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Chemistry

Option C: Energy

Standard and Higher Level

Valid for 2016 exams onwards

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FSC

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Chemistry
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Introduction

As with the other option topics, '*Energy*' builds on core Diploma Chemistry knowledge and allows you to develop some more in depth understanding of one area. The option has interesting links with physics, biology and environmental systems. '*Energy*' is, after all, a concept that bridges all of the sciences. However, many working chemists and chemical engineers find themselves particularly involved in managing or developing new energy sources, solving energy-related issues, or in helping to supply the day-to-day energy needs for our increasingly energy hungry world. This makes this option of particular importance for understanding the relevance of chemistry today.

This guide aims to provide a summary of what you need to know for the exam and follows the syllabus sequence. Some revision questions are included, but you should supplement these with as much practice as possible on real examination questions! Pay attention to words and phrases that have been placed in separate text boxes. These are important scientific terms that need to be particularly well understood and applied.

At the end of each of the first eight chapters (corresponding to C1 to C8 of your IB syllabus) are two or three '*example problems*' to show how you might be expected to apply your knowledge. In addition, in Chapter 9, there are several exam-style questions for further practice. Answers, including a few examination tips, are in Chapter 10.

The problems associated with resourcing society's energy needs and addressing global warming have been political and social issues for my generation. They are likely to continue to provide challenges for yours. Rightly, the IB values world issues and knowledge links. You should pay attention to the sections of your syllabus headed '*International Mindedness*' and '*Theory of Knowledge*'. However, since this is a revision guide, the main focus here is on helping you to understand the chemistry content and how this links to areas of your core syllabus and the nature of science.

Chemistry plays a central role in understanding fossil fuels, in how to harness nuclear energy, and how to develop our use of biofuels. At Higher Level we also apply and develop our core knowledge of redox and other chemistry to look at how fuel cells, rechargeable batteries, and photovoltaic devices work. For HL students there is more detail required in understanding nuclear energy.

In order to prepare this guide I would like to express gratitude to my science colleagues at ACS Egham International School, Ghulshan Karagul, and Philip McAvoy. They gave many helpful suggestions for improvements. I would also like to thank my son, Andrew Hickling, who produced all of the original diagrams.

Tony Hickling

Contents

Chapter 1: Energy sources

You should be familiar with Topic 5 of your syllabus (*Energetics and Thermochemistry*) before studying this chapter.

Forms of energy

At the molecular level particles possess two types of energy, **kinetic** and **potential** energy.

> ***Key Terms***
>
> **Kinetic energy** is energy associated with movement.
> **Potential energy** is energy associated with position.

Systems of particles can gain potential energy when chemical bonds are broken. (This is because work needs to be done to separate particles that are electrically attracted to each other.) Forming bonds releases energy, usually as heat. Hence exothermic reactions involve a net loss of particle potential energy, with more bond energy in the products than the reactants. Particle potential energy is converted to particle kinetic energy. This is the origin of the energy supplied by chemical fuels, such as fossil fuels or biofuels, when they burn.

A different, non-chemical, form of potential energy is released when we are using nuclear fuels as energy sources – changes to the composition of an atom's nucleus involves energy changes because of the forces at work inside the nucleus.

Light carries energy that can either be modelled as a stream of energy particles (photons) or as waves. As light energy from the sun interacts with matter we can harness '*solar energy*'.

Sources of energy – chemical, nuclear, or solar – are able to do mechanical or electrical work as well as provide heat where needed. Energy sources can ultimately provide us with electricity for distribution to homes and industry, energy for transportation, heating fuel, and even power sources for portable devices.

Conservation and degradation

It's interesting to note how we can trace most available energy sources on Earth to nuclear changes in the sun. Solar energy arises from these nuclear changes in the sun, some of which, via the natural process of photosynthesis, gives rise to the energy available to us from fossil fuels or biofuels.

Energy changes occur naturally although we are mainly interested, in this option, with how we can get energy where we want it and in the form we want it. As changes occur to energy, from one type of energy to another, or from one location to another, the total energy remains **conserved**.

> ***Key terms***
>
> The **'Law of conservation of energy'** says that the total energy in all forms stays the same. Energy cannot be created or destroyed.

Unfortunately, energy changes (and materials) tend to go from a concentrated form to a dispersed (spread out) form, and from an organised system to a less-organised system. The quantity of energy available for doing work decreases.

> ***Key terms***
>
> **Degraded energy** is energy that is no longer available for doing work; it has irreversibly been transferred as heat to the surroundings.

At the particle level, processes lean towards producing an **energy-degraded** world where there is completely random kinetic energy of particles everywhere, and with all locations at the same temperature!

What makes an energy source useful?

Here are five factors:

1) A useful source releases sufficient energy quickly enough, but not explosively.

2) A useful source produces a very small (minimal) amount of pollution.

3) A useful source is readily obtainable and won't run out quickly.

Renewable or non-renewable energy?

> ***Key terms***
>
> **Renewable energy** are sources that are naturally replenished.
>
> **Non-renewable** are sources that are finite.

Biofuels based on agriculture involve careful land management so that the fuels are only used at the rate at which the new crops are grown – they would therefore be classed as renewable. Fossil fuels on the other hand are being used at a rate that is of the order of a million times faster than any natural process of regeneration, so they are non-renewable.

4) A useful source is concentrated.

For a chemical or nuclear fuel this is quantifiable as either **energy density** or **specific energy**.

$$\boldsymbol{ENERGY\ DENSITY = \frac{Energy\ released\ from\ fuel}{Volume\ of\ fuel\ used}}$$

$$\boldsymbol{SPECIFIC\ ENERGY = \frac{Energy\ released\ from\ fuel}{Mass\ of\ fuel\ used}}$$

Notice that:

$$\frac{Energy}{Volume} = \frac{Energy}{Mass} \times \frac{Mass}{Volume}$$

So,

$$\textbf{ENERGY DENSITY} = \textbf{SPECIFIC ENERGY} \times \textbf{DENSITY}$$

Be careful with units! Look carefully to see the units of any data given in tables or graphs. You may need to convert between grams and kilograms, or cm^3, dm^3, and m^3!

5) A useful source transfers energy to the form and location needed efficiently.

$$\boldsymbol{Efficiency\ of\ Energy\ Transfer} = \left(\frac{Useful\ Output\ Energy}{Total\ Input\ Energy}\right) \times 100\%$$

Example problems

1) Hexane and methanol are being considered as liquid fuels for a model rocket.

FUEL	Density (gcm^{-3})	Enthalpy of Combustion ($kJmol^{-1}$)
hexane	0.655	-4,163
methanol	0.792	-726

a) ***Determine*** the specific energy of each fuel.

b) ***Determine*** the energy density of each fuel.

c) ***State***, with a reason, which fuel would be the best choice based on your calculations.

d) ***Give*** two other factors to consider when choosing the fuel.

2) A large power station supplies electrical energy at a rate of 4,000 MJ every second from burning powdered coal. (1 MJ = 1,000,000 J).

The efficiency of energy transfer for the power station is 30%. The specific energy for this coal is 24 $MJkg^{-1}$.

a) ***Define*** *'efficiency of energy transfer'* and *'specific energy'*.

b) ***What*** mass of coal is burnt each second by the power station?

Chapter 2: Fossil fuels

You should be familiar with Topic 10 of your syllabus (*Organic Chemistry*) before studying this section.

Energy from fossil fuels

Fossil fuels were formed by the chemical reduction of biochemical molecules containing mainly carbon, hydrogen, nitrogen, sulphur, and oxygen. Processes underground lasting between about fifty million to about three hundred million years converted what were originally sediments of decomposing organic material into the reserves of coal, petroleum (crude oil), and natural gas available to us today.

Converting carbon dioxide and water into complex organic chemicals is an endothermic process. The energy enabling green plants to perform this miracle comes from the sun, i.e. photosynthesis. This energy can again be released if the material is burnt, with the complex organic molecules returning to carbon dioxide and water again as a result. Hence the biochemical molecules, and fuels derived from these chemicals, can be used as energy sources.

The reduction of oxygen-rich organic molecules from living material in the formation of fossil fuels produce molecules such as **hydrocarbons**.

> ***Key terms***
>
> **Hydrocarbons** are molecules containing only the elements carbon and hydrogen. Petroleum is mainly a complex mixture of hydrocarbons.

Hydrocarbons have more exothermic enthalpies of combustion than oxygen-rich organic molecules such as sugars or alcohols. Carbon atoms in hydrocarbon molecules have a lower oxidation state than those in oxygen-rich organic molecules. In general, the more the carbon atoms need to be oxidised to become carbon dioxide, the more energy is available from the fuel.

Compare the following two examples of complete combustion, with enthalpies of combustion taken from your data book:

Example 1:

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

Glucose: Burning glucose gives out 2,803 $kJmol^{-1}$

The oxidation state of carbon in glucose is 0. (You should be able to work this out from the usual oxidation numbers for hydrogen (+1) and oxygen (-2) in their compounds.)

Example 2:

$C_6H_{12}(l) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

Cyclohexane: Burning cyclohexane gives out 3,920 $kJmol^{-1}$. This produces the same amount per mole of fuel of carbon dioxide and water as glucose in the example above.

The oxidation state of carbon in cyclohexane is -2. (Since hydrogen has an oxidation number of +1 in its compounds.)

Petroleum (crude oil)

The hydrocarbons in petroleum are separated and converted to useful fuels in an oil refinery. Gasoline (petrol) is a particularly valuable product so that the processes in a refinery try to maximise its output as well as produce other commercially important chemicals.

There are many processes taking place in an oil refinery, and products are used as raw materials for the chemical industry as well as fuels for specialised purposes. In combination with other raw materials, the product range is of course huge and a revision guide can't do justice to this. Why are we are burning most of these non-renewable resources instead of conserving them for the production of important chemicals in the future?

From the refinery...	Example of a non-fuel product
Ethene	Polythene
C4 hydrocarbons	Synthetic rubbers
Benzene	Epoxy resin

You need to know only a little about three important processes in the refinery only. The processes are **fractional distillation**, **cracking**, and **catalytic reforming**.

Fractional distillation

> ***Key terms***
>
> **Fractional distillation** is the physical separation of a mixture of many pure substances by maintaining liquid and vapour in equilibrium at a range of temperatures.

Short chain hydrocarbons have a low boiling point, long chain ones a high boiling point. A vertical fractionating column has a temperature gradient with the highest temperature at the bottom where the liquids with the highest boiling point (longer chain) are collected by condensation. Lighter molecules rise as gases and heavier ones fall as liquids in the fractionating column until they find a temperature at which they are in equilibrium. They are then collected as liquid fractions (groups of similar sized molecules) with a well-defined boiling point range.

Fractional distillation occurs at several stages in a refinery, at different pressures and different temperature ranges, with the ultimate goal of producing fuels of the desired quality, and usually with a small boiling point range. For example a gasoline (petrol) might finally be collected at a narrow boiling point range of about 90-110°C (at atmospheric pressure). However, no matter how narrow a boiling point range is collected, a gasoline is far from being a pure substance. For example, heptane and 2,2,4-trimethylpentane (which has the older name of 'iso-octane') have almost identical boiling points (99-100°C), so cannot be separated physically by distillation – even though it would be very helpful if this were possible! (see key term *'Octane number'*.)

Main fractions from petroleum

Sources of information vary widely on the main products of primary fractional distillation simply because crude oil and refineries are complex and highly variable. There are also alternative names for the main fuels in different countries, shown in brackets! This table just gives you an approximate idea and includes some names you ought to be familiar with.

Fraction	Approximate carbon chain length	Approximate boiling point range (°C)
Liquefied petroleum gas (LPG) from the top of the fractionating column	1-4	<20 These are the most volatile molecules.
Naphtha and Gasoline (includes petrol)	5-11	30 - 150
Kerosene (paraffin)	6-16	150-300
Diesel	10-20	200-350
Lubricating oils, fuel oils, and residue from the bottom of the fractionating column	>20	>300 These are the least volatile molecules.

Cracking

> ***Key terms***
>
> **Cracking** is a process where some of the larger and less valuable hydrocarbon molecules are broken down into smaller and more valuable ones.

Cracking is conducted at high temperature without a catalyst or at low temperature with a catalyst. The long chain hydrocarbons are broken down in a fairly random way to produce shorter molecules. These need to be distilled again to obtain the desired products. Low temperature catalytic cracking produces more branched chain isomers than high temperature cracking.

Example equation:

$C_{15}H_{32} \rightarrow C_8H_{18} + C_3H_6 + 2C_2H_4$

Cracking is an endothermic reaction so both the kinetics and equilibrium theory suggest that a high temperature will give the best yield most quickly. A fairly high pressure is also used to increase the collision rate between molecules even though equilibrium theory (Le Chatelier's Principle) would suggest that a lower pressure might be better!

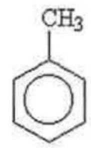
Catalytic reforming

> ***Key terms***
>
> **Catalytic reforming** is a process involving molecular rearrangement. Straight chain alkanes are converted into branched chain or cycloalkanes.

Catalytic reforming improves the *'Octane number'* of the fuel (see key term below). Useful bi-products of reforming are benzene and its derivatives as well as hydrogen – these are mainly used by the chemicals industry. Reforming requires a high temperature and high pressure. The catalyst used might typically be aluminium oxide.

Example equations:

1) $CH_3(CH_2)_6CH_3$ → $CH_3C(CH_3)(CH_3)CH_2CH(CH_3)CH_3$
octane → 2,2,4-trimethylpentane



2) $CH_3(CH_2)_5CH_3$ → $4H_2$ +
heptane → hydrogen + methylbenzene

Octane number

A gasoline engine uses a spark plug to ignite a mixture of the fuel vapour and air to provide the power stroke for the engine at exactly the correct moment in time during an engine cycle. Unfortunately, many of the molecules in a gasoline tend to ignite without a spark, at the wrong time. This produces something called **knocking** in a car engine, resulting in loss of power and less fuel efficiency.

> ***Key terms***
>
> **Knocking** is the process of an engine misfiring due to its fuel burning too easily when mixed with air.
> **Octane number** is the extent to which a fuel won't 'knock' when used in a petrol engine. It is an empirical scale. Pure heptane (the worst) has an octane number of zero. Isooctane has an octane number of 100.

Of the molecules in gasoline, heptane has a strong tendency to 'knock'. Pure heptane is given an octane number of zero. 2,2,4-trimethylpentane has a much lower tendency to cause **knocking**. Pure 2,2,4-trimethylpentane (iso-octane) is given an octane number of 100. Real fuels are compared in a test engine with different percentage mixtures of heptane and iso-octane to obtain an **octane number**. Some fuels can therefore have an octane number greater than 100 since 100% iso-octane is not the best molecule! The more branched-chain isomers have less of a tendency to knock because greater activation energy is needed for them to react with oxygen. Benzene has a similar octane number to iso-octane so is used as a gasoline additive but there are environmental and health problems associated with benzene. Its use is therefore regulated in many countries. The compound tetraethyl lead used to be added to improve octane number but no longer. This is due to the poisonous nature of lead compounds.

