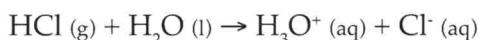


Chemical Equilibrium

1.1 REACTIONS

Most of the chemical equations you have experienced have been those that go to completion.



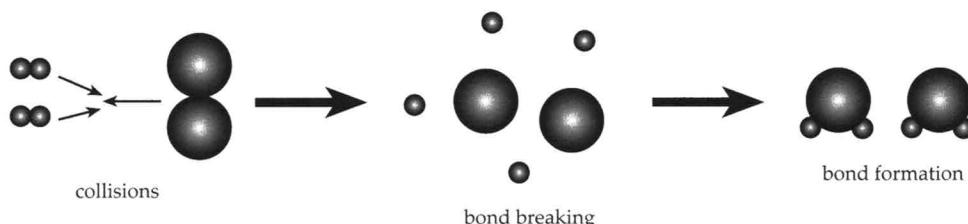
The arrow shows that all of the HCl has been converted into hydronium and chloride ions. However, chemical changes can be almost instantaneous like the one above, or may take many years to complete, depending upon many factors, such as closeness of particles and temperature.

Not all reactions convert all the reactants to products. Often products can also react to reform the reactants. Thus an intermediate equilibrium situation is obtained. The products are converted to reactants as quickly as they are formed.

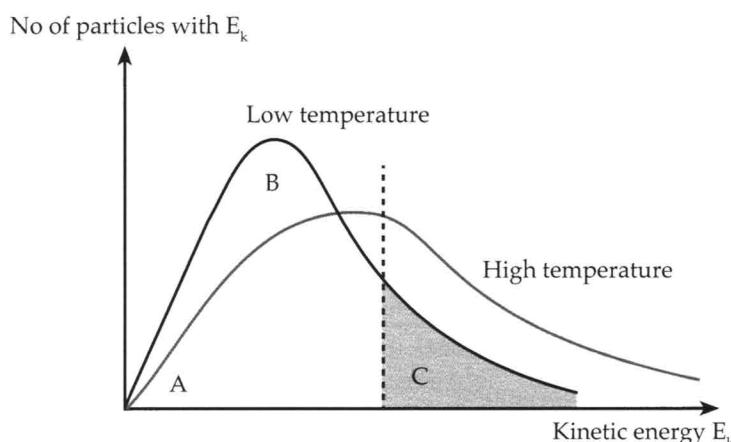
This Dynamic Equilibrium situation is the main focus of this chapter.

1.2 COLLISIONS ARE CRITICAL

Any reaction between two molecules requires the following to occur: a) collisions between molecules, b) breaking of bonds, c) re-joining of new bonds.



Collisions must occur with sufficient energy to cause bonds to break, but only a fraction of the total number of particles will have this critical energy, called Activation Energy (E_a). Sometimes reactions occur spontaneously (e.g. sodium in water) other times kinetic energy has to be added to particles (by heating) to cause critical collisions to occur (e.g. $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$). Therefore reaction rates always rise with temperature because the colliding particles move faster and collide more frequently. The graph below shows the distribution of fast-moving and slow-moving particles in a gas or solution.



1.3 REACTION RATE

In the gaseous or liquid phases, particles are moving in random directions with a random distribution of speeds (kinetic energies).

The graph on page 1 shows the distribution of energy amongst the gas molecules, i.e. the number with a particular kinetic energy. It can be seen in the left-hand part of the graph that at point A where the molecular speed is very low, the number with this E_k is small and at point C, the number with a very high velocity is also very small. The most frequent E_k of the particles is shown at point B.

The Activation Energy (E_a) of a reaction is the amount of kinetic energy with which molecules must collide in order to break bonds and form an **activated complex**. This transferred state then reforms into the final products. There is always a wide range of molecular kinetic energies at any temperature and so only a fraction of molecules collide with the correct orientation (the right way round) and sufficient energy to produce this high energy (activated complex) Transition State. Others simply rebound without reacting. The activated complex then reforms into a more stable product and gives out or takes in a net amount of energy called Heat of Reaction (ΔH).

In order to collide and break bonds the particles must be moving with a velocity corresponding to the Activation Energy (E_a), which only a fraction of the total particles will possess. This fraction is shown as the shaded area in the diagram on page 1. If E_a is higher then the shaded area will be smaller and the rate of the reaction will therefore be low at a particular temperature.

