

AWS

**ENVIRONMENTAL
CHEMISTRY
OPTION
BOOK LET**

ENC 03

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1. THE ATMOSPHERE

(a) Introduction

About 3.5 billion years ago, one billion years after the formation of the planet, life first appeared on Earth. The first primitive forms may have survived through obtaining energy directly by the anaerobic fermentation (i.e. fermentation in the absence of oxygen) of organic compounds. Carbon dioxide was obtained as a by-product. About 2.5 million years ago, oxygen-producing photosynthetic organisms appeared and the concentration of atmospheric oxygen increased. Eventually, the composition of the atmosphere settled to the proportions of gases that are associated with an unpolluted atmosphere today.

The approximate concentrations by volume of the environmentally important gases in the unpolluted atmosphere are:

nitrogen 78%, oxygen 21%, carbon dioxide 0.035% (350 parts per million, ppm), methane 1.5 ppm, dinitrogen oxide, N₂O, 0.3 ppm, with the noble gases and water vapour making up most of the remaining volume.

The atmosphere provides special conditions for chemical reactions, very different to those usually met in the laboratory. The concentrations of the gases decrease with altitude, the temperatures are variable and dust particles can provide catalytic surfaces. Many reactions of great environmental consequence occur during daylight hours when the greater intensities of high energy ultraviolet radiation from the Sun are sufficient to cause the breaking of chemical bonds. Such reactions are called photochemical and are important in protecting life on the surface of the Earth from an excessive exposure to radiation.

It is helpful to recall a section of the electromagnetic spectrum which is shown in Fig 1.

Wavelength/nm	50	400	750	100000
Type of wave	X-rays	ultraviolet	visible	infra-red

Fig 1 - diagram of part of the electromagnetic spectrum

The wavelengths present in solar radiation have the greatest intensities in the visible region of the electromagnetic spectrum, between 400 nm and 700 nm, with a maximum intensity at about 480 nm. These wavelengths are not absorbed by an unclouded atmosphere but are partially absorbed at the Earth's land and sea surfaces and the energy is re-radiated as infra-red radiation (i.e. heat, at much longer wavelengths) thus maintaining the temperature close to the Earth's surface. See Fig 2.

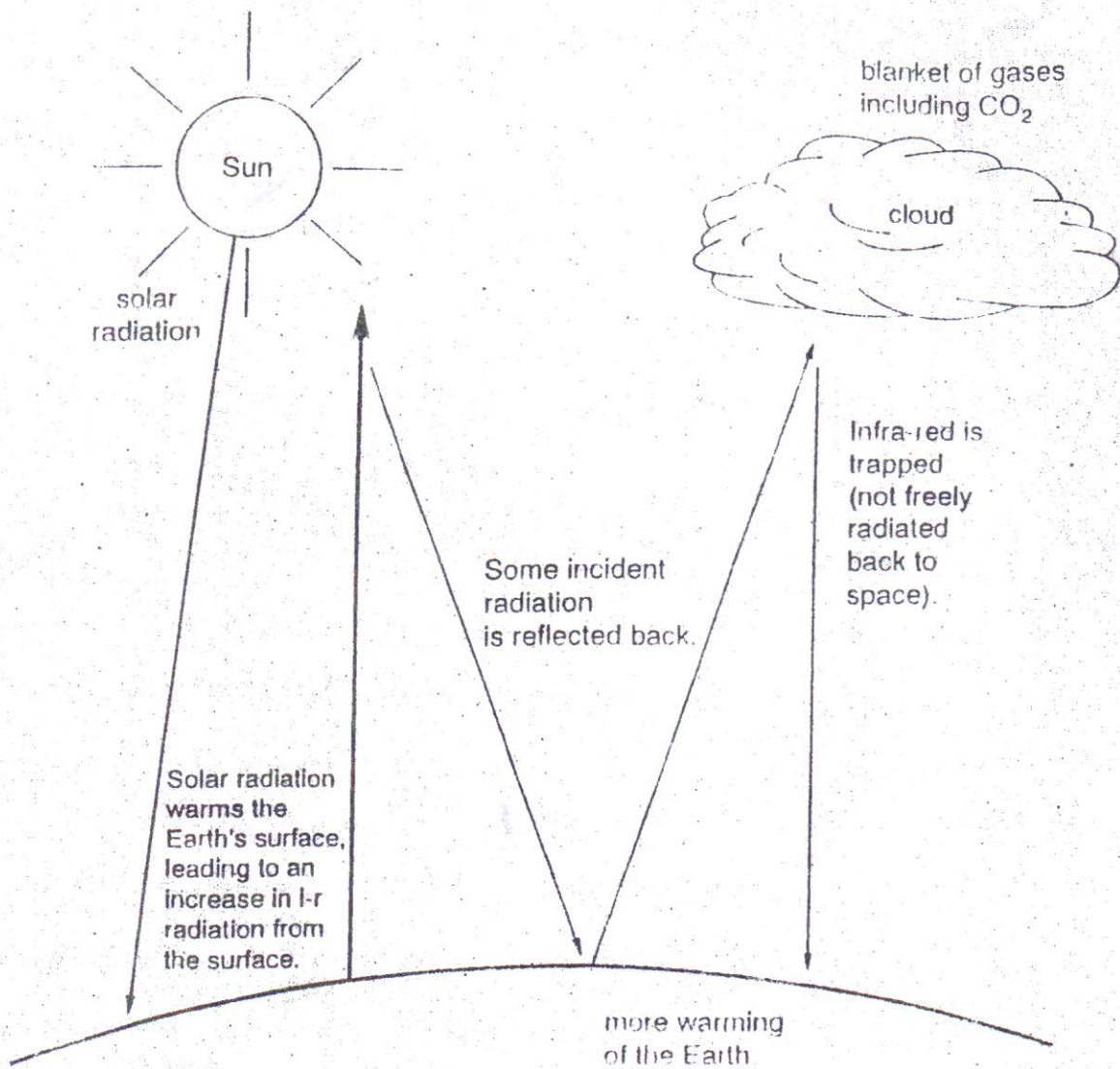


Fig 2 - global warming

(b) The structure of the atmosphere

Four distinct layers can be recognised within the atmosphere. In increasing altitude from the Earth's surface, these are the troposphere, the stratosphere, the mesosphere and the thermosphere. Of these, only the first two will be considered in detail.

The troposphere

This layer extends to a height of approximately 15 km. The gases in it are extensively mixed both by convection currents from the Earth, which has been heated by solar radiation, and also as a consequence of the Earth's rotation about its axis. The temperature decreases with increasing altitude in the troposphere because heating due to convection decreases with increasing distance from the Earth's surface. A further effect is that, as the pressure decreases, the rising gas expands and therefore cools.

The stratosphere

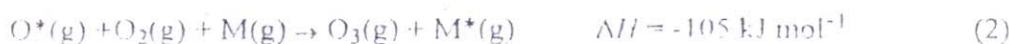
This is a layer of stable atmosphere extending from about 15 km to 60 km. The temperature increases with altitude as a result of the following two pairs of photochemical reactions which, in both cases, are exothermic overall.

(i) The first pair of reactions is as follows. Initially, there is a breakdown of oxygen molecules into oxygen atoms, $O(g)$, and excited (high energy) oxygen atoms $O^*(g)$.



This requires energy, which is supplied by ultraviolet radiation (represented in the equation as hf) with wavelengths of less than 242 nm. The shorter the wavelength, the more energetic the wave is and the more energy is given to the excited oxygen atom.

Ozone, O_3 , can then be formed, in an exothermic reaction, as a result of a reaction between the excited oxygen atoms and molecular oxygen in the presence of an inert third body (M), usually molecular nitrogen or oxygen.

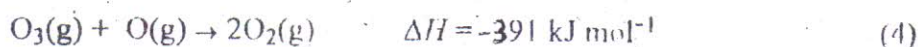


In the absence of the third body, the yield of ozone is much less because the third body carries away the excess energy which would otherwise cause decomposition of the ozone back to molecular oxygen and oxygen atoms again.

(ii) The second pair of reactions is initiated by the breakdown of ozone to re-form molecular oxygen and oxygen atoms. The energy required, in this case, is supplied by ultraviolet radiation of wavelengths between 290 nm and 330 nm.



An exothermic reaction between ozone and oxygen atoms then occurs and two molecules of oxygen are formed.



These two sets of reactions are particularly important in the stratosphere because the intensity of ultraviolet radiation is high enough to dissociate the oxygen and ozone to an appreciable extent, while the concentration of molecular oxygen is still sufficient to react with oxygen atoms to form ozone. In the troposphere, much of the ultraviolet radiation has been already absorbed at higher altitudes so its intensity is insufficient to generate enough oxygen atoms. At altitudes above the stratosphere, very little molecular oxygen is present and any oxygen atoms formed generally recombine to form oxygen molecules again.

The main reactions involved in the formation and destruction of ozone are shown in equations (1),(2),(3) and (4). These reactions, in an unpolluted atmosphere, maintain a layer of ozone which is about 25 km above the Earth's surface and has an average depth of about 15 km, though wide variations occur. It is unsurprising that it should form a layer. At lower altitudes, there is insufficient ultraviolet energy to dissociate oxygen; at higher altitudes, the concentration of oxygen is too low to react with oxygen atoms to form ozone. Although this depth may appear to be substantial, it must be remembered that the pressure at this altitude is low. If the same mass of ozone were to form a gaseous layer on the Earth's surface, it would be no more than 3 mm thick.

The stratospheric ozone plays a vital role in that the reactions which lead to its formation and destruction absorb a significant amount of the incoming ultraviolet radiation. This protects organisms on the Earth's surface from an excessive exposure to high-energy radiation which can be very damaging. Without it, an increase in the incidence of skin cancer in humans would, for example, occur.

The mesosphere and thermosphere

Above the upper limit of the stratosphere (60 km), two further layers can be identified, the mesosphere and the thermosphere. In the mesosphere, the temperature, once again, starts to fall as the concentrations of the reactants which provide the energy diminish. However, in the thermosphere, the temperature rises as the incident radiation from the Sun becomes the dominant feature.

A summary of the changes in atmospheric temperature and pressure with increasing altitude is shown in Fig 3.

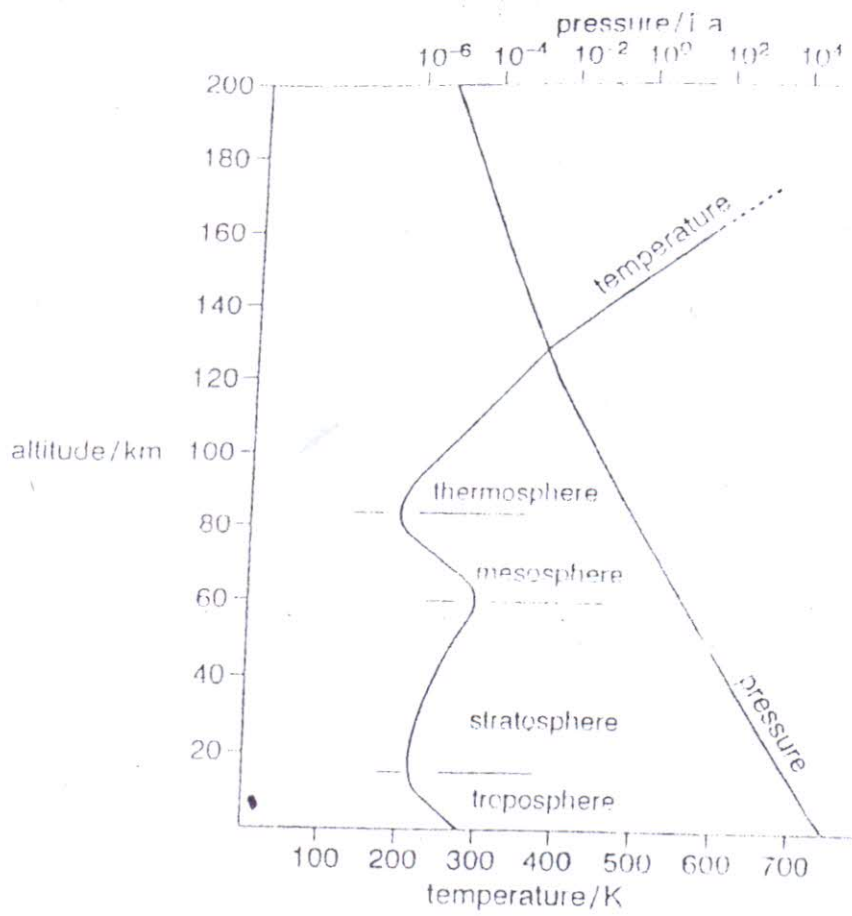


Fig 3 - structure of the atmosphere

(c) Residence time

That the composition of an unpolluted atmosphere remains largely constant over many years can only be explained if the sources which produce a particular gas are balanced by sinks - i.e. processes which remove the same gas. If the rates of production and removal are the same, a steady state is obtained in which the concentration of the gas remains essentially constant over time.

The term residence time is used to express the average time that a molecule of a particular gas spends in the atmosphere from its introduction by a source to its removal by a sink. This time is affected not only by the rate at which it is removed by the sinks but also by the concentration of the gas that is naturally present. Residence time may, therefore, be stated more formally as:

$$\text{residence time} = \frac{\text{steady state concentration of the gas present in the atmosphere}}{\text{rate of removal of the gas from the atmosphere}}$$

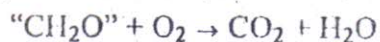
The appropriate residence times of some of the gases discussed in this booklet are listed below

Gas	Approximate Residence Time
nitrogen dioxide	4 days
nitrogen monoxide	4 days
sulphur dioxide	5 days
ozone	4 weeks
carbon monoxide	6 weeks
methane	3.5 years
carbon dioxide	4 years
dinitrogen oxide	25 years

It is important to stress that these figures apply only to unpolluted atmospheres: human activity has introduced such large quantities of some gases that sinks cannot effectively remove them, resulting in dramatic increases in their atmospheric concentration.

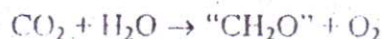
(d) The carbon cycle

The main naturally occurring source of carbon dioxide is the aerobic respiration of living organisms, an exothermic process in which carbohydrate is converted into carbon dioxide and water. Carbohydrate may be represented as "CH₂O".



Carbon dioxide is also produced in smaller quantities by photochemical oxidation of hydrocarbons in the atmosphere. Methane is the most abundant of these hydrocarbons and is produced by micro-organisms such as the bacterium *methanobacter* in marshes and in paddy fields. The main source of carbon dioxide resulting from human activity is the combustion of fossil fuels for power generation, heating and transportation. Natural combustion processes, such as forest fires, are another source which increase atmospheric carbon dioxide concentrations.

The most important process which removes carbon dioxide is photosynthesis by green plants. Photosynthesis is the reverse of respiration and is endothermic.



Carbon dioxide is also removed when it dissolves into surface water. An increase of pressure results in increased solubility, but an increase of temperature reduces the solubility. Since only about 30% of the Earth's surface is above sea-level, the oceans are a major factor in stabilising the atmospheric concentration of carbon dioxide. The sinking of surface water in cold latitudes serves to ensure continued absorption of carbon dioxide by unsaturated water at greater depths.

Carbon dioxide is further removed when it is incorporated into the shells of aquatic animals. Carbon dioxide reacts with water to produce soluble hydrogencarbonate ions.

Henry's Law then states that

$$[\text{CO}_2(\text{aq})] = c(0.00035 \times 101.3)$$

where c is a standard constant (with units of $\text{mol dm}^{-3} \text{ kPa}^{-1}$) with values which may be readily obtained from tables. For carbon dioxide, c is $3.34 \times 10^{-4} \text{ mol dm}^{-3} \text{ kPa}^{-1}$ at 298 K.

This gives a value for the solubility of carbon dioxide as

$$[\text{CO}_2(\text{aq})] = 3.34 \times 10^{-4} \times 0.00035 \times 101.3 = 1.18 \times 10^{-5} \text{ mol dm}^{-3}$$

(e) The nitrogen cycle

Nitrogen gas is very unreactive and has a very long residence time. It is removed from the atmosphere through biological fixation, by oxidation to nitrate ions and by atmospheric conversion to nitrogen oxides by lightning. However, the small quantities removed by these processes are balanced by the release of nitrogen or one of its gaseous compounds into the atmosphere as a result of the action of bacteria. A simplified version of the nitrogen cycle is shown in Fig 5.