Octane numbers are precisely defined in different ways in different countries and in different situations, for particular engines running in a certain way. If you were to do a web search on the acronyms 'RON', 'PON', and 'MON' you will find out more, but you don't need to know the details.

Natural gas

Natural gas is a fossil fuel mainly composed of methane. It is possible to convert natural gas into liquid fuels or to use it in the chemicals industry but a large amount is used as a heating fuel or as a fuel for power stations.

Coal

Coal is a fossil fuel composed mainly of carbon. Much of the coal that is mined is the fuel for power stations. Coal can also be converted into the more environmentally friendly solid fuel **coke**.

As with the other fossil fuels, chemicals from coal are also used to help produce a wide variety of chemical products.

> ***Key terms***
>
> **Coke** is a solid fuel derived from coal that burns cleanly. Unlike coal it doesn't contain sulphur, so burns without producing sulphur dioxide.

Converting coal into gas or liquid fuels

> ***Key terms***
>
> **Coal gasification** and **coal liquefaction** are the names given to the formation of gaseous or liquid fuels from coal via syngas.
> **Syngas** is mainly a mixture of carbon monoxide and hydrogen.

Coal is converted to **syngas** (*synthesis gas*), mainly by the action of water at high temperature. The process actually involves blasting hot coal alternately with steam and air until the coal is used up but can be considered as mainly a reaction between carbon and steam.

Simplified equation for coal gasification:

$C + H_2O \rightarrow CO + H_2$

Syngas can then be converted into synthetic natural gas or synthetic liquid fuel. Production of synthetic liquid fuel uses a cobalt/iron catalyst.

In general, an equation for coal liquefaction:

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

Therefore, for producing octane with a cobalt/iron catalyst:

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

Syngas can also be converted into methanol, which can be used as a fuel or as a fuel additive. It involves using a different catalyst, one containing copper, zinc oxide, and aluminium oxide,

$CO + 2H_2 \rightarrow CH_3OH$

Carbon footprint

Global warming and environmental problems associated with increasing amounts of carbon dioxide (and other greenhouse gases) in the atmosphere will be described in Chapter 5.

> ***Key terms***
>
> **Carbon footprint** measures how much CO_2 is produced by an activity (or 'CO_2 equivalent' if including other greenhouse gases such as methane).

Example problems

3) Butane and methanol are being compared as two possible fuels for a camping stove. Which has the highest carbon footprint given that the enthalpy of combustion of butane is -2,877 $kJmol^{-1}$ and the enthalpy of combustion of methanol is -726 $kJmol^{-1}$? What ***assumptions*** do you need to make?

4)

- **a)** ***Explain*** what is meant by '*octane number*'.
- **b)** ***Why*** do heptane and 2,2,4-trimethylpentane have a similar boiling point?
- **c)** ***Explain*** how cracking and reforming can improve the yield of high quality gasoline from an oil refinery. Give ***example equations*** as part of your answer.

5) ***Outline*** with equations how coal can be converted into gasoline.

Chapter 3: Nuclear fusion and fission

Topic 2 (*Atomic Structure*) contains essential background to this section. (More details and more advanced problems for HL are in Chapter 7. Your teacher will probably combine Chapter 3 and Chapter 7 for HL students.)

Nuclear energy is energy that is released when atomic nuclei change. There are two ways this can happen: **nuclear fusion** and **nuclear fission**.

Nuclear fusion

> ***Key terms***
>
> **Nuclear fusion** occurs when two very light nuclei (such as hydrogen) combine together to make a larger nucleus.

Enormous heat and pressure are required to overcome the electrical repulsion of protons but there is a net release of energy in the process.

Example equation:

$$^1_1H + \, ^2_1H \rightarrow \, ^3_2He$$

In the example above, the symbols represent the nuclei of hydrogen. They combine to make a helium nucleus, a helium-3 isotope in this example. Some of the energy produced is carried away as gamma ray photons.

The lower number to the left of each symbol is the atomic number and is the same as the number of protons. This represents the relative charge of the nucleus. Charge is conserved so that 1 + 1 = 2 on the bottom line of the equation.

The upper number is the mass number. It is the sum of the protons + neutrons. Mass is also conserved so that 1 + 2 = 3.

Nuclear fission

> ***Key terms***
>
> **Nuclear fission** occurs when a very heavy nucleus (such as uranium or plutonium) splits into medium sized nuclei.

In addition to releasing energy this process also releases neutrons, some of which might be absorbed by other heavy nuclei to produce more fission! Only a few heavy nuclei are 'fissionable' in this way and the fission products are varied.

Example equation:

$$^{235}_{92}U + \, ^1_0n \rightarrow \, ^{236}_{92}U \rightarrow \, ^{144}_{56}Ba + \, ^{89}_{36}Kr + 3\, ^1_0n$$

^1_0n is the symbol for a neutron. You will again see that both charge and mass are conserved.

Mass (the top line): 235 + 1 = 236 = 144 + 89 + 3

Charge (the bottom line): 92 + 0 = 92 = 56 +36 + 0

In your exam you might be set problems *'balancing'* these nuclear equations. (See example questions at the end of this section.) You do not need to learn any specific nuclear equations but you do need to be able to deduce mass numbers and atomic numbers or the name of the elements for the nuclei involved, if given enough information.

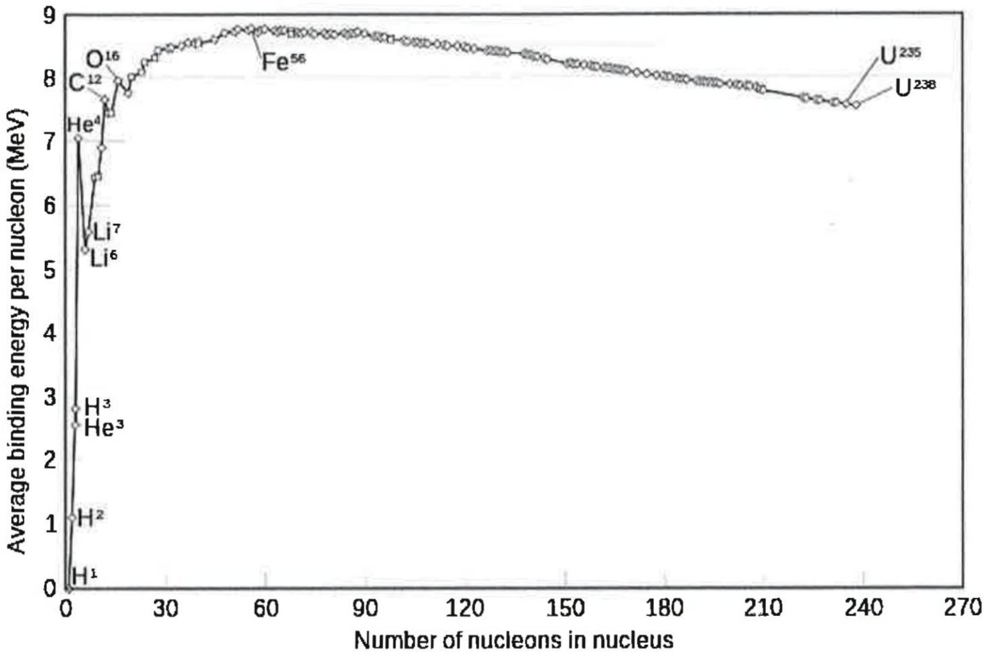
Binding energy

There is electrical repulsion between protons in a nucleus. There are also nuclear forces of attraction keeping protons and neutrons together in the nucleus, but these forces of attraction only work over a very short distance. In energy terms the most stable nuclei are those of iron and nickel and this is expressed by saying that they have the maximum **binding energy**.

> ***Key terms***
>
> The increase in **binding energy** is the amount of energy given out in fusion or fission.

Binding energy graph

A version of the following graph is in your data book, but smoothed out:



The graph above shows, approximately, how the average binding energy per proton or **neutron** in the nucleus varies with mass of nucleus.

> ***Key term***
>
> A **nucleon** is the name given to a proton or a neutron.

Binding energy and mass defect

$\Delta E = \Delta m \times c^2$

In Einstein's famous relationship between energy change and mass change, he tells us that the rest mass of something giving out energy must go down. ΔE is the energy change in joules, Δm is the mass change in kg and c^2 is an enormous constant, the speed of light squared (9×10^{16}). When there is either fusion or fission the measured rest mass goes down in proportion to the energy given out. Due to this enormous constant there is only a microgram (1 μg) reduction in mass when a nuclear reactor gives out 90 megajoules (90 MJ) of heat for example. On a particle level, energy changes are often measured in electron-volts (eV) or mega electron-volts (MeV). 1 MeV = 1.6×10^{-13} J.

Since energy is released by fusion of light nuclei there is what is termed a **mass defect** that can be calculated by adding together the masses of the protons and neutrons that come together to form a nucleus and subtracting the mass of the nucleus. Nuclei are always slightly lighter than the sum of their separate protons and neutrons, but the change in mass is tiny compared to the energy released.

> ***Key terms***
>
> **Mass defect** is the reduction in mass when protons and neutrons come together to form a nucleus.

This relationship between matter and energy explains how the sun is able to provide energy at an enormous rate for billions of years without *'running out of fuel'*. The *'fuel'* in the sun is of course hydrogen, and the process releasing energy is nuclear fusion.

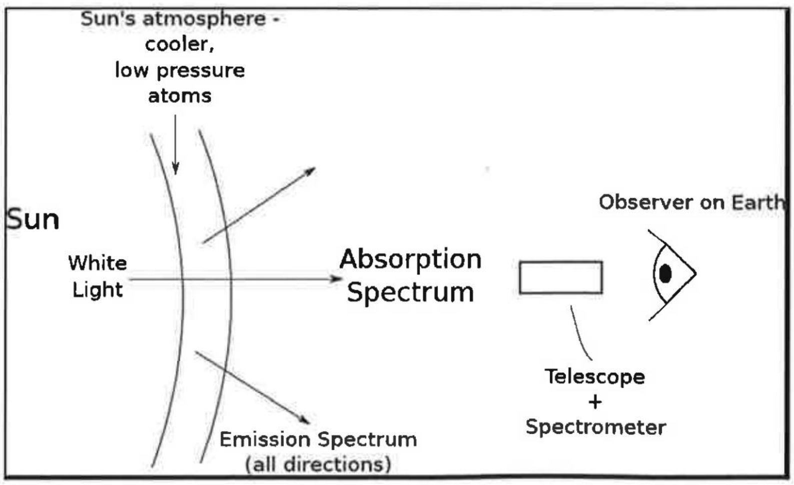
Stars and atomic absorption spectra

Stars, including our own Sun, produce energy as a result of nuclear fusion, combining hydrogen nuclei to make helium and eventually producing small amounts of heavier nuclei. This process occurs deep within stars, under enormous gravitational pressure and high temperature, where matter exists in a state called plasma – separate nuclei and unattached electrons.

Complete atoms only exist in the cooler outermost *'atmosphere'* of a star.

Atoms of different elements can be identified in stars by means of analysing **absorption spectra** of the light that has passed through this atmosphere on its journey to our telescopes.

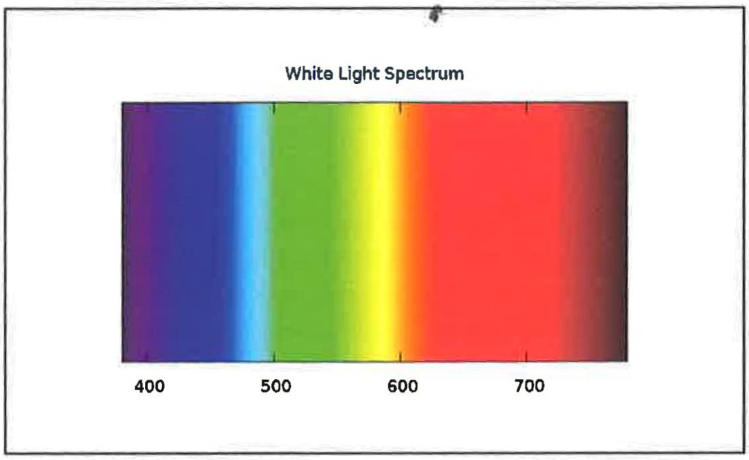
> ***Key terms***
>
> An **atomic absorption spectrum** is a sequence of dark lines in an otherwise continuous spectrum of light. It is due to atoms absorbing light photons of particular energies. These energies have equivalent frequencies or wavelengths (see section 2.2 of your core syllabus.)

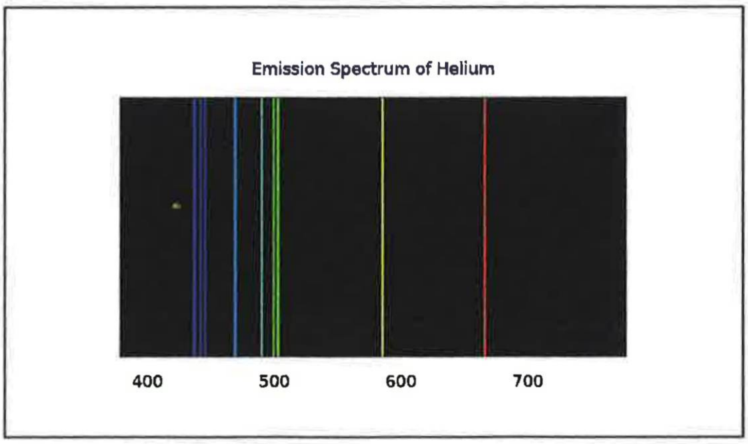


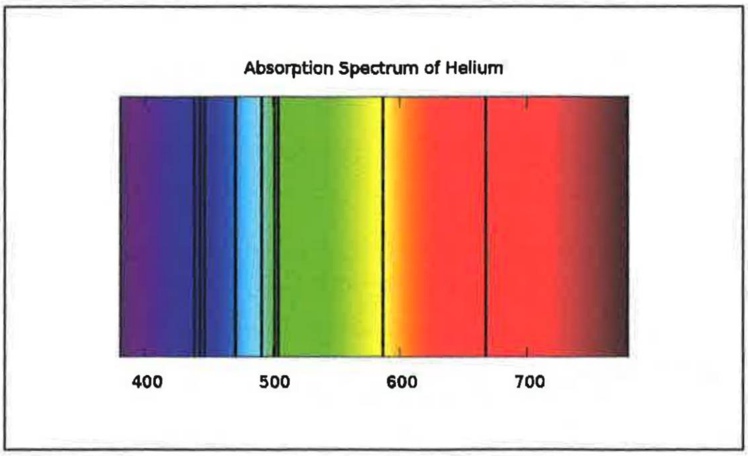
Comparing emission and absorption spectra

Individual atoms of hydrogen or helium will *'absorb'* particular frequencies of light, enabling us to identify the element. You should be familiar with *'emission'* spectra from section 2.2 of your syllabus. The specific frequencies that occur in an atomic emission spectrum appear as dark lines at the same frequencies in the absorption spectrum for the same element. The difference is that, with absorption, electrons are promoted from a lower to a higher energy level by absorbing light photons of a particular energy and frequency. The appearance of an absorption spectrum for a particular element is therefore of a continuous spectrum with dark lines at well-defined frequencies or wavelengths. It was these well-defined absorption patterns that enabled helium to be discovered on the sun before it was discovered on Earth!

