CHEMISTRY FOR WIMPS

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ATOMIC THEORY

The theories which describe the nature of atoms and other subatomic particles are unbelievably complex and well outside the needs of everyday life (it has been said that only a couple of people in the entire world actually understand the higher levels of quantum mechanics, and some people even claim that they are making it up as they go!). However it is essential in chemistry to have some understanding of the atomic model, as it is this model which allows us to predict and explain so much of the chemistry we see around us.

History

Democritus (500 BC, or quite a while ago)
Democritus, a greek philosopher and experimentalist put forward the idea that all matter was made up of very small indivisible particles called atoms. He claimed there were many different types of atoms and that the physical properties of substances was the result of the different shapes and packing of these particles. However other greek philosophers, especially Plato and Aristotle, thought that Democritus was full of it and basically put an end to atomic theory for more than 2000 years. By the 17th century people were still claiming that everything consisted of the four elements; earth, wind, water and fire.

Dalton (1808)
By Dalton's time a number of the elements which are familiar to us today had been discovered and the earth, wind, fire and water bit was losing ground (also by this stage the Christian church had stopped burning people for saying novel things like 'the earth is round!'). He stated that Democritus theory was on the right track, and that each individual element was made up of only one type of atom. He also stated that compounds were made up of atoms combined in whole number amounts, ie you could not make something by adding together bits of atoms.

Thomson (1897)
Thomson discovered that atoms were made up of positive and negative parts that combined to form a neutral whole. He demonstrated that the negative bits could be forced off the atoms and he called these small negatively charged particles electrons. This was the basis for the theory of electricity. His model of the atom was a large positive bit with small negative bits stuck in it, like the fruit in a plum pudding. This became known as the plum pudding model of the atom (names were a lot more descriptive back then).

Rutherford (1911)

Two of Rutherford's (who was a native of New Zealand) students found that when they shot alpha particles at gold foil most of them went straight through with only a small amount being deflected. This led Rutherford to suggest that the atom consisted of mostly space, with a small positive middle called a nucleus and the electrons orbiting around it. Later experiments were to show that the nucleus consisted of two type of particles, positively charged protons and neutral neutrons. Because the charge of a proton was essentially equal to that of an electron there must be an equal number of electron and neutrons.

Bohr (1913)
To explain inconstancies in Rutherford's model Bohr proposed that the electrons must occupy very specific orbitals (or energy levels) around the atom and that they could only move between these stable energy levels, and not remain between them. If an electron moved from an orbital of higher energy to one of lower energy a set amount of energy (a quantum) is emitted and for an electron to move from an orbital of lower energy to one of higher energy it must absorb a specific amount of energy.

Quantum Theory (1920's $\rightarrow$)
It gets a bit complicated from here, so we might just summarise what it means to us.

The Important Bits

1)Atoms are made of three different types of particles Protons (small positive particles that reside in the nucleus), electrons (even smaller negative particles that orbit the nucleus in specific orbitals) and neutrons (neutral particles about the same size as a proton that also reside in the nucleus).

2)In the neutral atom the number of electrons and the number of protons are equal.

3)Any given element always has the same number of protons.

4)An element may have different numbers of neutrons. Different types of the same element which have differing numbers of neutrons are called isotopes. (they must however have a constant number of protons).

5)Electrons can only change energy levels (specific orbitals) by gaining or losing a specific amount of energy.

6) Electrons fill up the lowest energy levels first.

Valance Theory

The most important concept to chemists is the concept of energy levels of electrons. It was noticed long ago that some elements are especially stable, these elements (all gases) were given the title of noble gases and include helium, neon, argon, krypton, xenon and radon. They were found to have filled specific electron orbitals and this led to them being unreactive. This is the basis of valance theory.

The electron orbitals can be put into specific groups that are progressively filled as the number of electrons increases. Each group can be thought of as forming a hard shell around the atom, that once filled is unreceptive to other electrons as it is an especially stable energy configuration. These groups fill in the order 2, 8, 8, 18, etc (the easy way to remember this is to count the elements in any row of the periodic table, but this will be discussed later). Hence the first inert element has 2 electron (helium) the next has 10 (neon) and so on.

The elements in between these especially stable elements have the outer group (or shell) of electrons only partly filled. For example, fluorine has 9 electrons. The first shell of 2 is filled first. This leaves 7 electrons in the outer shell which, since it can hold 8 electrons, is incomplete. This outer shell of electrons is called the valance shell and because it is incomplete the atom is open to attack by other species.

To reach its most stable configuration fluorine needs to gain one electron so that it has the same electron configuration of the nearest noble gas (neon with an electron configuration of 2, 8). It tries to achieve this by reacting with other species which are willing to either donate or lend it an electron. Another example is magnesium which has 12 electrons. It can totally fill the first 2 shells leaving two electrons to go into the third shell (ie an electron configuration of 2, 8, 2). Hence the easiest way for magnesium to achieve its most stable electron configuration (ie that of the nearest noble gas) is to lose 2 electrons so that it has the same has the same configuration as neon. Once again it achieves this by reacting with other species.

The Periodic Table

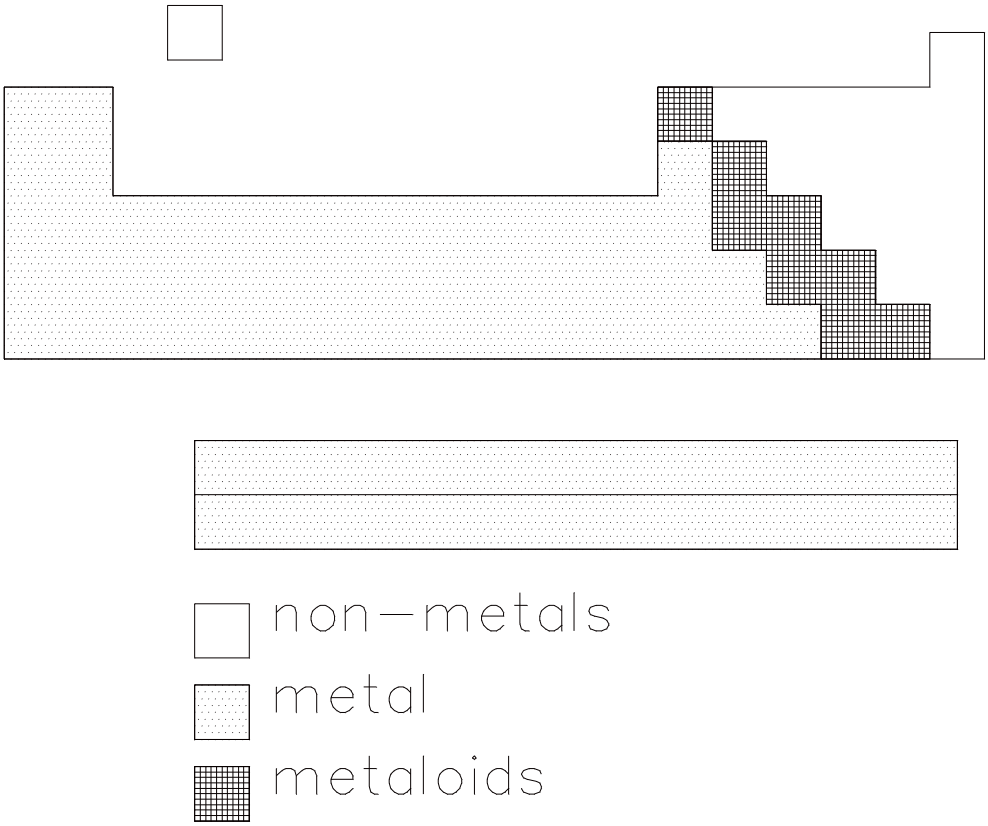
So where is all this information kept, how can you know how many electrons must be gained or lost to reach the most stable configuration. The answer is the periodic table. The periodic table has all the elements on it, their atomic number and their atomic weight. This table is one of the most important tools a chemist can have. A short summary of the important information it is given below.

-The Chemical Symbol for the element is usually included and consists of one or two letters, the first always being a capital. It is this shorthand method of representing the elements that is used in chemical equations.

-Atomic Number, this is the smaller of the two number given for each element. It is equal to the number of protons the element has. In the neutral species this also equals the number of electrons present.

-Atomic Weight, this is the mass of the atom in atomic mass units. It is equal to the number of proton plus the number of neutrons. It is often not a whole number because the different isotopes of an element can have differing numbers of neutrons, so an average of the number of neutrons is used to get this number.

The periodic table is often divided into groups based on the nature of the elements within it, ie it is broken up into metals, non-metals and metalloids. These will be discussed separately.



CHEMICAL BONDING

INTERATOMIC BONDING

The driving force behind chemical bonding is the need of atoms to fill their outer electron energy level, ie their valance shell. To achieve this they must either gain or lose electrons (except in the casse of the noble gases which already have full valance shells). This goal may be achieved by the inter action with other atoms. It is this interaction which contributes to chemical bonding.

There are three basic types of bonding;

a) ionic bonding

b) covalent bonding

c) Metallic bonding

Ionic bonding occurs mostly in metal and non-metal interactions.

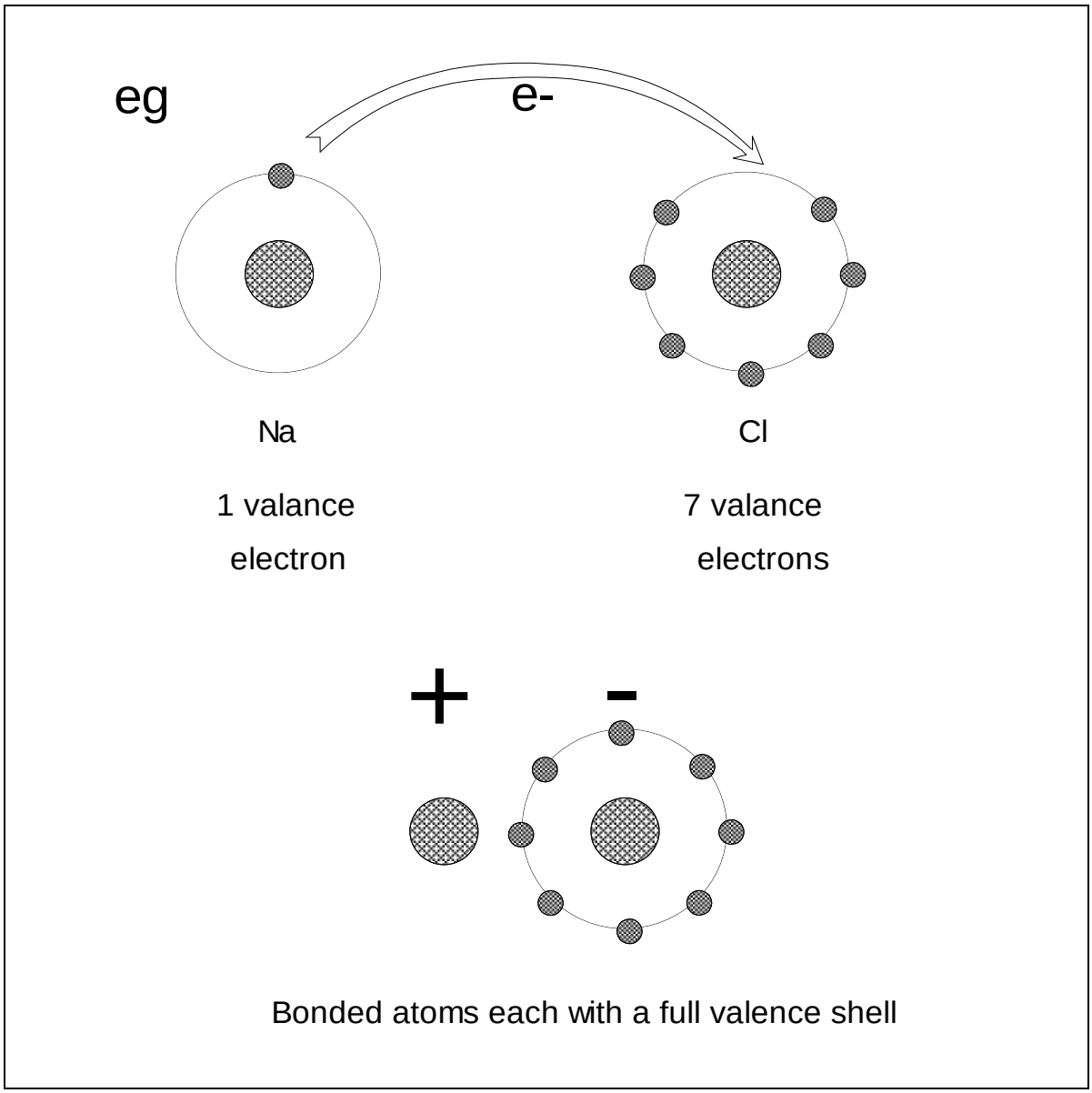
Covalent bonding is mainly present in bonds between non-metals.

Metallic bonding occurs in bonding between metals.

Ionic Bonding

Metals can usually more easily lose electrons than gain them, while non-metals usually find it easier to accept electrons. In both cases this is done to leave the atom with a full outer shell. Thus under the right conditions metals may donate electrons to non-metal resulting in both atoms acquiring a charge, the metal a positive charge and the non-metal a negative charge. The unlike charges then attract each other thus holding the atoms together.

The number of electrons accepted or lost depends on the number of electrons in the valance shell of the atoms (or alternatively the number of spaces left in the valance shell which need to be fill to complete te shell. Remember atoms are trying to achieve the most stable possible electron configuration by having a complete valance shell.



Atoms that carry a *negative* charge are called *anions*.
Atoms that carry a *positive* charge are called *cations*.
In general any atom that carries a charge is called an *ion*.

Because the different atoms whish to lose or gain differing amounts of electrons they may end up with different charges, ie magnesium tends to lose two electrons and hence has a charge of 2+ while chlorine generally only gains one electron resulting in a charge of 1-.

To balance out these charges (which must be done because electrons cannot be left floating around getting bored) we combine two of the chlorine atoms for each of the magnesium atoms, ending up with a three atoms in the molecule. This balancing of charges to achieve a neutral species must be done whenever you combine atoms to form an ionic compound.

Because of the charges on the atoms ionic molecules tend to gather together in well ordered large structures. These large structures are known as *ionic lattices* and it is because of them that the distinctive properties of ionic solids arise .

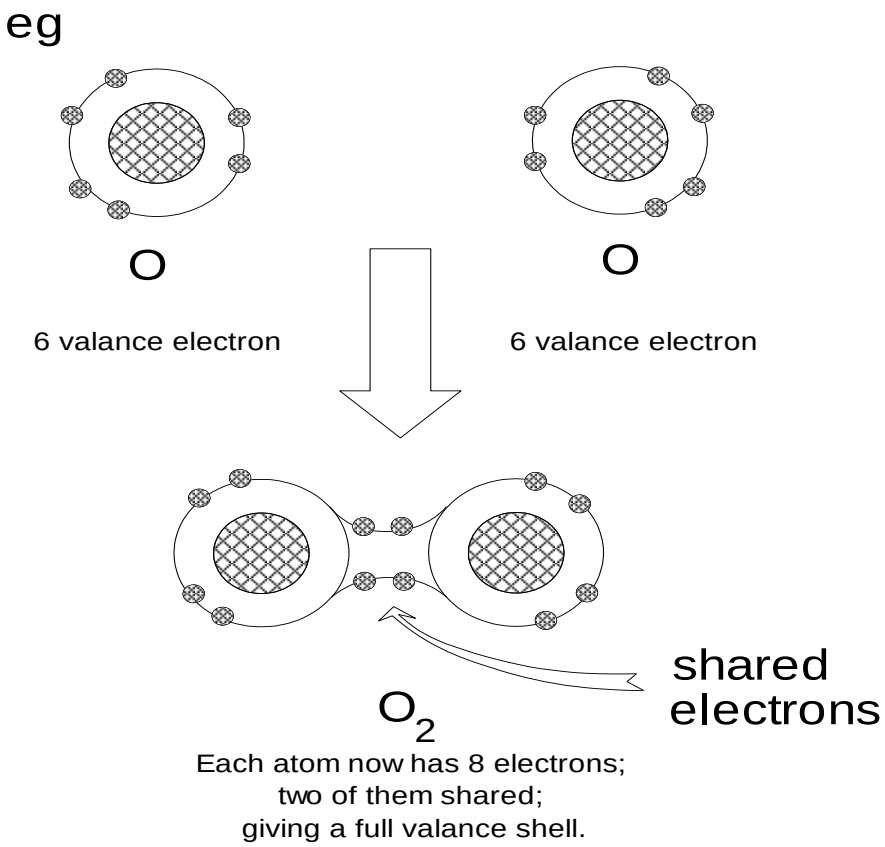
This well ordered network of atoms held together by strong forces of attraction result in compounds that tend to be *crystalline solids*. Many of them will *dissolve in water* and when they do the free ions allow them to *conduct electricity* (when they dissolve the ions become separated and allowed to move, this means that charge can flow from one point to another which means that electricity may flow). They tend to have *high melting points* and will *conduct electricity as a melt*. The solids however *will not* conduct electricity because the ions (and hence the charges) are held in their position in the lattice.