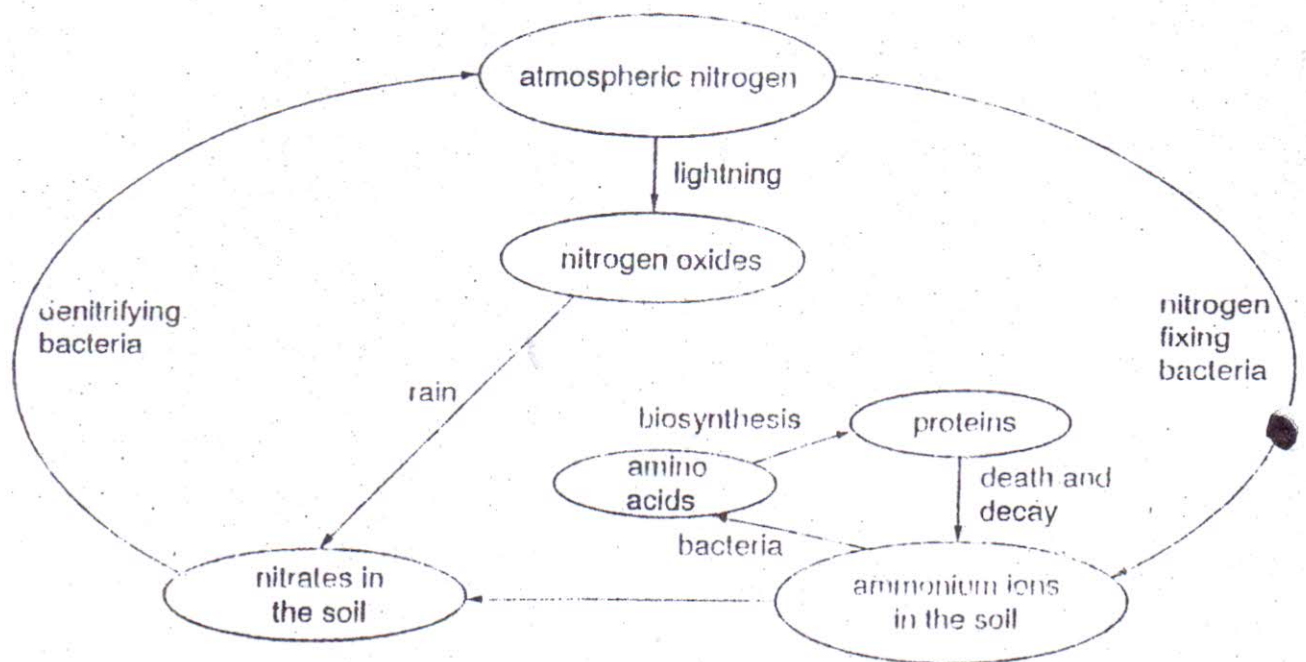


Fig 5 - the nitrogen cycle

Dinitrogen oxide, N_2O , occurs in trace quantities in the troposphere. Some rises into the stratosphere where, as explained later, it is thought to be involved in the decomposition of ozone.

Ammonia is another nitrogen compound found in the atmosphere. It is produced by micro-organism decay of proteins and is readily soluble in water (18 mol dm^{-3} at 298 K and 101.3 kPa). It may be important in controlling the pH of river water. Nitrogen dioxide, present in small quantities, is also very soluble in water, but gives an acidic solution (a mixture of nitrous acid and nitric acid), again affecting the pH of water.



Nitrogen dioxide plays an important part in photochemical reactions in the troposphere.

(f) Pollution

The carbon and nitrogen cycles described above have natural sources, but these are being enhanced by further inputs of gases as a consequence of human activity. Many of these extra inputs are associated with processes involved in energy production and they have upset the existing balance in the atmosphere. The sinks for the gases are no longer adequate to retain the existing steady state as the concentrations steadily rise. In addition, chemicals, which had previously not been present in the atmosphere to any significant extent, may become involved in a complex web of interactions that is only now beginning to be understood. Pollution may be defined as: "The direct or indirect alteration of the physical, thermal, biological or radioactive properties of any part of the environment in such a way as to create a hazard or a potential hazard to the health, safety or welfare of any living species."

Governments may be keen on the principle of reducing pollution but implementing policies which will have a beneficial effect on the environment may (i) be costly, (ii) cause unemployment, (iii) increase prices of goods needed by many of the population.

Before considering some specific effects of atmospheric pollution, various aspects of energy production and the methods of control of their waste products are now considered.

(g) Energy production

The non-photochemical reactions of greatest environmental consequence involve the combustion of fossil fuels, especially for the large-scale generation of electricity. The impact of the internal combustion engine in this context is discussed later.

It is anticipated that power consumption is likely to increase, both nationally and internationally, as a result of population increases, increasing prosperity and technological developments.

At the present time, the main sources of power are based on the use of fossil fuels (coal, oil, natural gas), nuclear fission and hydroelectricity. The World's stocks of fossil fuels are finite as fossil fuels are a non-renewable resource. Such is the likely increase in demand for power that increasing efforts are being made to develop other energy resources.

Question

It has been estimated that the World's crude oil reserves may be used up within the next 20 years.

- (i) *What processes will be affected if oil is unavailable?*
- (ii) *What steps should be taken to preserve the World's oil reserves?*
- (iii) *What are the best alternative sources of power for (a) vehicles, (b) the production of electricity, in your country?*

Fossil Fuels

Fossil fuels are used directly in space-heating and in the generation of electrical power. A difficulty associated with electrical power is that electrical energy cannot, on a large-scale, be readily stored. [Consider the bulk and cost of suitable batteries for large-scale consumption in relation to the accumulators in cars and electrically driven vehicles and in the use of batteries in portable devices such as radios, cassette players, cameras etc.]

The use of fossil fuels essentially exploits energy resources that were 'stored' from times past. In this respect, therefore, power consumption increases the present-day rate of energy dissipation and might lead directly to an increase of global warming. This can affect the climate pattern - leading possibly to locally extreme weather occurrences, such as unusually low rainfall or unusually vigorous wind strengths. Increased warming might lead to melting of polar ice masses, an increase in the mean sea-level and permanent flooding of low-lying land.

Question

It has been estimated that the global average air temperature will rise by 2.5°C by the year 2100. At the same time, the sea level will rise by approximately 45 cm.

- (i) *What are the likely consequences of these changes?*
- (ii) *What steps could be taken to control these increases?*

Nuclear Energy

In principle, a more efficient source of energy might be obtained by using nuclear power. It is essentially harnessing the energy released by the radioactive decay of the isotope uranium-235. This isotope has an abundance of only 1% and its production, by extracting the uranium from its ore and then separating the ^{235}U isotope, is complex and, therefore, expensive. There are also the problems associated with ensuring safe handling of both the ^{235}U and the products of its radioactive decay. Consideration has to be given to the safe operation of the power plant and the protection of the local and wider environments.

Understandably, especially in view of a few widely publicised accidents that have occurred, people have strongly held views on the advisability of employing such potentially dangerous methods of power production. A particular issue also concerns the safe disposal of the radioactive waste products which sometimes have half-lives of many years. Some countries do not have the facilities for dealing with such waste and, therefore, have to 'export' it to countries that are prepared to deal with it.

Considerable effort has been put into another approach which is to obtain energy by combining nuclei, i.e. nuclear fusion. It can be calculated, for example, that combining four moles of hydrogen atoms to create one mole of helium atoms would release in the order of 10^9 kilojoules of energy. This reaction, which occurs in the centre of the Sun, produces energy many millions of times greater than a chemical process.

The main products of the natural decay of radioactive nuclei are α -particles (^4He nuclei), β -particles (highly energetic electrons) and γ -rays (short wavelength, and hence highly energetic, electro-magnetic waves). γ -rays, in particular, are very penetrating and require a thick sheet of lead to stop them. The damaging effect of these emissions on biological tissue is not fully understood but they undoubtedly have a role in distorting biochemical processes thus creating cancers and cell mutation.

Background radiation occurs naturally and is mostly considered to be harmless but a particular hazard on which attention has been focused is associated with the noble gas radon. Granite rocks, in particular, may contain small amounts of uranium: radon is one of the products of its decay. Because radon is a gas, it can seep out of the rock and concern has been expressed at the apparently higher incidence of cancer amongst the inhabitants of houses built on granite.

Other energy sources

There are several other methods of generating power. Currently, they have only been successful on a local scale but they may have the potential for future development. The merit of each of these is their utilisation of natural resources and the absence of polluting by-products. Their attraction is therefore obvious, although it is unlikely that these methods would be able to cope with a large-scale power output. In some instances too, the equipment required to convert the power source into a useable power supply may disfigure the landscape.

(i) Hydroelectric power

In areas with a sufficiently high rainfall and with rivers suitable for damming, it may be possible to use the release of water to drive turbines. This can then provide a relatively cheap and efficient source of electricity. Environmental issues concern the damage to local ecology caused by drowning river valleys and the positioning of the cables for transmitting the power.

The absorption of sunlight by suitable panels on the roofs of houses can be used to heat water circulating in pipes and passing through the panels. Small devices, such as watches and calculators, can also exploit sunlight as a direct source of energy by using solar cells made of semiconductors.

(iii) *Wind and wave power*

Windmills convert the kinetic energy of the wind into electricity. However, assuming a consistently windy site, as many as 800 windmills with rotors of 50 m diameter might be required to provide the power equivalent to that supplied by a normal power station. A large number of windmills may be unacceptable in an area that depends largely on tourism for its income.

Suitably designed floats can be designed to convert the up-and-down motion of the sea into a useful energy output or tidal motion may be effectively employed.

Other methods include using the surface heating of the oceans or local hot-spots (e.g. volcanoes or hot springs) as an energy source.

(h) **Fossil fuel combustion**

By their nature, fossil fuels generally occur underground and have to be extracted. Immediate environmental considerations include the hazards involved in the extraction (e.g. mining accidents, fire hazards of oil-wells, oil spillages), and the disposal of spoil (e.g. slag heaps, spent ash).

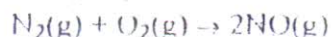
Sulphur compounds occur naturally both in oil and coal and also in mineral ores, e.g. as iron pyrites, FeS_2 , in iron ore. Some typical sulphur contents are listed below.

Substance	Typical Sulphur Content (by mass)
coal	between 0.5% and 6%
petrol (gasoline)	0.04%
diesel	0.22%
fuel oil	between 0.75% and 3%

An average sulphur content of coals might typically be approximately 1.5%. Of this 1.5%, most (0.7% to 1.0%) is present as organic sulphur compounds, with less than 0.1% as sulphate, the remainder being iron pyrites. The burning of such fuels involves dealing with the sulphur either by its removal before combustion or by reducing the emission of sulphur dioxide into the atmosphere after combustion.

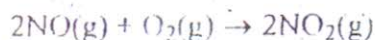
Power generation by using fossil fuels has other consequences; one being the products formed by such combustion, especially under confined situations, e.g. car-engines, furnaces, generators. These products include sulphur dioxide, carbon dioxide, carbon monoxide and nitrogen oxides.

Fossil fuel combustion is, for obvious reasons, normally in air rather than in oxygen. At the high temperatures involved, the endothermic oxidation of nitrogen in the air occurs.

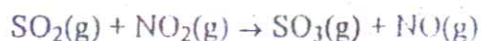


The drive for greater efficiency through the use of combustion at higher temperatures has led to a marked increase in the emission of oxides of nitrogen.

* In the atmosphere, further oxidation readily occurs.



Nitrogen dioxide dissolves in water to form both nitric acid and nitrous acid which is itself further oxidised to nitric acid - an additional contribution to atmospheric acidity. Moreover, the following gaseous reaction occurs.



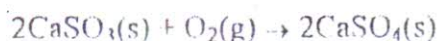
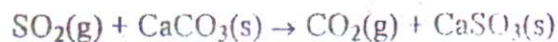
From these two equations, it can be seen that nitrogen monoxide catalyses the oxidation of sulphur dioxide to sulphur trioxide, an important step in the formation of acid rain. In addition to their contribution to acid rain, oxides of nitrogen also play important roles in other processes. They can cause respiratory problems in humans and interfere with nitrogen metabolism in plants. They are also heavily implicated in the formation of photochemical 'smog', which is discussed later in the context of the pollution caused by motor vehicles.

The removal of sulphur dioxide from coal

In the past, much of the sulphur in coal was released into the atmosphere as sulphur dioxide, but various methods are now used to remove sulphur dioxide such that it can then itself be used in the manufacture of sulphuric acid, which is of major importance in industry.

(i) *Fluidised Beds*

When gas is forced through a suitably powdered solid, the solid is said to be 'fluidised' and the surface area of the solid in contact with the gas is greatly increased. By burning coal in a bed of fluidised limestone, a high proportion of the sulphur can be removed, though, at the temperatures employed, nitrogen may react with oxygen to increase the proportion of nitrogen oxides. The sulphur in the pyrites is oxidised by air to sulphur dioxide, which then reacts with the limestone.

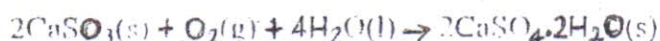
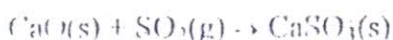


* (ii) Alkaline Scrubbing and Flue Gas Desulphurisation

The removal of sulphur dioxide from the flue gases is becoming increasingly important as many governments are committed to a reduction in sulphur dioxide pollution. Although the sulphur dioxide content of the flue gases from power stations is low (less than 1%), various 'scrubbing' methods are used to remove the gas. The acidic sulphur dioxide is often reacted with an alkali, a basic oxide or a carbonate.

Limestone and lime, as a slurry

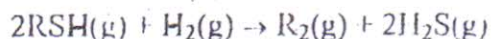
Calcium carbonate and calcium oxide each absorb sulphur dioxide to form calcium sulphite which may be oxidised by air to calcium sulphate.



The sludge of hydrated calcium sulphate may be used in plaster-board or cement manufacture.

The removal of sulphur from oil and gas

Crude oil and natural gas, like coal, often contain unwanted sulphur compounds. By being mixed with hydrogen, under pressure, and passed over a metallic salt catalyst, these sulphur compounds can be reduced to hydrogen sulphide.



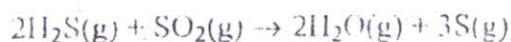
R is the organic part of the sulphur compounds.

The resulting hydrogen sulphide can be separated from other gases present by using a suitable solvent, followed by heating to release the gas and regenerate the solvent.

The hydrogen sulphide is burnt in a limited supply of air. Under these conditions, most of the hydrogen sulphide is oxidised to sulphur or to sulphur dioxide.



The sulphur vapour is condensed and separated. Any unreacted hydrogen sulphide is converted into sulphur by reacting it with the sulphur dioxide produced over a bauxite (aluminium oxide) catalyst.

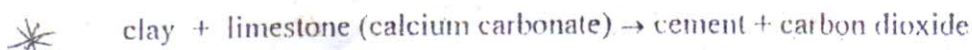


By repetition of these steps, over 95% of the sulphur can be recovered. Sulphur obtained in this way is the major source of the element for the manufacture of sulphuric acid.

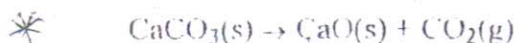
Natural gas, as supplied to consumers, contains a negligible amount of sulphur. Governments may wish to use gas for power generation in order to reduce pollution levels, but this may be a difficult decision if a country has to import natural gas.

(i) Lime and cement manufacture

A further process of considerable industrial importance which generates carbon dioxide as a potentially polluting by-product is the manufacture of cement. The annual worldwide production of cement is of the order of 1 billion tonnes. The essential reaction is as follows.



Lime (calcium oxide) manufacture also involves the decomposition of limestone, carbon dioxide again being a product.