Wavelengths in the atomic spectra for helium are shown in the diagram below:







Nuclear power stations

All electricity from nuclear power is generated today using nuclear fission although in the future we may be able to economically harness nuclear fusion. At present, controlled nuclear fusion presents difficulties in trying to contain plasma for sufficient time at the high temperature and pressure needed.

The **advantages** of nuclear fusion compared to fission are:

1) There are cheap and readily obtainable fuel sources since light nuclei are involved in fusion. By comparison, fission requires uranium ore as a raw material – uranium ore is a finite energy source and a rare mineral.
2) Fusion is likely to be environmentally much friendlier than fission. For nuclear fission, radioactive waste is a problem. (See section on radiation later in this chapter)
3) The steep slope on the fusion part of the binding energy curve shows that the energy available from fusion (per **nucleon**) is generally greater than for fission.

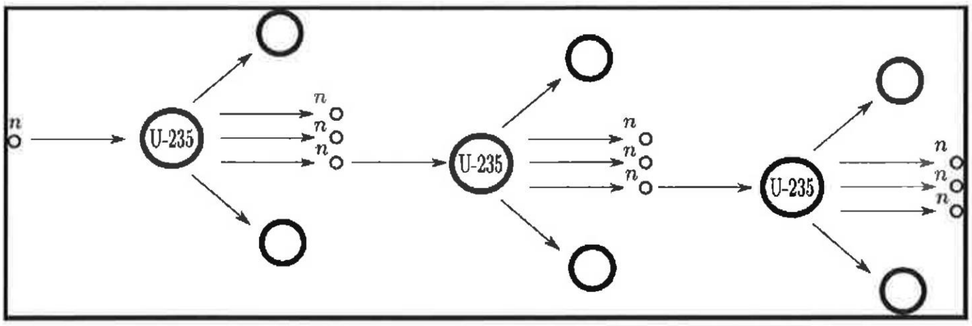
> ***Key terms***
>
> A **nucleon** is the name given to a proton or a neutron in a nucleus.

Nuclear fission reactors

Near the beginning of this chapter we met the following example equation for nuclear fission:

$$^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{236}_{92}U \rightarrow {}^{144}_{56}Ba + {}^{89}_{36}Kr + 3\,{}^{1}_{0}n$$

In a nuclear reactor the production of neutrons produces a '*chain reaction*'.



A neutron produced by fission is released with a very high kinetic energy. It is then slowed down by passing through a material called a '*moderator*'. This enables it to remain in the reactor core for sufficient time to be absorbed by another nucleus of U-235 and so continue the chain reaction. Control rods placed between the fuel rods of uranium absorb sufficient neutrons to prevent any undesirably high rate of release of energy. After start-up a reactor will, in this way, be able to produce a steady supply of heat energy to the coolant. This heat in turn supplies energy for the steam turbines of the power station. (Note that you will not be assessed on the details of a how a nuclear power station works!)

Naturally occurring uranium is 99% uranium-238, an isotope that is '*non-fissionable*'. In order for a controlled chain reaction to take place in a nuclear reactor using uranium, the uranium must first be enriched so that there is about 4% uranium-235. However, in *'breeder reactors'*, generally with a higher percentage of U-235 in the fuel rods, some of the non-fissionable uranium-238 absorbs slow moving neutrons, becoming another important nuclear fuel, plutonium-239. Like uranium-235, plutonium-239 is fissionable, so the use of breeder reactors enable more energy to be extracted from the uranium ore.

> ***Key terms***
>
> **Critical mass** is the mass of nuclear fuel needed for a sustained chain reaction.

The critical state for a reactor is when the power output is steady (the fuel has reached its **critical mass**). If less than one neutron per reaction (on average) continues the chain reaction then the reactor will become 'sub-critical' with a decreasing power output. In a 'super-critical' state, such as when the reactor is first started up, the power is increasing.

Advantages and disadvantages of nuclear power

On the positive side, nuclear power stations produce very low levels of greenhouse gas emission and use fuels with an extremely high energy density. Chemical pollution released by nuclear power stations is low.

The low concentrations of fissionable material in fuel rods are such that reactor cores cannot become atom bombs.

However, on the negative side, Plutonium-239 is the main fissionable material used in nuclear weapons. Plutonium is obtained by reprocessing fuel from breeder reactors. In addition to atom bombs, fission *'primaries'* are also used to set off the thermonuclear *'hydrogen bombs'*, releasing energy explosively from fusion as well as fission.

Accidents have also occurred in the past with nuclear power stations resulting in the release of radioactivity and radioactive materials. There are significant hazards associated with the accidental release of radioactivity and storage of nuclear materials. If a working reactor core is insufficiently cooled then there is the possibility of a catastrophic accident. *'Core meltdown'* might occur if there is more heat produced than can be removed by the coolant. In this situation at least some of the fuel rods might begin to melt. This could cause a structural failure and a release of radioactive material.

In addition, when a nuclear reactor reaches the end of its economic life it needs to be *'decommissioned'*. Decommissioning a nuclear power station is an expensive process to carry out safely. Since the consequences of an accident can be a major disaster, modern nuclear power stations invest a large amount of money into safety and control systems.

Radioactivity

In addition to fusion and fission it is possible for a nucleus that is unstable (a radioisotope) to give out one or more particles of radioactivity in order to become more stable. This happens spontaneously and by chance. It is not possible to control the emission of radioactive particles. You are not required to know details of the nuclear equations involved or properties of the types of particle given out, but you do need to know about the general hazards of radioactivity, and factors involved in the safety of nuclear power.

All heavy isotopes such as uranium and plutonium are radioactive. Any isotopes with an imbalance between protons and neutrons are also radioactive, such as the fission products in a nuclear reactor.

Particles of radioactivity are very high energy and can be classified as *alpha* (α), *beta* (β) and *gamma* (Y). They all cause ionization as they travel through the air or materials, but the intense ionization caused by alpha and beta means that they don't travel so far and so are usually less dangerous than the highly penetrating gamma rays.

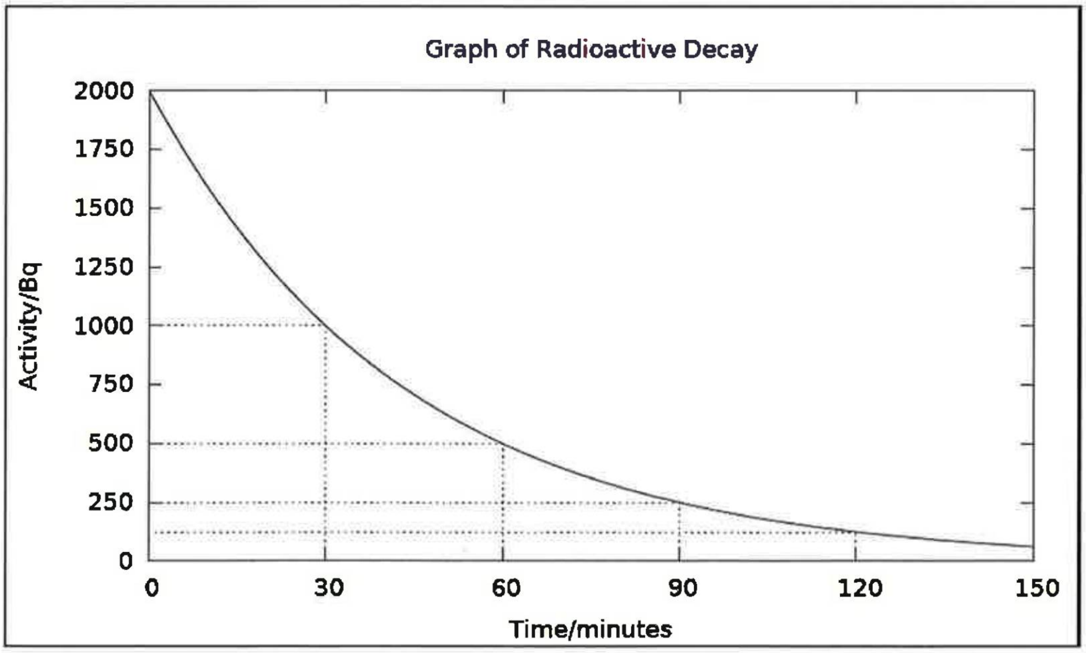
Health risks of radioactivity

Any ionizing radiation can cause cancer to form as a result of the chemically reactive ions and free radicals producing changes to human biochemistry. There is natural radioactivity in our environment due to radioactive rocks and cosmic rays and there is a very low chance of getting cancer associated with such low levels of radioactivity. The higher the dose of radioactivity we are exposed to (due to particles of radioactivity absorbed by or passing through the body), the bigger the risk from that exposure. The risk is reduced by shielding dangerous radioactive sources with concrete or other dense materials and disposing of radioactive waste from nuclear power stations (etc.) in a safe fashion. This depends on how active it is and how long the **half-life** is of any radioactive isotope involved. Used fuel rods from a reactor for example are sometimes vitrified (made into glass) then encased in stainless steel and buried deep underground in a geologically stable zone, where they need to remain for hundreds of years.

Half-life

> ***Key terms***
>
> **Half-life** is time it takes for the amount of radioactive isotope remaining to halve.
> **Activity** is the number of radioactive particles given out each second.

Every radioactive isotope has a **half-life** that is a unique property of a particular isotope. It is the time it takes for the activity to halve as well as the amount remaining to halve. Activity is measured in Becquerels (Bq), the number of radioactive particles per second emitted, or nuclei decaying each second. It can also be called the '*decay rate*'. The activity never reaches zero but continues to halve in equal time intervals (see graph below).



Example:

If a source gives out 20,000 Bq of radioactivity and has a half-life of 30 minutes, how active is it after 2 hours? You can work this out by halving the initial activity of 20,000 Bq every 30 minutes until you get to 2 hours. As follows:

<u>Time</u> (minutes)	**<u>Decay rate</u> (Bq)**
0	20,000
30	10,000
60	5,000
90	2,500
120	1,250

If you were to continue this halving game with this particular example you will see that after about 7 hours the activity of this source has reached about 1 Bq.

Instead of halving again and again the shortcut is to say:

7 hours = 14 half lives

Activity after 7 hours is therefore = 20,000 x $(0.5)^{14}$ = 1.2 Bq

What makes reaching about 1 Bq important is that this is comparable to the natural background level – one way of judging if a source is safe.

However, a nucleus remaining after radioactive decay, called a '*daughter*' nucleus, will often itself be unstable, giving out its own radioactivity, and with its own new half-life – this might be short or long!

Nuclear waste usually contains a mixture of radioisotopes.

Nuclear waste that needs to be stored underground indefinitely is not only the highly radioactive kind, but also the kind that contains or produces one or more highly active isotopes that have long half-lives. For example, the Plutonium-239 for fast-breeder reactors and atomic warheads has a half-life of about 24,000 years!

Example problems

6) ***Complete*** the following nuclear equation by identifying the missing mass and atomic numbers as well as the correct symbol for the element marked as 'X':

$$^{239}Pu + \quad n \rightarrow \quad Mo + {}^{134}X + 6 \quad n$$

7) Iodine-131 has a half-life of 8 days. A radioactive source contains 0.0024 grams of this isotope. ***How much*** will remain after 32 days?

Chapter 4: Solar energy

Photosynthesis

Green plants use light energy to produce *'chemical energy'* by combining carbon dioxide and water to form glucose and oxygen. You can confirm for yourself from average bond enthalpy data that the products have less total bond enthalpy than the reactants.

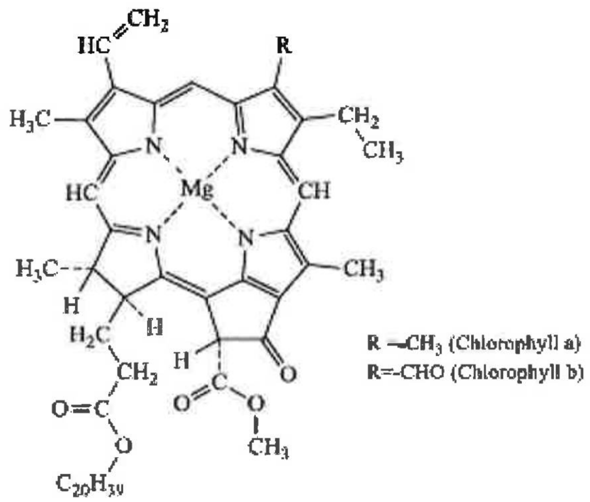
$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

What looks like a simple equation is in fact a complex biochemical mechanism, the key to which is the action of the green pigment called chlorophyll.

Chlorophyll and other pigments absorb light of particular wavelengths. They need a **conjugated electronic structure** to do this.

> ***Key terms***
>
> A **conjugated structure** in a molecule is an alternating series of double and single bonds.

You need to be able to recognize a part of a molecule that enables it to absorb light. In these molecules resonance can occur because there is more than one possible location for the double bonds. These resonance structures have energy differences that correspond to the energy of a visible light photon. Effectively a bonded electron absorbs this energy to configure the double bond differently. For chlorophyll, it strongly absorbs light photons in both the red and blue parts of the spectrum leaving the colour green as the main colour reflected from plant leaves. In the molecule of chlorophyll in the data booklet (IB Chemistry Data Book 2014) a structure of alternating double and single bonds surrounds the Magnesium atom at the heart of the molecule.



chlorophyll

The equation below shows the general principle of how a conjugated part of a molecule can resonate between a low energy (ground) state and a higher energy excited state as a result of absorbing energy. The actual situation is a little more complex for chlorophyl.

CH=CH-CH=CH	$\Leftrightarrow$	**•CH-CH=CH-CH•**
Low energy state		**High energy state**

The energy absorbed by the chlorophyll molecules in this way is released to enable the endothermic production of glucose in the plant. Hence chlorophyll acts as the principle catalyst in photosynthesis.

Biofuels

Sugars and oils from plants can be converted to fuels, increasingly used today as an alternative or additive to petrol or diesel for transportation. Although these fuels, like the fossil fuels, produce carbon dioxide when they are burnt, if crops are specifically grown as renewable biofuels then their use can be nearly **carbon neutral**.