Covalent Bonding

It is difficult for non-metals to lose electrons from their valance shell (they much prefer to gain them). So is it possible to bond to non-metals?

The problem is overcome by both atoms sharing electrons from their valance orbitals. This allows both non-metal atoms to *attain a full valance shell* while at the same time retaining all their own valance electrons.

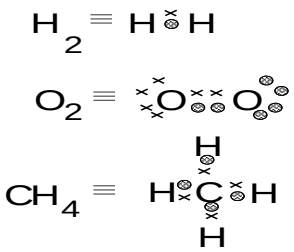
Since both atoms still have a hold on the electrons that they are sharing the atoms are held together by the shared electrons. It is this form of bonding which predominates in biological compounds.



Because covalently bound molecules are not comprised of charged ions, they are not held together in groups in the same way as ionic lattices. The forces of attraction between molecules tend to be much weaker (see intermolecular forces latter in this chapter) which results in covalently bound compounds often being gases or liquids. Even the those that are solids tend to have low melting points. They do not conduct electricity as either a solution or a melt.

Electron Dot Diagrams

Covalent compounds are often drawn using dots and crosses to represent the sharing of valance electrons. In such diagrams only the valance electrons are shown as the other electrons (those in the lower energy shells which are already complete) are not considered to take part in bonding. It is important however that all the valance electrons be represented, even if they are considered not to formally take part in the bonding process.



Metallic Bonding

In general metals lose electron easily. Hence when metal atoms bond it is easy for them to donate electron to each other to form filled valance shells. This happens to such an extent that the metals of the valance orbitals are not considered to belong to any single atom. Rather the metal atoms are considered to be floating in a sea of freely moving valance electrons.

It is this form of bonding which gives metals their characteristic properties. These include its *lustre* (ie they are shiny when freshly cut), *malleability* (the ability to be shaped, which arrises because the atom centres may move about in relation to each other through the sea of electrons), *ductility* (the ability to be stretched out into a wire) and their *conductivity* (the sea of electrons can freely move to carry charge).

INTERMOLECULAR BONDING

We have seen that atoms are held together to form molecules by interaction between their valance electrons. However what holds the various molecules together to form liquids and solids.

In the case of ionic solids it has already been shown that the molecules are held together by the unlike charges of their component ions. This however is just an extension of the forces which holds the atoms together. In the case of large organic molecules (a special class of covalent compounds) the actual size and shape of the molecule comes into play (this will be discussed in later chapters). There are however a group of relatively weak forces that contribute the physical state (ie gas, liquid or solid) of molecules. These forces are especially important to covalent molecules where there is little else to hold the molecules together. Such forces are known as intermolecular forces because they work between molecules.

The three main types of inter molecular bonding are;

a) dipole-dipole interactions
b) hydrogen bonding
c) Van der Waal's forces

It is the variations in these forces that account for the differences in the boiling and melting points of various covalent compounds. They should not be

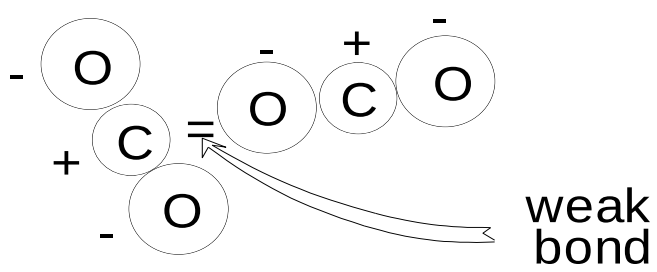
confused with the interatomic forces discussed earlier which are much stronger and generally are not broken when melting or boiling a substance (except in the extreme case of melting ionic solids).

Dipole-Dipole Interaction

In covalent bonding we usually talk of an equal sharing of electrons. However in reality some atoms have a greater hold over the electrons than others. This leads to the electrons spending slightly more time with one other than another in the molecule.

This ability to draw to itself is referred to as the atoms *electronegativity*.

The result of this is that the end of the molecule that has the greater affinity for the electrons (is more electronegative) will aquire a slightly negative charge while the other atom (which is said to ne electron deficient) becomes slightly positive. Such a molecule is referred to as a *dipole* and the bond between the atoms (while still being considered a covalent bond) is referred to as a *polar covalent bond*.

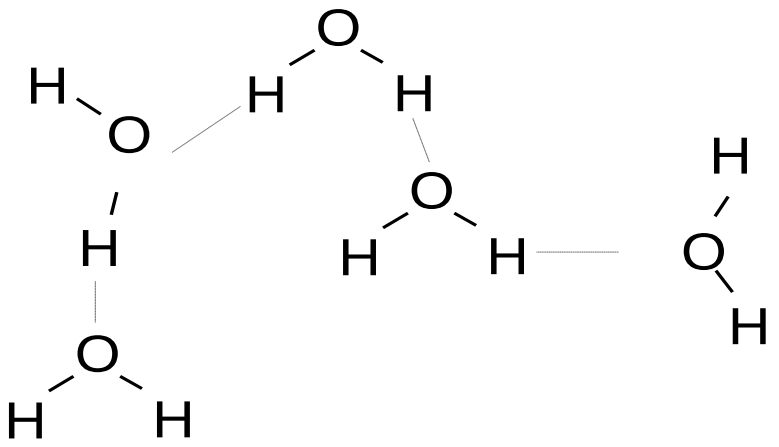


This results in an *attraction* between the charged ends of the molecules and other similar molecules. This attraction is much weaker than the bonding found between ionic molecules in ionic solids and is called a *dipole-dipole interaction*. The attraction between molecule means that they are not as free to move about each other and as a result boiling and melting points of such compounds are higher.

Hydrogen Bonding

This is a special case of dipole-dipole interaction in which one of the atoms is hydrogen. Hydrogen tends to form the positive end of a dipole, especially when bonded to strongly electronegative atoms such as oxygen. The resulting dipole-dipole interaction is quite strong (although still very weak compared to the interactions in ionic solids).

It is this interaction that operates between water molecules, forcing water to be a liquid at room temperature.



Hydrogen bonding is important in many aspects of chemistry;

eg.

*It helps to control the shape of biologically important molecules such as DNA and some proteins. It is this shape which controls many of their functions.

*It creates the surface tension in water which allows water to travel through the xylem tissue of plants.

*The polarity of water allows ionic and polar substances to be dissolved in it.

Van der Waal's Forces

Electrons are continually moving around a molecule. This implies that the location of the negative charge is continually changing and creating very weak dipoles for incredibly short periods of time. These are called instantaneous dipoles. The interactions between instantaneous dipoles is very weak but plays an important part in compounds of non-polar molecules such as many hydrocarbons.

CHEMICAL EQUATIONS

For many people it is sufficient to describe a chemical reaction in terms such as "They mixed some yellow stuff and some clear liquid in a tube, not long after a b-----y awful smell came off and we all had to leave the lab".

While this is a reasonable description of what takes place on the reaction of iron sulfide and sulfuric acid it does not tell us some important facts;

* what was each of the reactants?
* in what proportions were they present?
* what was actually made?
* what was that smell!!?

For people who work with chemicals it is vitally important that these questions be answered. It is for this reason that we use chemical equations as a shorthand method of describing chemical reactions. For example the reaction described above would be written,

$$FeS_{(s)} + H_2SO_{4(aq)} \text{ ------- } H_2S_{(g)} + FeSO_{4(aq)}$$

This equation describes the reaction of iron(II) sulfide and sulfuric acid to produce hydrogen sulfide (rotten egg gas) and a solution of iron(II) sulfate. The small subscripted letters in brackets tell us what form the reactant was in (s=solid, l=liquid, g=gas and aq=aqueous solution). The letters represent the various atoms as described in the periodic table that make up each molecule taking part in the reaction. The small subscripted numbers tell us the numbers of each atom in each molecule, eg. $FeSO_4$ has one iron atom, one sulfur atom and four oxygen atoms. Thus from the above equation we can say that one molecule of iron sulfide will react with one molecule of hydrogen sulfate (sulfuric acid) to form one molecule of hydrogen sulfide and one molecule of iron sulfate.

But what happens when we need more than one molecule of some compound. Let's look at another example;

$$CH_{4(g)} + 3O_{2(g)} \text{ --------- } CO_{2(g)} + 2H_2O_{(aq)}$$

In this case we need three molecules of oxygen for every molecule of methane to produce one molecule of carbon dioxide and two molecules of water. The number of molecules of the compound we need is represented by a normal size number in front of the compound in question. It is also important to note that there are the same number of each type of atom on each side of the equation (ie 4 x H, 6 x O and 1 x C). This is important as you cannot create or destroy atoms in a chemical reaction and as such must have the same number of atoms of the various types before the reaction as after.

But given an observed reaction how would you go about writing its reaction. The general procedure is as follows. You do an experiment in which you place the metal magnesium in hydrochloric acid. You observe a gas coming off which turns out to be hydrogen and you are told the solution left over contains magnesium chloride. First you should write down the reaction in words,

magnesium + hydrogen chloride ---- hydrogen + magnesium chloride

Next, using the periodic table you should write down the correct formulae for each of compounds involved,

$$Mg + HCl \text{ ------- } H_2 + MgCl_2$$

Now you must balance out the number of atoms on each side of the equation. It is important to remember that you cannot change the number of atoms in a compound (ie the subscript number), this number is fixed by its valency. You may only change the number of molecules of individual compounds or atoms. There are two hydrogens and two chlorines on the right and only one of each on the left. To remedy this we multiply the HCl by 2.

$$Mg + 2HCl \text{ ------- } H_2 + MgCl_2$$

We now have equal numbers of atoms on both sides of equation and it can be said to be balanced. Another example is the reaction between sodium hydroxide and sulfuric acid to give sodium sulfate and water.

Word equation,

sodium hydroxide + hydrogen sulfate --- sodium sulfate + water

Chemical equation,

$$NaOH + H_2SO_4 \text{ ------ } Na_2SO_4 + H_2O$$

Balanced equation,

$$2NaOH + H_2SO_4 \text{ ------ } Na_2SO_4 + 2H_2O$$

THE MOLE

When we have been talking about chemical reactions so far we have been talking in terms of single atoms reacting with each other. Since the largest known atom weighs only 2.57×10^{-22} g this is probably not very useful. Chemists and other people who use chemical equations and chemicals find it much better to scale the whole thing up and to talk in much larger amounts of atoms. The question was by what factor to scale up all the results, and it here that the mysterious beast the mole comes into play.

It was found that if you took one gram of atomic hydrogen that it contained 6.02×10^{23} atoms. A bit of cunning thought led people to realise that if this was true, then since helium weighed four times as much that four grams of it must contain the same number of atoms. And in the same way 12 g of carbon which has an atomic weight of 12 must also have 6.02×10^{23} atoms and so on for the rest of the atoms. This means that if we take the equivalent of the atomic weight of any atom in grams that it will contain 6.02×10^{23} atoms. This number of atoms is called a mole of atoms. This is very useful because now instead of talking in numbers of atoms we can talk instead in numbers of moles. When we do this we are not talking of the number of small furry (and relatively cute) burrowing animals we have but about the relative numbers of atoms present. For example in the equation

$$FeS_{(s)} + H_2SO_{4(aq)} \text{ ------- } H_2S_{(g)} + FeSO_{4(aq)}$$

we talk about one mole of iron sulfide reacting with one mole of sulfuric acid instead of one atom reacting with one atom. We are still talking about the same thing only scaled up.

It also tells about how much compound is produced. In the example above if we start with one mole of each of the reactant we must end up with one mole of each of the products. We can calculate the molecular weight of H_2S;

$$(2 \times 1.01) + 32.06 = 34.08.$$

Therefore we can predict 34.08 grams of hydrogen sulfide will be produced.

We do not have to work in whole number amounts either. If we have half a mole of each of the reactants then we must end up with half a mole of each of the products! How can we calculate exactly how many moles we have, the formulae below is the normal method.

$$\text{number of moles} = \frac{\text{mass of compound}}{\text{molecular weight}}$$

For example, if we have 36 g of magnesium hydroxide how many moles do we have?

molecular weight of $Mg(OH)_2$ $= 24.305 + (15.9994 + 1.01) \times 2$

= 58.3238

number of moles = 36 g / 58.3238
= 0.6172 moles

Now lets use this information in an example. Magnesium hydroxide reacts with hydrochloric acid to produce the salt magnesium chloride and water. Given that we have 36 grams of magnesium hydroxide how much magnesium chloride will be produced?

Word equation,

magnesium hydroxide + hydrogen chloride ---- magnesium chloride + water

Chemical equation,

$$Mg(OH)_{2(aq)} + HCl_{(aq)} \text{ ----- } MgCl_{2(aq)} + H_2O_{(l)}$$

Balanced equation,

$$Mg(OH)_{2(aq)} + 2HCl_{(aq)} \text{ ----- } MgCl_{2(aq)} + 2H_2O_{(l)}$$

For every mole of magnesium hydroxide used one mole of magnesium chloride is produced. Therefore if we have 0.6172 moles of magnesium hydroxide then we must produce 0.6172 moles of magnesium chloride. We can rearrange our original equation to give;

mass of compound = number of moles x molecular weight

The molecular weight of $MgCl_2$ = 24.305 + (2 x 35.453) = 95.21

Hence grams of $MgCl_2$ produced = 0.6172 x 95.21
= 58.7636 grams

So if we react 36 grams of magnesium hydroxide with hydrochloric acid we produce about 56.9 grams of magnesium chloride.

From the equation we can also see that we use twice as much hydrochloric acid as magnesium hydroxide. That is if we have 0.6172 moles of magnesium hydroxide we use 2 x 0.6172 = 1.2344 moles of hydrochloric acid. The molecular weight of the HCl is;

1.01 + 35.453 = 36.463

Therefore the amount of hydrochloric acid used is;

1.2344 x 36.463 = 45.010 grams

A similar calculation can be done for the amount of water produced in the reaction.

Concentration Units

While it is all very well to know exactly how many atoms of something you have got if you know its weight, very few reactions take place in a solid form. In general most reactions take place between components in solution. There is good reason for this. In solution atoms may react on a one to one basis and the reagents may be thoroughly mixed, as opposed to only being able to react at the surfaces in solids.

As such it is necessary to have a system to describe the amount of substance in a given volume of solution. The most commonly used system today is the molarity system. The molarity of a solution is defined as the number of moles of substance per litre of solvent (usually water). The value can be worked out using the equation;

$$\text{molarity} = \frac{\text{moles of substance}}{\text{volume of solvent in litres}}$$

The units for molarity are *mol* l^{-1} (ie moles per litre) and a solution that is 5 *mol* l^{-1} is said to be a 5 molar (5M) solution.

For example if you dissolve up 28 grams of NaOH in 500 millilitres of solution, what is its final concentration.

The first task is to calculate the number of moles of substance;

$$\text{moles} = \frac{\text{mass of sample}}{\text{molecular weight of substance}}$$

Since we know the molecular weight of sodium hydroxide to be approximately 40, we can use the above equation to calculate the number of moles;

$$\text{moles} = \frac{28 \text{ grams}}{40}$$

$$\text{moles} = 0.7 \text{ moles}$$

We can now use our molarity equation to work out the concentration of the solution;

$$\text{molarity} = \frac{\text{moles of substance}}{\text{volume of solvent in litres}}$$

$$\text{molarity} = \frac{0.7 \text{ moles}}{0.5 \text{ litres}}$$

$$= 1.4\ mol\ l^{-1}$$

Note that it is important to use the number of litres on the bottom of the equation and not thee number millilitres!. This basic equation may be rearranged to give the number of moles in a solution of given concentration or the amount of solvent needed to achieve certain concentration.

EQUILIBRIUM

All chemical reactions are theoretically reversible, but sometimes the reverse reaction is so small that it is proper to say that the reaction is not a reversible one, ie it goes to completion in one direction.