(j) Acid rain

The carbon dioxide, oxides of nitrogen and oxides of sulphur which occur naturally in an unpolluted atmosphere would be expected to give rainwater a pH of about 5.6 - 5.0. Acid rain is the term used to describe rainwater which has an acidity greater, i.e. of lower pH, than the natural value. In much of the industrialised world, the pH can reach values as low as 4.0 - ten times more acidic than the unpolluted value. Globally, the natural and industrial emissions of acidic gases are similar, but in the northern hemisphere over 90% of all sulphur dioxide emissions arise as a result of technological activities.

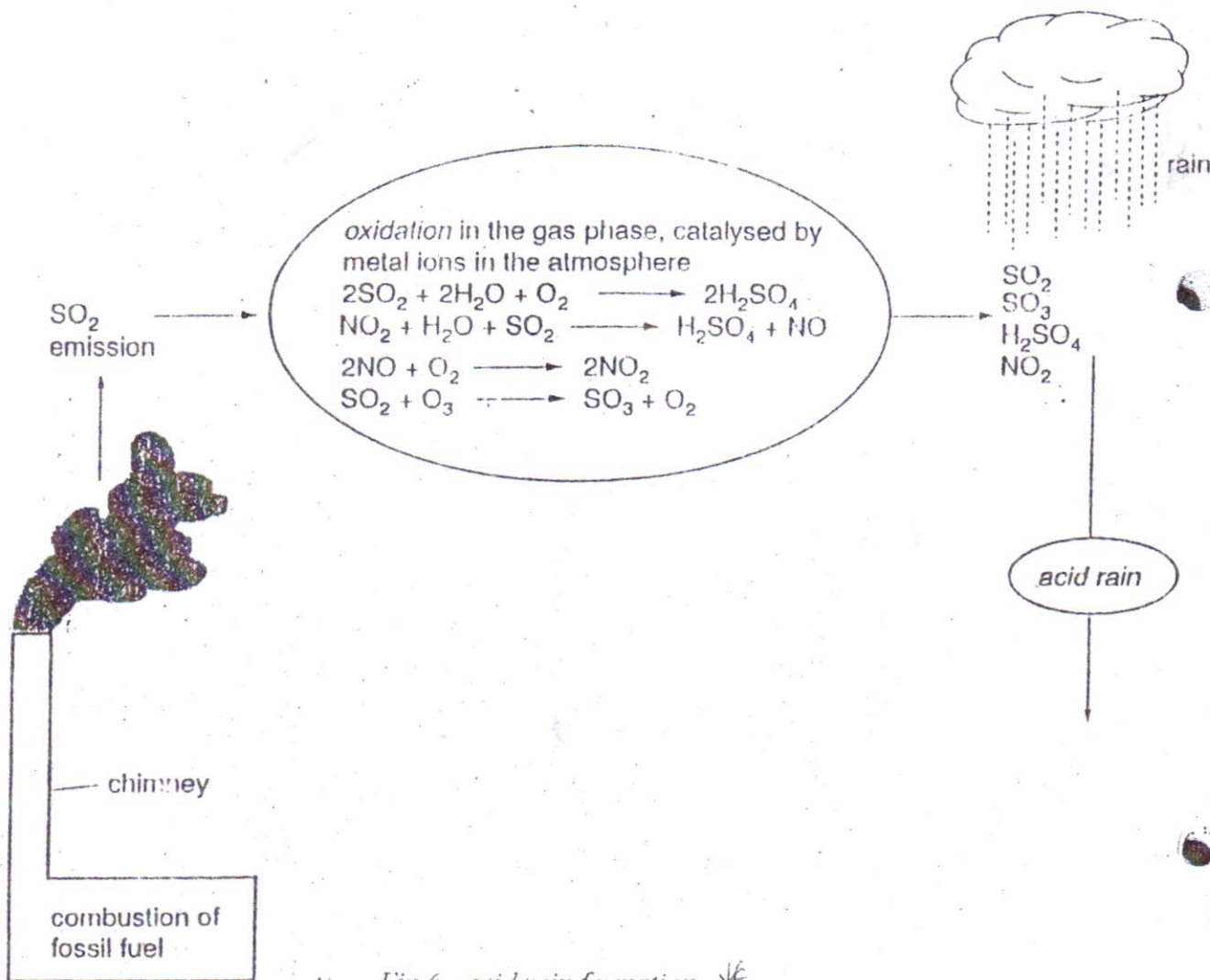
The details of the reactions which lead to the formation of acid rain are not fully understood but may be summarised as shown in Fig 6.

It is now realised that the acidity of the rain itself is only one factor in its damaging effects on the environment - its effect on the transport of metal ions in the soil, both beneficial and harmful, is at least as important.

The Effects of Increasing Acidity on Aquatic Life

Although it is difficult to separate the direct effects of a decrease in pH and those associated with other changes, such as cation concentrations, there is a growing body of evidence that many species of aquatic insects are affected by increasing acidity alone. Acidic waters support a reduced range of important food insects for fish, such as mayflies, caddis flies, stoneflies and snails. The decrease in the numbers of food insects for game fish, such as trout, has had a particular impact on Scandinavian economies, where tourism and game fishing are closely linked. What is beyond dispute is the considerable reduction in fish populations in Scandinavian waters.

There is some evidence that fish are directly affected by increasing acidity, though the greater solubility of both aluminium compounds and heavy metal compounds in soils under such circumstances may well be more important. The gills of fish are covered with a protective mucus which can thicken and lose its protective qualities in the presence of heavy metal ions such as cadmium and zinc. A further complication can occur through circumstances in which two or more pollutants have a much greater effect when present together than either has on its own. Small amounts of zinc can greatly increase the toxicity of cadmium, for example.



* Fig 6 - acid rain formation *

The Effects of Acid Rain on Trees

It was the sight of vast tracts of dead and dying trees which first alerted people to the seriousness of the threat posed by acid rain. Acid rain can affect the soil in that nutrients are washed away and heavy metal ions are 'mobilised'. These toxic ions can then be taken up by the tree roots and weaken the tree's resistance to disease and extremes of weather. The acid rain falling on the trees may cause direct damage and leaves may be shed and growth restricted. There is still a wide divergence of opinion as to the causes of damage by acid rain. It is likely that the relative importance of the various factors which contribute to the eventual death of trees varies with climate, location and the nature of the bedrock.

The greenhouse effect

Energy is radiated from the Earth's surface as infra-red radiation which is prevented from escaping completely into space (even in an unpolluted atmosphere) by the following mechanism.

Molecules such as water and carbon dioxide can undergo molecular vibrations which involve a change in the dipole of the molecule. These vibrations have frequencies within the infra-red region of the electromagnetic spectrum and some of the infra-red radiation is absorbed, resulting in an increase in the temperature of the troposphere. Such molecules are said to be infra-red active.

For example, carbon dioxide has three characteristic vibrations. These are illustrated below. It should be noted that only two of these, the asymmetrical stretch and the bending mode, involve a change in dipole. The third, the symmetrical stretch, is therefore not able to absorb in the infra-red region. See Fig 7.

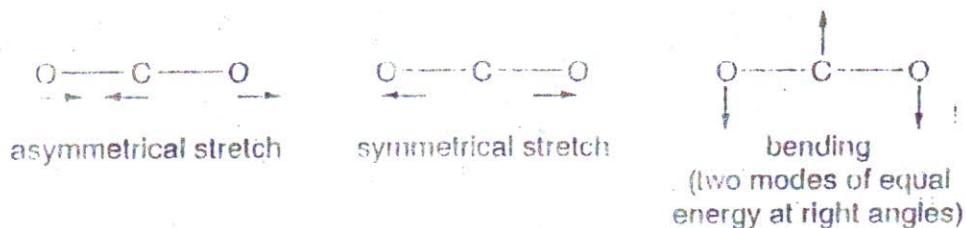


Fig 7

It is important to appreciate that what is commonly known as the 'greenhouse effect' might more accurately be described as the 'enhanced greenhouse effect' in that a mechanism for the trapping of infra-red radiation (i.e. for global warming) exists even in an unpolluted atmosphere. It is estimated that without this natural greenhouse effect the temperature of the Earth's surface would be below -20°C . Human activity has simply increased the level of carbon dioxide and other 'greenhouse gases' well above those found in the atmosphere even a few centuries ago. Instead of escaping into space, more of the infra-red radiation from the Earth's surface is retained by the atmosphere.

The atmospheric gases themselves radiate infra-red wavelengths in all directions, some of which heats the Earth's surface, and this results in an increase in mean global temperatures. This increase, since 1880, is rather less than 1°C . The efficiency of the greenhouse effect is well illustrated by Venus, which maintains a surface temperature of around 450°C as a result of its atmosphere, which is 97% carbon dioxide.

The greenhouse effect arises from the fact that if there is, as a result of human activity, an increase in the concentration of infra-red active molecules in the troposphere, there is a corresponding increase in the infra-red absorption. This then leads to an overall increase in the average global temperature. See Fig 8.

The table below shows the effectiveness of various substances as greenhouse gases relative to carbon dioxide. The variation in the 'greenhouse factor' occurs partly because molecules differ in the number of modes of vibration that absorb infra-red radiation.

greenhouse gases

Gas	Formula	Greenhouse Factor	Percentage present in the troposphere
carbon dioxide	CO ₂	1	3.5 x 10 ⁻² %
methane	CH ₄	30	1.7 x 10 ⁻⁴ %
dinitrogen oxide	N ₂ O	200	3.0 x 10 ⁻⁵ %
ozone	O ₃	2000	4.0 x 10 ⁻⁶ %
a CFC (see later)	CCl ₂ F ₂	25000	4.8 x 10 ⁻⁸ %

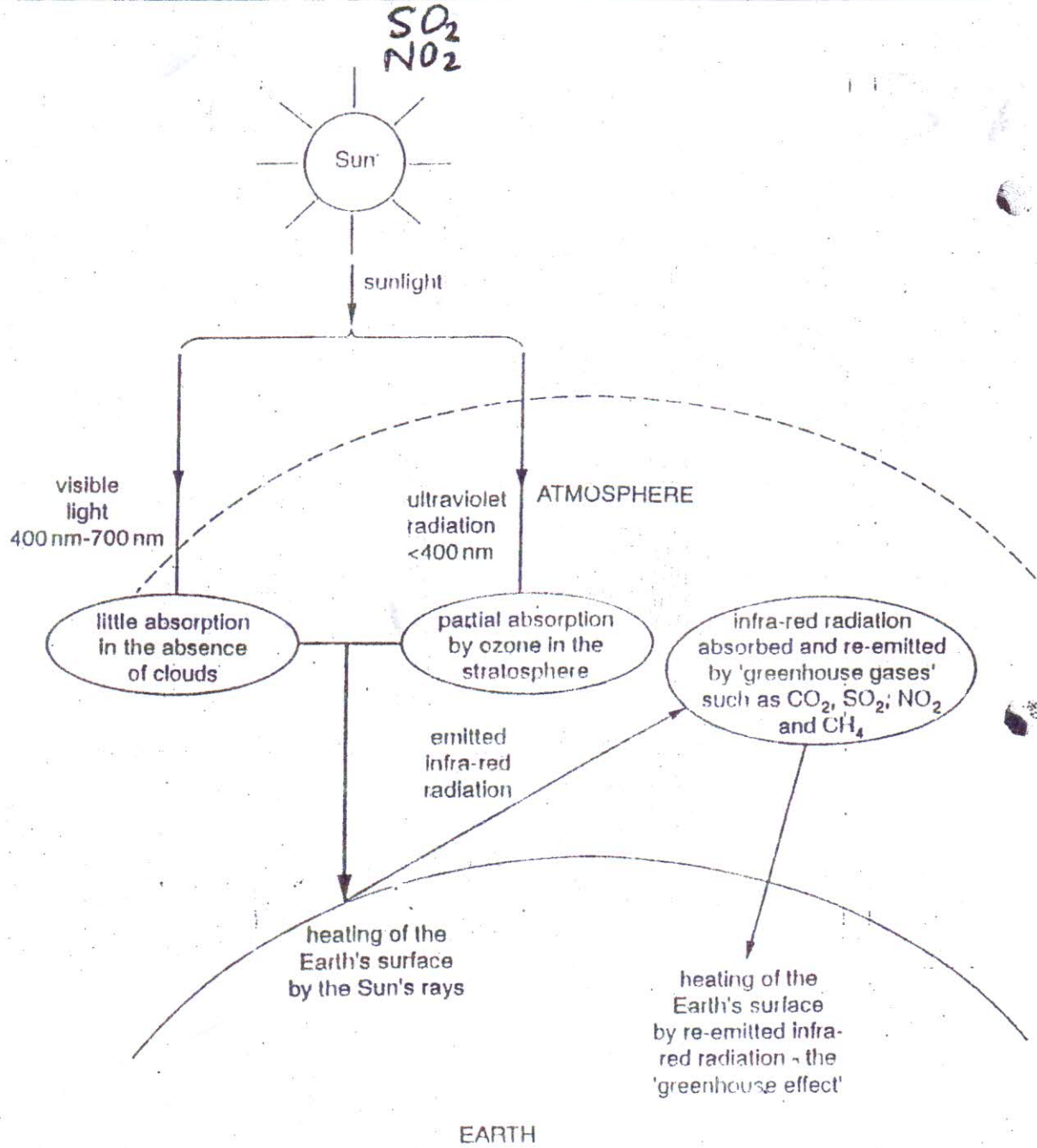
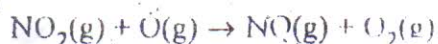
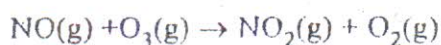
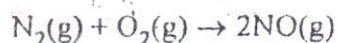


Fig 8 - global warming, the greenhouse effect

Reactions which damage the ozone layer

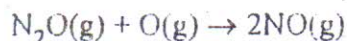
Nitrogen Monoxide

There is evidence that naturally occurring nitrogen oxides are involved in the destruction of ozone. Nitrogen monoxide is first formed during lightning discharges and may then be oxidised, by ozone, to nitrogen dioxide. The nitrogen dioxide can then react with oxygen atoms formed by the breakdown of ozone.



It can be seen from these equations that because NO is regenerated in the third reaction the nitrogen oxides can destroy many ozone molecules and can be seen to catalyse ozone destruction.

A further source of nitrogen monoxide in the stratosphere results from the reaction of dinitrogen oxide (produced by bacterial action at the Earth's surface) and oxygen atoms from the dissociation of ozone.



Nitrogen monoxide is also a product of the high temperature combustion of nitrogen in car engines or during the use of fluidised beds mentioned previously.

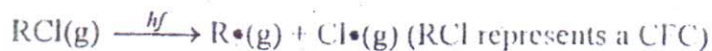
Fortunately, the stratospheric concentration of oxides of nitrogen is currently thought to be too low to reduce the thickness of the ozone layer appreciably although, as with all aspects of the chemistry of the atmosphere, the situation requires careful monitoring.

(m) CFCs

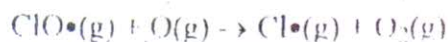
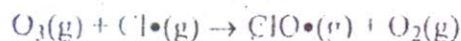
A more significant threat to the ozone layer arises through the use of chlorofluorocarbons (CFCs) in aerosols, air-conditioning systems, refrigerants and in packaging. They have obvious advantages in these applications because they are chemically inert, have low toxicity and are non-flammable. Their very inertness was the clue to the environmental problems which they have caused. They diffuse upwards through the atmosphere unchanged, until they reach the stratosphere, where in the presence of ultraviolet light they dissociate photolytically, generating chlorine atoms which behave as free radicals.

The chlorine atoms behave as free radicals as shown in the following sequence of reactions.

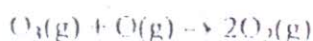
Initiation



Propagation

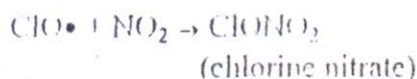
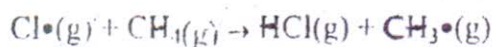


Overall, these two reactions represent destruction of ozone according to the following equation.

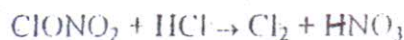


It can be seen that, because a chlorine atom is re-formed in the second propagation step, many molecules of ozone may be decomposed per atom of chlorine. This is, of course, similar to the behaviour of nitrogen monoxide.

There are termination steps for the removal of chlorine-containing free radicals which might limit the destruction of ozone. Two possibilities are given below.