> ***Key terms***
>
> **Carbon neutral** describes the use of the product or process which does not involve any net increase or decrease in the quantity of greenhouse gases in the atmosphere.

This means that burning the fuel releases a similar amount of carbon dioxide to that locked away by photosynthesis. This is important, as we will discuss in the next section on global warming. In addition, biofuels are more easily biodegradable than fossil fuels if spilled. However, growing crops as biofuels reduces ecosystems and removes land that might otherwise be used for food production.

There are two main types of biofuel: **ethanol** and **biodiesel**.

Ethanol

Fermentation of glucose from sugar cane, corn, or potatoes (for example) in the presence of yeast (and absence of oxygen) produces ethanol:

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

The ethanol produced can be blended with petrol in cars with modified petrol engines. At present about 10% ethanol with 90% petrol is common.

Biodiesel

The energy content of vegetable oils is similar to that of diesel fuel but they are not used in internal combustion engines, as they are too viscous, i.e. they don't flow easily. Vegetable oils are composed of triglycerides. A triglyceride is an ester formed from propane-1,2,3-triol (glycerol) and three long chain carboxylic acids. It has a very large molecular mass hence the Van der Waals bonding between triglyceride molecules is very strong – this is why the viscosity is so high.

A successful biodiesel needs to have a similar viscosity and boiling point to diesel fuels derived from crude oil. This is accomplished by the **transesterification** of the vegetable oil with methanol or ethanol.

> ***Key terms***
>
> **Transesterification** is a chemical process whereby the alcohol end of an ester molecule is replaced by a different alcohol.

The conditions for **transesterification** are to reflux the oil with the alcohol in the presence of a strong and concentrated acid or base. In general, where **-OCOR$_2$** represents one of the long chain carboxylic acids in the triglyceride,

C_2H_5OH + -$CHOCOR_2$ $\rightleftharpoons$ -$CHOH$ + $C_2H_5OCOR_2$

This will happen for each of the three different long chain carboxylic acids in the triglyceride molecule to give, mainly,

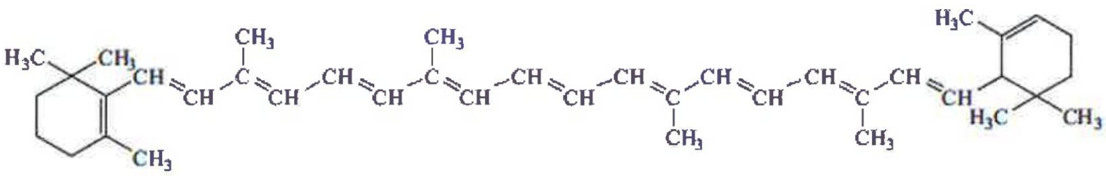
Ethanol + triglyceride $\rightleftharpoons$ Glycerol + mixture of ethyl esters

You need to be able to deduce the equations for different triglycerides and alcohols. The glycerol (propane-1,2,3-triol) is removed as a bi-product. The biodiesel produced (a mixture mainly of these esters) has a lower average molecular mass than the original vegetable oil and so has the lower viscosity needed in a diesel engine.

Example problems

8)

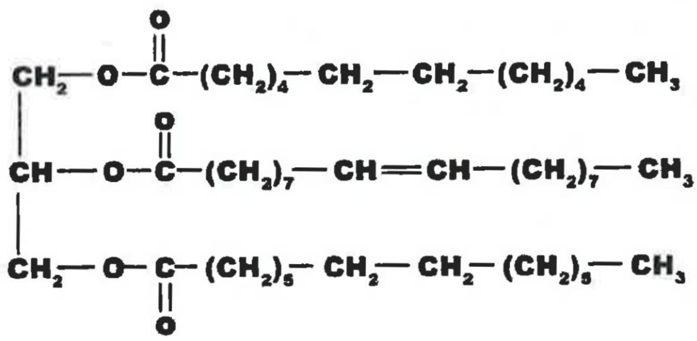
a) ***Circle*** on the following molecule that part of the molecule responsible for it having a specific colour. (IB Chemistry Data Booklet, 2009)



α-carotene

b) ***Explain*** how molecules of this sort might work as catalysts in reactions requiring light energy.

9) Used cooking oil can be used to make biodiesel when it reacts with methanol. One triglyceride in the used cooking oil is shown below.



Draw out the possible new esters that might be produced from this triglyceride.

Chapter 5: Environmental impact and global warming

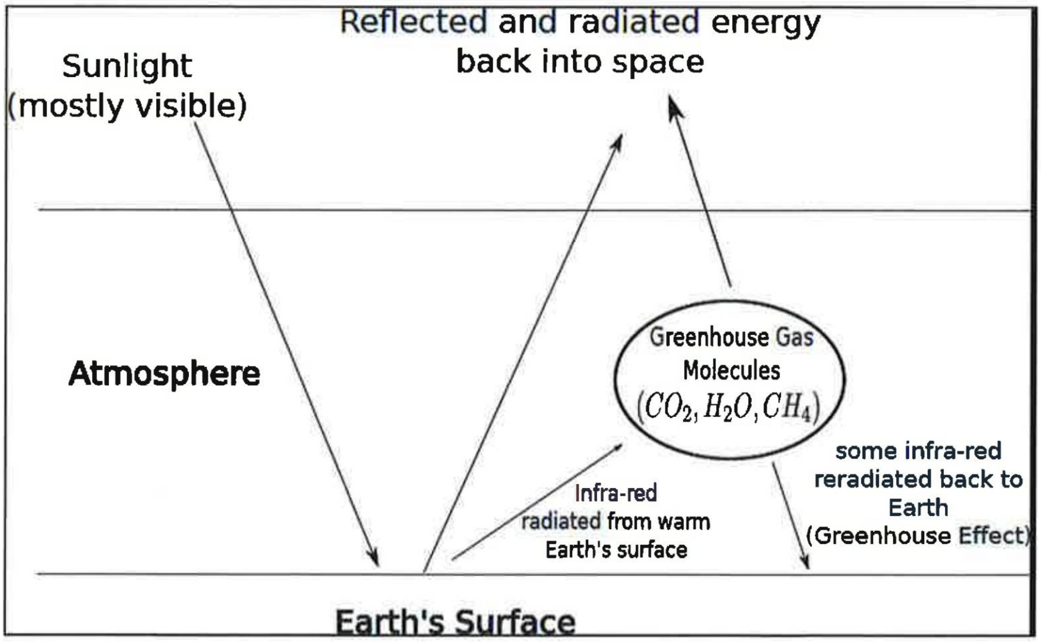
Greenhouse gases and the greenhouse effect

Greenhouse gases in our atmosphere allow the passage of incoming solar short wavelength radiation but absorb a proportion of the longer wavelength radiation from the Earth. Some of the absorbed radiation is re-radiated back to Earth. This means that our atmosphere maintains the Earth's surface at a higher temperature than it would have without an atmosphere. The average surface temperature on Earth is about 15°C. Without an atmosphere, the temperature would be more like -30°C (but would also fluctuate much more wildly between day and night extremes, like it does on the Moon). Perhaps not surprisingly, having an atmosphere is generally a good thing, but more surprising, perhaps, is that having a '*greenhouse effect*' is also a good thing.

Our concern is about any '***enhanced** greenhouse effect*' caused by a rise in the proportion in the atmosphere of those molecules, called greenhouse gases, which are particularly good at absorbing infrared given out by the Earth. The gases mainly responsible are CH_4, H_2O and CO_2. (There are others!)

Mechanism of the greenhouse effect

Molecules can vibrate in different ways as a result of their bonds being '*springy*'. The possibility of bending and stretching of the bonds when energy is supplied means that a molecule, such as carbon dioxide, will vibrate at certain frequencies. In a greenhouse gas these frequencies correspond to the same particular frequencies of infrared photon strongly absorbed by the molecule. This is a type of '*resonance*', if we model infrared as an electromagnetic wave vibration.



Bonds in molecules without a dipole moment, such as those in nitrogen (N_2) and oxygen (O_2) do not absorb infrared very much since a '*changing dipole moment*' (as molecules stretch and bend) is involved in absorption of infrared photons. Hence nitrogen and oxygen are not greenhouse gases.

After a photon has been absorbed, the excited, vibrating state of the molecule exists for only a tiny fraction of a second before an infrared photon is again given out by the molecule, this time in a random direction, and possibly back to the Earth's surface to warm it further.

Global warming and climate change

The earth's climate is complex. However, the mechanism above suggests that, as greenhouse gases are added to the atmosphere we would expect average surface temperatures to rise. In addition, relatively small changes in average temperature can have dramatic local consequence to the weather. Human activity has been increasing the emission of greenhouse gases.

Two factors might to some extent reduce some of the negative impact of greenhouse gas emissions – carbon dioxide dissolving in the oceans and particulates being emitted into the atmosphere.

Carbon dioxide in the oceans

There is a vast reservoir of carbon dioxide dissolved in the Earth's oceans. Some carbon dioxide is used by sea creatures to make limestone (calcium carbonate) minerals, used for making shells and for support. A both warmer and increasingly acidic ocean causes this carbon dioxide to be released back into the atmosphere where it will increase the amount of greenhouse gas present. However, the oceans work as a carbon dioxide sink, meaning that some of the gaseous CO_2 produced artificially will dissolve at the ocean's surface. Understanding how this balance works is part of the problem with predicting the effect of artificial carbon dioxide emissions.

There is a heterogeneous equilibrium between the concentration of atmospheric carbon dioxide and the aqueous carbon dioxide in the oceans. It is quite difficult for the gas to dissolve initially at the surface of the oceans.

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

Since this is a heterogeneous equilibrium the carbon dioxide is much more soluble at high pressure. This of course is how cans of fizzy drink work! Deep in the oceans the pressure is enormous. By Le Chatelier's principle, at equilibrium, the oceans will therefore dissolve a huge quantity of carbon dioxide at great depth, but the question is will the carbon dioxide reach those depths?

Once dissolved there is partial dissociation in solution to the weak acid, carbonic acid.

$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \rightleftharpoons 2H^+(aq) + CO_3^{2-}(aq)$

As the concentration of carbon dioxide in the atmosphere rises, so more dissolves in the oceans, but this lowers the water's pH. This lowering of pH has harmful effects on sea life, particularly affecting those sea organisms trying to make solid calcium carbonate for shells or structure, since the increase in hydrogen ion concentration will shift the equilibria above towards the left and reduce the stability of solid carbonate minerals.

Particulates – global dimming

> ***Key terms***
>
> **Global dimming** is a reduction in sunlight reaching the Earth's surface

Particulates such as smoke, dust, and condensed water in clouds cause global dimming as they reflect sunlight. Various industrial processes and the burning of fossil fuels produce solid particles (soot etc.). Global warming also increases the amount of cloud formation. Sunlight is reflected from clouds and particles back into space and this reduces the amount of radiation reaching the Earth's surface during daytime. This has the effect of cooling daytime temperatures and, unfortunately, reducing photosynthesis despite also reducing global warming to a small extent. There is some evidence that average day and nighttime temperatures are becoming closer in some parts of the world as a result of both global warming and global dimming happening at the same time.

Three important greenhouse gases

Name	Source	Abundance in atmosphere, ppm (parts per million)	Effect
Water vapour	Mostly natural, evaporation of surface water	Increasing only a little with global warming About 10,000 ppm	Important greenhouse gas, but condensed water in clouds also causes dimming, so not regarded as a significant problem
Carbon dioxide	Partly artificial -from burning fossil fuels and less photosynthesis due to deforestation	Has increased dramatically About 400 ppm	Not as strong a greenhouse gas as methane but a bigger problem due to abundance in atmosphere and dramatic increase
Methane	Partly artificial due to growing rice, rotting rubbish in dumps, animal farming, and mining activities	Not very abundant in atmosphere but rising About 2 ppm	Extremely strong greenhouse gas but not so important as CO_2 due to low abundance

Controlling carbon dioxide emissions

1) **International cooperation to reduce carbon emissions** – Most famously the Kyoto Protocol in 1997 introduced *'carbon trading'*. The objective was to head towards carbon neutral economies, absorbing as much carbon dioxide as created.
2) **Making more use of carbon neutral energy sources** – essentially anything except burning fossil fuels!
3) **Measures taken to reduce emissions** – from transportation of commodities and people.
4) **Reducing deforestation**
5) Various methods are used to prevent carbon dioxide from power stations and industrial sources from entering the atmosphere:
    a) **Carbon capture and storage** – carbon dioxide from fossil fuel power stations can be stored deep underground.
    b) **Sequestration** – this involves using common silicate minerals to absorb carbon dioxide as carbonate mineral.
    c) **Using carbon dioxide for new fuels** – for example, the waste gas might be bubbled through illuminated ponds containing algae, to convert some of the carbon dioxide back to biomass.

Three energy sources compared

Three energy sources	Advantages	Disadvantages
Fossil fuels	• Available • Has high energy density • Fits existing technologies	• Non-renewable • Produces chemical pollution • Emits greenhouse gases
Nuclear fission	• Extremely high energy density • Few pollutants and very little CO_2	• Non-renewable • Risks working with radioactive materials • Big costs associated with safe disposal of radioactive materials and decommissioning power stations
Biofuels	• Renewable • High energy density • Almost carbon neutral	• Limits food production • *'Monocultures'* of one fuel crop damage ecosystems

The evidence for man's impact on the environment

Here is a checklist showing some of the evidence, in recent years, linking human activity to climate change:

- Measureable rise in atmospheric concentration of carbon dioxide
- Measureable rise in global temperatures
- Melting of permafrost and ice sheets
- Less measured daylight radiation reaching the Earth's surface
- Record extreme weather events such as floods, droughts, and wild fires

Overall, changes to the climate are likely to have serious long-term effects on food production and the availability of water resources. Rising sea levels due to warming are putting coastal areas at risk around the world.

Example problems

10)

a) ***Give*** one man-made and one natural source for each of the following:

i) Carbon dioxide

ii) methane

b) ***How*** might water be responsible for both global warming and global dimming? ***Describe*** briefly the mechanism for each of these effects and explain the possible consequences to the environment.

11)

a) ***Outline*** three different ways by which the amount of greenhouse gases added to the environment might be reduced as a result of human behaviour.

b) ***Describe*** three different types of evidence that lead the majority of scientific opinion to link human activity to climate change.

Chapter 6: Electrochemistry, rechargeable batteries and fuel cells (AHL)

You should be familiar with Topics 9 and 19 of your syllabus (*Redox Chemistry*) before studying this section.

Types of cells and their properties

Practical electrochemical cells have a wide variety of different designs and applications. Although there are sometimes issues connected with the disposal of toxic materials used to make electrodes or electrolytes, they often provide an environmentally clean alternative for energy sources for transport (cars, buses etc.) or portable devices (laptops, mobile phones etc.). Batteries and fuel cells use exothermic redox reactions to produce electrical energy from chemical energy.