A reversible reaction is written

$$A + B \text{ ===== } C + D$$

But this could also be represented by two equations as such;

$$A + B \text{ ------ } C + D$$
$$\text{and} \quad C + D \text{ ------ } A + B$$

Note that the symbol ===== indicates that the reaction is a reversible one (ie. goes in both direction at the same time.) In biological systems many of the metabolic reactions that occur are reversible.

At some point in time all reversible reactions come to what is called an equilibrium. This means that the speed (better called the rate) of the forward reaction equals that of the reverse reaction, so the system is balanced with the relative amounts of all reactants and products and reactant remaining the same. For this reason, reversible reactions are called *equilibrium reactions*.

Characteristics Of Equilibrium Reactions

1) An equilibrium reaction is *reversible.* That is, the substances on the left react to produce those on the right and at the same time those on the right react to change back into those on the left.
2) The equilibrium is *dynamic.* The reversible reaction occur continuously, even though their appear to be no change.
3) An equilibrium system is *closed,* no substance is added to or removed from the system. Also the temperature and pressure remain constant.

When a chemical system is at equilibrium, the forward and reverse reaction occur at the same rate, Therefore the *concentrations* of the components of the system *do not change.*

Le Chatelier's Principle

Le Chatelier's principle states that if a change is imposed on any chemical system at equilibrium, that the system will react in such a way that the effect of change is reduced. In other word, systems at equilibrium try to remain at equilibrium.

For example, an equilibrium system which occurs in the blood and is a step in the method by which carbon dioxide is expelled from the body, is

$$CO_2 + H_2O \text{ ===== } H_2CO_3$$

If this system is suddenly bombarded by extra CO_2 (possible as the result of increased metabolic activity due to exercise by the individual.), the reaction will move to the right (producing more H_2CO_3) to remove that extra CO_2, until the system is once again at equilibrium.

The Equilibrium Constant

Because the relative amounts of all the participating substances in an equilibrium reaction stay the same, it is possible to express the reaction as a ratio of these substances. This makes it possible for us to know how much of any participant substance in the reaction we will have, given any other part.

The law of chemical equilibrium states that, when a reaction reaches equilibrium, the product of the concentrations of each substance on the right hand side of the equation divided by the product of concentrations on the left hand side is constant (at a given temperatureand pressure) and is called the equilibrium constant K.

That is, for the reaction,

$$aA + bB \text{ ===== } cC + dD$$

the equilibrium constant is given by the equation;

$$K = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

For example, in the reaction

$$N_2 + 3H_2 \text{ ===== } 2NH_3$$

The equilibrium constant is given by the equation.

$$K = \frac{[NH_3]^2}{[N_2] \times [H_2]^3}$$

Where the square bracket mean the concentration of whatever is inside the brackets or in the case of gasses their pressures.

Solids and Water in Equilibrium Expressions

The concentration of solids and water is essentially constant (concentration of water is 55.5 M) and in equilibrium equations they are given the value 1. That is we substitute 1 as their value in the equation.

ACIDS AND BASES

Many of the chemicals you will come across in reactions will be either acids or bases.

Acids were first associated with the sour taste of some citrus fruits, the sour taste we now know coming from citric acid in the fruit. The name derives from the Latin *acidus* (sour); vinegar is a good example of a common acid, as is it mainly a dilute solution of acetic acid.

Bases, also sometimes called alkalis, are also bitter in taste and often have a slippery feel.

Common acids like sulfuric acid and nitric acid have been known for almost 700 years, but it was only in the eighteenth century that the common property of acids was discovered.

This concept was that an **acid** *is a substance which produces H^+ ions (called protons) when dissolved in aqueous solution.*

Strong acids like HCl, HNO_3 and H_2SO_4, when placed in water, virtually completely dissociate into protons and anions. One mole of HCl in water dissociates into one mole of H^+ ions and one mole of Cl^- ions. At the same time, it was discovered that aqueous solutions that exhibit behaviour as a base always contains hydroxide ions, OH^-.

So a **base** was defined as *a substance which produces hydroxide ions in aqueous solution.*

Typical bases are NaOH and KOH, with these strong bases again completely dissociating into cation and hydroxide anions. For a simple acid and a simple base, we could write the following equations for dissolution:

$$HCl \xrightarrow{water} H^+(aq) + Cl^-(aq)$$

$$NaOH \xrightarrow{water} Na^+(aq) + OH^-(aq)$$

Another property of these acids and bases which we should be aware of is their reaction when mixed.

The fundamental reaction when a strong acid and a strong base is mixed is the formation of water from combination of protons with hydroxide ions:

$$H^+(aq) + OH^-(aq) > H_2O\ (l)$$

This reaction to form the stable water molecule occurs readily, usually accommodated by release of energy as heat. Mixing of strong acids and bases can therefore be dangerous due to the vigorous reaction.

The other cation and anion in the reaction of an acid and base are preserved unchanged; they are mere spectators in the reaction. We could write a reaction as follows:

$$HCl + NaOH > NaCl + H_2O$$

The acid and the base have reacted to produce water and a **salt**, in this case sodium chloride.

We could write the equation in terms of ions, rather than just compounds (an **ionic equation**):

$$H^+ + Cl^- + Na^+ + OH^- > H_2O + Na^+ + Cl^-$$

where you can see clearly that the sodium and chloride ions simply carry over without reacting.

If the solution were evaporated to dryness, removing all the water, we would be left with a **neutral** (not acidic or basic) solid, NaCl. The solution when equal molar amounts of HCl and NaOH are mixed is also neutral.

In Table 1 are listed some common acids, as well as the anions which they form in solution. Some acids contain more than one proton per molecule, which they can 'lose' successively, so that several anions may exist.

Table 1. Some common acids and their anions

Acid	*Anion*
HCl (hydrochloric acid)#	Cl^- (chloride ion)
HNO_3 (nitric acid)	NO_3^- (nitrate ion)
H_2SO_4 (sulfuric acid)	HSO_4^- (hydrogen sulfate ion)
	SO_4^{2-} (sulfate ion)
H_2CO_3 (carbonic acid)#	HCO_3^- (hydrogen carbonate ion)
	CO_3^{2-} (carbonate ion)
HNO_2 (nitrous acid)#	NO_2^- (nitrite ion)
H_3PO_4 (phosphoric acid)	$H_2PO_4^-$ (dihydrogen phosphate ion)
	HPO_4^{2-} (hydrogen phosphate ion)
	PO_4^{3-} (phosphate ion)
$HClO_4$ (perchloric acid)	ClO_4^- (perchlorate ion)
H_2SO_3 (sulfurous acid)#	HSO_3^- (hydrogen sulfite ion)

(# known only in aqueous solution; cannot be isolated)

Most bases you will come across first will be simple hydroxide compounds like NaOH, KOH, and $Mg(OH)_2$. Other compounds, including organic molecules, can be bases as well. One of the simpler ones of this type is sodium carbonate, Na_2CO_3.

With a compound like the latter, which does not have an obvious hydroxide ion part, how can one tell if it is a base or not? The simplest experiment, of course, is simply to dissolve the compound in water, and detect whether there are concentrations of hydroxide ions (or protons if it suspected of being an acid) beyond the levels normally existing in pure water.

Measuring Acidity and Basicity - The pH Scale

To do the measurement of proton or hydroxide concentration conveniently, we need a measurement scale. The scale employed commonly is based on hydrogen ion (proton) concentration. The limits of the scale in water are set effectively by considering water itself. Water is an example of an **amphoteric** substance, or one capable of behaving as either an acid or a base. It can ionize itself, according to the following reaction:

$$H_2O + H_2O \text{ === } H_3O^+ + OH^-$$

One water molecule acts as a base by accepting a proton and the other as an acid by furnishing a proton.

Note also that the reaction is in equilibrium, ie it goes in both directions. We can write a **constant** for this equilibrium reaction, called in this case the **ion-product constant**, or **dissociation constant**,
which is expressed as

$$K_W = [H_3O^+][OH^-]$$

or more frequently simply as

$$K_W = [H^+][OH^-]$$

where the square brackets mean the concentrations of the species in the bracket.

Experiment shows that $[H^+] = [OH^-] = 1.0 \times 10^{-7}$,
which leads to

$$K_W = [H^+][OH^-] = 1.0 \times 10^{-14} .$$

This number is a constant at a particular temperature. This means, in this case, that no matter what it contains, the product of $[H^+]$ and $[OH^-]$ must **always** be 1.0×10^{-14}.
If one of the numbers go up, the other **must** go down to compensate.

We can define acid, neutral and basic solution in terms of the proton and hydroxide concentration:

neutral solution: $[H^+] = [OH^-]$
acidic solution: $[H^+] > [OH^-]$
basic solution: $[H^+] < [OH^-]$

where in all cases the product of the two concentrations is constant at 1.0×10^{-14}.

Such small numbers are inconvenient to deal with, so log units have been devised.
The common scale is the **pH scale**, where we define

$$\mathbf{pH = -\log_{10}[H^+]}$$

Because $K_W = [H^+][OH^-] = 1.0 \times 10^{-14}$

then $pK_W = pH + pOH = 14.00.$

In a neutral solution, $pH = pOH = 7.0.$

Table 2. Relationship of pH to proton and hydroxide concentration

$[H^+]$ *(mol/L)*	*pH*	$[OH^-]$ *(mol/L)*	
10^{1}	-1	10^{-15}	
10^{0}	0	10^{-14}	
10^{-1}	1	10^{-13}	
10^{-2}	2	10^{-12}	acidity
10^{-3}	3	10^{-11}	increases
10^{-4}	4	10^{-10}	
10^{-5}	5	10^{-9}	
10^{-6}	6	10^{-8}	
10^{-7}	7	10^{-7}	neutral
10^{-8}	8	10^{-6}	
10^{-9}	9	10^{-5}	
10^{-10}	10	10^{-4}	
10^{-11}	11	10^{-3}	basicity
10^{-12}	12	10^{-2}	increases
10^{-13}	13	10^{-1}	
10^{-14}	14	10^{0}	

Simple measurement with a modern pH meter will place a solution as either acidic, neutral or basic. Most meters measure conveniently between approximately 0 and 14 pH units. Measurement of pH of a strong acid or base in solution permits determination of concentration from the relationship between pH and $[H^+]$ (and $[OH^-]$).

Not all acids (and bases) are 'strong'; for example, many 'weak' acids are so named because they do not dissociate completely into protons and anions, in the same sense that water does not dissociate completely.

A strong acid is 100% ionized into protons and anions; a weak acid may be ionized to even less than 1%.

This means that the pH of solutions of weak acids are usually higher (lower proton concentration) than you would anticipate from the concentration alone.

COLLOIDS

If you stir up a solution with finely divided clay particles the particles will eventually settle back to the bottom.

In a solution the molecules stay suspended and evenly distributed.

Between these two extremes is the situation in which dispersed particles are larger than molecules, but not so large that the component of the mixture settle under the influence of gravity.

These kinds of suspensions are called ***colloids***.

Definition;

Colloids are particles that are larger than normal molecules, but that are small enough to remain suspended in the dispersing medium indefinitely.

Relative Sizes

0.1 to 10 nanometers	ions and molecules
10 to 100 nanometres	colloids
greater than 100 nanometres	solids

In discussing colloids we talk of *dispersed particles* and *dispersing medium.*

The dispersed particles are the *colloidal particles*.

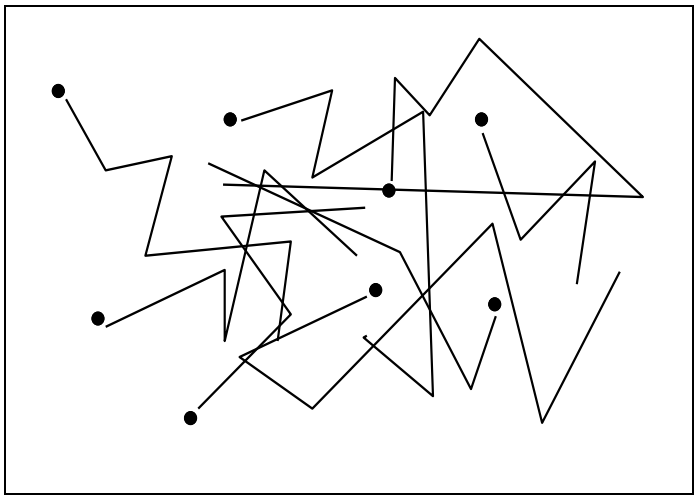
Colloids can exist as solids liquids or gases.

Phase of colloid	Dispersing substance	Dispersed substance	Colloid type	Example
gas	gas	gas	-	none (all are solutions)
gas	gas	liquid	aerosol	fog
gas	gas	solid	aerosol	smoke
liquid	liquid	gas	foam	whipped cream
liquid	liquid	liquid	emulsion	milk
liquid	liquid	solid	sol	paint
solid	solid	gas	solid foam	marshmallow
solid	solid	liquid	solid emulsion	butter
solid	solid	solid	solid sol	ruby glass

Colloids exist in biological systems, for example, the haemoglobin molecule in blood (carries oxygen) is a colloid as are many enzymes and antibodies.

Brownian Motion

This refers to the random movement of colloidal particles that can be seen through powerful microscopes.



This random zig-zag motion is due to the constant collisions between the colloidal particles.

The Tyndall Effect

Colloidal particles are very small, however they are large enough to effectively scatter light.

For this reason colloidal suspensions often appear opaque or cloudy.

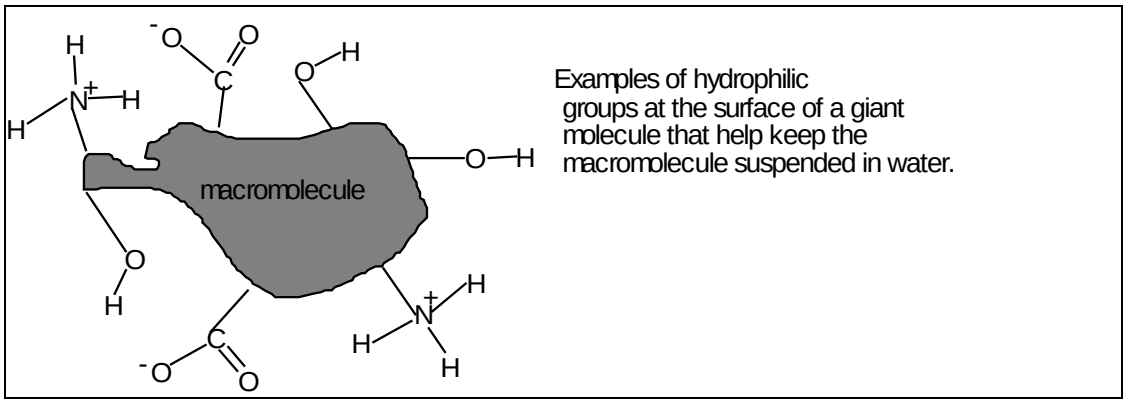
This scattering of light is known as the *"Tyndall effect"*.

You can see this effect when driving a car through fog at night. The beams of light from the headlights become visible because the fog is a colloidal suspension and scatters light according to the Tyndall effect.

Hydrophilic and Hydrophobic Colloids.

The most important colloids are those in which the dispersing medium is water. Such colloids are classed as either *hydrophilic* or *hydrophobic*.

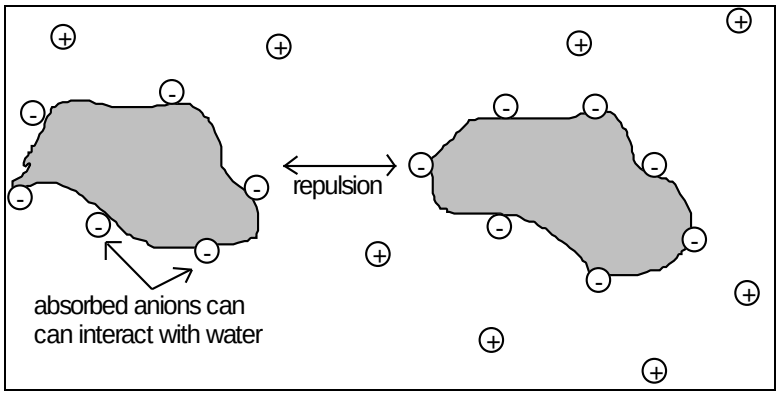
Hydrophilic means attracted to water.
Hydrophobic means repelled by water.
Hydrophilic colloids contains particles whose surface is covered in *polar* or *charged groups* which interact with water molecules.