However, the hydrogen chloride and chlorine nitrate can react together in the presence of ice particles such as those found in the stratospheric clouds in polar regions.



The chlorine and nitric acid stay trapped in the clouds until sunlight intensities increase in the polar spring. The chlorine molecules may then dissociate into chlorine atoms and play a significant part in the particularly severe depletion of ozone which occurs in polar regions at this time of the year, particularly in the Antarctic.

CFCs with a relatively high proportion of chlorine are potentially the more damaging in this context and are said to have high ozone depletion potential (ODP). The ODP value is defined as the ratio of the % (by mass) of the compound in the atmosphere to its residence time in years.

es of the ODP values of major commercial CFCs are shown below.

Formula	ODP	Residence time/years
CCl_3F	1.0	75
CCl_2F_2	0.9	111
$\text{CCl}_2\text{FCClF}_2$	0.8	90
$\text{CClF}_2\text{CClF}_2$	0.6	185
CClF_2CF_3	0.3	380

The inertness (and, hence, relatively long residence times) of CFCs is explained by their molecules being completely halogenated.

Alternatives to CFCs that have been proposed include hydrocarbons with an appropriate volatility, such as butane, and CFCs which contain at least one hydrogen atom in their molecule. These are known as HFCs or HCFCs. The hydrogen atom can readily be displaced by reactive chemicals in the troposphere (e.g. by hydroxyl free radicals). This process helps initiate the breakdown of the entire molecule. The chlorine contained in HCFCs cannot then reach the stratosphere and damage the ozone layer.

Even with successful recycling programmes, it has been estimated that by the end of the century the amount of CFC substitutes released into the atmosphere will be measured in terms of hundreds of thousands of tonnes.

Human technological activity is on the increase and will continue to have an influence on the environment. That is why it is essential that continuing research is devoted to investigating and understanding the complex chemistry involved.

The environment has never been static but the rate of change has been relatively slow. However, it is now being realised that profound and rapid changes are being brought about by human activity and that the cumulative effects of this activity can have potentially damaging consequences for the environment. See Fig 9.

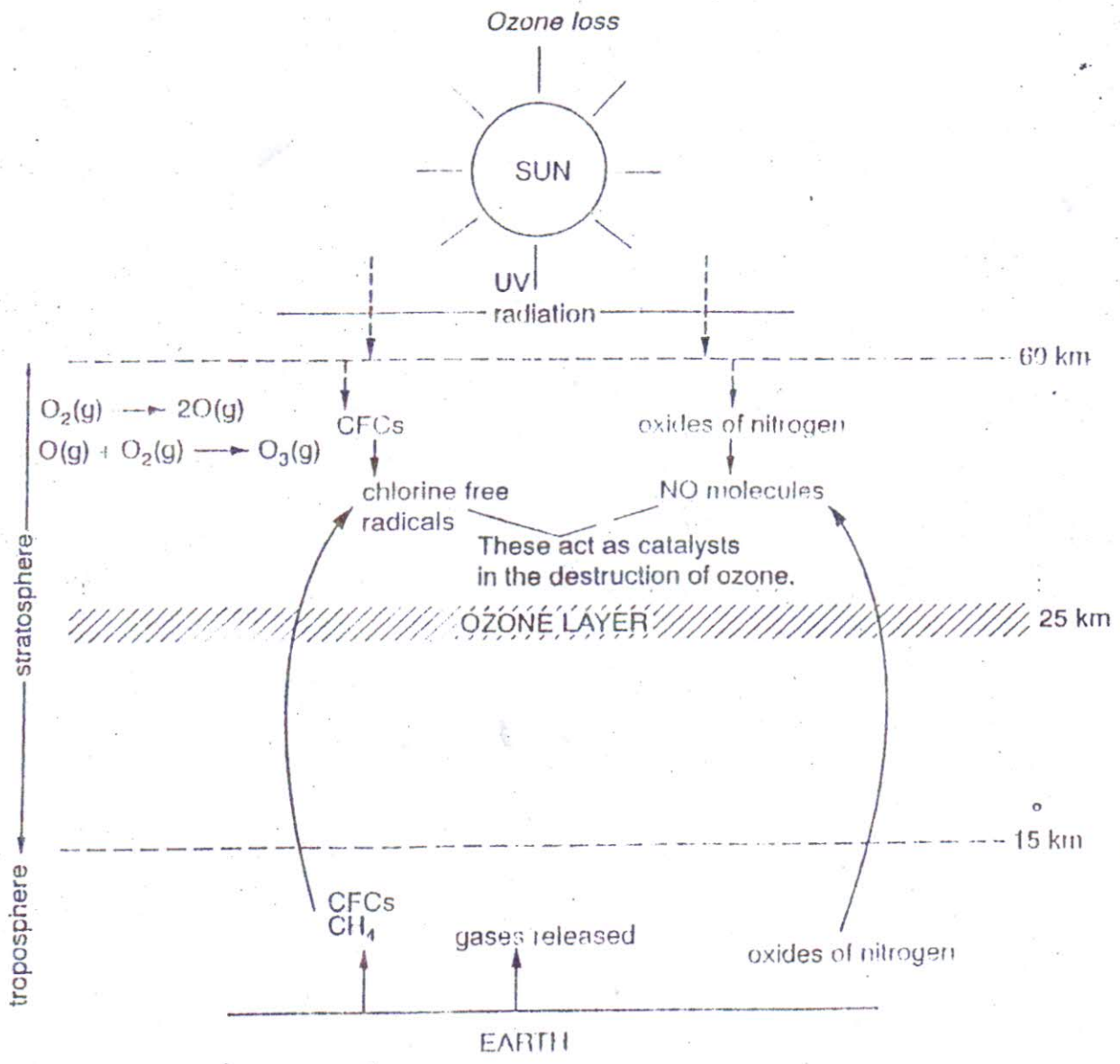


Fig 9 - atmospheric processes

n) The chemistry of the internal combustion engine

Refined fossil fuels (hydrocarbon fuels), as used in vehicles, are a major source of emissions such as carbon monoxide, oxides of nitrogen, and unburnt hydrocarbons. (Leaded petrol is a source of lead compound pollution in the atmosphere.)

There is considerable variation in the composition of vehicle exhausts depending on its mode of operation. The table below gives some typical values.

Mode of operation	Some exhaust gases present		
	unburnt hydrocarbons (ppm)	nitrogen oxides (ppm)	carbon monoxide (%)
idling	500-1000	10-15	4-9
accelerating	50-800	1000-4000	0-8
cruising	200-800	1000-3000	1-7
decelerating	3000-12000	5-50	2-9

Carbon monoxide is a colourless and poisonous gas which is always formed when carbon compounds have insufficient oxygen for complete combustion, such as in the internal combustion engine. It is fatal in an enclosed space. In many cities, especially at peak times of heavy traffic, the concentrations of carbon monoxide exceed recommended limits and there is a good correlation between increased concentrations of carbon monoxide and increases in recorded heart attacks. Arctic explorers who used small stoves in tents kept as air-tight as possible often reported severe headaches or dizziness, apparently caused by increased carbon monoxide concentrations.

Carbon monoxide can also take part in a complex series of reactions which leads ultimately to an increase in the presence of undesirable low-level ozone (not to be confused with the ozone in the stratosphere). The two regions of ozone, tropospheric and stratospheric, do not appear to mix and exist independently of one another.

Oxides of nitrogen, collectively known as NO_x , are produced by burning fuels in air (which is approximately 79% nitrogen). The high combustion temperature provides sufficient energy to dissociate oxygen molecules into atoms which can then cause the following free-radical reactions to occur.



which, overall, is $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$

As with other reaction sequences that have been described, the second reaction produces an oxygen atom which can initiate the first reaction again. The resulting nitrogen oxides contribute to many effects, one of the most prominent being acid rain.

Emissions from vehicles also contribute to heavy metal pollution. Lead in the form of an organo-metallic compound tetraethyl-lead, $Pb(C_2H_5)_4$, has been used as an additive to petrol in vehicles for some time. It is used to ensure a smooth running engine. The weak lead-carbon bonds are easily broken, giving $CH_3CH_2\cdot$ (ethyl radicals) which initiate smooth burning.

To prevent lead oxide being deposited on the cylinders, 1,2-dibromoethane, $(BrCH_2CH_2Br)$, is also added to the petrol. Volatile lead compounds are formed which are swept out with the exhaust gases. Lead can be ingested either directly or indirectly through the food chain and is the cause of considerable concern. It has been associated in humans with general mental depression, slowness in reaction times and brain damage, particularly in young children. It is dangerous because it cannot easily be eliminated by the body.

Lead concentrations can be diminished by using non-leaded high-octane fuel. An octane rating is a measure used by petroleum technologists to characterise the efficiency of a given hydrocarbon as a fuel for engines. It is based on a scale in which the compound 2,2,4-trimethyl pentane (which contains eight carbon atoms) is given a value of 100 and other fuels are compared to it. The higher the octane rating of the fuel, the higher the temperature and pressure it can withstand and the more effective the fuel is. When leaded petrol burns in the internal combustion engine, the lead additives effectively raise the octane rating of the fuel. Fuel with a low octane rating can be converted into high octane fuel by being vaporised and passed over a catalyst so that the hydrocarbon chains reform and produce those that can stand the high temperature.

Because of the hazards associated with the use of leaded petrol, increasing use is being made of unleaded petrol. However, such petrol still results in the emission of nitrogen oxides, carbon monoxide and unburnt hydrocarbons. The hydrocarbons present in unleaded petrol include benzene which is known to be carcinogenic (cancer inducing). Problems associated with these emissions have already been discussed. One way of reducing these emissions is the fitting of catalytic converters into the exhaust systems of petrol-driven vehicles.

There has, in fact, been much progress in reducing emissions from vehicles but there are also some unforeseen consequences of these changes. Diesel engines are more efficient than petrol engines since, as they operate at higher temperatures, there is more complete combustion of the fuel. Diesel fuel also contains more carbon atoms per molecule than petrol so the energy released on burning one litre of fuel is greater. This leads to greater fuel economy. However, vehicles using diesel as a fuel can emit dangerous aromatic hydrocarbons which produce carcinogenic products when incompletely burnt. Such vehicles also produce approximately fifty times as much particulate matter (PM) as a vehicle fuelled by petrol.

The black smoke that may be released from the exhaust system of a diesel engine consists of tiny particles suspended in the air and such emissions are measured on a PM scale. Particles with a diameter less than 10 μm are described by the notation PM_{10} and there is much evidence that particles of this size are damaging to health as they are small enough to penetrate deep into the lungs. Increasingly strict regulations controlling the allowable emissions from engines are being brought into effect in many countries.

The emissions standards for gases such as sulphur dioxide, nitrogen oxides and for particulate matter vary between countries.

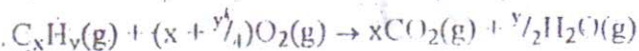
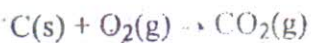
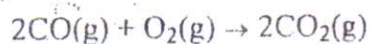
- (i) Do you think that it is necessary or acceptable for there to be national differences in standards of pollution control?
- (ii) Do you think that it would be politically possible to achieve World emission standards?

(b) Catalytic converters

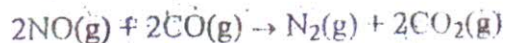
The catalyst used is a mixture of expensive transition metals, palladium, platinum and rhodium. They are used to coat the surface of a honeycomb structure which maximises the surface area on which heterogeneously catalysed reactions take place. These three catalysts are selective in the reactions they promote. Palladium and platinum promote the oxidation of carbon monoxide and of the unburnt hydrocarbons; rhodium promotes the reduction of nitrogen monoxide to nitrogen. The reactions involved are favoured at typical exhaust temperatures (750 K to 800 K) but they do need an exact air/fuel ratio of 14.7 to 1. Catalytic converters are de-activated by lead (i.e. the lead is preferentially adsorbed on the catalyst surface thereby occupying their active sites). Cars with catalytic converters have to use lead-free petrol.

The operation of catalytic converters may be summarised as follows:

- (i) Carbon monoxide, carbon soot and unburnt hydrocarbons (represented as C_xH_y) are oxidised to carbon dioxide and water.



- (ii) Oxides of nitrogen are reduced to nitrogen.



There is a difficult compromise between developing more power from the internal combustion engine and obtaining better fuel economy. More fuel (a richer mixture) results in more power but this produces more unburnt hydrocarbons and more carbon monoxide. More air (a leaner mixture) is more economical but produces more oxides of nitrogen. Catalytic converters certainly go some way to helping achieve a balance between power output, better economy and the reduction of harmful emissions. However, it must be remembered that, like so many chemical reactions, those in the converter do not occur at any appreciable rate until the catalyst is hot. A vehicle which is used for many short journeys will be much more polluting than one that is used for fewer but much longer journeys.

(p) Lean-burn engines

An alternative approach to the reduction of pollution exploits improved engine technology which now makes it possible to manufacture engines which use an air/fuel ratio of 18:1. These lean-burn engines require specially designed combustion chambers and electronically controlled fuel systems but, equipped with catalytic converters, are amongst the least polluting systems available.

(q) Photochemical smog and PAN

Carbon dioxide, carbon monoxide, oxides of nitrogen and sulphur dioxides are examples of *primary pollutants*, being produced separately by the operation of the internal combustion engine itself. *Secondary pollutants* are formed as a result of subsequent reactions between these primary pollutants and other exhaust constituents, such as unburnt hydrocarbons (fuel).

The most serious secondary pollutant which arises as a result of the motor vehicle is photochemical smog. It consists of a mixture of oxidising substances including ozone, nitrogen dioxide, and peroxyacetylnitrate (PAN, which is described later in these notes), which together are extremely irritating to the respiratory system. Photochemical smog is very prevalent when, in sunny weather, there is heavy traffic. It is especially prevalent in certain geographical locations (the most famous being that of Los Angeles).

The chemistry of photochemical smog formation is incompletely understood in detail, though the following processes represent the principal stages.

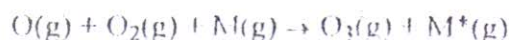
The formation of photochemical smog is most likely when there is:

- bright sunlight,
- a temperature inversion near the ground (i.e. a situation where the air at low altitudes is cooler than the air which lies above it),
- a relatively static air mass,
- relatively high concentrations of primary exhaust pollutants.

Reactions involving free radicals are complex and it is not necessary for them to be learned in detail. However, an example showing how a, somewhat surprising, organic compound is generated through atmospheric free-radical processes serves to illustrate some features of the chemistry involved. These processes involve species, such as the hydroxyl free radical, which are not normally generated under laboratory conditions. Many sets of reactions similar to those outlined below may result in a range of pollutant organic products with effects which are only beginning to be fully understood.

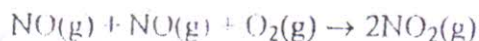
The sequence of reactions leading ultimately to the formation of PAN involves firstly the production of ozone. Nitrogen oxides largely generated from the high temperature combustion of nitrogen within petrol engines, followed by reactions utilising hydrocarbons, enhance the production of ozone. It must be remembered that photochemical smog is formed in the troposphere, where the intensity of incident ultraviolet radiation is much less than in the stratosphere.

It is known that the only viable mechanism for the formation of ozone in the troposphere involves the dissociation of nitrogen dioxide followed by a reaction between the oxygen atoms so formed and molecular oxygen.



(M is an inert molecule, such as nitrogen, which removes some of the excess energy of the reaction as M*.)

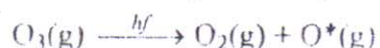
However, the oxide of nitrogen present in highest concentration in car exhausts is NO and this must first be converted to nitrogen dioxide by the following reaction.



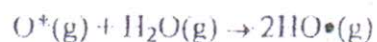
As this involves three molecules, it is extremely slow at the concentrations of nitrogen monoxide that are present in the atmosphere.