There are some general considerations:

1) The **voltage** of a cell depends primarily on the materials used. The biggest voltage available, the **e.m.f.**, can be deduced from the redox potentials for the half reactions occurring at each electrode, defined in topic 19 of the core syllabus. Redox potentials also depend on conditions – temperature and concentrations of chemicals. (See, '*Nernst equation*', later on.)

> ***Key terms***
>
> **Voltage** or **e.m.f. (V)** is the electrical energy changed per unit charge that has passed.

2) Any electrochemical cell has **internal resistance.** Since ions take time to diffuse through a cell, there is a limit to the **current** (flow of electric charge) through the cell and this must be the same as the electric current in the external circuit.

> ***Key terms***
>
> **Internal resistance** is the extent to which the cell limits the flow of electric charge carried by ions and electrons.
>
> **Electric Current (A)** = the flow rate of charge caused by movement of ions inside a cell
>
> = Flow rate of charge caused by movement of electrons in external circuit

3) At higher temperature ions diffuse faster, lowering the internal resistance, but also increasing the tendency for a battery to discharge its energy without being used usefully.

$$Maximum\ electric\ current\ (A) = \frac{emf\ (V)}{internal\ resistance\ (\Omega)}$$

Some of the energy output from a redox reaction is wasted as heat produced within the cell because of this internal resistance.

By increasing the surface area of electrodes the internal resistance can be reduced so larger batteries tend to both store more energy and have a lower internal resistance.

The total **work done** or energy output from an electrochemical cell depends on the quantities of chemicals as well as the nature of the materials.

$$\boldsymbol{Work\ done}\ (J) = Voltage\ (V) \times\ Current\ (A) \times Time\ (s)$$

In this chapter we contrast three types of electrochemical cell:

- **Primary cells**
  Non-reversible redox reactions. Use once and throw away or recycle the materials!
- **Rechargeable (secondary) cells**
  Reversible redox reactions. Use and recharge to use again and again!
- **Fuel cells**
  Non-reversible redox reactions. Use and refill with more fuel to use again!

Primary cells

Primary cells need to be thrown away or the materials recycled once the cells have stopped generating electricity. They are non-rechargeable for a variety of reasons. The diffusion of ions in the electrolyte might stop the reaction, the oxidation of the anode might be irreversible, or other *'side'* redox reactions might occur such as the production of gases at the electrodes.

Rechargeable (secondary) cells

When in use to supply electrical energy the battery is being *'discharged'*. You will need to be able to explain how rechargeable cells work, and be able to give half equations. In each case the redox equations for recharging the battery are the reverse of those for discharging the battery, so just learn the equation for *'discharging'* for the three examples below! A schematic diagram in each case involves labelling the two electrodes and the electrolyte.

You should be able to recall these three common types:

Nickel-cadmium cells

This is the common type of small rechargeable cell. The electrolyte is usually potassium hydroxide solution. This separates a cadmium metal anode from a nickel oxide hydroxide cathode.

During discharge:

At the anode: $Cd(s) + 2OH^-(aq) \rightarrow Cd\,(OH)_2(s) + 2e$

At the cathode: $2NiO(OH)(s) + 2\,H_2O(l) + 2e \rightarrow 2Ni(OH)_2(s) + 2OH^-(aq)$

Lithium ion cells

This is the common type of battery for a laptop. The electrolyte is an organic solvent and polymer layer through which ions can move. The negative anode is graphite combined with absorbed lithium atoms. The cathode is made of lithium cobalt dioxide. There is no water so don't write (aq) for the following reactions!

During discharge:

At the anode: $Li(s) \rightarrow Li^+ + e$

At the cathode: $Li^+ + e + CoO_2 \rightarrow LiCoO_2(s)$

Lead-acid cells

This is the common type of car battery. It is also used as a heavy-duty energy storage device with **solar cells** for example to ensure a supply of energy even when the sun isn't shining (See Chapter 8). Two plates of lead, one coated with lead (IV) oxide act as the electrodes are separated by an electrolyte of sulphuric acid.

During discharge:

At the anode: $Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq)\_ + 2e$

At the cathode: $PbO_2(s) + HSO_4\text{-}(aq) + 3H^+(aq) + 2e \rightarrow PbSO_4\ (s) + 2H_2O(l)$

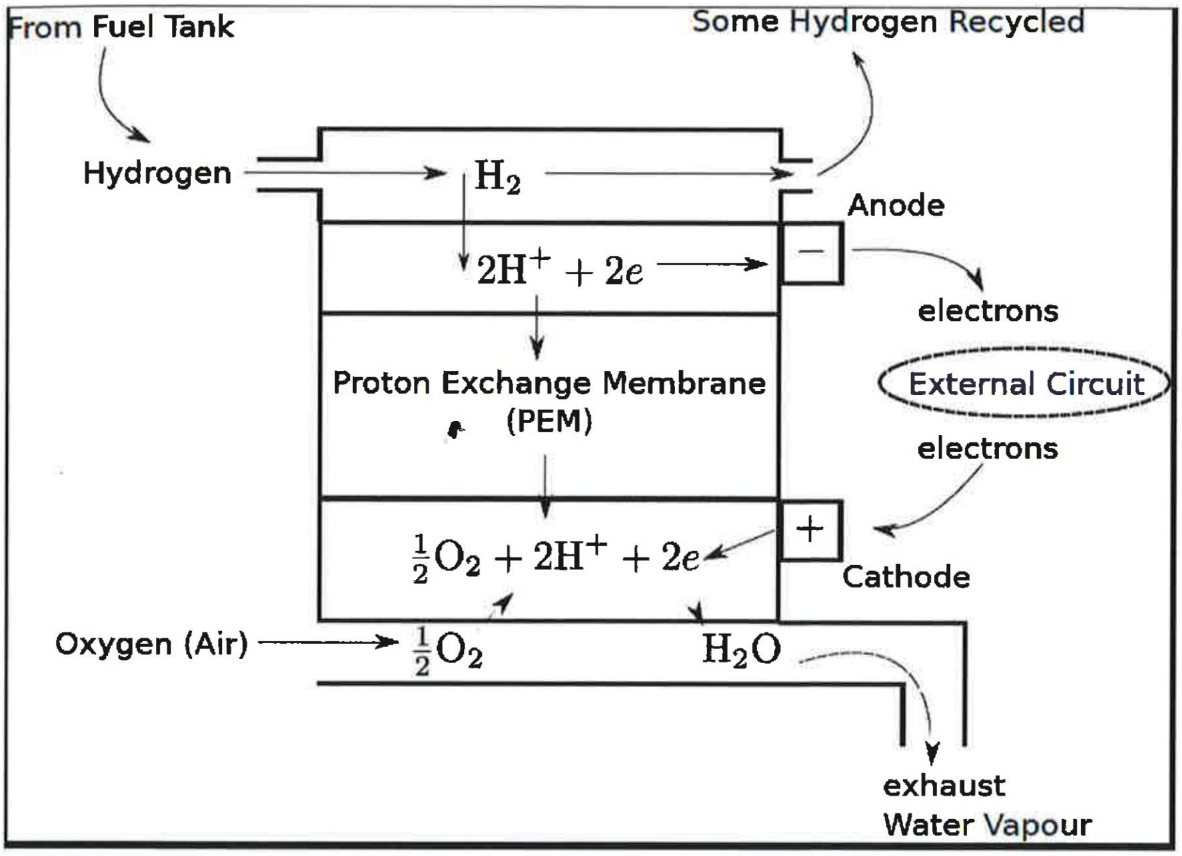
Hydrogen fuel cells

Combustion of a fuel is of course a redox reaction. In a fuel cell, instead of releasing this energy from combustion directly as heat, the reaction is separated into two half-cell reactions occurring at the two electrodes of the fuel cell. The result is the production of electrical energy as the useful product instead of heat.

By using hydrogen as the fuel in a fuel cell there is very little chemical pollution and a small carbon footprint. This is of course because water is the only product when hydrogen reacts with oxygen. Hydrogen can be obtained as a bi-product from an oil refinery, from the manufacture of '*synthesis gas;* from coal, or from the electrolysis of water. However, it is possible to use other fuels as the energy source for fuel cells, including alcohols, or quite complex molecules (see '*Microbial fuel cells*', below).

Hydrogen fuel cells differ in design. In an alkaline hydrogen fuel cell an electrolyte of potassium hydroxide solution separates the electrodes, but a phosphoric acid electrolyte or an exchange membrane are used in other designs.

Design of a hydrogen fuel cell (acid electrolyte example)



Under the acidic conditions, shown in the diagram, the water is produced at the cathode and hydrogen ions at the anode:

At the anode: $H_2(g) \rightarrow 2H^+(aq) + 2e$

At the cathode: $O_2(g) + 4H^+(aq) + 4e \rightarrow 2H_2O(l)$

Under alkaline conditions:

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

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

Hydrogen passes over an inert electrode, and is oxidised, producing an exhaust of water. Oxygen (or air in some designs) passes over an inert cathode to be reduced to hydroxide ions.

Microbial fuel cell

Microbial fuel cells enable organic wastes to be used as fuel in a fuel cell. Anaerobic bacteria release energy from organic molecules such as glucose without the presence of oxygen. Since the overall reaction is a redox reaction it is possible to separate the complete oxidation of glucose into two half cells with bacteria catalytically and anaerobically oxidising the glucose solution at the anode.

In the presence of anaerobic (Geobacter) bacteria, with glucose used as this example of one of the organic waste molecules:

At the anode: $6H_2O(aq) + C_6H_{12}O_6(aq) \rightarrow 24H^+(aq) + 6CO_2(g) + 24e$

A flow of air or other oxidant:

At the cathode: $O_2(g) + 4H^+(aq) + 4e \rightarrow 2H_2O(l)$

Thermodynamic efficiency of fuel cells

Fuel cells provide, potentially, a very efficient means of harnessing chemical energy.

The biggest efficiency that can be made, called the cell's **thermodynamic efficiency**, is typically 90%-95% for a fuel cell, and is given by the ratio of the free energy change of the overall chemical reaction to the enthalpy change for the overall chemical reaction. *'Topic 5'* explains how to calculate enthalpy changes for reactions and *'Topic 15'* explains how to calculate free energy changes.

$$\boxed{\textit{Thermodynamic Efficiency} = \frac{\textit{Free Energy Change}}{\textit{Enthalpy Change}} = \frac{\Delta G}{\Delta H}}$$

Since **$\Delta G = \Delta H - T\,\Delta S$**, for reactions where the entropy change (ΔS) for a reaction is close to zero, this efficiency will approach 100%.

However, due to internal resistance of the cell, the output voltage is always lower than the value predicted from redox potentials alone. This lowers the energy available to do work in the external circuit to between (typically) 50% and 70% of that supplied by the fuel overall.

Nernst equation

We normally calculate enthalpy changes, free energy changes, and thermodynamic efficiency under standard thermodynamic conditions. Cell potentials are also defined at the same conditions of 298 K, 100 kPa pressure for gases, and 1 moldm^{-3} concentrations for solutions. However, with different conditions the potential of a cell will be different.

In general it is possible to apply a correction to calculate the cell potential when the conditions are not standard thermodynamic conditions. The **Nernst equation** is what we use to work this out.

The **Nernst equation:** $E = E° - \left(\frac{RT}{nF}\right) log_e Q$

E = cell potential

$E°$ = standard conditions cell potential

R = Universal Gas Constant (data booklet);

T = thermodynamic temperature in kelvins;

F = the Faraday constant (data booklet);

n = the number of moles of electrons transferred per mole of ions.

Q = the ratio of the concentration of the ions being oxidised divided by the concentration of the ions being reduced.

Concentration cell

One consequence of the Nernst equation is that by simply having different concentrations of ions in two half cells, but the same electrodes and electrolytes in both half cells, a small potential will be generated. This is called a **concentration cell.**

Imagine, for example, the situation where an iron rod is immersed in seawater. Due to slightly differing concentrations of oxygen and iron ions dissolved in different spots of sea water on the iron's surface small cells are set up, causing the iron to rust rapidly since parts of the iron will become anodes and other parts cathodes.

In another example, suppose a cell is made up at 298 K of two half cells, each with copper immersed in copper sulphate solution. If one solution has twice the concentration of the other, what will the cell potential be?

Clearly, the standard cell potential is 0 volts since the electrodes and electrolytes are identical. Q, the concentration ratio = 2, and n=2 electrons per copper ion, since:

At the cathode: $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$

At the anode: $Cu(s) \rightarrow Cu^{2+}a(aq) + 2e$

Actual cell potential: $E = \mathbf{E°} - (RT/nF) \log_e Q$

$= 0 - (8.31 \times 298 / 2 \times 96{,}500) \log_e 2 = 0.0089$ volts

This shows that this is a small effect and concentration cells will in general have very low cell potentials.

Summary comparison of types of cell

Type	Voltage per cell/ V	Energy/ mass	Environment	Other factors
Lithium ion cell	4.2	High	Rechargeable Materials non-polluting	Hazard of overheating
Lead acid cell	2.1	High	Rechargeable	Liquid electrolyte and heavy
Nickel cadmium cell	1.2	Moderate	Rechargeable Cadmium is highly toxic	Can be made very small and compact
Hydrogen fuel cell	0.7	High	Refuel-able Minimal pollution in use	Needs substantial new infrastructure if used for transportation

Example problems

12) The enthalpy of combustion of methanol is given in your data book. The free energy change of combustion of methanol under certain conditions is found to be -690kJmol^{-1}. If methanol is to be used as the fuel in a fuel cell, calculate the maximum thermodynamic efficiency. ***Explain*** why the efficiency is less than this in practice.

13) A primary cell is composed of a copper electrode immersed in copper sulphate and a zinc electrode in a solution of zinc sulphate. The cell is at 15°C and the concentration of the zinc ions are 2.0 moldm^{-3}, while the copper ions are 1.0 moldm^{-3}. ***Determine*** the e.m.f. of this cell under these conditions.

Chapter 7: Nuclear fusion and nuclear fission (AHL)

Energy from fusion and fission: more advanced calculations

As we saw in Chapter 3 there is energy released in both nuclear fusion and nuclear fission and we now look at a more advanced problem using the concepts of **mass defect** and **binding energy**, linked to Einstein's equation already discussed: $\Delta E = \Delta m\, c^2$

> ***Key terms***
>
> **Mass defect** of a nucleus is the difference between the mass of the nucleus and the sum of the masses of its individual protons and neutrons.
> **Binding energy** is the energy required to separate a nucleus into protons and neutrons. (A binding energy curve is given in the data booklet and in Chapter 3.)

Example problem

14)

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

The masses are $^{1}_{1}H$ = 1.007825 u , $^{3}_{2}He$= 3.016030 u , $^{2}_{1}H$= 2.014102 u
(1 atomic mass unit (u) or (amu) = 1.661×10^{-27} kg ; speed of light, c = 2.998×10^{8} ms^{-1})

a) ***Explain*** why the mass decreases in this nuclear reaction

b) ***Calculate*** the energy released when 3 grams of Helium-3 atoms are produced in this way.

c) Use the binding energy curve data below to ***determine*** the energy released when 3 grams of U-235 is converted into Ba-143 and Kr-90 by nuclear fission.