Stabilisation of Hydrophobic Colloids

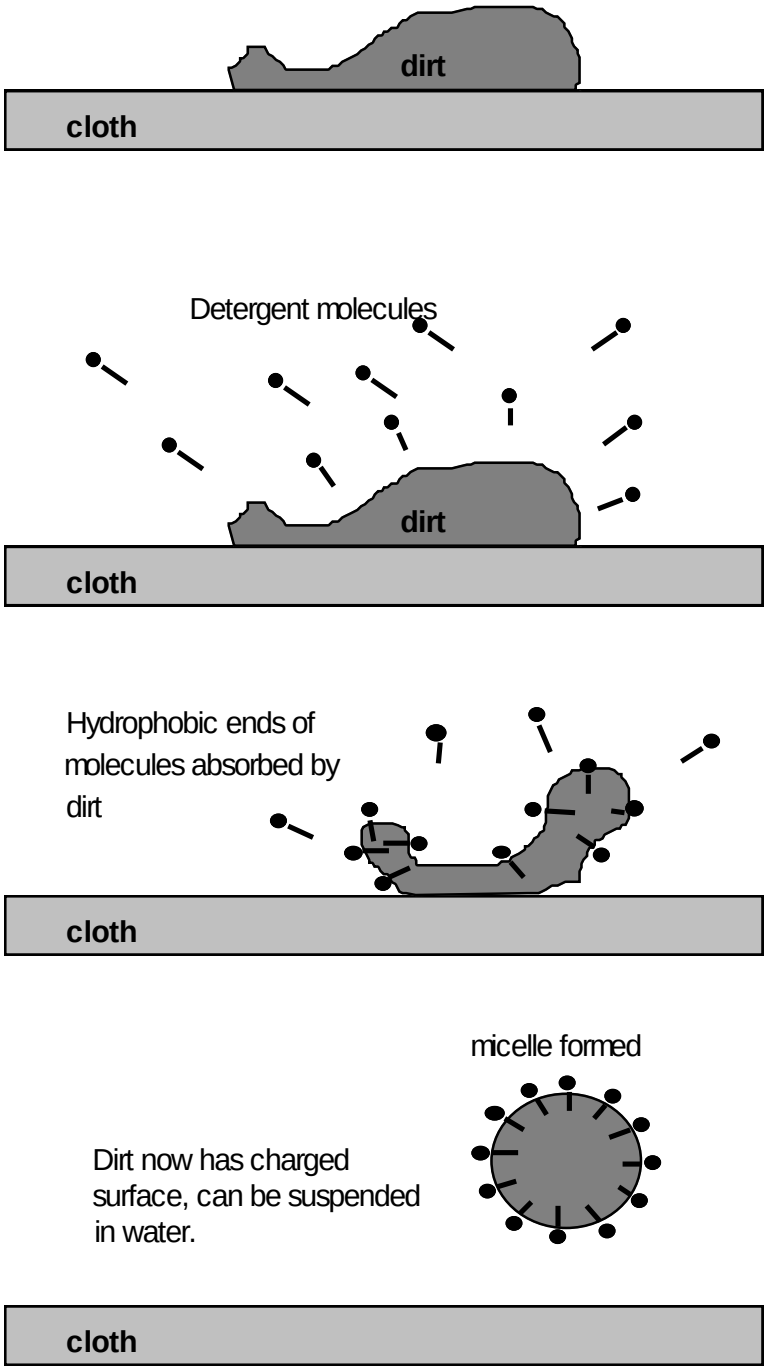
In hydrophilic colloids it is the presence of polar groups which help to keep the molecules suspended in water.

Hydrophobic colloids have no such groups so by themselves in water they soon separate out. To remain suspended in water they must absorb charged species (ions) onto their surface. These absorbed ions will result in repulsions of particles with like charges on their surface preventing *coagulation* and *precipitation*.



Soaps and Detergents

The cleansing action of soaps and detergents are due to their ability to stabilise hydrophobic colloids.



Detergents and soap are usually molecules that have one hydrophobic end and one hydrophilic end.

Grease and oil and other forms of dirt are often hydrophobic and will not dissolve in water. The hydrophobic end of the detergent however can be absorbed by the dirt particle.

This leaves the particle surrounded by hydrophilic groups which can interact with the water allowing the dirt particle to be suspended as a colloid and lifted away from the object being cleaned.

The particle surrounded by detergent molecules is called a *micelle*.

Common Colloids

Emulsions are a type of colloid commonly found in the household (eg. mayonnaise and moisturising cream). These consist of an *oil-water* emulsion in which an emulsifying agent stabilises the oil to keep it suspended in the water. In mayonnaise from oil and vinegar, egg yolk act as the emulsifying agent.

Large molecules in the body such as *enzymes and antibodies* must stay suspended in water. To do this these large organic molecules, which are largely hydrophobic bend so that they present their hydrophilic sections to their outer surface. In this way they stay suspended in the bodies fluids.

COLLIGATIVE PROPERTIES

Since solutions are mixtures the properties of the solutions depend on the amounts of the various substances that make up the solution.

Some of the physical properties of solutions depend only on the *concentration of particles in solution,* regardless of what these particles are. These properties are known as ***colligative properties***.

The colligative properties of solutions include vapour pressure, freezing point, boiling point and osmotic pressure.

Vapour Pressure Lowering

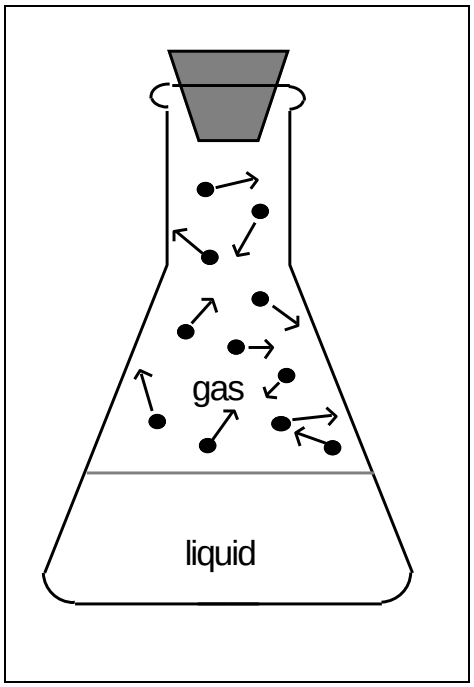
If a liquid is placed in a closed container the gas that evaporates from the surface will cause a pressure on the container walls.

After a very short period of time the rate at which molecules are leaving the liquid becomes equal to the rate at which they condense back into the liquid. At this equilibrium point the pressure exerted by the molecules becomes constant.

This pressure is known as the ***vapour pressure***.

Definition;

Vapour pressure is the pressure exerted by vapour being given off by a liquid, at a given temperature.



For example, water has a vapour pressure of 23.8 mmHg at 25^{o}C and 733.2 at 99^{o}C.
The same principle applies to all liquids, not just water.

If a non volatile solute (eg. salt or sugar) is added to a solvent, *the vapour pressure of the solvent is decreased.*

When you dissolve a solute in a solvent, you replace some of the solvent particles at the surface of the solution with solute particles. This means there are fewer particles at the surface to escape, hence reducing the vapour pressure. Also there is a positive attraction between solute and solvent particles, which makes it more difficult for solvent molecules to escape.

If you add a more volatile solute, *the vapour pressure is increased.*

Boiling Point Elevation

When the vapour pressure of a liquid becomes equal to that of the atmosphere around it, the liquid boils.

Definition;

The boiling point is the temperature at which the vapour pressure of a liquid is equal to the atmospheric pressure.

As atmospheric pressure increases, boiling point increases.

As atmospheric pressure decreases, boiling point decreases.

Hence if you decrease the vapour pressure of a liquid by adding a non-volatile solvent, you increase the boiling point.

Freezing Point Depression

The freezing point of a liquid is the temperature at which it changes from a liquid to a solid.

Addition of a non-volatile solute to a liquid physically prevents the liquid from forming into a rigid crystalline structure necessary for freezing.

Addition of a non-volatile solute to a liquid lowers the freezing point.

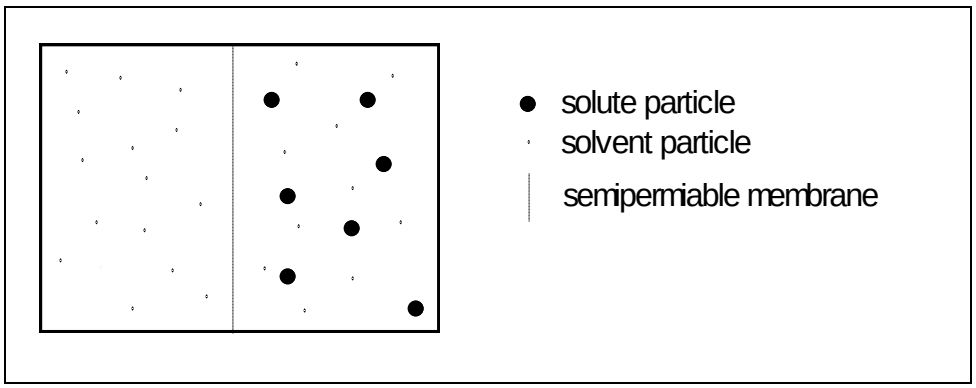
It is this principle that is used when we add antifreeze (ethylene glycol) to radiators to prevent them freezing up.

Osmosis and Osmotic Pressure

Many materials in biological systems are semipermeable, meaning that they allow some particles to pass through and not others.

Osmosis *is the net movement of solvent particles from a region of lower solute concentration to one of higher solute concentration.*

Semipermeable membranes can be thought of as a very fine mesh, through which only very small molecules may pass. These particles usually include solvent molecules like water, but not solute particles (eg. salt or sugar).



In a situation where there is a higher solvent concentration (lower solute concentration) on one side of a semipermeable membrane than the other, *there is a net flow of solvent molecules from high solvent concentration side of the membrane to the other*.

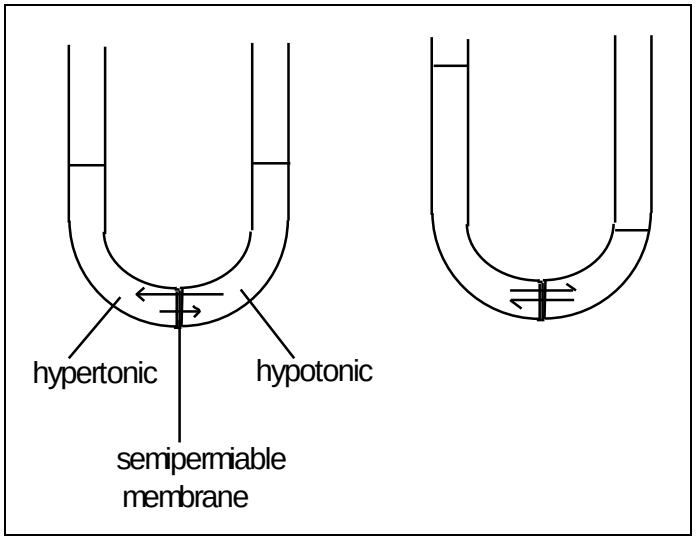
This process continues until the solvent concentrations on either side of the membrane are equal.Solvent molecules are always moving in both directions

through the membrane, but since there are more on one side than the other the rate of flows are uneven until the concentrations *equilibrate.*

Because it is the number of molecules and not the type dissolved in the liquid that controls osmosis, three terms are used to describe the relative numbers of solute particles in these situations.

The term ***isotonic*** is used to describe two or more solutions that contain equal numbers of dissolved particles per unit volume. In this situation there is no net flow of solvent molecules.

In comparing solutions of different concentrations, the solution that has the greater number of solute particles per unit volume is known as ***hypertonic,*** the one with less solute is known as ***hypotonic.***

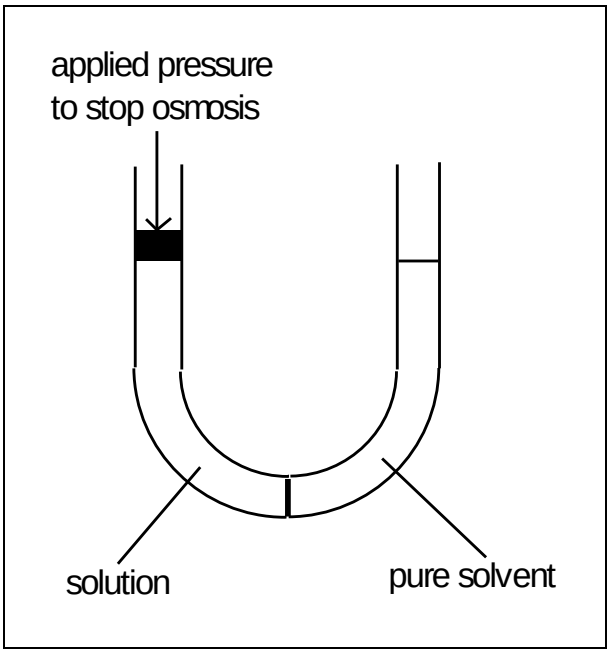


In osmosis, water molecules pass from the hypotonic side of a semipermeable membrane to the hypertonic side.

In biological systems the cell membrane acts as the semipermeable membrane. It is important that a careful balance is kept between the solute concentrations inside and outside the cell. If to much water flows into the cell it may rupture, if too much water flows out of the cell it will become desiccated.

Osmotic Pressure

The pressure that is required to stop the osmotic movement of water into a solution is called the *osmotic pressure.*



Osmotic pressure is measured using an instrument known as an osmometer. Osmotic pressure is important to plants and is used to measure the molecular weight of large molecules such as polymers and proteins.

CHEMICAL ENERGY

Temperature

Temperature is a measure of the hotness or coldness of an object.

The three common temperature scales are ;

(i) Fahrenheit (units: ^{o}F)
(ii) Celsius (units: ^{o}C)
(iii) Kelvin (units: K)*

*There is no degree sign for the Kelvin scale. This scale is sometimes called the absolute scale.

The accepted scientific unit (**SI unit**) for temperature is the Kelvin scale.

Conversion: $K = {}^{o}C + 273.15$

Energy

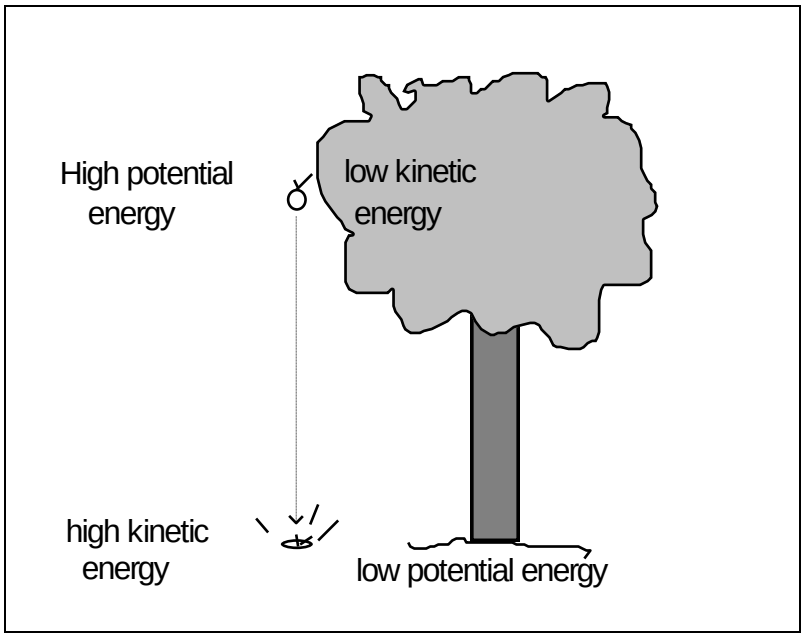
All changes in nature, whether physical or chemical are accompanied by changes in energy.

Energy may either be *potential* or *kinetic.*

Potential energy is the energy possessed by a substance due to its position in space.

Kinetic energy is the energy possessed by a substance due to its motion in space.

For example, a brick held 10m in the air has a high potential energy, but a low kinetic energy.
If the brick is dropped, as it hits the ground it can be said to have a low potential energy, but a high kinetic energy.



The molecules or atoms of all substances have kinetic energy; in other words *molecules* and *atoms are always in motion.*

0 K (-273º C) is known as *absolute zero,* and is the theoretical temperature at which all motion in a substance stops.

The SI unit for energy is **Joules (J)**.