Once ozone has been formed, it is believed that the following reactions occur.

photodissociation of ozone to give oxygen molecules and excited oxygen atoms



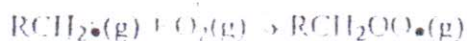
reaction of excited oxygen atoms with water vapour to give hydroxyl radicals



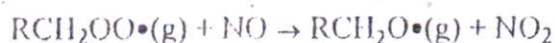
formation of an alkyl radical



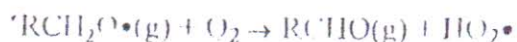
formation of a peroxy radical



rapid oxidation of NO to NO₂

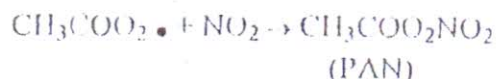
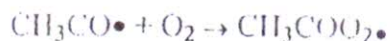


oxidation to an aldehyde



Peroxyacetylnitrate (PAN), $\text{CH}_3\text{COO}_2\text{NO}_2$, can be formed if the aldehyde generated by the above sequence is ethanal.

The following reactions can then occur.



It should be emphasised again that there is no need to recall this sequence but it does serve to illustrate the intricacy of atmospheric chemistry and the unexpected products that may ultimately be obtained. PAN is particularly irritating to the mucous membrane and is believed to be largely responsible for the irritant effects of photochemical smog. The brown haze characteristic of photochemical smog is largely due to the presence of nitrogen dioxide.

In cities such as Los Angeles, the peak incidence of photochemical smog occurs some time after the morning rush hour: although the concentrations of primary exhaust pollutants are high during the rush hour, the intensity of the sunlight is insufficient to drive the necessary photochemistry until later in the morning.

The disadvantages of low-level (i.e. in the lower troposphere) ozone may be summarised as:

- the formation of photochemical smog is enhanced, the compounds thus produced irritate mucous membranes;
- photosynthesis within plants is adversely affected, their growth is inhibited and their resistance to pests is diminished.

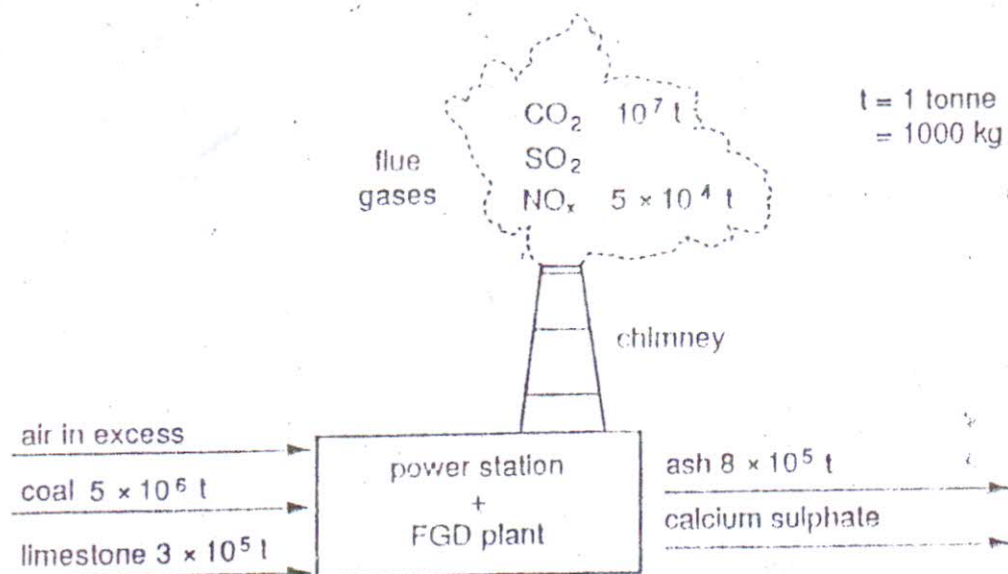
Example questions

1. What is the importance of the stratosphere in the protection of life on Earth?
2. Make a diagram of the nitrogen cycle, labelling each process and including the formulae of the principal nitrogen compounds involved. You should clearly distinguish between those processes which take place in soil and those which take place in the air.

A coal-fired power station (which generates electricity) is fitted with a Flue Gas Desulphurisation (FGD) plant, which removes some of the sulphur dioxide from waste gases.

In the FGD plant, the waste gases are treated with powdered limestone, CaCO_3 , producing calcium sulphite, CaSO_3 . This is oxidised by air to form solid calcium sulphate, CaSO_4 .

The diagram below shows the amounts of substances used, and produced, by such a coal-fired power station with an FGD plant in one year.



- (a) (i) What process provides the energy used in the power station?
- (ii) Which gas, not listed in the diagram, is the chief component of the flue gases?
- (iii) Explain why oxides of nitrogen (NO_x) are present in the flue gases.
- (b) Write a balanced equation in each case to show how
- (i) limestone reacts with sulphur dioxide,
- (ii) air oxidises calcium sulphite.
- (c) (i) Use the equation in (b)(i) to determine the maximum mass of sulphur dioxide which could be removed by 3×10^5 t of limestone in the FGD plant. [t = tonne = 1000 kg.]
- (ii) Use the equations in (b) to determine the maximum mass of calcium sulphate which would be produced from the 3×10^5 t of limestone.

- (d) The FGD plant removes 90% of the sulphur dioxide from the waste gases.

Using your answer to (c)(i), calculate the mass of sulphur dioxide which is released into the atmosphere each year by this power station when 5×10^6 t of coal are burnt.

- (e) Which other substances, as well as calcium sulphate, will be formed by the limestone acting on the flue gases?
- (f) Suggest two possible disadvantages of the use of an FGD plant.

4. Read the passage below and answer the questions that follow.

There has been considerable debate about the definition of acid rain. Until quite recently, any rain with a pH level of less than 5.6 was assumed to be unnaturally acid, whereas research now shows that pH can be as low as 4.5 due to natural factors.

One of the most contentious issues in the acid rain debate has centred on the nature of the relationship between the amount of sulphur dioxide in the atmosphere and the pH of rain. Early researchers tended to assume that this relationship was linear. This view fell from favour in the early 1980s when evidence began to emerge which suggested that the amount of sulphuric acid produced in the atmosphere depended ultimately on the supply of photochemical oxidants rather than SO_2 levels: once the oxidants had been exhausted, any excess of sulphur dioxide would remain in the atmosphere unchanged. A logical development of this could be that decreasing emissions of the precursors of oxidants, i.e. nitrogen oxides and hydrocarbons, might be more effective in decreasing acid precipitation than cutting down SO_2 emissions.

- (a) Outline, using appropriate equations, why rainwater with a pH of 5.6 can be considered 'naturally acidic'.
- (b) Suggest a further natural (i.e. not man-made) occurrence which might cause rainwater to have a pH as low as 4.5.
- (c) Explain, using appropriate equations, how nitrogen oxides are involved in the formation of sulphuric acid in the atmosphere.
- (d) Explain what is meant by the expression *photochemical oxidants*.
- (e) Briefly explain whether you think that, without oxidation processes, an excess of sulphur dioxide in the atmosphere would represent less of an environmental hazard.

The strength of the C-F bond is 467 kJ mol^{-1} . Free chlorine atoms, initially formed in the upper atmosphere by the action of ultraviolet light on chlorofluorocarbons, CFCs, are believed to be responsible for the destruction of the ozone layer.

By reference to the *Data booklet* suggest why CFCs, such as CF_2Cl_2 , are being replaced by fluorohydrocarbons such as $\text{C}_2\text{H}_2\text{F}_4$.

- 6.
- (a) What are the chief gases in the exhaust fumes of a motor car?
 - (b) What are the advantages of fitting a catalytic converter into the exhaust system of a car?
 - (c) What is meant by *lean burn*?

2. PROCESSES INVOLVING SOILS AND WATER

(a) The components of soil and their formation

The complex chemical mixture called soil is an obviously important part of the environment and, although its compounds differ from place to place, there are common features which make it possible to describe in general terms.

Originally, the Earth's crust was formed by precipitation from a liquid mass called magma. As the molten magma cooled, different components crystallised and the diversity of materials on the Earth's surface represents the changing circumstances at the temperature of the melt. Most of these solids, although stable at the different temperatures of their formation, are thermodynamically unstable at present day temperatures. The process of weathering is the kinetic movement towards greater stability. Substances such as rocks and the soil formed from them have giant molecular and ionic structures so that the processes leading to their breakdown are very slow. It may be centuries before a change becomes apparent but nonetheless it is important to realise that it is an active process over which human beings exert considerable influence.

The study of the chemical constituents of soil does not concern itself particularly with the identification of simple compounds with fixed compositions (except maybe a few oxides, carbonates and sulphides) but attempts to identify structural patterns and similarities within the components. Soil is, in fact, a mixture of decomposing organic matter and inorganic compounds dominated by anions created from a relatively small number of elements such as silicon, aluminium, oxygen and sulphur which are counterbalanced by common cations such as the Group I and II elements or iron. To gain an appreciation of the features of these complex anions and their important chemical properties, it is necessary to understand the structure of the simple silicate anion and its role in generating compounds of greater complexity.

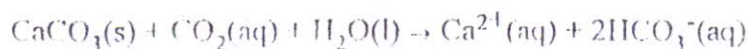
(b) Other components of soil

Although silicates can be amongst the more valuable components of soil, there are clearly many other important materials present. Not surprisingly, their actual nature varies enormously depending not only on the nature of the original rock but also on the extent and type of weathering that has taken place. The chemical processes involved in weathering are complex but always directed towards the generation of more stable materials. Although it should not be viewed as a simple sequence of events, the following stages in the breakdown of rocks can be recognised in broad terms.

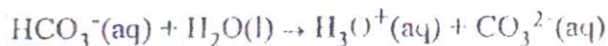
1. Release of soluble components such as Group I compounds.
2. Precipitation of insoluble carbonates as a result of the action of rain containing dissolved carbon dioxide - mostly Group II carbonates

B. van der

Aqueous solutions of carbon dioxide react with carbonate rocks, e.g. limestone, according to the following equation.



However, the hydrogencarbonate ion can also provide carbonate ions



and this can cause the re-precipitation of Group II carbonates in soils and water.

3. The slow breakdown of silicate materials.
4. The ultimate formation of highly weathered residues - mostly very insoluble oxides such as aluminium oxide, silicon(IV) oxide (sand) or iron(III) oxide.

Throughout weathering, there is a steadily increasing presence of organic material which adds a further complexity. Organic matter decomposes over a period of time and the mix of compounds is called humus. Humus, quite apart from improving the physical structure of the soil, can store cations which are absorbed on to the many carboxylate (RCO_2^{-}) groups present. This adsorption is notably pH dependent since hydrogen ions can take the place of the cations to form RCO_2H units.

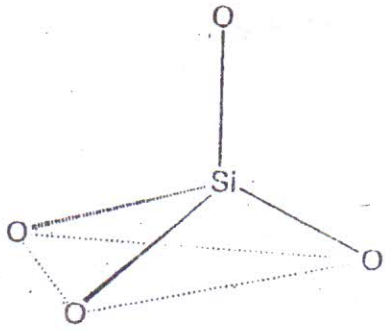
Overall, soil can be regarded as a mixture of steadily decomposing organic and inorganic material - rich in silicates, oxides and carbonates - containing compounds with the important ability to hold and exchange cations for use in plant growth. Soils with a high sand content drain freely and retain nutrients poorly; on the other hand, too much clay can lead to waterlogging and anaerobic conditions. A 'good' soil falls somewhere between these extremes.

(c) Silicate structures

Hydrolysis (or hydration as it is sometimes confusingly, and mistakenly, called) is particularly important in the weathering of rocks such as granite and basalt which contain silicate minerals. The structural units in these minerals are tetrahedra consisting of silicon bonded to 4 oxygen atoms, SiO_4^{4-} . See Fig 10.

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the basic SiO_4^{4-} unit with Si at the centre of a tetrahedron with an oxygen at each vertex



simplified representation of the unit (viewed from above)

Fig 10 - diagram of simple silicate tetrahedron

These tetrahedra can share oxygen atoms at their vertices to generate a large variety of structures. An example is the mineral, mica, shown below in Fig 11.

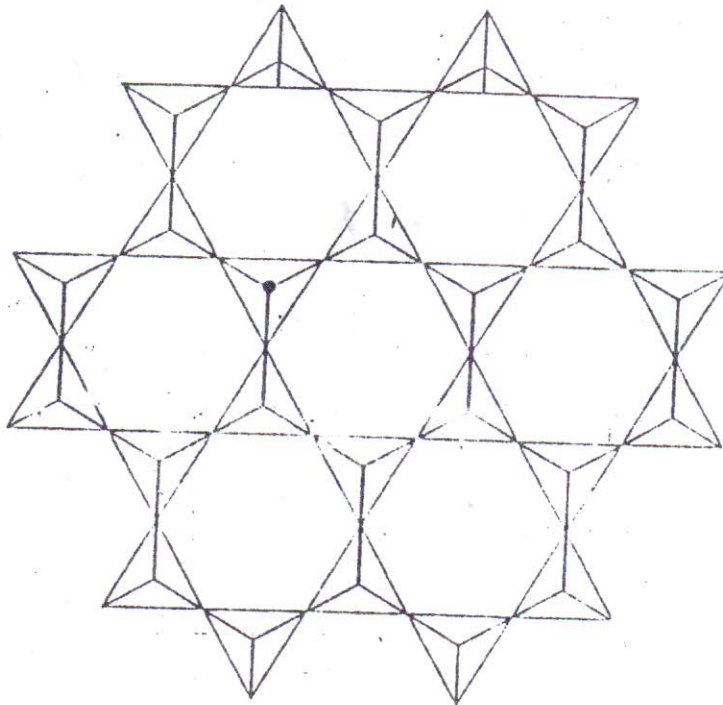


Fig 11 - diagram of mica.

A detailed discussion of the structures of the silicate minerals is not important here and it is sufficient to regard them as containing oxo-anions based on SiO_4^{4-} , with cations present in sufficient number to balance their negative charges. The range of possible compositions is enormous since, as long as overall electrical neutrality is maintained, substitution of one cation by another readily occurs. Similarly, the substitution of anions is possible. If, for example, Mg^{2+} replaces Fe^{3+} , oxide (O^{2-}) might be replaced by hydroxide (OH^-) or fluoride (F^-) to balance the lower positive charge.

Clay Minerals

The chemistry of the weathering of silicate minerals is complex but important, since clays are among the products and these have an essential role in soil formation.

The formation of a sheet structure involving silicate units has already been illustrated in the diagram of mica above. It is also possible for aluminium and oxygen to generate a sheet structure although, in this case, the structural unit consists of an octahedron of six oxide or hydroxide ions with an aluminium ion at the centre of each unit. See Fig 12.

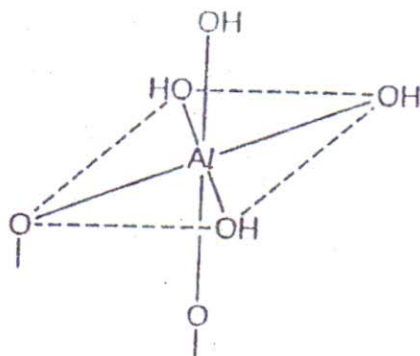


Fig 12 - diagram of single ' AlO_6 ' unit

An important, and perhaps rather surprising, feature of sheets of silicon/oxygen tetrahedra and aluminium/oxygen octahedra is their ability to link together by sharing oxygen atoms. It is therefore possible to build up layer structures consisting of combinations of the two types of sheet, and these are often referred to as silicate clays.

Whilst it is not important to be able to recall the geometry of the way in which the sheets are linked, the general features of the following two types of silicate clay should be understood.

1:1 Layer Silicates

In this type of layer silicate, the 'SiO₄' unit and the 'AlO₆' unit share two oxygen atoms to create a structural unit in which four oxygen ions have been replaced by hydroxide ions.

These individual units are linked through Si-O bridges and it is possible to extend this so that sheets based on 'SiO₄' units may be joined to those derived from 'AlO₆' units. The combined sheets are usefully referred to as lamellae.

Lamellae may now themselves be joined together by hydrogen bonds to create a giant structure, illustrated below. The silicon and aluminium are effectively buried within layers of oxide or hydroxide and the structure has considerable strength because of the presence of so many hydrogen bonds. The presence of these hydrogen bonds also effectively excludes cations from the spaces between the layers. See Fig 13.