Binding energy per nucleon read from graph (values are approximate)

U-235 is	7.6 MeV	Kr-90 is	8.6 MeV
Ba-143 is	8.3 MeV	(Use: 1 MeV = 1.6×10^{-13} J)	

d) ***Comment*** on your answers to (b) and (c).

Radioactive decay: more advanced problems

We had a first look at radioactive decay in Chapter 3. We need to look at this more mathematically and compare with the mathematics and graphs of first order chemical reactions, covered in HL topic 16. In your data book there are two equations to use:

$\boldsymbol{\lambda = \log_e 2 / t_{1/2}}$

$\boldsymbol{N = N_o e^{-\lambda t}}$

In these equations, λ is the **decay constant,** $t_{1/2}$ is the half-life of the radioactive isotope. N_o is the initial number of un-decayed nuclei in the sample and **N** is the number remaining after time **t**. Note that **N, N_o** could also represent final and initial masses or even activities – they all decay in the same way exponentially with the same decay constant. These equations follow mathematically from the rate of decay being proportional to the number of nuclei remaining.

Example problem

15) The intensity of radiation given out by a radioisotope falls from 1,600 units to 100 units in 24 years. There is initially 0.001 mol of the isotope.

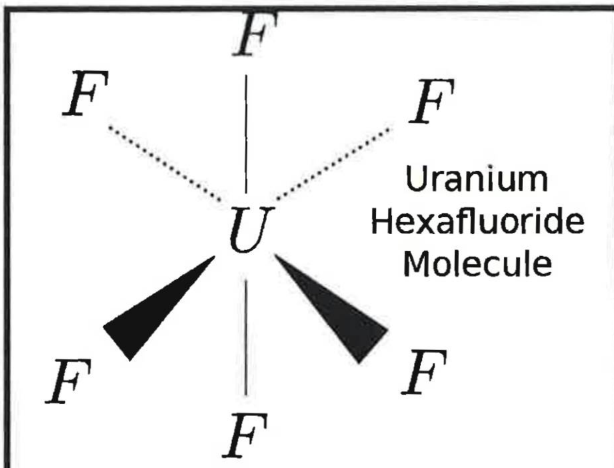
a) ***What*** fraction of the original isotope has decayed in 24 years?

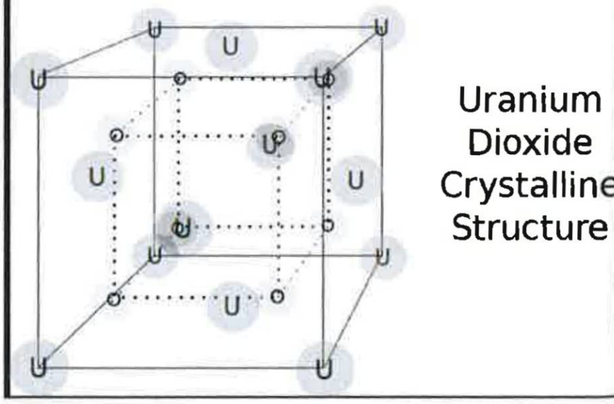
b) ***What*** is the half-life?

c) ***What*** intensity would be expected after 25 years and ***how many*** moles of the original isotope remain at this time?

Radiation produced by the radioactive fuels and waste products of nuclear energy are dangerous due to the ionizing nature of the radiation as previously mentioned. At Higher Level you need to refer specifically to the production of '*hydroxyl radicals*', H-O, and '*superoxide*' radicals, O_2^-. As with other free radical mechanism (such as when halogens reactant with alkanes in sunlight for example), a relatively small number of free radicals can initiate a chain reaction of collisions between radicals and biochemical molecules. This can involve DNA or enzymes, causing damage to living cells, and potentially malignant cancers.

Fuel enrichment and Graham's Law





Uranium dioxide (UO_2) is used in fuel rods in reactors. To produce uranium dioxide from naturally occurring uranium minerals involves a complex process of physical and chemical processing steps. Most importantly, for the fuel rods to be able to attain '*critical mass*' in a reactor the concentration of the fissionable U-235 needs to be increased since naturally occurring uranium is mainly the isotope U-238.

Uranium dioxide is a crystalline solid with a very high melting point – this high melting point is useful since the reactor core becomes extremely hot during operation. However, in order to separate the isotopes of uranium a volatile compound of uranium needs to be used. Uranium hexafluoride (UF_6) is that volatile compound. It is composed of octahedral molecules. It turns from a solid into a gas at 56°C at atmospheric pressure so can easily become free moving molecules. This is the key to separating the naturally occurring isotopes, using the fact that molecules containing the different isotopes have different masses. In addition, fluorine only exists as the fluorine-19 isotope – any difference between the masses of different uranium hexafluoride molecules is only due to the different uranium isotopes present in the sample.

There are two physical separation methods used to concentrate the amount of U-235. They are called **centrifugation** and **gaseous diffusion**.

- In **centrifugation** the uranium hexafluoride enters a rapidly rotating cylinder in a vacuum. A bigger proportion of heavier molecules move to the fast moving end of the cylinder where they are removed. By repeating the process an increasing proportion of U-235 containing molecules can be produced until the desired percentage is reached for manufacturing the fuel rods.
- In **gaseous diffusion** the uranium hexafluoride enters a container with slightly porous walls. The lighter molecules move faster on average at a particular temperature. This is because the kinetic theory says that the temperature of a gas is proportional to its average molecular kinetic energy. Kinetic energy depends on both mass and velocity. When the lighter molecules hit the porous walls they are therefore more likely to pass through the small holes in the porous material.

Effusion is the name given to the way that a gas passes through a small hole and because of kinetic theory, the rate at which this occurs depends on mass, in a mathematical way given by **Graham's Law**.

Graham's Law says that:

$$\frac{Rate\ of\ effusion\ of\ molecule\ 1}{Rate\ of\ effusion\ of\ molecule\ 2} = \sqrt[2]{\frac{M_2}{M_1}}$$

In this formula M_1 and M_2 are the molar masses of the two different molecules being compared.

Example problem

16) ***How many*** times faster does a molecule of UF_6 effuse if it contains U-235 compared to a molecule containing U-238? ***Suggest why*** fuel enrichment is an expensive process.

Chapter 8: Photovoltaic cells and dye-sensitized solar cells (AHL)

This section is about how to directly convert solar energy into electrical energy. It builds on ideas from both Chapter 4 and Chapter 6.

Semiconductors

When you studied bonding you discovered that electrical conductivity of metals arose from the ease of movement of delocalised electrons. For insulating solid elements (such as a diamond) there are no delocalised electrons since all valence shell electrons are associated with particular atoms or localised to a pair of atoms in a covalent bond. You are probably not surprised to learn that elements between metals and non-metals in the periodic table can have a semiconducting property due to an intermediate nature between metallic and covalent bonding. Metal atoms have a lower first ionisation energy than semiconductor atoms, so valence electrons are mostly localised in semiconductors and mostly delocalised in metals.

Silicon for example exists as a diamond-like macromolecular structure. However, a few of the valence shell electrons in a silicon crystal at a given temperature are delocalised, available to freely conduct electricity. In addition, where these delocalised electrons have left a gap in the covalent structure we have a **hole** that can freely move through the crystal lattice, behaving like the movement of a positive charge (of the same size as the charge on an electron)!

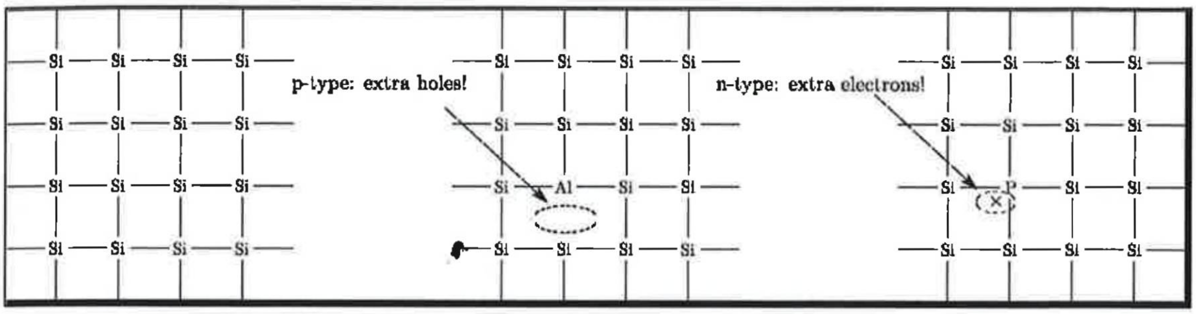
> ***Key terms***
>
> A **hole** is a gap (missing electron) in a covalent lattice that can move through the semiconductor, behaving like a moving positive charge.

Pure semiconductor materials (called *'intrinsic'* semiconductors) are fairly poor conductors of electricity. The conductivity increases a little as the temperature rises because at higher temperature more electrons and holes are available for conduction. (For a metal the electrical resistance increases with increasing temperature, but even at high temperatures metals are much better conductors than semiconductors.) By adding small quantities of a Group 3 element (e.g. aluminium) or Group 5 element (e.g. phosphorus) to the crystal lattice of a semiconductor more holes or electrons are made available for conduction respectively. This is called *'doping'*.

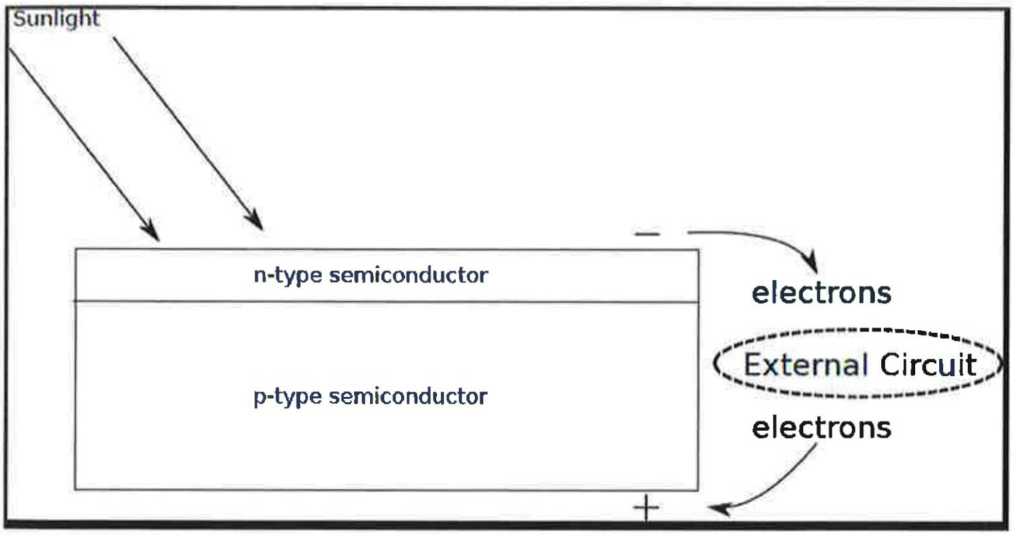
With an occasional aluminium atom (for example) in place of a silicon atom in the lattice there is a missing electron for bonding in that location since aluminium atoms only have 3 electrons in their valence shells. These *'doped'* semiconductors are called **p-type** (p for positive) since they conduct mainly because of the movement of positively charged holes through the lattice.

With an occasional phosphorus atom (for example) in place of a silicon atom there is an extra electron available for bonding in that location since phosphorus atoms have 5 electrons in their valence shells. These doped semiconductors are called **n-type** (n for negative) since they mainly conduct because of delocalised electrons.

> ***Key terms***
>
> **p-type** is a semiconductor that conducts mainly by the movement of holes.
> **n-type** is a semiconductor that conducts mainly by the movement of electrons.



Silicon solar cell ('photovoltaic cell')

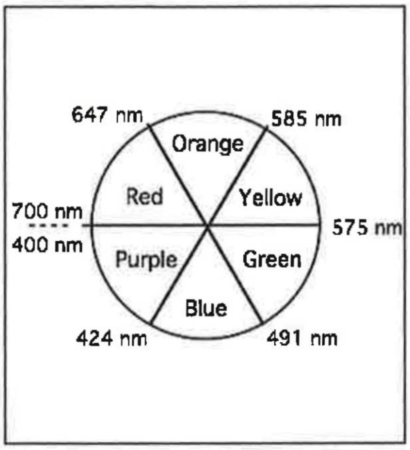


The combination of a thin layer of **n-type** silicon on top of a layer of **p-type** silicon works as a solar cell. At the boundary between the two semiconducting layers a few electrons from the n-type material *'fall'* into the valence shell holes on the p-type side. This creates an electric field inside the cell, at the boundary, preventing more electrons from moving through the silicon into the p-side (and preventing holes from moving the other way). Light photons are absorbed by the solar cell on the free surface of the n-type material (see diagram above). This energy promotes some electrons from the '*valence band*' energy levels to the higher energy '*conduction band*'. There is then a movement of electrons and holes in opposite directions across the p-n boundary as a result, separating positive and negative charges across the cell while the light is shining. This provides the voltage (e.m.f.) that drives electrons around the external circuit connected to the solar cell. Electrons flow from the n-type side to the p-type side in the circuit connected to the photovoltaic cell. In this way solar energy is converted to electricity.

Dye-sensitized solar cells

Dye-sensitized solar cells (DSSCs) imitate the way in which plants harness solar energy using dye molecules with an **extended conjugated electronic structure** (see Chapter 4). At Higher Level we can understand this in terms of pi electrons being delocalized across the length of the conjugated structure in the same way that pi electrons are delocalised around a benzene ring.

As the number of alternating pairs of single and double bonds increases so the maximum wavelength of photon that can be absorbed by the dye molecule increases, because the energy difference between an excited state and ground state of the molecule gets less. An organic dye molecule that absorbs a narrow range of visible colours in the visible spectrum will *'reflect'* light of other wavelengths. It is of course the reflected colour that we see and due to the way that the eye detects and the brain perceives colour we will see a colour that is complimentary to the colour that is absorbed by the molecule. This is the colour opposite to the absorbed colour on the *'colour wheel'*. The colour wheel is in the IB Data Book.



For example, if the molecule absorbs yellow light of wavelength 580 nm, the colour wheel above shows that it will actually appear purple, the colour opposite on the wheel.

In a DSSC a glass sheet is coated with titanium (IV) oxide **nanoparticles**. Nanoparticles are extremely small so have a very large surface area to volume ratio. These nanoparticles are covered with covalently bonded dye molecules. The high surface area of the nanoparticles means that a lot of light is able to reach the light sensitive dye molecules.