The Kinetic Theory

Kinetic theory links the concepts of temperature and energy.

The temperature of a substance is a measurement of the average kinetic energy of the molecules that make up a substance.

This can be seen by a comparison of gases, liquids and solids.

Solids, fixed shape and volume, are incompressible , have a high density and cannot diffuse. This is because the molecules of a solid have little kinetic energy, and as a result can only vibrate around a fixed point in space.

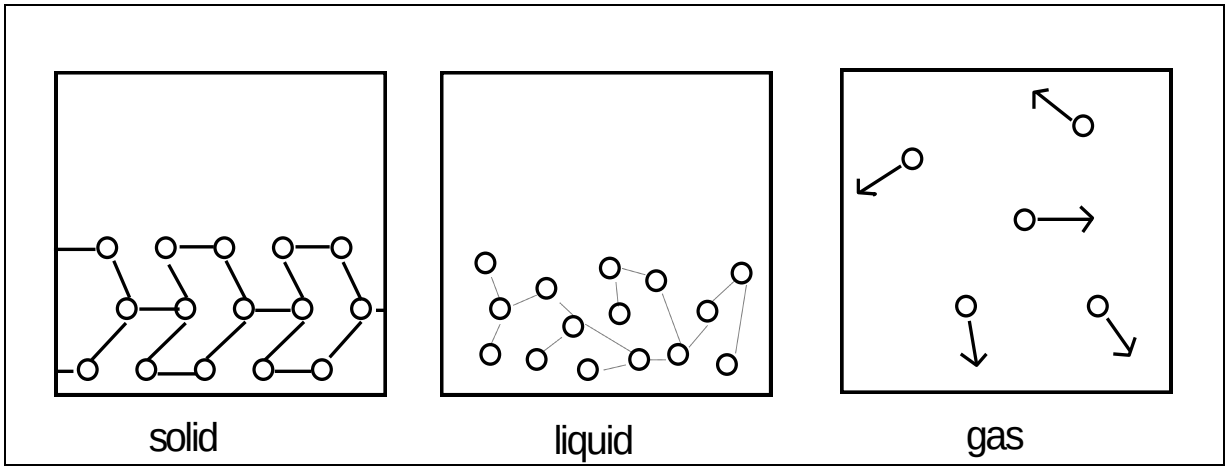
If we add enough energy in the form of heat the molecules will overcome the intermolecular forces acting and the solid will change to a **liquid**.

Since the molecules are now free to move about each other they are able to take on the shape of their container and are able to diffuse with other liquids.

They are only slightly compressible and have a fixed volume because the molecules do not have enough kinetic energy to move far away from each other.

If we supply even more energy in the form of heat the atoms or molecules may gain enough energy to overcome all intermolecular forces resulting in a **gas**.

Because there are no real forces of attraction between the molecules they move to fill whatever space is available. This leaves a lot of space between the molecules, which means that they are easily compressed and have a low density.



Gas Pressure

Gas pressure can be described in terms of *kinetic theory.*

The molecules of a gas have a great deal of kinetic energy and are in constant random motion. This results in them continually colliding with the walls of their container. It is these collisions which result in the gas exerting *pressure*.

The more *kinetic energy* they have, the harder they collide and hence the greater the pressure.

The SI unit for pressure is **Pascals** (Pa).

If we have a number of gases present, it is the sum of their partial pressures that gives the total pressure.

Energy and Chemical Reactions

The law of conservation of energy states that *energy can neither be created or destroyed, it merely changes form.* This law holds for all situations of change.

In all chemicals energy is stored in the form of chemical bonds, electronic energy, the energy which holds the protons and neutrons together (binding energy) and kinetic energy.
In chemical reactions energy is either gained or lost (in the form of heat) as the atoms rearrange, destroying old bonds and creating new ones.

Reactions which take in energy are called **endothermic** reactions.

Enthalpy

The heat change, or change in heat content, in a chemical reaction, is often referred to as the change in enthalpy.

This quantity is designated by the symbol **ΔH**. (This is read as 'delta H').

We cannot measure the actual heat content of any substance. We can however measure the energy lost or given off during a reaction. That is we can measure the *enthalpy*.

eg.

$$CH_4 + 2O_2 ==== CO_2 + 2H_2O$$

This reaction gives off 802 kJ of heat. Hence the enthalpy of the reaction is $\Delta H = -802$ kJ.

If the enthalpy of a reaction has a *negative* value the reaction gives off heat and is said to be **exothermic**.

If the enthalpy for a reaction has a *positive* value the reaction takes in heat and is said to be **endothermic**.

Entropy

Entropy can be described as the randomness or disorder of a system. In nature, all things tend towards maximum entropy, that is they like to be as disordered as possible.

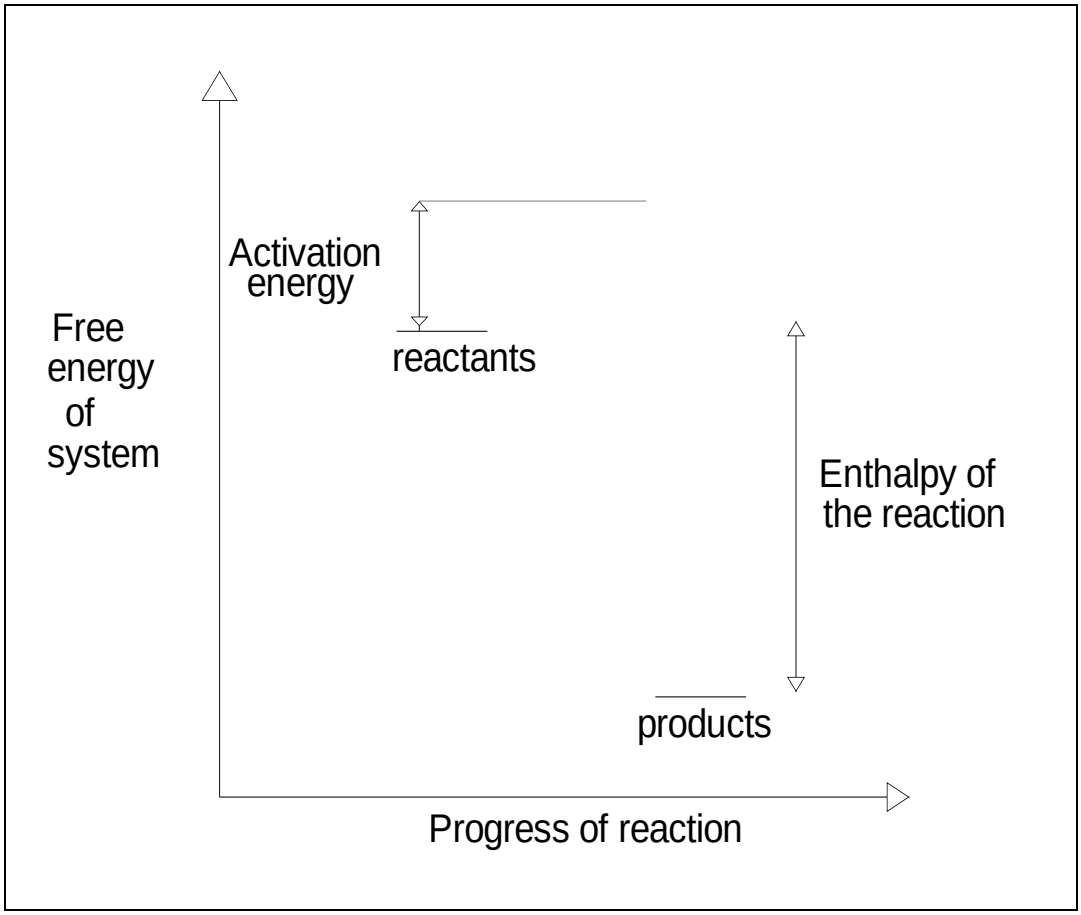
Entropy plays a part in determining whether a reaction will occur spontaneously.

FACTORS AFFECTING THE RATE OF CHEMICAL REACTIONS

Chemical reactions can only occur if the atoms or molecules involved in the reaction come into physical contact. That is they must collide with each other!

This means that the atoms and molecules must be moving, which in turn suggests that energy is necessary.

The energy necessary for effective collisions between atoms and molecules in a chemical reaction is known as the **activation energy**.



The activation energy can be thought of as the extra bit of energy we need to add to get a chemical reaction going.

For example petrol vapour needs extra energy in the form of a spark to explode. There are a number of factors that control the rate at which a reaction can occur once it has been initiated.

Temperature

If a chemical reaction is supplied with more energy (eg. heat) the reacting atoms and molecules involved in the reaction *will be moving more quickly.* As a result they will collide with one another more frequently and with greater force.

This leads to an *increase in reaction rate.*

Collision Geometry

Note that if atoms or molecules don't collide with one another in the right orientation (direction) then it will be less likely that they will react.

If, on the other hand, they collide dead on , they will be sure to react provided the collision occurs with sufficient energy for a reaction to result.

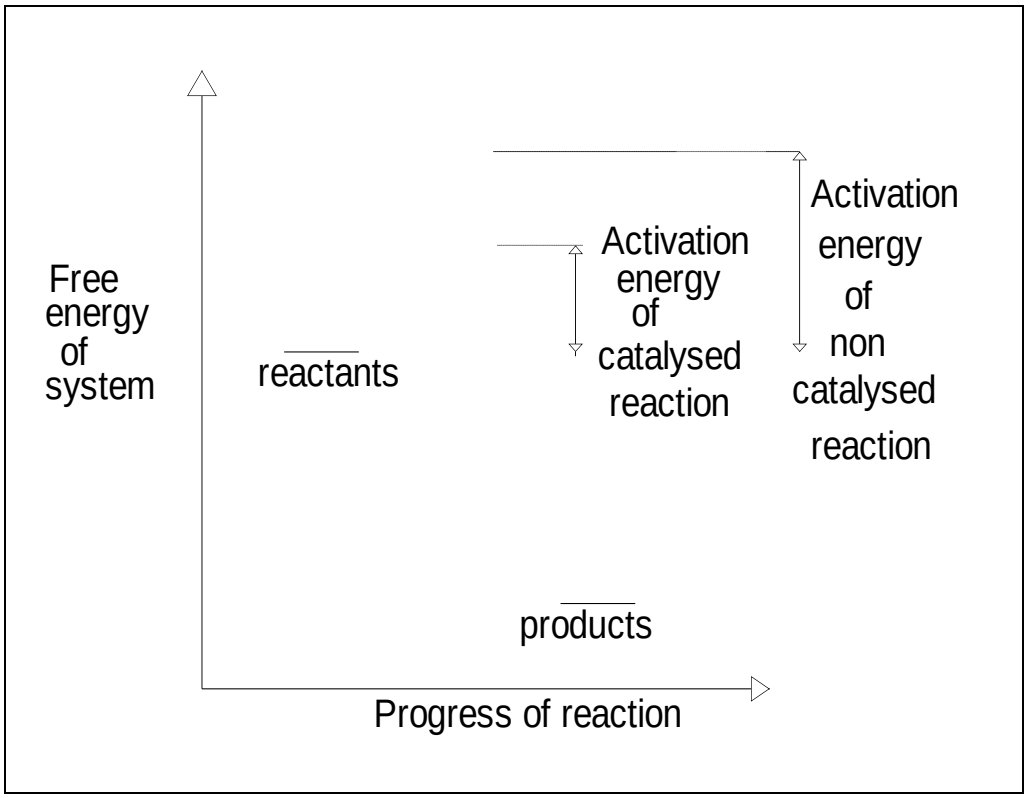
Concentration

The higher the concentration of reactants in a chemical reaction, the more atoms and molecules are present. Hence at higher concentrations the more likely collision are to occur.

Therefore higher concentrations usually lead to *higher reaction rates.*

Catalysts

Catalysts are substances which increase the rate of a chemical reaction without participating chemically in the reaction. They usually achieve this by bringing the reactants closer together, thus lowering the activation energy of the reaction.



This leads to an *increase in reaction rate.*

Enzymes are biological catalysts. All enzymes are proteins. All metabolic reactions need enzymes because most metabolic reactions must occur at very high speed and low temperature.

There are over 2000 different types of enzymes known to man, and each of these is capable of catalysing a specific reaction.

ORGANIC CHEMISTRY

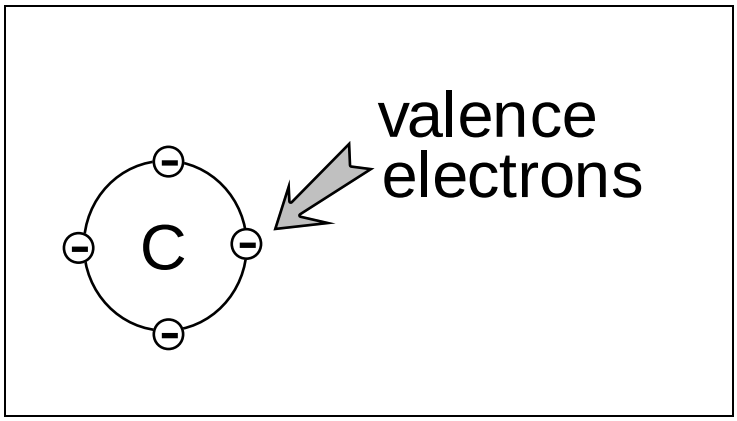
Introduction

Organic chemistry deals with substances that contain the element carbon.

Millions of organic chemicals exist in biological systems. These include carbohydrates, polysaccharides, lipids, amino acids, proteins (antibodies and enzymes) and nucleic acids.

In short most life forms on earth are composed of carbon based compounds, hence the name organic chemistry.

But why does carbon fill this role in living systems. The answer lies in its availability and its electronic configuration.



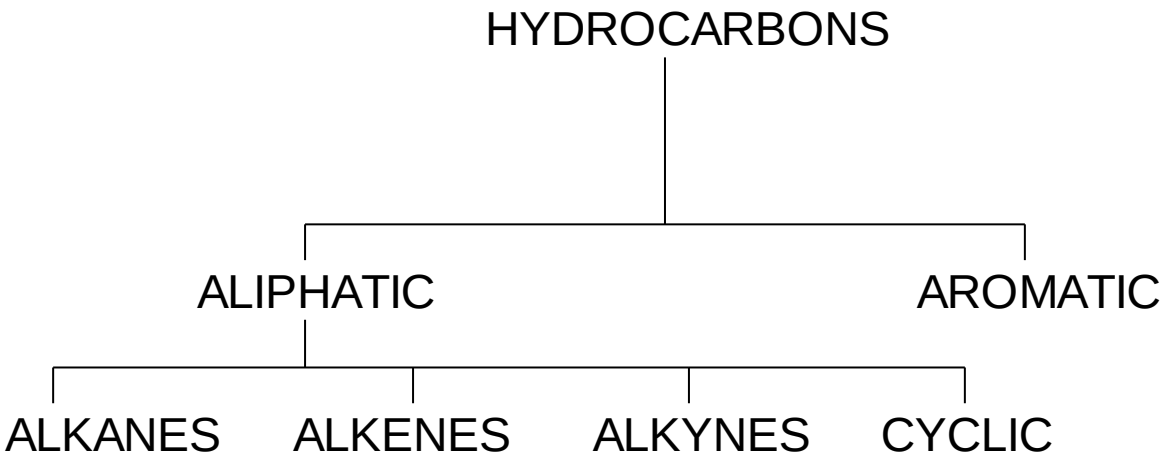
Carbon has only four valance electrons and as such needs to gain an extra four electrons to complete it outer shell. (That is to gain its most stable electron configuration.)

In organic compounds, carbon achieves a full valance shell by covalently bonding to non-metal atoms such as itself, hydrogen, oxygen, nitrogen, sulfur, phosphorous and the halogens such as chlorine and fluorine.

The ability to bond to itself allows carbon to form large linear, branched and cyclic molecules; or any combination of these.

Organic molecules (or **hydrocarbons**) can be broadly classified into groups; **aliphatic** (straight chained) and **aromatic** (based on benzene). These can be further classified into subgroups.