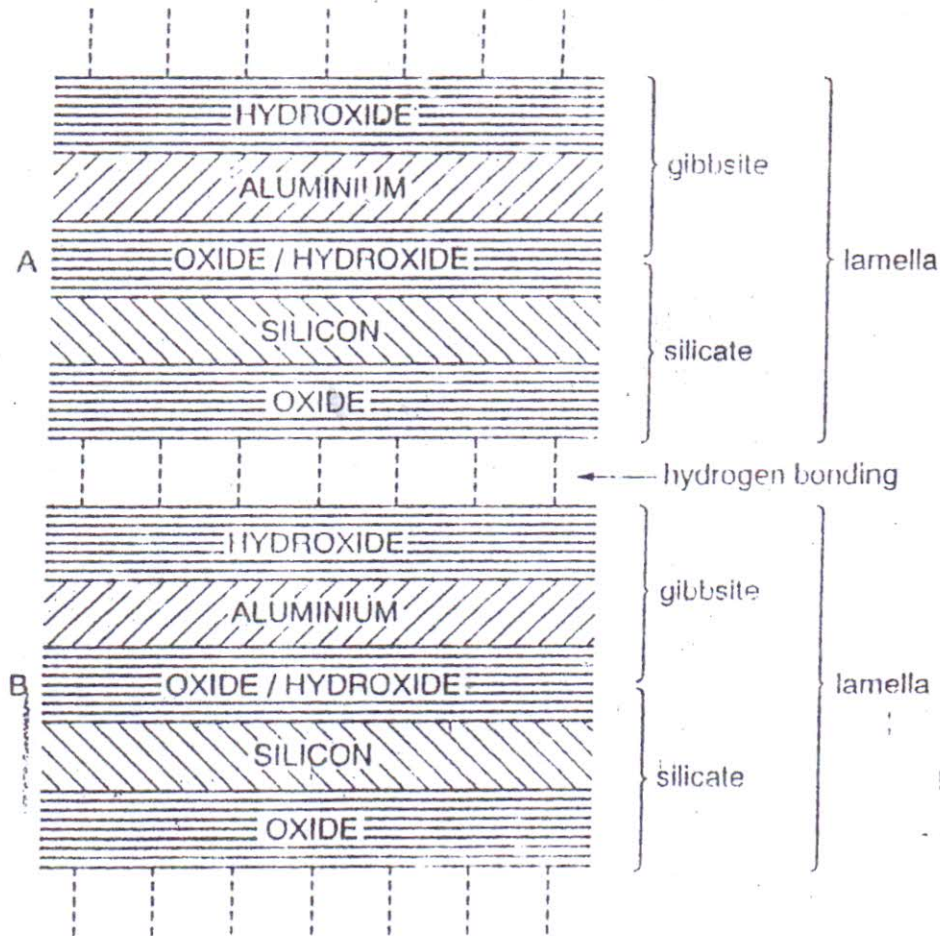


Fig 13 - sheet structure of kaolinite - a typical 1:1 clay

1 Layer Silicates

An alternative arrangement involves the sharing of 4 oxygens between one AlO_6 unit and two SiO_4 units. Such a structure is weaker than a 1:1 layer silicate because the lack of hydroxide ions on the outer surfaces of the lamellae means that no hydrogen bonding is possible. However, water can easily enter the spaces between the lamellae and hydrogen bonding then occurs between the water molecules and the lamellae, thus binding the structure together. See Fig 14.

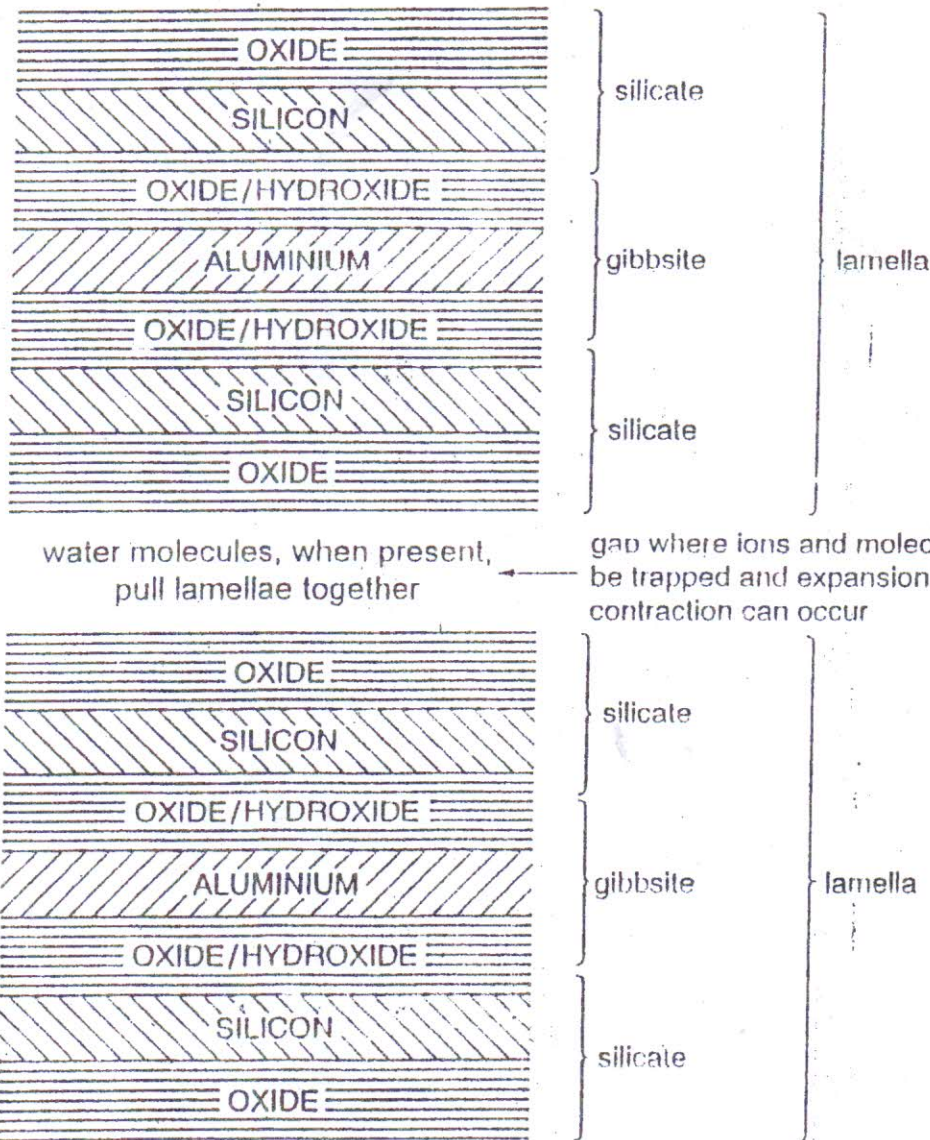


Fig 14 - sheet structure of montmorillonite - a typical 2:1 clay

An important consequence of the lack of strong hydrogen bonds between lamellae in 2:1 structures is that they are able to expand and contract more readily. The well-known cracking that appears when a wet soil dries out occurs because the removal of water causes the lamellae to fall apart. The subsidence of houses after prolonged dry spells of weather is one unfortunate way in which this effect can be observed.

(d) Cation substitution

The above layer structures are 'ideal' and do not exist in soil clays because of cation substitution which takes place at the time of formation of the mineral. This occurs when a 'foreign' cation becomes incorporated into the structure in the place of either a silicon or aluminium ion. For example, Al^{3+} can be found in place of ' Si^{4+} ' within the Si/O layers or Mg^{2+} instead of Al^{3+} within the Al/O/OH layers. Such substitutions typically occur randomly within a structure. However, the commonly found minerals called feldspars, have a regular substitution where one or two in every four tetrahedra have Al^{3+} in place of ' Si^{4+} '.

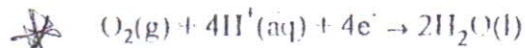
It may be noted that each substitution that occurs results in the loss of one positive charge - Al^{3+} for ' Si^{4+} ' or Mg^{2+} for Al^{3+} . This loss of positive charge must be accounted for to allow the overall structure to be electrically neutral. This is achieved by the adsorption of other positive ions on the surface of the clay. These ions can be either a specific or varied collection and, importantly, they can be substituted by other cations which may be present in soil water. Most minerals, particularly clays, have an ability to retain and exchange cations at their surface - a 'cation exchange capacity' which is a permanent and measurable feature of a silicate clay.

Even if an individual clay structure has little ion substitution, the oxide ions at the surface of the clay do not have their charges neutralised as effectively as the oxide ions in the bulk of the clay. The surface of the clay thus has an additional capacity for cation exchange which can be quite significant. This capacity to adsorb cations at the surface depends on the soil pH since hydrogen ions may preferentially adhere to the oxide surface in place of other cations in acidic conditions.

The ability of clays to adsorb cations is a vital part of their capacity to act as an effective means of ion supply for plant growth. For example, soil treated with either potassium ions or ammonium ions has the ability to retain these ions at the clay surface by displacing the ions already present. The ions therefore remain available rather than being washed away when rain falls. This behaviour is vital in maintaining growth over an extended period of time and the cation exchange capacity effectively controls the extent to which a soil may be described as 'good' with regard to its potential agricultural use.

The effect of soil oxygen levels on nutrient availability

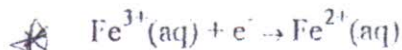
In general, plants use ions for growth in an oxidised form and this is achieved by adequate oxygen availability in the soil. The following process has a standard redox potential of 1.23 V and is therefore quite strongly oxidising.



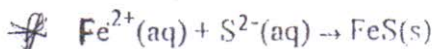
Although conditions within soils are far from standard - the acidity is considerably less and oxygen concentrations are much lower - this reaction is nonetheless responsible for maintaining oxidising conditions. The redox potential, which is around 0.8 V in a well-aerated soil, is sufficient to ensure that most ions in soil exist in their oxidised forms (e.g. iron as Fe^{3+} , nitrogen as NO_3^- and sulphur as SO_4^{2-}) and to allow organic carbon to be lost as carbon dioxide. The oxygen may diffuse into the soil as a gas or be carried downwards in solution.

When oxygen circulation is inadequate, e.g. when a soil is waterlogged, the redox potential of the above reaction decreases and it may be impossible to maintain all the ions in their oxidised state. In these anaerobic conditions, other conversions may be favoured which are disadvantageous to plant growth. For example, the following reductions may occur.

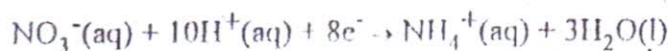
- iron(III) to iron(II):



The presence of iron(II) and sulphide ions together results in the loss of available iron in solution due to formation of the very insoluble iron(II) sulphide.

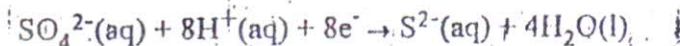


- nitrates to nitrites, NO_2^- , or finally to ammonium ions, NH_4^+ :

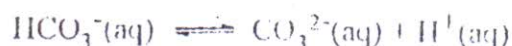


Nitrite ions are toxic to plants and ammonium ions may be absorbed less efficiently.

- sulphates to sulphide ions:



Under sufficiently acidic conditions, S^{2-} can occur in the soil as hydrogen sulphide - a toxic and foul-smelling gas. Note, also, that these reactions also remove hydrogen ions from solution and hence increase the pH of the soil. This increase in pH can result in the precipitation of metals such as iron and aluminium as their hydroxides. An increase in pH also forces the following reaction to the right.



This decreases the availability of metals such as calcium and magnesium, which have insoluble carbonates.

Severely anaerobic conditions can lead to the conversion of carbon dioxide to methane, which deprives the soil of the buffering action of the carbon dioxide/hydrogencarbonate/carbonate system.

(f) Pollution by organometallic compounds

The use of tetraethyl-lead as a fuel additive has previously been mentioned. It is an example of the unnecessary introduction of an organometallic compound into the environment. There are equal concerns about the formation of other organometallic compounds which may be well illustrated by the formation of dimethyl mercury.

In the anaerobic conditions that are likely to occur in the muddy sediments of rivers, mercury(II) ions, Hg^{2+} , can be converted into gaseous dimethyl mercury, $Hg(CH_3)_2$ by the action of bacteria which utilise unoxidised hydrocarbons, such as methane. The dimethyl mercury diffuses through the water and during this process may be absorbed by fish. Although the concentrations are initially very low, the dimethyl mercury steadily accumulates in the body of the fish until it has a significant presence. If these fish are then consumed, the mercury enters the food chain and may cause significant health problems.

A well-publicised example of mercury poisoning occurred at the fishing village of Minamata in Japan where a chemical plant, using Hg^{2+} as a catalyst in a process leading to the manufacture of poly(chloroethene), discharged residues containing mercury into Minamata Bay. Fish absorbed the mercury as the dimethyl compound and subsequently many hundreds of people died as a result of eating the contaminated fish.

(g) Soil acidity

For most agricultural purposes, the pH of soil should be in the region of 6; values lower than this have noticeable effects on the nature and efficiency of the soil as a growth medium. In addition, since most of the water in lakes and rivers has percolated through the surrounding soil, a change in soil properties may have significant effects on the local ecology. It is clear that in many areas soil acidity has been increasing in recent years and a possible reason is the decreasing pH of rainwater as a result of the increase in the concentrations of dissolved gases such as sulphur dioxide, carbon dioxide and the oxides of nitrogen. Acid rain certainly contributes to increasing soil acidity but it is difficult to quantify its impact because there are several other processes which may also be involved.

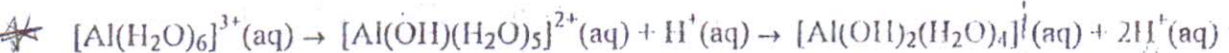
Factors causing increased soil acidity

Respiration is perhaps the most important natural soil acidification process. Soil organisms can degrade organic materials to carbon dioxide and water and the subsequent formation of HCO_3^- and H^+ ions increases the acidity. Decomposing organic material (humus) is also acidic in its own right since it contains a high proportion of $-\text{CO}_2\text{H}$ groups, though these are of greatest importance in the control (buffering) of soil pH. Growing material also enhances acidity by extracting ions that are required from the exchange sites which may then become occupied by hydrogen ions. Although these ions might be replaced when the plant eventually dies, this will not be the case if the plant is used for food or if, as is the case with forests, the growth is sustained for many years. A well-aerated soil may generate hydrogen ions as a result of the oxidation of the ammonium ions to nitrate ions.



A less obvious cause of acidity is the presence of aluminium ions. These ions may be present as free ions within soil naturally but they are mostly generated by the weathering of rock materials. Such weathering is, in fact, enhanced as the pH is lowered by decomposition of silicate clays such as the mineral kaolinite.

However, instead of alleviating some of the effects of acidity, the highly polarising Al^{3+} ion complexes with water molecules and then regenerates hydrogen ions as follows.

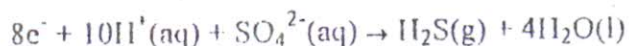


These hydrated aluminium ions, $[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ may occupy the exchange sites (to which they adhere strongly because of their high charge) and maintain the local acidity.

Factors causing decreased soil acidity

The most important counter to increasing soil acidity is the weathering of the underlying rock material. Carbonate-based rocks, e.g. limestone, have a directly neutralising effect but other materials may also consume hydrogen ions as weathering proceeds. For example, potassium feldspar takes up hydrogen ions when it is converted into mica.

Unfortunately, although the potential for such neutralisation is very great (since a small mass of rock could adsorb a considerable number of hydrogen ions), weathering processes of this type are extremely slow and cannot compete with the more rapid production of acidity. Many reduction reactions also involve the use of hydrogen ions. The formation of ammonium ions from nitrate as a reverse of the reaction mentioned previously is a case in point: the reaction of sulphate ions is another example.



Sulphate ions together with hydrogen ions may also be adsorbed on to aluminium oxide or iron(III) oxide surfaces in deeper soil and, in some areas, this is believed to contribute significantly to the control of acidity.

Some Effects of Increasing Soil Acidity

Some of the undesirable effects of increasing acidity have already been implied. It is clear that a soil dominated at its cation exchange sites by hydrogen ions is not able to supply plants with the necessary nutrients for effective growth. In addition, an acid soil medium encourages the reduction of oxo-anions and may thereby render them unavailable to the roots of plants which are usually adapted to accept ions only in a particular, mostly oxidised, form. Acidity also encourages many metal ions to dissolve more readily in the soil solution and, although this may be unimportant for some ions, it is of considerable concern if the element is one of the toxic heavy metals such as mercury, cadmium or lead or indeed if it is aluminium. These toxic ions may selectively accumulate in plants, or other organisms, and thereby enter the food chain.