> ***Key term***
>
> A **nanoparticle** is a particle which is less than 100 nm across. Typically a nanoparticle is less than a few hundred atoms across.

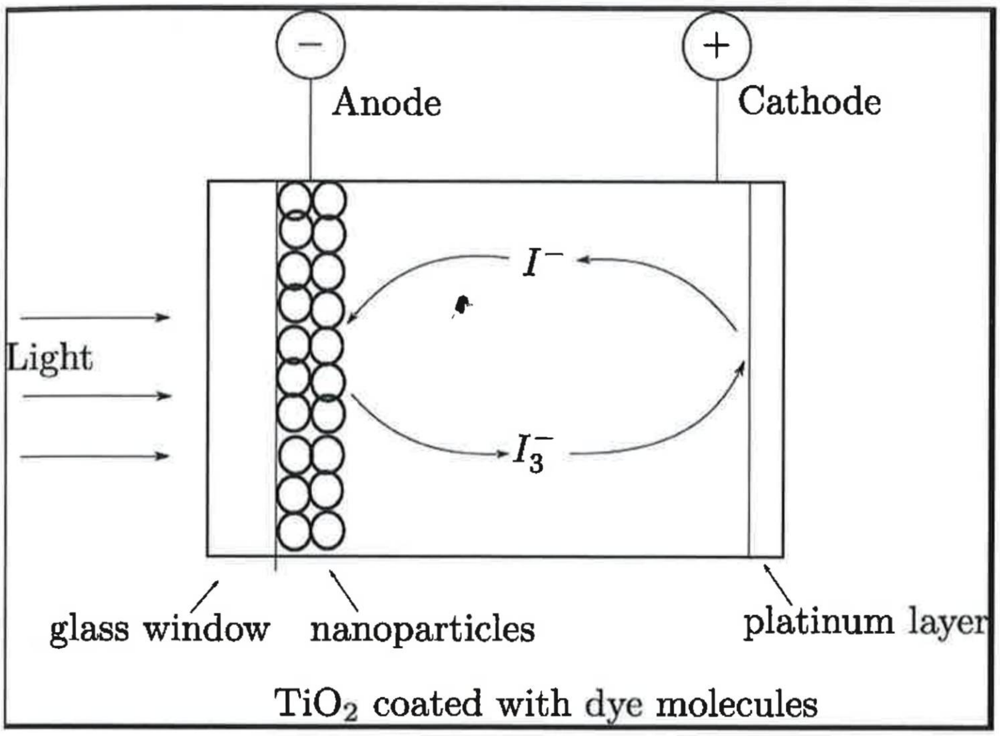
The titanium (IV) oxide (TiO_2) works as the anode in the cell. It has semiconductor properties, receiving the energetic electrons from the excited dye molecules. In the **Grätzel DSSC** an electrolyte contains iodide ions so that as electrons are lost at the anode they reduce tri-iodide ions back to iodide at the platinum cathode.

Overall redox half-equations for the Grätzel DSSC:

Anode equation: $3I^- \rightarrow I_3^- + 2e$

Cathode equation: $I_3^- + 2e \rightarrow 3I^-$

In a photovoltaic cell (silicon solar cell) the light is absorbed and the charges separated in the silicon semi-conductor. The processes of absorption and charge separation are separated in a dye-sensitized solar cell.



Research and development of DSSCs has developed rapidly over the past thirty years with the evolution of more efficient designs incorporating new dye molecules but they have a number of clear advantages and disadvantages when compared to silicon solar cells at present.

Comparing dye-sensitized solar cells with silicon solar cells

Advantages

- DSSCs work in lower light intensity than silicon solar cells. They work in cloudy conditions and might also work inside homes.
- The high surface area provided by the nanoparticles means that a lot more light is collected on a smaller electrode area when compared to silicon cells.

Disadvantages

- Silicon solar cells are entirely solid state whereas DSSCs have a liquid electrolyte. The liquid electrolyte might freeze in very low temperatures or expand too much in hot weather.
- The materials such as platinum and the dyes used are expensive despite the fact that manufacturing techniques are simple and cheap.

Despite the disadvantages it has been predicted that DSSCs will be able to compete with other renewable sources for generating electricity in the future.

Example problems

17) Dye-sensitized solar cells to some extent mimic the action of photosynthesis in green plants.

- **a)** ***Describe*** how light is absorbed by the dyes used and how this energy is converted into electrical energy in this type of solar cell
- **b)** Dye-sensitized solar cells are able to work in low light intensity. ***Explain*** how.

18) Semiconductor materials have enabled cells to be constructed which convert solar energy directly into electricity.

- **a)** ***Explain*** how silicon conducts electricity and how the addition of a few gallium or arsenic atoms to the silicon crystal lattice affects how it conducts.
- **b)** ***Describe*** briefly the structure of a silicon solar cell.

Chapter 9: General revision problems on Option C (examination style)

You need to be familiar with the IB ***command terms***. They are in one of the appendices of your IB chemistry syllabus guide and relate directly to the objectives on your IB syllabus, helping to tell you how much detail is required in giving an answer. When you try the following questions, please pay careful attention to the command terms in ***italicised bold type!***

19) In Britain it was recently announced that a large state-owned museum situated on the coast of Wales is having its old oil-fired heating system replaced with a large electrically operated '*heat pump*'. The heat pump will take warm water from the Irish Sea in pipes and use it to supply under floor heating to the museum galleries. A heat pump of this type is able to use a joule of electrical energy to supply up to three joules of heat energy to the museum.

- **a)** ***Explain*** why this does not conflict with the idea that energy is conserved.
- **b)** The heating oil that is currently used is produced in a refinery from crude oil. It is a type of heavy kerosene with a density of 0.81 gcm^{-3} and specific energy of 43 $MJkg^{-1}$. The kerosene consists mostly of alkanes with about 15 carbon atoms per molecule. Its use as a heat source for the museum is nearly 100% efficient.
  - **i)** ***Outline*** why the energy source has such a high efficiency in this situation.
  - **ii)** ***Calculate*** the energy density for this fuel.
  - **iii)** ***Determine*** the mass of carbon dioxide produced when 100 m^3 of this fuel oil are completely burnt.
  - **iv)** ***Suggest*** and ***explain*** one method that could be used to reduce the carbon emissions into the atmosphere when burning kerosene as heating oil.
- **c)** The use of a heat pump to replace the heating oil may or may not be nearly 'carbon neutral'. ***Outline*** what 'carbon footprint' and 'carbon neutral' mean and ***comment*** on what needs to be considered when assessing the carbon emissions of a heat pump of this type.

20) In Brazil ethanol from sugarcane is blended with gasoline (petrol) as the fuel for motor vehicles. At present 25% ethanol is combined with 75% gasoline by volume.

- **a)** ***Describe*** with an equation how ethanol is produced from sugarcane.
- **b)** ***State*** one environmental advantage and one environmental disadvantage of using ethanol as a fuel additive for motor vehicles.
- **c)** Gasoline is obtained as a valuable product from an oil refinery. ***Outline*** three processes involved in producing a high yield of good quality gasoline from an oil refinery.
- **d)** Ordinary gasoline engines need to be redesigned to run on this ethanol blend. This is partly because ethanol has a much lower boiling point than gasoline. ***Explain*** why ethanol has a lower boiling point.
- **e)** ***Explain*** whether you would expect the ethanol-gasoline blend to have a higher or lower specific energy than pure gasoline.

21) India generates about 3% of its electrical energy from nuclear power stations. In one new reactor design uranium-233, derived from thorium, is used as the fuel. This is being developed since India has naturally occurring thorium minerals, avoiding the need to import uranium.

a)

i) ***State*** an equation to show what happens when a uranium-233 nucleus captures a neutron, before any fission occurs.

ii) ***Describe*** how a chain reaction occurs by nuclear fission.

iii) ***Define*** *'critical mass'*.

b) Uranium-233 has a half-life of 160,000 years.

i) ***Calculate*** the fraction of uranium-233 will have decayed after 480,000 years, assuming no fission is occurring.

ii) Periodically fuel rods need to be replaced or a reactor comes to the end of it useful life. ***Describe*** one method by which highly radioactive nuclear waste with long half-life can be safely disposed of.

c) In the future nuclear fusion reactors may be a possible source of energy. ***Explain*** why the development of this type of nuclear energy has been difficult and ***state*** two advantages nuclear fusion is likely to have over nuclear fission.

22) Fuel cells are becoming increasingly important for increasingly diverse energy applications. (HL only)

a)

i) Bacteria of the genus *Geobacter* might be used in a microbial fuel cell to extract energy from organic molecules and ions in domestic food waste or waste water. ***State*** the anode equation for this reaction, using ethanoate ions in your example.

ii) Coal, natural gas, and biomass can all be used to produce methanol, used by one type of proton exchange fuel cell. ***State*** the anode equation for this fuel cell under alkaline conditions.

iii) ***Explain*** one environmental advantage of using hydrogen in a fuel cell used for transportation instead of organic molecules.

b) Fuel cells, silicon solar cells, and lithium ion cells might all be used to provide electricity to portable electronic devices. ***Compare*** in general terms, one advantage and one disadvantage of each power source in this situation.

Chapter 10: Answers to example problems

In this final chapter I have provided all of the numerical answers with explanations, and some suggestions for how to approach your answers to other types of questions.

Chapter 1

1)

a) Specific energy = Energy per mole / mass per mole
Hexane is 86.2 $gmol^{-1}$
Methanol is 32.0 $gmol^{-1}$

For hexane: Specific energy = 4,163 / 86.2 = 48.3 kJg^{-1}

For methanol: Specific energy = 726 / 32.0 = 22.7 kJg^{-1}

b) Energy density = Energy per unit mass x density

For hexane: Energy density = 48.3 x 0.655 = 31.6 $kJcm$-^{3}

For methanol@ Energy density = 22.7 x 0.792 = 18.0 $kJcm^{-3}$

c) Hexane would be the best choice.

Possible explanations, give **only one**:

- Since the rocket needs to lift itself and its fuel, the hexane supplies the most energy for its weight
- The hexane fuel tank will take up less space to provide a given amount of energy for the journey.

d) State your two factors clearly. **Don't give more than two!**

Two of the following:

- Fuel releases energy quickly enough but not explosively
- Fuel makes the least pollution when burnt
- Fuel is renewable or won't run out more quickly
- Fuel can be made to transfer the energy from combustion most efficiently

2)

a) $$\boldsymbol{SPECIFIC\ ENERGY} = \frac{Energy\ released\ from\ fuel}{Mass\ of\ fuel\ used}$$

$$\boldsymbol{Efficiency\ of\ Energy\ Transfer} = \left(\frac{Useful\ Output\ Energy}{Total\ Input\ Energy}\right) \times\ 100\%$$

b) Total input energy = (100/30) x 4,000 = 13,000 MJ each second

Mass of coal needed each second = 13,000 / 24 = 560 kg

Chapter 2

3) First write a balanced equation for the complete combustion of each fuel:

$2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$

$2CH_3OH + 3O_2$ □ $2CO_2 + 4H_2O$

Notice that butane produces 4 times as much carbon dioxide per mole of fuel. Each mole of butane produces 4 moles of carbon dioxide. We need to compare the amount of carbon dioxide per kilojoule of energy produced.

For butane this is 4 /2,877 = 0.00139 $molkJ^{-1}$

For methanol this is 1/726 = 0.00138 $molkJ^{-1}$

The carbon footprints are therefore almost identical! The assumptions that need to be made include complete combustion and 100% efficiency of energy transfer in both cases. In addition, the manufacture of each fuel has an unknown carbon footprint!

4)

a) '*Octane number*' is a measure of how much a fuel resists the tendency to self-ignite ('*anti-knocking*' tendency). It is measured in a test engine with 100 being equivalent to a fuel of pure isooctane and 0 equivalent to pure heptane.

b) Despite iso-octane having a higher molecular mass, it is heavily branched so that molecules have less surface area in contact with each other. This means that Van der Waals bonding is similar for the two molecules.

c) Cracking produces shorter C7-C8 length molecules from longer molecules. Reforming produces molecules that are more branched chain, cyclic molecules, and benzenes, all of which have a higher octane number. Give example equations as in the notes above.

5) Coal is heated at high temperature with alternate blasts of steam and air until it is converted to syngas:

$C + H_2O \rightarrow CO + H_2$

Syngas is then passed over a cobalt/ iron catalyst, producing a mixture of synthetic liquid fuel which can be separated by fractional distillation –

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

Chapter 3

6) First, you should know that a neutron has one mass unit and no charge. This enables you to balance the mass on the top line of the equation.

$^{239}Pu + {}^{1}n \rightarrow {}^{100}Mo + {}^{134}X + 6\,{}^{1}n$

239 + 1 – 134 – 6 = 100

Next you should balance the charge (atomic number) on the bottom line, using the periodic table to look up the atomic numbers you need.

Useful tip: *Don't* use the periodic table to look up mass numbers since this depends on the isotope!

$$^{239}_{94}Pu + {}^{1}_{0}n \rightarrow {}^{100}_{42}Mo + {}^{134}_{52}X + 6{}^{1}_{0}n$$

This gives you the atomic number of the unknown element X, which is therefore Tellurium (Te).

$$^{239}_{94}\mathrm{Pu} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{100}_{42}\mathrm{Mo} + {}^{134}_{52}\mathrm{Te} + 6{}^{1}_{0}\mathrm{n}$$

7) The half-life is not only the time for the activity to halve but is also the time for the amount of radioisotope to halve.

Number of half-lives = 32/8 = 4 half-lives.

Initial mass = 0.0024 grams which we need to halve four times.
0.0012, 0.0006, 0.0003, 0.00015

So the answer = 0.00015 grams

Mathematically it is a little more elegant to show this as:
0.0024 grams x $(0.5)^4$ = 0.00015 grams

Useful tip: It is also possible to use formulae from the data booklet to solve these problems. You would need to use the formulae if the time is not a whole number of half-lives. Here is the method:

First find the decay constant: $\lambda = \log_e 2 / t_{1/2} = 0.0866\ \text{days}^{-1}$

Then use $N = N_0 e^{-\lambda t} = 0.0024 \times e^{-0.0866 \times 32}$

Since the half-life is in days you only need to use this formula with t=32 days and N_0= 0.0024 grams.

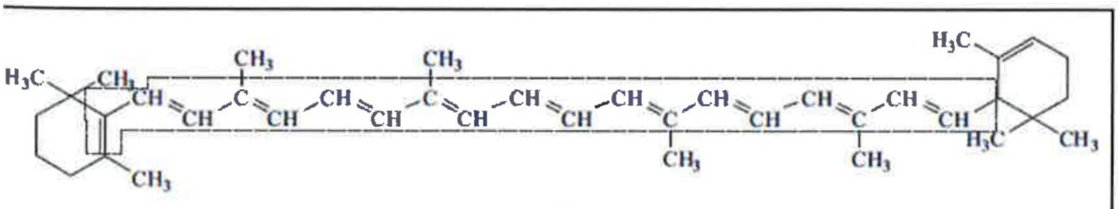
On your calculator you will again get the same answer, 0.00015 grams.