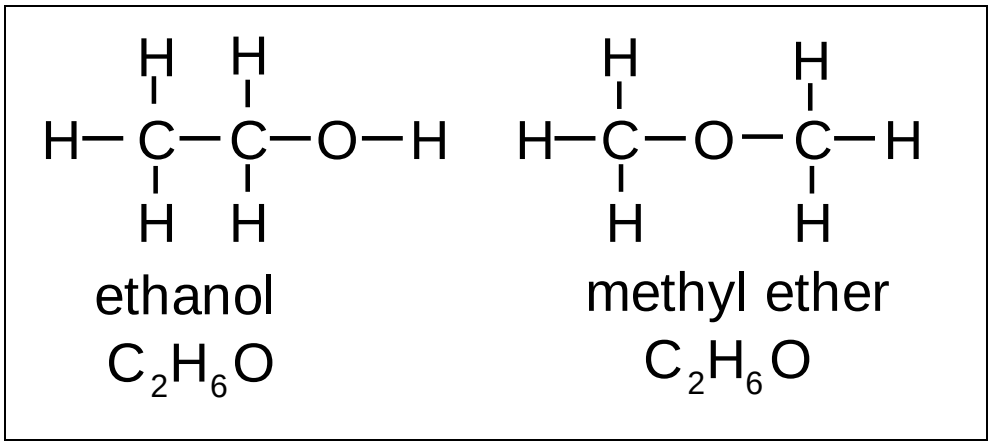
The ones dealt with by this course can be classified as follows.



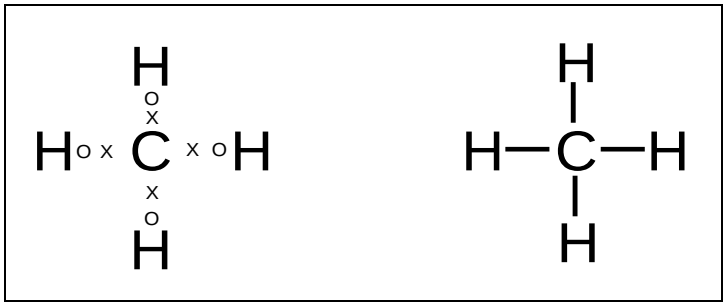
Structural Formulas

Although organic molecules generally contain only a few types of element, they may contain many atoms of each element per molecule in arrangement very specific to that molecule. For this reason molecular formulae are of little use in organic chemistry.

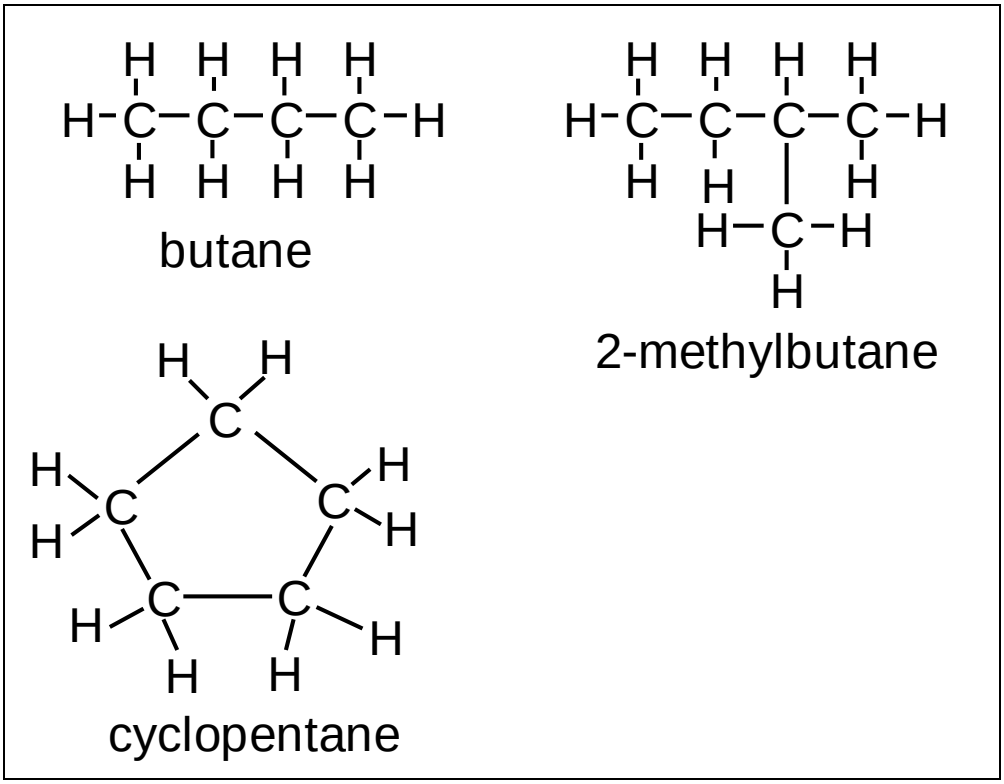
In organic chemistry it is the arrangement of the various atoms that is important. It is arrangement that infers the properties of organic compounds. It is possible for two organic compounds to have the same molecular formulae but different structures and properties.
eg



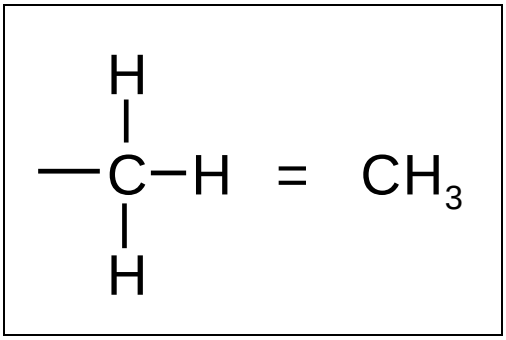
In structural formulae each two electron bond is represented by a single dash as in the example below.
ie.



Some examples of structural formulae follow.



Rather than represent the single bonds between carbon and hydrogen atoms (there are usually a lot of these in a given compound), it is acceptable to use the following shorthand method:



Isomerism

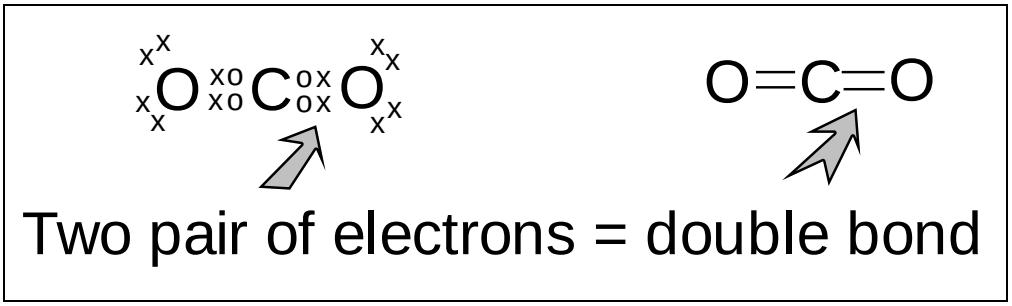
The existence of several different compounds having the same molecular formulae is called isomerism.

Compounds having the same molecular formulae but different structural formulae are called *structural isomers*.

Multiple Bonds Between Atoms

Atoms may share more than two electrons between them. If they share two pairs of electron, the bond is said to be a *double bond.* If they share three pair, it is called a *triple bond.*

This can be seen by looking at the carbon dioxide molecule.



As you can see from the electron dot diagrams each carbon oxygen bond consists of two shared pair of electrons. This means that each bond is a double bond.

An example of a molecule with a triple bond is ethyne.

Hydrocarbons with only single bonds between carbon atoms are known as *saturated hydrocarbons*, while those with one or more double or triple bonds are known as *unsaturated hydrocarbons*.

ALKANES

Petroleum and its associated natural gases are now the major source of hydrocarbons. Liquid petroleum is a complex mixture in which saturated hydrocarbons (alkanes) predominate. Large scale distillation and extraction processes are employed by the petroleum industry to separate crude oil into its useful fractions.

Organic compounds can divided into groups which have the same general formula.
Alkanes are aliphatic or cyclic hydrocarbons in which each carbon is bonded to *four* other atoms.
These compounds form what is known as a homologous series with the general formula:

$$C_nH_{2n+2}$$

Definition: a homologous series is a succession of hydrocarbons that have the same general formula.

The first ten hydrocarbons in the alkane family are as follows:

No.	Name	Formula
1	methane	CH_4
2	ethane	$H_3C\text{-}CH_3$
3	propane	$H_3C\text{-}CH_2\text{-}CH_3$
4	butane	$H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_3$
5	pentane	$H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$
6	hexane	$H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$
7	heptane	$H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$
8	octane	$H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$
9	nonane	$H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$
10	decane	$H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2CH_3$

The above compounds all follow the general formulae

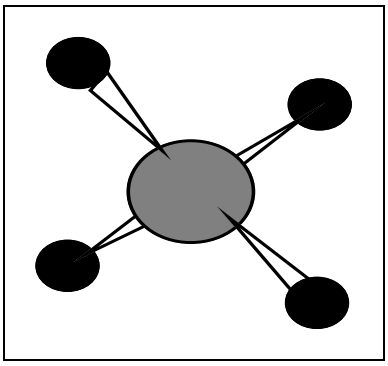
C_nH_{2n+2}

NAME	FORMULAE	M. Wt	B.Pt	M.Pt
methane			-162	-183
ethane			-89	-183
propane			-42	-178
butane			0	-138
pentane			36	-130
hexane			69	-95
heptane			98	-91
octane			126	-57
nonane			151	54
decane			174	-30

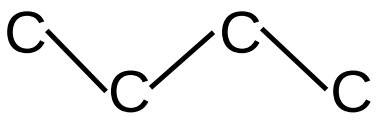
You can see from the table that trends in both boiling point and melting point occur. In short both melting point and boiling point increase as the length of the hydrocarbon chain increases.

This occurs because as the carbon chain gets longer it becomes harder for the molecules to move about each other. That is it takes more energy.
Although the structural formulae for hydrocarbons make the molecules appear flat (2-dimensional), they are really 3-dimensional. When a carbon atom bonds to 4 other atoms, electron repulsion causes the bonds to move as far away from each other as possible.

The result is an angle of 109.5º between all the bonds in saturated hydrocarbon.



This means that carbon chains tend to form zig-zags.



Functional Groups

When we look at the structural formula of an aliphatic hydrocarbon, it should be possible to see a carbon "backbone", made up by the longest available chain of carbon atoms in the molecule. This backbone could be methane, ethane, propane, butane (ie. the parent compound) etc..

In some cases, however, one or more of the hydrogen atoms on the backbone will have been replaced by what we call *functional groups*.

Examples of functional groups are:

methyl group	$-CH_3$
ethyl group	$-CH_2CH_3$
propyl group	$-CH_2CH_2CH_3$
butyl group	$-CH_2CH_2CH_2CH_3$
chloro group	-Cl
bromo group	-Br
iodo group	-I
amino group	$-NH_2$
hydroxy group	-OH
carbonyl group	=O
nitro group	$-NO_2$

These functional groups impart certain chemical properties to the molecule they are a part of.

Of course, naming alkanes once they have functional groups attached is somewhat more complicated than the naming of the basic alkanes.

Reactions Of Alkanes

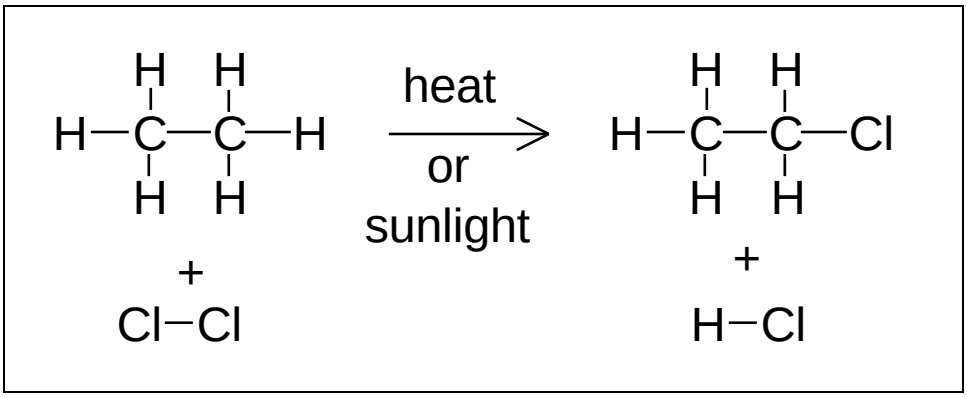
Saturated hydrocarbons (alkanes) are relatively inert; they react with few chemical reagents.

They will, however, react with *halogens, concentrated nitric acid and oxygen.*

Halogenation

The process where hydrogen atoms in an alkane are replaced by halogen atoms is called halogenation.

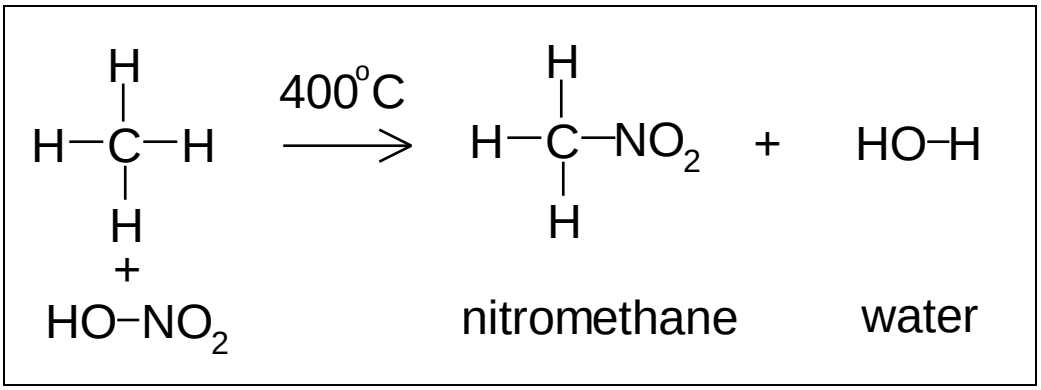
example;



More than one halogen atom can be substituted onto any one alkane. Alkanes which have one or more halogen (chlorine, bromine, fluorine, iodine) atoms attached to the carbon backbone are known as haloalkanes.

Nitration

Nitration of alkanes is a commercially important reaction.



Products from nitration reactions of alkanes are excellent solvents, ingredients of special racing and model engine fuels, as well as the intermediates for the synthesis of drugs, insecticides and explosives.

Oxidation

Perhaps the most important use of hydrocarbons is as fuels. Hydrocarbons burn in excess oxygen to form carbon dioxide and water. The reaction is accompanied by the evolution of large quantities of heat.

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ ΔH= -889 Kj/mol

$2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$ ΔH= -2876 Kj/mol

Reactions of this type constitute the major sources of energy in the modern world.

In the absence of sufficient oxygen for complete reaction, partial combustion may occur. The products can be carbon monoxide or even carbon.

$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$

$CH_4 + O_2 \rightarrow C + 2H_2O$

Nomenclature Of Alkanes

So that the nomenclature of the organic compounds is standard all over the world, the International Union of Pure and Applied Chemists (IUPAC) have devised a simple naming system.

Rules Nomenclature Of Alkanes

The naming system for branched alkanes is as follows;

1. If the hydrocarbon chain is branched, determine the longest continuous chain of carbon atoms (known as the carbon backbone) in the molecule. The name of your compound will end in the name of the alkane corresponding to this number of carbon atoms.

2. Number the carbon atoms of the continuous chain, in such a way that the functional groups are attached to the lowest possible numbered carbon atoms.

3. The functional groups which are attached to the carbon backbone are given the appropriate names, and these names written before the name of the carbon backbone, in alphabetical order, are part of the same word formed by the name of the parent alkane from which the hydrocarbon is derived.

4. If more than one of any type of functional group is present on the one backbone, a prefix is added to indicate the number present. The prefixes used are;

number of groups	prefix
2	di
3	tri
4	tetra
5	penta
6	hexa

6. All numbers in the IUPAC name are separated by a comma, and numbers and text are separated by a horizontal dash. All text is written as one word.

ALKENES

Petroleum and its associated natural gases are now the major source of hydrocarbons. Liquid petroleum is a complex mixture in which saturated hydrocarbons (alkanes) predominate. Large scale distillation and extraction processes are employed by the petroleum industry to separate crude oil into its useful fractions.

Alkenes and *cycloalkenes* are hydrocarbons that possess one or more carbon-carbon double bonds.

Alkenes have the homologous formula:

$$C_nH_{2n}$$

They are said to be unsaturated because they do not have the maximum number of atoms each carbon is able to accommodate.

Their physical properties are closely related to those of the corresponding alkanes.