Lead, for example, is usually immobilised in the environment as insoluble compounds such as its sulphide or carbonate. Lead ions may also be held on the surface of silicate clays. In acidic conditions, these compounds become appreciably more soluble and hydrogen ions may displace lead ions at the cation exchange sites of clays. In both cases, the concentration of lead ions will increase in the surrounding water.

Aluminium is also of particular note since, as already explained, it is present in potentially very large amounts within soil structures. Its generation as a free hydrated ion and its passage through the soil are both enhanced as the pH value decreases and it also tends to dominate cation exchange sites. Its adverse effects are not fully established but there is little doubt that its presence is undesirable. For example, it is certain that the concentration of uncomplexed aluminium ions in lakes is responsible for the loss of fish.

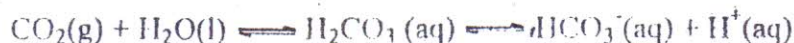
The Control of Soil and Water Acidity

The ability of clay minerals to adsorb cations, including hydrogen ions, has been mentioned earlier. Although important in controlling soil pH, clays are not considered a buffer in the chemical sense. Similarly, liming simply neutralises the acid present but exerts no buffering action. Buffers involve aqueous equilibria between a weak acid and its conjugate base in aqueous solution. Soils contain natural buffers. A buffer is a system which changes its pH only to a small extent when moderate amounts of acid or alkali are added. Soil is a complex mixture of inorganic and organic constituents and the buffering mechanism of greatest importance in a given soil depends on several factors, most importantly on the nature of the bedrock from which the soil was formed and the proportion of organic matter which it contains.

The principal aqueous buffering mechanisms in soil are as follows.

- The carbon dioxide - hydrogencarbonate system

When carbon dioxide dissolves in water, the following equilibria are established:



As the pH falls, the carbonic acid becomes less dissociated until at $\text{pH} < 4.5$ the extent of ionisation is almost negligible and so the concentration of hydrogencarbonate ions becomes too low for this buffering system to remain effective.

- Humic acids

Plants, particularly their woody parts, are largely composed of polymers such as cellulose (ca. 60%) and lignin (ca. 30%). These substances are hydrolysed in acidic conditions to smaller molecules, the most important of which in the context of the maintenance of soil pH are the humic acids. Lignin contains benzene rings and these, being particularly stable, survive in the humic acids, some examples are given in Fig 15.

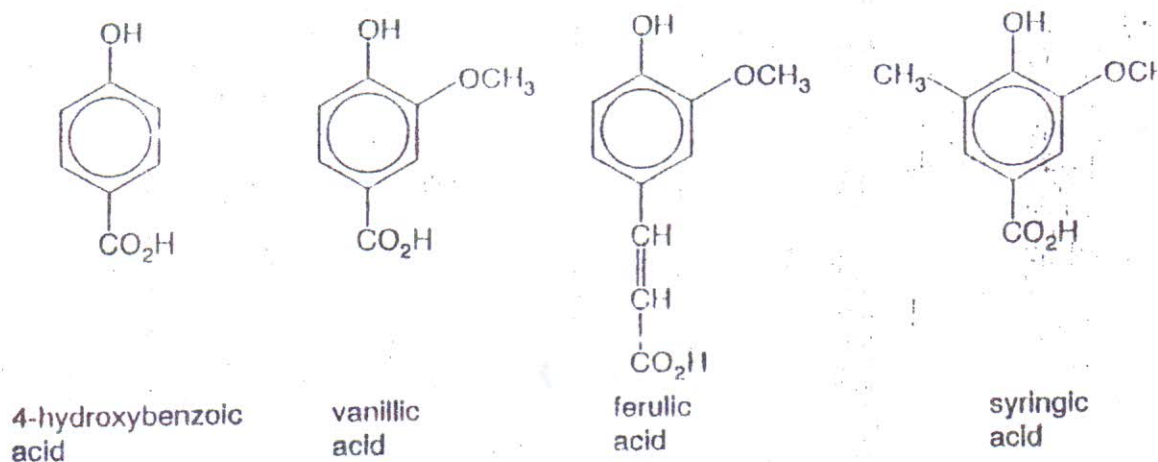
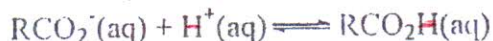


Fig 15

These acids are weak and, with their corresponding conjugate bases (their acid anions), they can act as buffers. An excess of hydrogen ions converts the conjugate base to its parent acid, while decreasing acidity deprotonates the acid.



Liming

There are some circumstances where soils or water may become too acidic and the natural means of control mentioned above are either insufficient or too slow to be effective. In these cases, some increase in the pH may be achieved by liming. This, as its name implies, is the addition of either calcium oxide or limestone, to the area concerned. Heavily farmed land tends to become acidic and farmers may routinely apply lime in order to adjust the pH to a value suitable for the crop they wish to grow. In some countries, such as Sweden, which are affected by acid rain, lime has been applied to lakes to try and restore the conditions necessary to preserve aquatic life. While this has met with some success, it is not always easy to gauge the quantity of lime required. For example, during Winter periods, the snow surrounding lakes in Scandinavia can accumulate considerable acidity and this creates a problem when the snow melts in the Spring. Such surges of acidity may be beyond the capacity of the lime to neutralise. Soils which have accumulated hydrogen ions or aluminium ions at their cation exchange sites may also be difficult to control since, although immediate neutralisation can be accomplished, the pH soon decreases as these ions are released from the soil surface.

(h) Nitrogen and phosphate fertilisers

A fertile soil is one that can consistently produce a desired crop and, while fertility is not solely related to nutrient supply, a soil that is deficient in either nitrogen or phosphorus is incapable of maintaining adequate plant growth.

The problem for nitrogen control is the maintenance of an adequate nitrogen supply in the soil to meet the demands made by the crop for the nutrient while, at the same time, keeping to a minimum the extent to which unused nitrogenous fertiliser is leached from soil into waterways.

Problems associated with phosphates are different from those with nitrogen, primarily because insoluble phosphates of aluminium, iron(III) and calcium are readily formed, making much of the applied phosphate unavailable to plants. The crops are, in fact, only able to take up about 15% of the applied phosphate during the year of application.

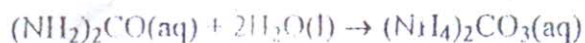
Sources of Nitrogen in Soils

A minority of plants can use micro-organisms contained in root nodules to convert atmospheric nitrogen into water-soluble forms which can then be taken up by plant roots: leguminous plants, such as peas, beans and clover have long been grown on fallow land and then ploughed in to enrich the soil.

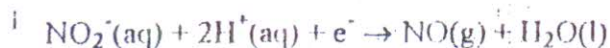
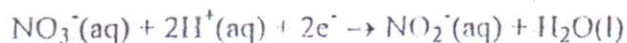
Rainfall is a useful supply of nitrates as a result of direct combination of atmospheric nitrogen and oxygen in lightning discharges, followed by subsequent oxidation and solution.

The decay of natural vegetation and the return of animal faeces (manure) to the soil would mean that the bulk of nitrogen is returned to the soil. However, agriculture produces a crop that is removed from the soil and a nitrogen deficiency results. Other major nitrogen losses include the following. Nitrate ions and ammonium ions are leached from the soil by water and they may pass either directly into streams and ponds or continue in percolating water down the water table. It is possible to locate bands of high nitrate concentration which can be related to the years when large amounts of nitrates were applied to the fields. The ions move steadily down to the water table at a rate of between 1 and 2 metres per year. An excess of nitrate spread on the fields today could still present a problem for the next fifty years.

Animal manure is a good source of nutrients but can lose a high proportion of the available nitrogen due to the formation of volatile compounds. Urea is hydrolysed to ammonium carbonate which, in turn, decomposes into ammonia and carbon dioxide.



Denitrification is the term used for the reduction of the nitrate ion into gaseous compounds and this is brought about by micro-organisms. In the absence of oxygen, the organisms have the ability to remove the oxygen from nitrates and its reduced products.



Each step in the reduction process is catalysed by a specific enzyme and the reaction scheme can stop at any stage as the gaseous products are released into the atmosphere.

In farming, the overall deficit for nitrogen is made up by the addition of nitrogenous fertilisers.

Eutrophication

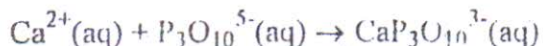
All fertilisers have to be soluble in water because they are necessarily applied to the soil surface and then have to be carried to the roots by rainwater percolating through the soil. All nitrates are sufficiently soluble to be carried rapidly downwards and are soon beyond the reach of plant roots. More fertiliser then has to be applied and the processes of rapid leaching and continued application soon lead to the accumulation of high concentrations of nitrates in waterways.

Eutrophication literally means 'well fed' and the high levels of nitrate in waterways ensure the rapid growth of plants, initially microscopic algae. These soon blanket the water surface and significantly diminish the amount of light able to reach water weeds growing on the bottom, leading to decreased photosynthesis and a lowering of the concentration of dissolved oxygen. The algae die and, when they decompose, cause a further decrease in the concentration and availability of dissolved oxygen. Rapid weed growth also has the effect of reducing the rate of flow, which reduces the efficiency of oxygen exchange at the surface. At this stage, small animals die, decompose and decrease the concentration of dissolved oxygen still further. The end result of this cycle can be the death of all animals, except those such as annelid worms and leeches, which can tolerate very low concentrations of dissolved oxygen.

The Use of Phosphates in Detergents

Eutrophication is largely controlled by the presence of excessive concentrations of nitrate ions but additional phosphate ions would also encourage further unwanted growth in lakes. This is, of course, particularly so if the water already has a substantial supply of nitrate ion. A potential source of phosphate can come from the use of detergents containing pyrophosphates.

The pyrophosphates (the ion being $P_2O_7^{4-}$) are added in order to improve the cleaning power of the detergent. They act as a water softener by complexing with the cations $Mg^{2+}(aq)$ and $Ca^{2+}(aq)$.



The ability of pyrophosphate ions to form a soluble complex with Ca^{2+} ions means that the formation of an insoluble scum is prevented.

Example questions

7. Blueberry plants only thrive on soils that are very acidic. Soils rich in organic material and fertilisers such as ammonium sulphate provide appropriate conditions.
- (a) Explain the use of (i) organic material, (ii) ammonium sulphate, in creating and maintaining soil acidity.
- (b) The addition of lime to a soil temporarily raised its pH from 4.5 to 7.5.

Explain why (i) more lime is needed than the acidity of the water present in the soil might suggest, (ii) the increase in pH is only temporary.

Redox processes are important in establishing healthy soil conditions suitable for plant growth.

- (a) Write a half-equation to illustrate the role of oxygen in maintaining inorganic ions in their oxidised forms within soils.
- (b) Typically, the redox potential of this reaction is about +0.8 V within soils. Explain why this value is substantially less than the standard potential quoted in the *Data Booklet*.
- (c) If this potential decreases, some ions within soils may exist predominantly in a reduced form. Give an example of circumstances where this might occur and, using the standard redox potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$, explain its effect on the oxidation state of iron.

- 9.
- (a) Explain the role of oxygen in maintaining soil in a suitable condition for plant growth. Illustrate your answer by reference to ions containing (i) nitrogen, (ii) iron. Include appropriate equations.
 - (b) Methane and dinitrogen oxide, N_2O , both cause atmospheric pollution and can be released from soils under certain conditions. Explain the circumstances that may cause these compounds to be formed.

10. Nitrate, phosphate and lead ions are among the ionic pollutants that may be found in small quantities in river water. Nitrate ions may be leached from agricultural lands and phosphate ions may result from the use of detergents. Lead ions can come from the surrounding land although it is amongst the least mobile of heavy metal ions.

- (a) Give two reasons why nitrate, rather than ammonium, ions are likely to be leached from soils.
- (b) Explain the function of phosphate ions as an additive to detergents.
- (c) What problem may occur in still water contaminated by both nitrate and phosphate ions?
- (d)
 - (i) Give two reasons why lead ions tend to be immobile within soil.
 - (ii) Explain the conditions under which lead ions may become more mobile.
- (e) State the long-term concern associated with the ingestion of lead by humans.

11. Many soils rich in silicate clays show signs of cracks in their structure during weather. These cracks are the result of the separation of the lamellae within the structure.
- Identify the type of clay that is liable to develop such cracks and draw a simple diagram of its structure.
 - Suggest how these cracks develop as wet soil dries out.
12. Oxygen circulation within soils is essential if many of the ions present are to be maintained in a form suitable for plant uptake.
- Use the *Data Booklet* to write the half-equation for the reaction responsible for maintaining oxidation and quote its electrode potential under standard conditions.
 - In practice, the redox potential within soils is considerably less than the standard value. With reference to the half-equation you have quoted in (a)(i), give two reasons why this is so.
 - Waterlogging is a major reason why oxygen circulation may be inefficient within soils. Such anaerobic conditions result in changes to the oxidation states of a number of ions.
 - State the sulphur-containing ion utilised by plants in fully oxidised soil and an ion formed from it under very reducing conditions. Write a balanced half-equation for the reduction.
 - State two further reductions of other ions that can take place under extreme reducing conditions.

13. Read the following passage and answer the questions that follow.

In addition to exposure to high levels for short periods, whether in wet forms, dry forms or in mists, trees experience the gradual, incremental effects of acid rain pollution mainly through soil changes.

Cations such as magnesium and calcium are gradually leached out by acid inputs, such as by sulphur deposited in wet or dry form. It has been calculated that the buffering capacity of Scandinavian soils is exceeded at deposition levels of sulphuric acid of about $5 \text{ kg ha}^{-1} \text{ yr}^{-1}$ and of Canadian soils at levels of $20 \text{ kg ha}^{-1} \text{ yr}^{-1}$. British levels are estimated to be in the range of $8\text{-}15 \text{ kg ha}^{-1} \text{ yr}^{-1}$.

The Forestry Commission has suggested that this is not a problem in Britain, although in Wales, at least, there is growing concern at acidification of pasture. In large areas, it is thought that hydrogencarbonate buffering is exhausted and aluminium buffers are in operation.

Prof B Ulrich of Gottingen University in Germany originated the hypothesis that forest decline was linked to aluminium toxicity caused by soil acidification (aluminium being much more soluble at pH below 6).

(ha = an area of 1 hectare)

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- (a) Explain briefly how magnesium or calcium is leached out by acid inputs.
- (b) Humus may also act as a soil buffering agent. Outline how humus can act in this way.
- (c) Suggest what limits the solubility of aluminium at pH values higher than 6.
- (d) Explain the prevalence of aluminium ions in soil solutions with pH values less than 6.
- (e) By considering the nature of the hydrated aluminium ion, explain how it might act as a buffer in soils which have become acidified.

3. WASTE MANAGEMENT

(a) Land-filling and incineration

A large quantity of domestic waste is disposed of by tipping the rubbish into old quarries, coastal marshlands or other suitable sites within economical handling distance. These landfill sites, when well-run, compact the rubbish into layers about 2 metres thick before covering the surface with soil or ashes to prevent habitation by small mammals and insects.

There are two potential problems with this method of disposal.

(i) Leachate

This is a black liquid that oozes from refuse tips when water percolates through. It contains partly decomposed organic matter and is often rich in a range of metal ions, some of which are hazardous.

(ii) Landfill Gas

The anaerobic conditions of compressed waste can cause the formation of hydrogen sulphide and methane (as explained previously on pages 44 and 30 respectively). The latter gas is both potentially explosive and is a greenhouse gas.

Incineration of domestic waste is an apparently attractive alternative to landfill but careful temperature control is necessary if the formation of toxic products is to be avoided. A group of chemicals of particular concern are the dioxins which are regarded as a significant health hazard. Dioxins are a group of 210 closely related compounds. An example is 2,3,7,8 - TCDD shown in Fig 16.