At HL we will need to use the formulae for more advanced problems.

Chapter 4

8)

a)



α-carotene

TAKE CARE! You need to circle most of the molecule, but not including the ring on the right or the left side of the ring on the left, or any of the methyl side chains. i.e. Just circle the long chain of alternating double and single bonds.

b) The long conjugated series of double and single bonds absorbs light energy in the visible part of the spectrum, forming an alternative, higher energy structure for the molecule. This energy is released to provide the activation energy for the chemical reaction and the coloured molecule returns to its original low energy state.

9) Trans-esterification is involved. Break off the carboxyl chains and attach them to methyl groups from the methanol. In this example we will get the three different methyl esters from the triglyceride oil:

- $CH_3COO(CH_2)_{10}CH_3$
- $CH_3COO(CH_2)_7CH=CH(CH_2)_7CH_3$
- $CH_3COO(CH_2)_{12}CH_3$

Chapter 5

10)

a)

i) *'man-made'*: e.g. burning fossil fuels

'natural': e.g. respiration

ii) *'man-made'*: e.g. cultivating rice

'natural': e.g. anaerobic respiration in swamps and marshes

b) Water is a greenhouse gas in the form of atmospheric water vapour. Water vapour molecules absorb photons of particular infrared frequencies that have been radiated by the Earth. They do this strongly because when water molecules vibrate they have a changing dipole moment. The molecules re-radiate part of this infrared energy back to the Earth when they de-excite. Hence water contributes to global warming. However, *'condensed'* water droplets in clouds reflect sunlight back into space causing dimming. As the average temperature of the Earth's surface rises an increase in water in the atmosphere will reduce the difference between average daytime and night-time temperatures.

11)

a) Replace fossil fuels with alternatives (give specific example:

- use less fossil fuel (e.g. more public and less private transportation)
- plant trees (or reduce deforestation)
- introduce systems that absorb or use carbon dioxide from chimneys (give specific example such as carbon sequestration).

Useful tip: Make your three examples as different from each other as possible and make it clear how the method reduces the amount of carbon dioxide being added to the atmosphere.

b) Refer to :

- measurement made over many years of increasing average temperatures
- average carbon dioxide concentration in atmosphere rising
- reduction in thickness of ice sheets
- other

State that this can be explained by the human activities of burning fossil fuels and deforestation adding carbon dioxide to the atmosphere.

Chapter 6

12) From the data book the enthalpy of combustion of methanol under standard conditions is -726 $kJmol^{-1}$.

Maximum efficiency = $\Delta G_{comb} / \Delta H_{comb}$ = (-690) / (-726) = 95%

The efficiency is much less since energy will be dissipated inside the cell because of the cell's internal resistance.

13) Use the standard electrode potentials:

for Zn^{2+}/Zn as -0.76 V and Cu^{2+}/Cu as +0.34 V.

Under standard conditions, E^o = +76V + 0.34 V = 1.10 V.

This means that the zinc ions are being oxidised.

Using the Nernst equation:

$E = E° - (RT/nF) \log_e Q = 1.10 - (8.31 \times 288 / 2 \times 96{,}500) \log_e 2 = 1.09$ V

Chapter 7

14)

a) The reduction in rest mass is equivalent to a release of energy when the nuclei fuse together.

b) Reduction in mass =

1.007825 + 2.014102 – 3.016030 = 0.005897 u

= 9.795×10^{-30} kg

Energy released from one fusion =

$\mathbf{\Delta m\ c^2}$

= $9.795 \times 10^{-30} \times (2.998 \times 10^{8})^2$

= 8.804×10^{-13} J

Mulitply by Avogadro's number to find the energy per mole. (3 grams of He-3)

= $8.804 \times 10^{-13} \times 6.022 \times 10^{23}$

= 5.30×10^{11} J

c) Total increase in binding energy

= (143 x 8.3) + (90 x 8.6) – (235 x 7.6)

= 175 MeV = 2.80×10^{-11} J

(for the fission of one U-235 nucleus)

For 3 grams of U-235, energy released by fission

= Avogado's number x Number of moles x energy released

= $6.022 \times 10^{23} \times (3/235) \times 2.80 \times 10^{-11} = 2.15 \times 10^{11}$ J

d) Per gram of nuclear fuel, nuclear fusion releases more energy than nuclear fission in this example.

15)

a) Since 1/16 remains there must have been 15/16 decayed.

b) Since the intensity has halved 4 times in 24 years, the half-life is 24/4 = 6 years.

c) This is not a whole amount of half-lives so we need to use the equations from the data book:

$\lambda = \log_e 2 / t_{1/2} = 0.6931 / 6 = 0.1155$ years^{-1}

Intensity = $N_o e^{-\lambda t} = 1{,}600\ e^{-(0.1155 \times 25)} = 89$ units

Moles remaining = $(89/1{,}600) \times 0.001 = 5.6 \times 10^{-5}$ mol

16) The uranium hexafluoride molecules containing U-238 have a molar mass = 238.05 + (6 x 19.00) = 352.05 $gmol^{-1}$

Those containing U-235 have a molar mass of:
235.04 + (6 x 19.00) = 349.04 $gmol^{-1}$

Using Graham's Law:
$\sqrt{(352.05/349.04)} = 1.004$

The molecules containing U-235 therefore effuse 1.004 times faster.

Since the molecules have a very similar mass, separation of isotopes is not very efficient and requires many repeated stages of separation by either gaseous diffusion or centrifugation in order to enrich the nuclear fuel sufficiently. In addition, for use as nuclear fuel the enriched uranium in the form of uranium hexafluoride needs to be chemically converted to the high melting point uranium dioxide.

Chapter 8

17)

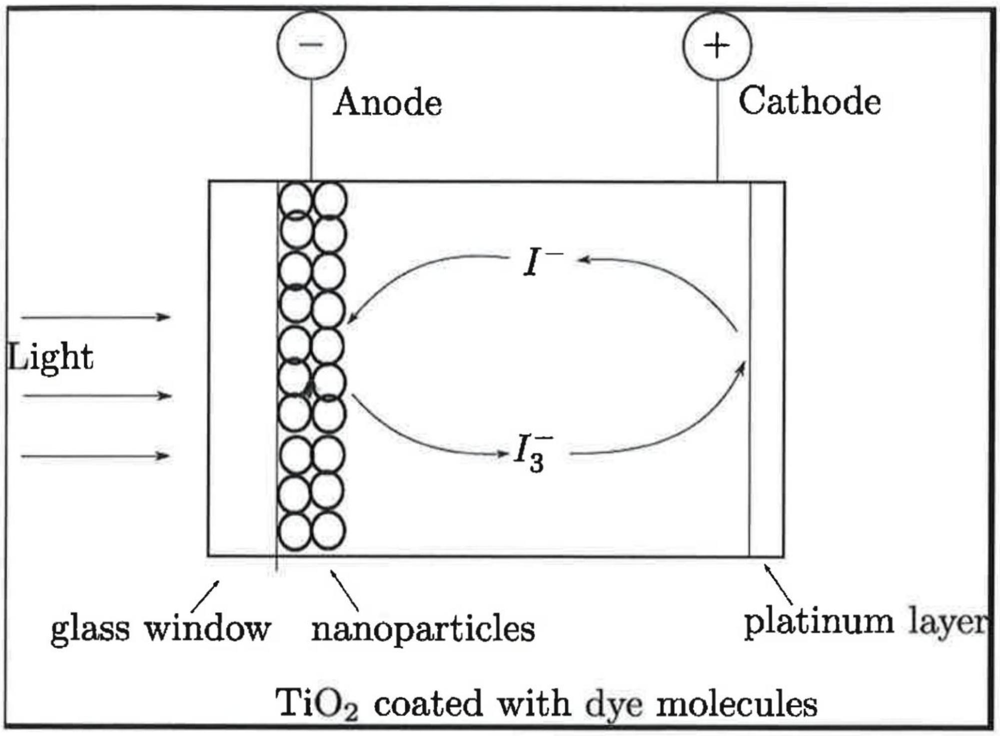
a) A dye molecule contains an extended conjugated structure of alternating double and single bonds which absorbs visible light photons. When a photon is absorbed, the dye molecule is put into an excited energy state. Excited dye molecules provide energy for oxidizing iodide ions to tri-iodide ions, with the electrons produced from this being transferred to the titanium IV oxide anode, making it negative. At the same time electrons are used to reduce tri-iodide ions to iodide ions at the platinum cathode. Overall the movement of the charges across the cell generates the emf (voltage) to drive electrons around the external circuit, with the energy to do this coming originally from light.

b) b) The dye molecules cover the extremely tiny nanoparticles at the anode. With such a large surface area in direct contact with light, a very high proportion of the light falling on the cell can be captured.

18)

a) Silicon conducts electricity by means of a small population of delocalised electrons and positively charged holes. Gallium is a Group 3 element. With a few gallium atoms replacing silicon in the crystal lattice the material will be a better conductor and mainly conduct by means of positively charged holes – a p-type material. Arsenic is a Group 5 element. With a few arsenic atoms replacing silicon in the crystal lattice the material will be a better conductor and mainly conduct by means of negatively charged electrons – an n-type material.

b) This diagram shows describes the structure of a silicon solar cell, but for a fuller explanation, look back at *'Dye-sensitized solar cells'* in Chapter 8.



Answers to general, exam style, revision problems (Questions 19-22)

a) You need to give a detailed account for perhaps 3 marks. For example:

The electric pump uses electrical energy to pump heat energy from the Irish Sea. **The warm water supplies its heat to the museum galleries** to maintain its temperature above the surroundings.

Overall, for every 1 joule of energy from the pump, **2 joules of thermal energy can be collected from the sea water** to supply 3 joules of thermal energy to the museum.

1 J (from pump) + 2 J (from sea) energy supplied to the museum = 3J of heat energy lost by the museum to the surroundings. So energy is conserved.

b)

i) For ***outline*** you only need to make brief points. For example, if there is only 1 mark, one of the following would be sufficient?

- when fuel is burnt all of the chemical energy is converted into heat
- entropy rises when fuel is burnt
- even though heat is lost by the building the combustion of fuel oil releases all of the energy from the reaction as heat

ii) Show your working! For 2marks,
43 $MJkg^{-1}$ x 810 kgm^{-3}
= **35,000 MJm^{-3}** (other units possible!)

iii) Mass of fuel = 100 m^3 x 810 kgm^{-3} = 81,000 kg

Assuming that the fuel is mainly $C_{15}H_{32}$

Molar mass = 212 $gmol^{-1}$

Moles of fuel = 81,000,000g / 212 $gmol^{-1}$ = 382,000 moles

Approximate moles of carbon dioxide produced

= 15 x 382,000 = 5.73 x 10^6 moles

Mass of carbon dioxide = 44 $gmol^{-1}$ x 5.73 x 10^6 moles = **250,000 kg**

iv) Propose a solution and give an account of how it works, e.g.

- carbon sequestration
- carbon dioxide can be removed from the exhaust gases/chimney (by means of chemical scrubbers for example)

c) **Carbon footprint**: amount of carbon dioxide produced as a result of some activity.

Carbon neutral: a process or activity that results in no net addition (or subtraction) of carbon dioxide from the atmosphere.

Comment means to give a judgment. The mark is for showing an understanding that the source of the energy for running the heat pump can lead to the pump being nearly carbon neutral or not. E.g. a wind or solar generator used to provide the electricity may make the pump nearly carbon neutral but connecting the pump to the National Grid or fossil fuel sources of electricity will not be.

20)

a) Include the following:

$C_6H_{12}O_6$ => $2C_2H_5OH + 2CO_2$

fermentation; distillation; removal of remaining water (rectifying).

b) **Advantage** (one of the following):

- renewable resource
- burns producing less carbon (soot) and carbon monoxide
- might reduce carbon emissions

Disadvantage (one of the following):

- lower specific energy
- uses up farming land that could produce food crops
- engines need to be modified

c) **Fractional distillation**: separates molecules of different boiling points and so of different chain length

Cracking: process where some of the less useful large molecules in crude oil are broken into smaller ones including gasoline

Catalytic reforming: process used to convert low octane (naphtha) molecules into molecules with a higher octane rating to blend into gasoline as a refinery product

d) **Despite** the hydrogen bonding between ethanol molecules, ethanol molecules have a **much** lower molar mass than gasoline molecules and so intermolecular forces are weaker in ethanol because of the very much weaker London dispersion forces.

e) Lower: carbon atoms in ethanol are *'more oxidised'* / have more positive oxidation number than in gasoline so enthalpy of combustion is greater for pure gasoline.

21)

a)

i) $^{233}_{92}U + ^{1}_{0}n => ^{234}_{92}U$

ii) You could draw a sketch to support your description!

Needs to include:

- one neutron collides with a nucleus
- resulting new nucleus is unstable and breaks up
- into two or more large fragments together with 2,3, or 4 more neutrons
- the neutrons produced can go on to create more fission, the chain reaction

iii) The amount of fissile material needed to maintain a chain reaction.

b)

i) Number of half-lives = 3.
Since 1/8 remain, answer = **7/8 decayed**

ii) Different sequences/ details. For example:

1. turned into a glass (so that radioactive dust doesn't escape)

2. put in stainless steel canisters above ground for some years (to lose much of its radioactivity)

3. disposal in geologically stable rock formations;

c) Sustained nuclear fusion needs extremely high temperature and pressure. To manage these conditions in a controlled (as opposed to an explosive) fashion presents engineering problems of containment and controlled extraction of the energy produced

Advantages:

- abundant raw materials as potential energy sources for fusion
- fewer and less hazardous radioactive products

22)

a)

i) $CH_3COO^- + 2H_2O \Rightarrow 2CO_2 + 7H^+ + 8e$

Note: You need to produce carbon dioxide! See your notes on balancing redox equations if stuck with this or the next one!

ii) $CH_3OH + 6OH^- \Rightarrow CO_2 + 5H_2O + 6e$

iii) The chemical product of a hydrogen fuel cell is only water so the carbon emissions are zero. Organic molecules used in a fuel cell will add carbon dioxide to the atmosphere so there are greenhouse gas emissions. (However, the source of both fuels should really be considered!)

b) Example answer, many possible pros and cons! With a question like this try to bring in a few contrasting ideas!

- **Fuel cell**: high specific energy but needs to exhaust water and be supplied with the chemical fuel, so might damage electronics (and might end up not being very portable to keep the electronics safe!).
- **Silicon solar cell**: energy supply (sunlight) has no cost but cell only works in the light (so needs to work alongside a secondary cell perhaps) (and won't work for higher power appliances).
- **Lithium ion cell**: high specific energy but has a tendency to overheat.

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