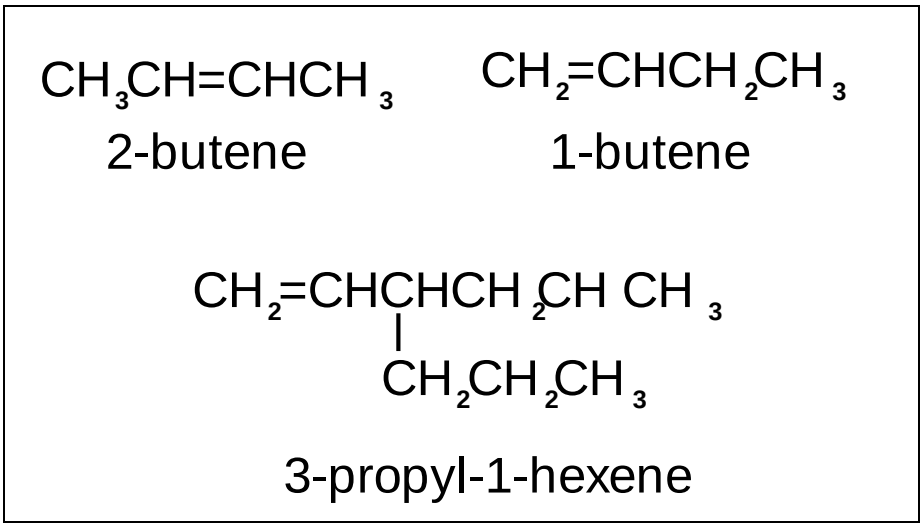
IUPAC naming for alkenes is similar to that for the naming of alkanes; the major difference is that the alkenes end with "ene" rather than "ane" as do the alkanes. The position of the double bond in an alkene provides the criterion for numbering the atoms in the IUPAC system, even if side chain groups must receive high numbers.

When a compound is named as a cycloalkene, numbering of the carbons in the backbone begin at one carbon atom of the double bond and proceed to the second atom of double bond and then around the ring.

Within this constraint the ring is numbered so as to give side chains the lowest possible numbers.

The number of double bonds present in an alkene is indicated by a prefix (di, tri, etc.) placed before the name of the backbone of the molecule.

For example.



In cycloalkenes, the carbon involved in the double bond (in the case of only one double bond) are numbered 1 and 2, and the remaining carbons named in order around the cyclic carbon backbone.

Physical Properties of Alkenes

The alkenes are similar to the alkanes in their physical properties.

name	formula	boiling point
ethene		-104
ethane		-89
propene		-48
propane		-42
1-butene		-6.3
butane		1

The boiling point of each alkene tends to be slightly lower than that of its corresponding alkane. This is the result of the electronic properties of the double bonds and their more rigid physical structure.

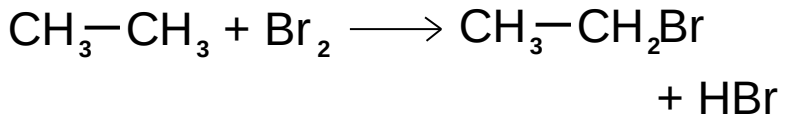
Reactions of Alkenes

The general distinction between saturated and unsaturated hydrocarbons is the general type of reaction they undergo.

Saturated hydrocarbons react by substitution (a hydrogen atom is substituted by another atom or group of atoms), whereas the characteristic reaction of a group of alkenes (unsaturated hydrocarbons) is addition to the double bond (addition reactions).

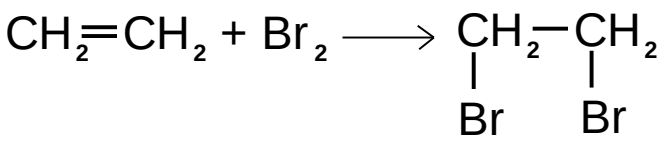
Contrast the reaction of ethane and ethene with bromine.

substitution



bromoethane

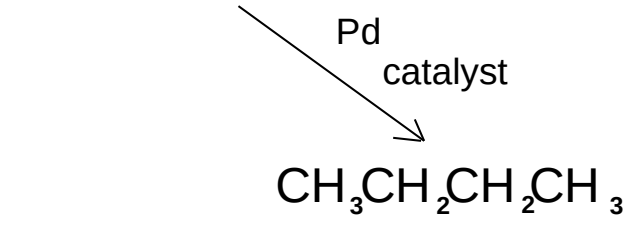
addition



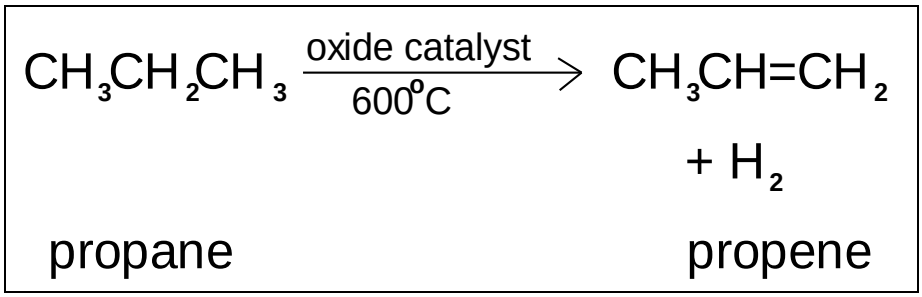
1,2-dibromoethane

This reaction can be used to distinguish between alkenes and alkanes because the substitution reaction is quite slow (under normal conditions) while the addition reaction occurs almost instantaneously.

Alkenes can be converted to alkanes by process known as *hydrogenation*.



Alkanes can be converted into alkenes by an elimination reaction known as dehydrogenation.



This kind of reaction is known as an *elimination reaction* because two of the hydrogens have been eliminated from the hydrocarbon and replaced by a double bond.

ALKYNES

Alkynes are unsaturated hydrocarbons that contain one or more carbon-carbon triple bonds.

The alkyne family can be represented by the homologous formula:

$$C_nH_{2n-2}$$

The simplest alkyne is the important industrial gas ethyne (also known as acetylene).

$$HC{\equiv}CH$$

The naming system for alkynes is the same as that for alkenes, with the triple bond taking precedence if both triple and double bonds are present.

The chemical and physical properties of alkynes are also similar to those of the alkenes. The only major difference is that alkynes undergo addition reactions slightly more slowly than alkenes.

ALKANOLS

Alkanols (alcohols) are probably the organic compounds with which students have the greatest familiarity. Ethanol (ethyl alcohol; C_2H_5OH) has been known since ancient times; it is the product of the anaerobic fermentation of the carbohydrates found in plants.

Alkanols may be thought of as being derived
from saturated or unsaturated hydrocarbons by replacing a hydrogen atom by a hydroxyl group (-OH).

Nomenclature

Alcanols are designated by the suffix -ol in the IUPAC nomenclature.

The longest continual chain to which the hydroxyl group is connected provides the root for the parent name. The final "e" of the corresponding hydrocarbon name is dropped and the "ol" suffix is added. Numbering begins at one end of the parent carbon chain and that end is chosen so as to give the hydroxyl group the lowest possible number.

Compounds which contain two, three or more hydroxy groups are classified as polyols; the IUPAC suffixes are -diol, -triol and so forth. The IUPAC name retains the final "e" of the parent hydrocarbon name because the suffix "diol" does not begin with a vowel.

Exercise

Draw structural formulae for each of the following alcohols:

1) methanol

2) ethanol

3) 1-propanol

4) 2-propanol

5) 1-chloro-2-pentanol

6) 2-methyl-1-propanol

7) cyclopentanol

8) 3-methylcyclopentanol

9) 1,2-ethanediol

10) 1,2,3-propanetriol

Physical Properties of Alkanols

name	M.Pt (^{O}C)	B.Pt (^{O}C)
methane	-182	-164
methanol	-94	65
ethane	-183	-89
ethanol	-117	79
propane	-190	-42
1-propanol	-127	97
2-propanol	-90	82

The melting and boiling points of alkanols tend to be much higher than those of their corresponding alkanes. This is due to the ability of the hydroxy group to undergo hydrogen bonding in the same way as water does.

The hydroxyl group is found in a wide variety of compounds of plant and animal origin. Because of the complex structures of some of the substances, they are usually referred to by common names.

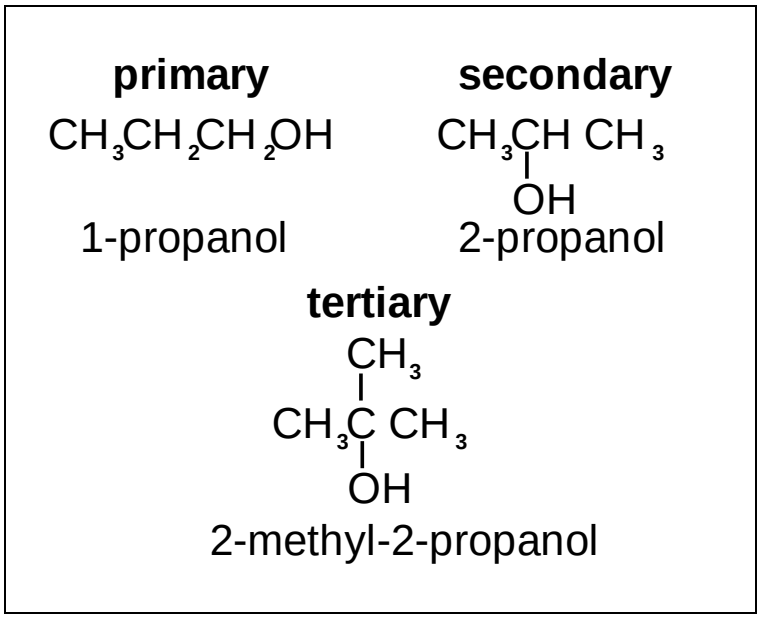
Primary, Secondary and Tertiary Alkanols

Alkanols can be classified by the number of carbon atoms attached to the hydroxyl-bearing carbon atom.

In **primary alkanols**, the hydroxyl-bearing carbon is bonded to one other carbon atom.

In **secondary alkanols**, the hydroxyl-bearing carbon is bonded to two other carbon atoms.

In **tertiary alkanols**, the hydroxyl-bearing carbon is bonded to three other carbon atoms.



Preparation Of Alkanols

Primary alkanols can be prepared by the hydrolysis of the corresponding haloalkane. This involves heating the primary haloalkane with NaOH (the -OH is the reactive part of the NaOH molecule in this case).

$$RCH_2X + OH^- \rightarrow RCH_2OH + X^-$$

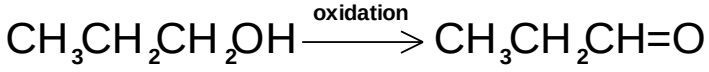
(X = Cl, Br, I R = a hydrocarbon group)

Oxidation of Alkanols

Alkanols are the most important precursors of the carbonyl compounds (those containing the carbonyl =O functional group).

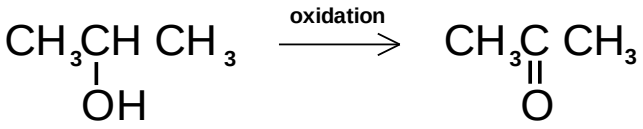
Oxidation of primary alkanols gives alkanals, oxidations of secondary alkanol gives alkanones and tertiary alkanols are not easily oxidised.

Oxidation of a Primary Alkanol



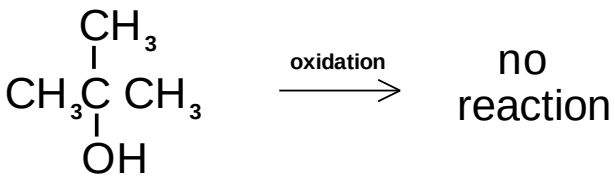
1-propanol propanal

Oxidation of a Secondary Alkanol



2-propanol 2-propanone

Oxidation of a Tertiary Alkanol



2-methyl-2-propanol

Oxidation is usually carried out using an oxidising agent such as sodium dichromate ($Na_2Cr_2O_7$) in the presence of an acid such as sulfuric acid.

Exercise

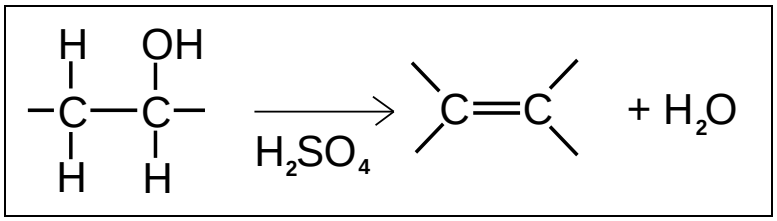
a) Write an equation representing the oxidation of 1-propanol.

b)Write an equation representing the oxidation of 2–butanol.

c) Write an equation representing the oxidation of 3-heptanol.

Dehydration of Alkanols

Alkanols can be dehydrated (H_2O removed) by acid (usually H2SO4 or H3PO4) to produce alkenes.



Exercise

a) Write the equation for the dehydration of 2-butanol. Name the product.

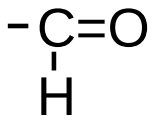
b) Write the equation for the dehydration of 3-hexanol and name the products.

CARBONYL COMPOUNDS; ALKANALS & ALKANONES

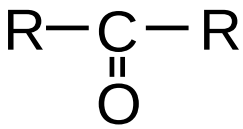
Formaldehyde, long known as a disinfectant and as a preservative for biological specimens, is the simplest of a series of compounds built around the carbonyl group (a carbon atom linked to an oxygen by a double bond). Compounds containing a carbonyl group are known as either alkanals (or aldehydes) or alkanones (ketones) depending on the location of the carbonyl group. Many natural substances are alkanals and alkanones. Among them are the various flavours from almonds, cinnamon, vanilla; many perfumes; camphor; certain vitamins and sex hormones.

Alkanals and Alkanones contain the carbonyl group C=O.

If one of the two groups attached to the carbonyl group is a hydrogen atom, the compound is known as an **alkanal**. It can be represented as shown below but is often abbreviated to -CHO.



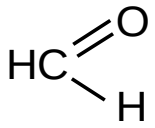
Those organic compounds in which both groups attached to the carbonyl carbon are part carbon backbone are known as alkanones. The attached groups do not need to be identical.



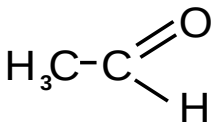
Nomenclature

Alkanals (aldehydes) are named by using the suffix **-al**. When a compound is named as an alkanal the functional group is always at the end of the parent chain and so the number -1- is omitted.

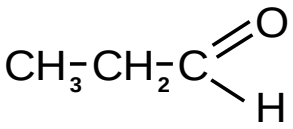
for example



methanal

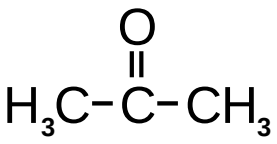


ethanal

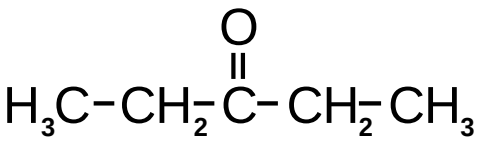


propanal

The IUPAC nomenclature employs the suffix **-one** to designate an alkanone (ketone). A number indicates the position of the carbonyl group along the parent chain.



propanone



3-pentanone

The carbonyl group takes precedence in assignment of numbers over all other functional groups discussed so far.