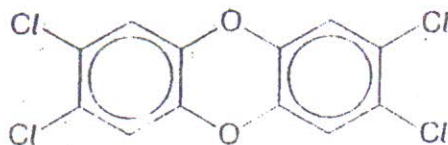


Fig 16 - diagram of the dioxin 2,3,7,8-TCDD

The presence of waste organic material which contains chlorine, e.g. pvc, has the potential to enhance the formation of the very toxic dioxin shown.

These compounds form at temperatures around 500 °C but above 850 °C and in the presence of sufficient oxygen they are destroyed. Modern incinerators can provide the necessary level of control.

sewage treatment

Sewage is a variable and complex mixture of organic matter (fats, soap, urine, oil, food material and faeces) and inorganic matter (nitrates, phosphates, clay, sand and a variety of metal ions) but over 99% is likely to be water. Untreated sewage is sometimes discharged into the sea but this method causes unacceptable pollution if applied to inland water courses. Quite apart from aesthetic factors, discharge of sewage would place an intolerable demand on the dissolved oxygen as bacteria use up the available supply.

Sewage is normally treated as follows.

Suspended matter is allowed to settle (sedimentation) and the sludge obtained is then aerated in the presence of a suspension of micro-organisms. This results in the decomposition of organic matter. Specific components may then be removed - e.g. phosphates can be precipitated using calcium ions or lime can aid the removal of ammonium ions as ammonia gas. Absorption of any remaining organic material is then effected using beds of charcoal.

At this stage, the treated sewage can be discharged provided that it has a satisfactory biological oxygen demand (BOD). The BOD measures the amount of oxygen (in parts per million) taken up by a sample over a five-day period. It is thus a measure of the level of organic matter present. The table below gives an indication of the interpretation given to measurements of BOD.

BOD/ppm	Water Quality
<2	unpolluted
2 - 5	doubtful quality
5 - 10	poor
>10	heavily polluted

Water with a BOD >10 would be unable to support fish life and would be offensive in respect of both odour and appearance. Some improvement in quality can be made by mixing polluted water with many times its own volume of pure water but this should not be necessary if the sewage treatment is effective.

Oil pollution

Marine pollution as a result of oil spills during transportation and exploration is a serious problem. It is likely to become worse as the size of tankers continues to increase and more marine oil fields are developed.

The most obvious effects of oil pollution are the deaths of marine creatures as a result of contact with the oil itself. The waterproofing secretions are removed from the feathers of sea birds and they die either from drowning or exposure. Shellfish are also poisoned by the oil or their respiratory organs clogged by it. These are obvious effects but comparatively little is known about the long-term effects on animals of oil pollution which results in absorption of hydrocarbons at lower concentrations.

A possible effect concerns animals and birds which rely on the distinctive smell of chemicals called pheromones to attract a partner prior to mating. The odour of the hydrocarbons can mask that of the pheromones leading to a reduction in breeding success.

Several initiatives have been taken to reduce oil loss from tankers, principally a ban on the flushing of tanks at sea and the increased use of double-hulled vessels, which may reduce the probability of a leak following a collision. Once oil has been spilled, the subsequent action taken to contain or disperse it depends very much on the quantity of oil involved and the site of the spillage. In coastal locations, particularly in estuaries, floating booms may be used to contain the oil prior to removal by pumping. Larger spillages at sea are usually dealt with by spraying with detergent.

Ion exchange

Industries that create pollutant waste containing dissolved metal ions (e.g. electroplating) can remove the ions using exchange resins. The method employs the same principle as is used by soils to exchange cations at their surface. The resin is an insoluble compound which may be prepared as a sodium salt, e.g. Resin-OSO₃Na. The waste solution may be discharged through the resin and cation exchange takes place so that the pollutant ions are now held by the resin and the relatively less harmful sodium ions pass into solution. The resins eventually become exhausted but can be restored by washing with sulphuric acid followed by regeneration with aqueous sodium hydroxide.

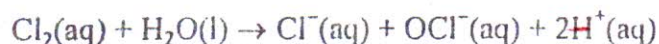
Potable water

Few natural waters are immediately suitable for domestic use and the process of purification to obtain, what is known as, potable water is important.

Simply storing water is the first step towards purification. Suspended matter tends to sink and harmful bacteria begin to die out; organic impurities are oxidised in the upper layers and sunlight has a bleaching effect on the colour.

Specific treatment involves several steps.

- Screening (filtering) removes larger particles of insoluble matter.
- Aeration, achieved by cascading or spraying the water, removes volatile substances such as H₂S or CH₄. Some metal ions are also oxidised (e.g. Fe²⁺).
- The carefully controlled addition of Al³⁺(aq) ions produces a precipitate of aluminium hydroxide which adsorbs finely suspended matter before sinking and being removed.
- Charcoal may be used to remove traces of organic substances.
- Chlorine is used in carefully controlled amounts to destroy bacteria. This is achieved by providing oxidising conditions through OCl⁻(aq) ions.



The use of chlorine can result in reactions with organic matter and the formation of chloroalkanes. For example, trichloromethane has been detected in water and this might marginally increase the risk of cancer developing as a consequence of drinking the water. However, this is a small factor compared to the benefits obtained from the destruction of bacteria.

(b) Recycling waste

Interest in the recycling of materials is primarily dependent upon social and economic conditions. Shortages during World War II meant that a high proportion of metals were recycled. The last few years have seen a dramatic change in public attitude and recycling is seen, once again, to be for the general good.

Recycling has a number of potential advantages:

- it leads to a reduction in environmental damage,
- there is a reduction in the demand for new landfill sites,
- it reduces costs of waste disposal,
- there may be substantial savings in energy costs.

Some examples of waste materials which can be recycled are as follows.

(i) Paper

- clean paper, e.g. offcuts
- old used paper, e.g. newspaper

The potential for the paper industry is up to 80% re-use, the main advantage being an energy saving of 50%.

(ii) Glass

Local collection points for used glass containers, often known as 'bottle banks', are becoming more popular and have provided a significant increase in recycled tonnage in the UK in recent years. The main advantage of bottle banks is that they cut down the demand for energy and the raw materials of sand, limestone and soda ash. The materials are cheap but their quarrying leads to an environmental impact and every tonne of used glass saves 140 dm³ of oil and 1.2 tonnes of raw material.

(iii) Plastics

About 30% of the plastics used in the UK is for packaging; this is commonly used once and then discarded. Although plastics are produced from oil in an energy-intensive and costly process, the recycling of plastic waste from mixed domestic refuse is too expensive. One solution (that is used in Japan) is to collect plastic as a separate waste item but the varied mix of domestic plastic means the recycled product has unpredictable properties.

Pyrolysis is the term used to describe thermal decomposition in the absence of air and, under these conditions, the plastics are not burned but converted instead into simple petrochemical raw materials.

(iv) *Metals*

Iron, steel, tin, copper and aluminium are the most easily recycled metals. Over half of all the steel produced in the UK comes from scrap.

The potential advantages of recycling metals are as follows.

- saving on imported iron ore,
- less demand for energy,
- the scrap is home-produced,
- air pollution is reduced,
- other resources used in the manufacture, e.g. water, are saved.

The judgement as to whether recycling represents a real saving in energy is a difficult one to make. Certainly the burden of bearing the energy costs is, in part, shifted from the manufacturer to the consumer, who uses his time and fuel to transport the waste to the recycling point. A precise analysis in energy terms is, perhaps, impossible to make, but the aesthetic environmental benefits, such as a reduction in mining and its associated waste and noise and the reduction of unsightly discarded packaging, are welcome.

Question

Discuss the effect that organisations like Friends of the Earth and Greenpeace have in protecting the Earth's environment.

Sample questions

14. Much domestic waste is disposed of by landfill methods. One problem associated with this method is the formation of 'landfill gases' which are mixtures containing variable quantities of methane and carbon dioxide. Explain how these gases are formed and state one environmental concern to which both these gases may contribute.
15. Sewage treatment involves primary, secondary and tertiary stages. The extent of the pollution at any stage may be estimated by measuring the biological oxygen demand (BOD). The BOD may fall to one tenth of its original value as a result of treatment.
- (a) Explain what is done at each of the stages of sewage treatment.
 - (b) Explain why treatment of sewage leads to such a significant drop in the BOD value.
16. The treatment of water for domestic purposes involves several stages. After filtering, the water is left to stand before the addition of carefully controlled quantities of $Al^{3+}(aq)$. This may be followed by chlorination in the presence of ammonia.
- (a) Explain
 - (i) the purpose of leaving the water to stand before further treatment,
 - (ii) the role of the $Al^{3+}(aq)$.
 - (b)
 - (i) Give an equation for the reaction of chlorine with water and explain the function of the chlorine.
 - (ii) Explain why ammonia may be added during the chlorination process.
 - (iii) Explain one possible hazard that may exist as a result of chlorinating water which still contains small quantities of organic matter.
17. Discuss the advantages and difficulties of recycling materials. You should mention the technical problems of recycling and limit your discussion to the recycling of paper, glass, plastics, aluminium and iron.

Petrol, diesel or neither?

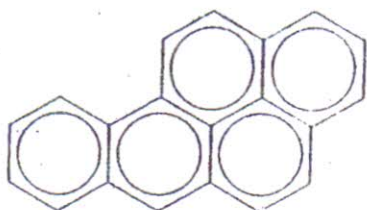
Improvements in the design of internal combustion engines mean that a modern vehicle generally causes less pollution than that by the same type of vehicle 20 years ago. Although the amount of pollution per vehicle may have declined, the number of vehicles present in the world has risen dramatically over the same period.

Although the use of unleaded petrol has greatly reduced pollution by lead compounds, its different hydrocarbon composition results in a greater risk to emission of potentially carcinogenic (cancer inducing) aromatic hydrocarbons. Like so many issues in environmental chemistry, it is a matter of balance between potential advantages and potential risks.

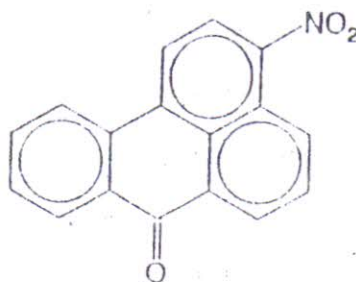
In terms of fuel economy, it may be preferable to use diesel engines because they generally enable vehicles to travel further on one litre of fuel. This advantage is partly due to the higher temperatures present in a diesel engine so, theoretically, the fuel should burn more completely. Diesel fuel, compared to petrol (gasoline), contains hydrocarbons with higher values of M_r . A litre of diesel fuel, therefore, contains more carbon than a litre of petrol. We would, therefore, expect a diesel powered vehicle to travel further on one litre of fuel compared to an equivalent petrol driven vehicle. However, it is difficult to say whether diesel or petrol engines, in terms of CO_2 emissions, are the more environmentally friendly.

Because the hydrocarbon molecules in diesel fuel are larger than those in petrol, there is a greater possibility of a series of molecular rearrangements which result in the formation of polyaromatic hydrocarbons (PAHs), such as compound X below, which is also found in cigarette smoke. Such compounds are often carcinogenic. It is estimated that car exhausts are responsible for thousands of tonnes of compound X being released annually into the atmosphere.

As reported in *New Scientist* (25th October 1997), researchers in Japan have detected traces of the compound Y in the exhaust gases of diesel engines and its concentration increases significantly when the vehicle is overloaded. Compound Y appears to be the most dangerous carcinogen so far detected.



X



Y

likely that particulate matter (PM) probably has PAHs adsorbed on to its surface as such compounds, having high values of M_r , are not very volatile.

All internal combustion engines have the potential for increased pollution if the engine is not maintained correctly. In the UK, all cars over three years old are required by law to be checked annually to ensure that their emissions do not exceed certain limits.

More recently, some vehicles have been developed that use compressed natural gas (CNG) as a fuel. Although this combustion of methane still releases carbon dioxide, the emission of carbon monoxide is very small and the formation of PAHs is very unlikely because the fuel only contains one carbon atom per molecule.

Electric cars seem to offer a pollution-free solution to many problems. However, it must be remembered that if they are operating from batteries, rather than solar cells, these need to be recharged on a regular basis. So, although the car is non-polluting, the power station generating the electricity to charge the car's battery may cause its own pollution problems. The transfer of pollution from a congested city to a distant power station may be advantageous locally, but it does not necessarily help the global problem. It may be possible, however, to control the pollution levels more easily in an efficient power station (or to have virtually none at all if the source is hydroelectric power).

Another seemingly attractive solution would be to use hydrogen as a fuel, as used in many space rockets. The main advantage is that the only combustion product is water. The disadvantage is that, in certain proportions, hydrogen and air form an explosive mixture, as can be demonstrated in the laboratory. Some scientists have argued that mixtures of methane and air can also be explosive, but that has not deterred the use of natural gas on a large scale.

Question

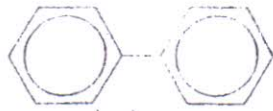
High performance cars produce higher levels of pollution. What would be the arguments for banning or allowing such vehicles to be used? Should the price of motor fuel be raised in order to reflect the enhanced greenhouse effect caused by excessive carbon dioxide emissions?

Question

In the UK, there is a telephone 'hotline' to enable members of the public to report the registration numbers of vehicles emitting very smoky diesel fumes. Do you think this is a good idea and how might its usefulness be limited without computerised records of vehicle registration numbers?

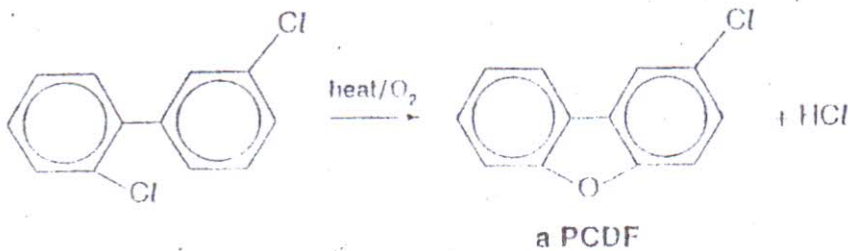
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PCBs - Polychlorinated Biphenyls



biphenyl

Chlorinated biphenyls found widespread use because they are inert, do not burn easily, and are good electrical insulators. They were, therefore, used as coolants in electrical transformers. Although PCBs are toxic themselves, trying to destroy them by burning can form a more dangerous product which is similar to a dioxin.



The disposal of PCBs, dioxins and PCDFs (polychlorodibenzofurans) presents a problem because very high temperatures are required if incineration is to be used. Special equipment has to be used and few communities would readily agree to the construction of such facilities in their locality in case of a leak.

Biodegradation of many compounds depends on the presence of C-H bonds which can be changed, by enzyme action, to C-OH which makes the compound more water soluble. The more chlorine substituents, the more difficult it is for the compound to biodegrade. However, extensively chlorine-substituted compounds often have the lowest toxicity for a group of compounds.

Water Purification

Chlorine reacts with water to form HOCl which reacts with 1,3-dihydroxy substituted benzene rings present in humic acids from soil. After a series of reactions, it is possible for trichloromethane to be formed.

The presence of trichloromethane in drinking water is believed to have caused thousands of cases of cancer of the bladder. Is the answer simply to stop chlorinating water? Over 20 million people world-wide die from waterborne diseases. Although other purifying agents can be used, such as ozone, these agents have no residual effect in the water - they purify the water at the time of treatment only. The advantage of chlorinating agents is that small quantities persist in the water and are, therefore, able to counteract bacteria which may enter the water system at a later stage.

Question

It is suspected in some areas that compounds such as PCBs have been allowed to leak into soils. How might these compounds enter the water system and why is chlorination ineffective against such compounds, whereas chlorination is very good at destroying bacteria?

Question

To what extent are we, as individuals, responsible for increases in pollution with regard to power consumption?

APPENDIX E

The numbering of CFCs

Designation	Formula
CFC-11	CCl_3F
CFC-12	CCl_2F_2
CFC-113	$\text{CCl}_2\text{FCClF}_2$
CFC-114	$\text{CClF}_2\text{CClF}_2$
CFC-115	CClF_2CF_3

The numbering system of CFCs is far from self-explanatory and an explanation may be of interest.

Counting from left to right

- the first number = number of carbon atoms - 1
- the second = number of hydrogen atoms + 1
- the third = number of fluorine atoms

If the first number is zero, this is omitted, i.e. CFC-011 becomes CFC-11. [The remaining atoms are chlorine to obtain a saturated molecule.]