Exercise

Draw the structural formulae for the following compounds:

1) 2-heptanone

2) 3-methylbutanal

3) 3-methyl-3-butenal

4) 6-chloro-5-methyl-2-heptanone

5) cyclobutanone

6) 2-methylcyclopentanone

7) 3-ethylhexanal

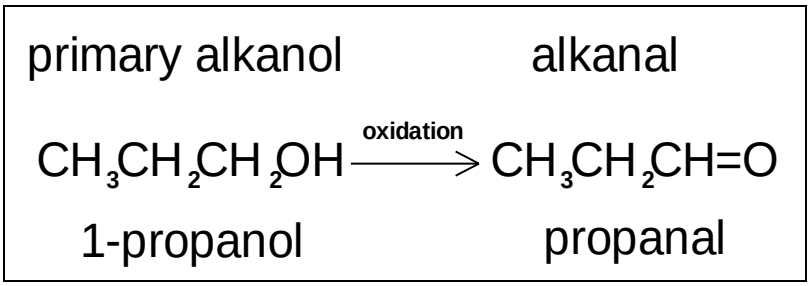
8) cyclohexanone

9) 4-pentenal

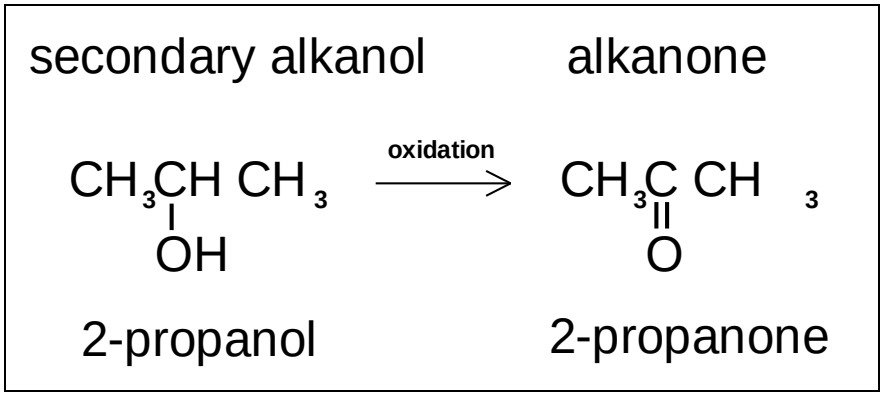
10) 7-chloro-5-ethyl-3-methyl-2-octanone

Reactions of Alkanals and Alkanones

Alkanals can be produced by the oxidation of primary alkanols:



Alkanones can be produced by the oxidation of secondary alkanols:



Exercises

a) Write the chemical equation for the oxidation of 1-propanol to propanal.

b) Write the chemical equation for the preparation of pentanal by the oxidation of a primary alkanol and name the alkanol.

c) Write the chemical equation for the preparation of 3-hexanone from a secondary alkanol and name the alkanol.

d) Write a chemical equation for the preparation of cyclobutanone from an alkanol and name the alkanol.

Distinguishing Tests

It is possible to distinguish between an alkanal and alkanone by using Tollen's silver mirror test and Fehling's test.

The **Tollen's test** involves the reduction of silver ions (Ag^{+}) to silver metal, which can be observed as a silver mirror on the walls of the test tube in which the test is being performed.

Alkanals give a **positive** result for the Tollen's test. At the same time that the reduction of silver is occurring another substance must be oxidised. In this case the alkanal is being oxidised to an alkanoic acid.

Alkanones give a **negative** result for this test.

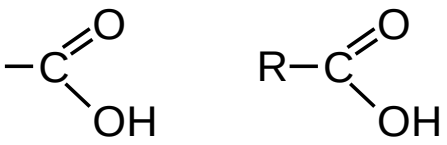
Fehling's solution consists of Cu^{2+} ions, complexed with tartrate ions. The solution is blue in colour. When **Fehling's solution** reacts with an **alkanal** a brick red precipitate of copper(I) oxide is produced.
Alkanones also give a **negative result** for this test.

These types are tests are sometimes used to clinically detect the presence of sugar in urine (glucose can be classed as an alkanal).

ALKANOIC ACIDS

It was known to the ancients that a sour taste developed in wine left exposed to the air, and this process is still used in the manufacture of vinegar. Ethanol in the wine is oxidised by bacteria to a dilute solution of ethanoic acid, one of the simplest members of a series of compounds known as the alkanoic acids (also known as the carboxylic acids). Many occur in nature, either free or in combination with other organic compounds. Alkanoic acids combine with alkanols to form esters, which occur in fruit flavours, perfumes, vegetable and animal fats and oils. Many of the intermediates in metabolic processes are alkanoic acids.

Alkanoic acids contain the **carboxyl group**:



carboxyl group alkanoic acid

Nomenclature

Because of their wide distribution and abundance in nature, the alkanoic acids were among the first organic compounds to be studied. Consequently, many of them are known by common names, often derived from a Latin or Greek name indicating the source of the acid. For example, formic acid (Latin, formica = ant) was obtained by the distillation of ants.

The IUPAC system employs the suffix **-oic acid**, and applies all the other rules previously discussed.

Because of its structure the carboxylate group must come at the end of a carbon chain; consequently no number is used to locate this group.

Exercise

Draw the structural formula for the following.

1) methanoic acid

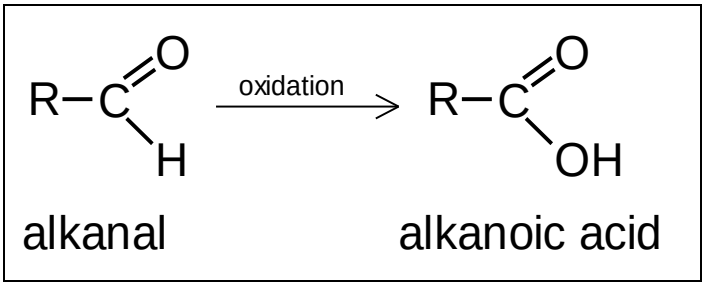
2) ethanoic acid

3) propanoic acid

4) 2-methylpropanoic acid

5) 3-chloropentanoic acid

Alkanoic acids can be produced by the oxidation of the corresponding alkanal:



alkanal alkanoic acid

Alkanal are the product of the **oxidation of primary alkanols** such as ethanol.

Therefor the oxidation of ethanol to ethanoic acid, the process which gives old wine and vinegar a sour taste, occurs in two steps. The first step is the oxidation of ethanol to ethanal, and the second is the oxidation of ethanal to ethanoic acid.

Exercise

Write a chemical equation for the oxidation of propanal and name the product. ($K_2Cr_2O_7/H^+$ is a suitable oxidising agent).

CHEMISTRY AND THE ENVIRONMENT

In recent times there has been a great deal of discussion in the media and at various levels of government about the role of chemicals and the chemical industry in society. While this has led to a much needed increase in the public awareness of the enviroment and man's impact upon it, it has also led to a number of misconceptions within the public; due either to a general misunderstanding of chemical concepts or misleading use of these concepts. It is only by having a reasonable grasp of these principles that you may make your own judgement on the environmental impact of various substances.

CHEMICALS AND NATURE

Probably the greatest misconception in the argument over the role of chemicals in everyday life is the differentiation between chemicals and natural products. The simple truth is that there is no such division. There are chemicals that are present in nature and there are man made chemicals but they are still essentially the same, ie they are groups of elements gathered together in a specific way that does not vary (see the definition of a compound earlier in this book). Many so called man made chemicals are also present in nature, but in small amounts or in forms difficult to access. Examples include many drugs such as aspirin and penicillin and chemicals such as ethanol and methane.

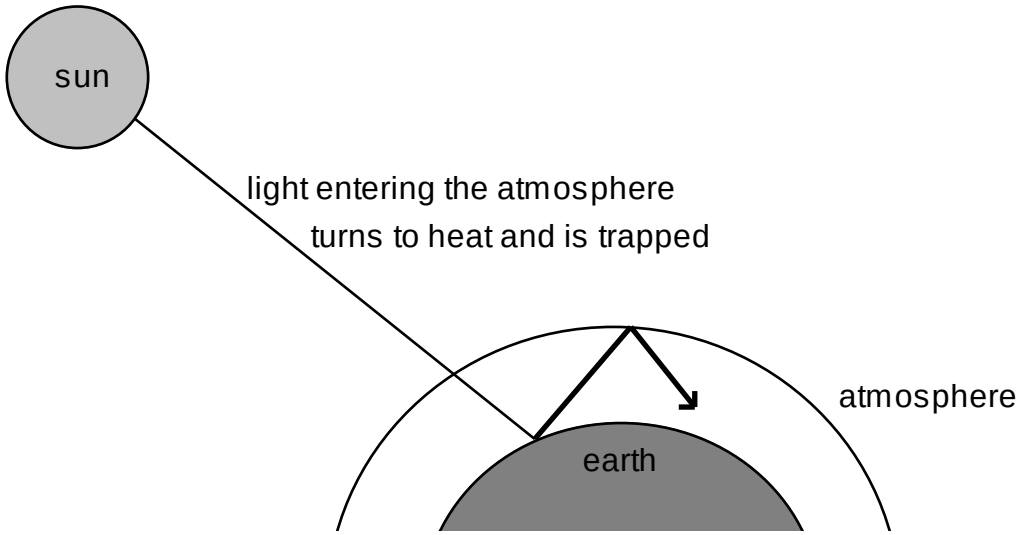
This artificial differentiation between man made and natural chemicals has also led to the misconception that all natural products are beneficial to health and the enviroment while man made chemicals are by definition dangerous. While many substances found in nature are beneficial for health it must also be noted that some of the most deadly poison that are known to man are also natural products. These include such things as arsenic and many of the classical poisons such as belladonna and curarie. Crude oil is a natural product resulting from the decomposition of millions of microscopic creatures, but you would hardly drink a cup of it on the basis that since it was natural it must be good for you. In the 1800's in the United States it was common practice for travelling salesmen to offer mineral spring water as a natural health tonic; unfortunately, these contained large quantities of naturally occurring arsenic salts, resulting in a number of deaths.

Inversely a large number of man made substances are highly beneficial to man and the enviroment. These obviously include many drugs and medicines but also includes building products that do not use up our valuable timber reserves, processed foods that last longer than natural ones and alleviate wastage, semiconductor materials used in microchip and solar energy conversion technologies and many others. It is the uses that chemicals are put to that determine their effect on man and his enviroment.

The Greenhouse Effect

The greenhouse effect is the result, predicted by a large body of scientist, of the increased use of fossil fuels and large scale agriculture by man in this century. They predict that the increase in greenhouse gases in the atmosphere will result in an overall increase in global temperature. This could result in climatic change and a rise in sea level due to the melting of the ice caps.

The heat increase is predicted to result from the influences on the process where light enters the atmosphere and hits the planet when it is converted to infrared radiation (heat) . This is a normal process and has been going on since the beginning of the planet. However, due to the presence of greenhouse gases, the infrared radiation, or heat, can no longer escape complete to outer space. The greenhouse gases act as a blanket keeping the heat in the planet's atmosphere. Once again this a natural effect which is necessary to keep the planet warmer than the space around it. However it is the chance of the effect increasing with an increase in greenhouse gases that concerns scientists.



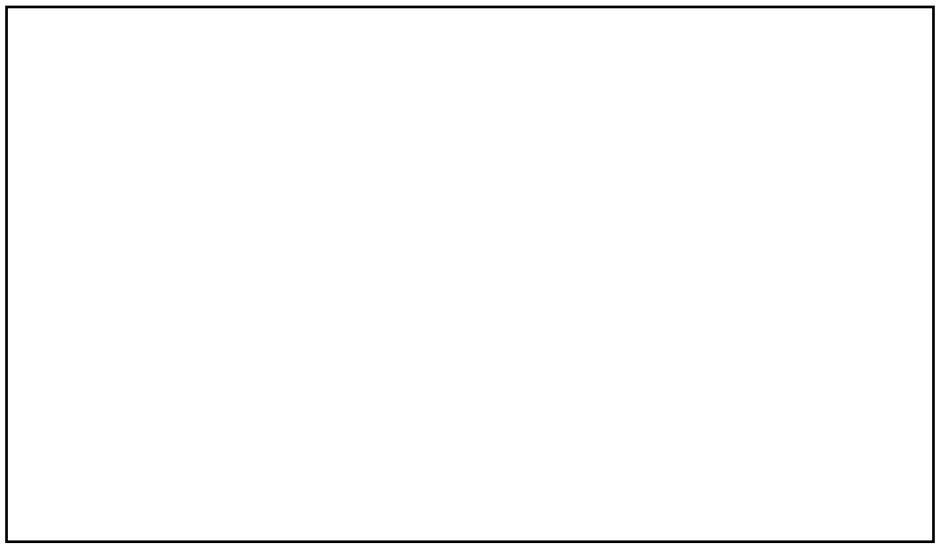
Two of the primary greenhouse gases are carbon dioxide (CO_2) and methane (CH_4). Carbon dioxide is produced by the burning of fossil fuels such as petrol.

$$C_5H_{12} + 8O_2 \text{ ------ } 6H_2O + 5CO_2$$

Other fossil fuels include coal and natural gas. These are often burnt to produce electricity. So even if not directly producing a greenhouse gas using electricity also contributes to the greenhouse effect.

Another surprising source of green house gases is cattle. Cattle eat mainly food made out of an organic molecule called cellulose. This is a fairly unreactive molecule and the digestive system of cattle produces the gas methane while trying to break it down. As the earths populating increases the demand for products from animals such as sheep and cattle increases and hence the

number of sheep and cattle increases. This leads directly to an increase in the amount of methane in the atmosphere.



The Breakdown of the Ozone Layer

Ozone is the molecule O_3. In the upper atmosphere it is formed by the action of ultraviolet radiation on the oxygen (O_2) molecule in a reaction that produces heat.

$$O_2 + UV \text{ ------ } O + O$$

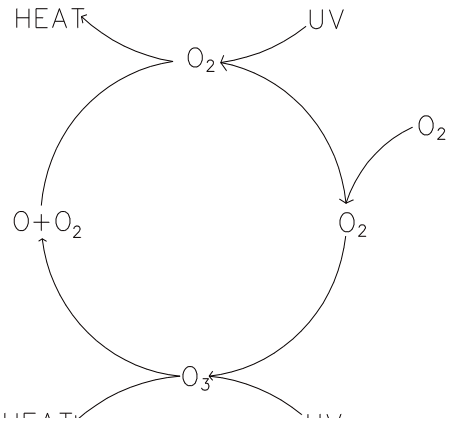
$$O + O_2 \text{ ----- } O_3 + \text{heat}$$

The ozone is then broken down by ultraviolet radiation in a reaction that once again produces heat.

$$O_3 + UV \text{ ----- } O_2 + O$$

$$O + O \text{ ----- } O_2 + \text{heat}$$

The overall effect is that ultraviolet radiation is converted to heat while a constant level of ozone is maintained.



Chlorofluromethanes such as CF_2Cl_2 and $CFCl_3$ (better known as CFCs) break down in the upper atmosphere to form atomic chlorine. This in turn reacts with the ozone to form O_2. while undergoing no change itself (ie it works as a catalyst).

$$Cl + O_3 \text{ -----} ClO + O_2$$

$$ClO + O \text{ -----} Cl + O_2$$

It is thought this leads to an overall depletion in the amount of ozone available, by consuming it at a greater rate than the rate of production and hence to an increase in ultraviolet radiation reaching the planets surface. This process is a slow one and as such evidence of the effect is hard to measure. Many companies are now looking for alternative propellants for aerosol products, rather than CFCs.

Acid Rain

One of the more noxious pollutants to be found in the atmosphere is sulfur dioxide (SO_2). This gas is a product of the smelting of many zinc and lead ores and is also a result of burning some types of coal and oil. Some studies suggest that this gas by itself endangers health when it is present in certain concentrations. However much of it is oxidised in the atmosphere to the more reactive form, sulfur trioxide (SO_3). This in turns reacts with water to form sulfuric acid.

$$SO_3 + H_2O \text{ -----} H_2SO_4$$

Sulfuric acid is a strong acid that does a great deal of damage to man made structures, especially those made out of carbonate materials such as cement and marble. Acid rain also does a great deal of damage to natural formations such as limestone caves and it has also been blamed for the extensive damage to the Black Forest in Germany.

Many governments in recent years have imposed strict regulations on the emission of sulfur compounds into the atmosphere and in response companies have been forced to drastically reduce the level of these emissions. Unfortunately many countries, especially in eastern Europe, still lag behind in this type of control and acid rain is still a major problem.

Photochemical Smog

Smog is the general name given to the yellow brown haze which hangs over many major cities, especially at those times the atmosphere is relatively stagnant. This smog is a mixture of gases and airborne particles but the distinctive yellow colour and the offensive odour are the result of the poisonous gas nitrogen dioxide (NO_2). This gas is produced in small amounts by car engines. However the majority of the pollutant arises from the reaction between ozone and the colourless and odourless gas nitric oxide (NO) which is emitted from cars in far greater quantities.

$$O_3 + NO \text{ ----- } NO_2 + O_2$$

This ozone is the result of the photochemical reaction (ie a reaction that need light to occur) between oxygen and nitrogen dioxide among others. While the presence of ozone is so beneficial in the upper atmosphere, it presence at sea-level leads to a number problems. It is capable of reacting with relatively unreactive hydrocarbons which are also emitted from car exhaust engines to create harmful aldehydes which may cause breathing difficulties and eye irritation.

Far stricter car emission controls has led to a marked decrease in the amount of dangerous gases released by car exhausts, promoted by the breakdown of dangerous pollutants by catalytic converters. However emission control devices are ineffective when fitted to a poorly maintained and tuned vehicle. Also it has been shown that the majority of pollution caused by motor vehicle is the result of the large number of old vehicles found on the roads, with modern cars built to far better controls and with self maintaining electronic tuning contributing very little of the pollution.