If the temperature is raised then E_a stays the same but the whole graph moves to the right and hence there will always be a larger fraction of the total number that have energies past that point i.e. the rate of any reaction will always increase if the temperature increases.

The diagram on the right illustrates an exothermic reaction where there is a net energy output from the system, i.e. ΔH has a negative value.

In exothermic reactions the surroundings (air, solution, etc.) will become warmer.

The activated complex is a temporary structure which will not be able to exist for any considerable time and breaks up almost immediately.

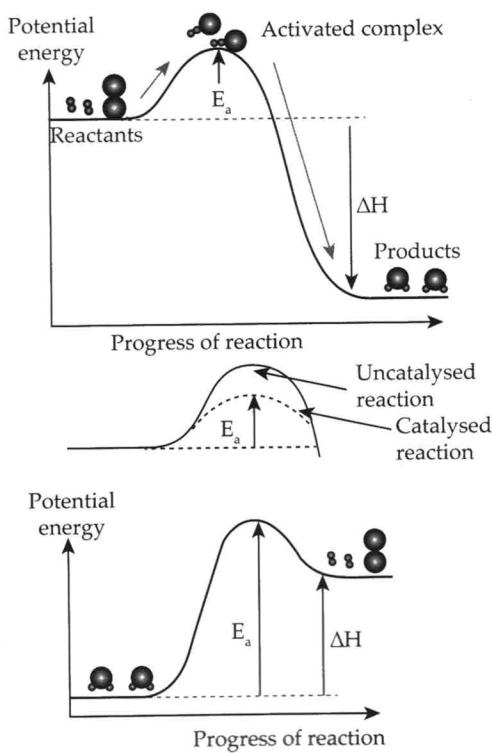
The effect of a catalyst is to provide a new pathway with a lower activation energy by combining with the reactants to form an intermediate product with lower energy content.

With an endothermic reaction, the activation energy is large and the final products have more potential energy than the reactants. There is a net energy gain by the reaction and so heat is taken in and the heat of reaction, ΔH , is positive. In endothermic reactions the surroundings will become cooler.

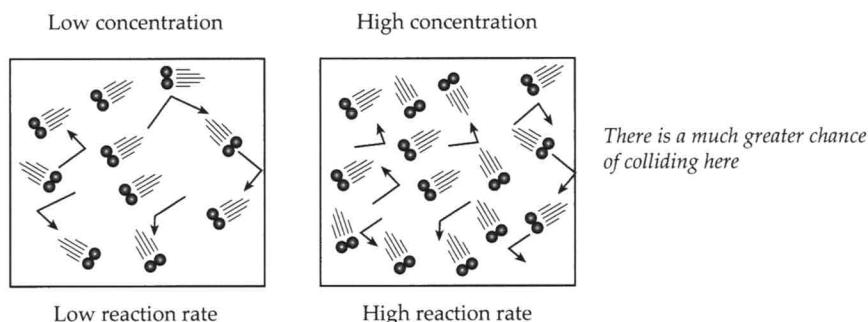
Other factors that affect reaction rate are:

Particle size: The same reactant divided into smaller particles will have a larger overall surface area exposed to the other reactant and there will be more collisions hence a higher reaction rate.

Concentration – the more concentrated an aqueous reactant is the closer the particles are and the shorter the distance to travel between collisions.

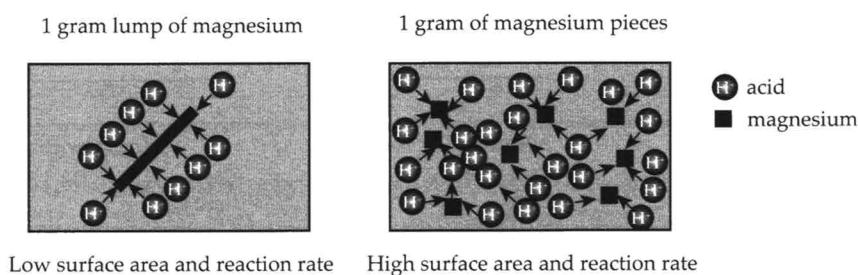


The **concentrations** of the reactants also affect reaction rates – see diagram below.



Molecules or ions in solutions can have a much higher reaction rate than in gases, as the particles are much closer.

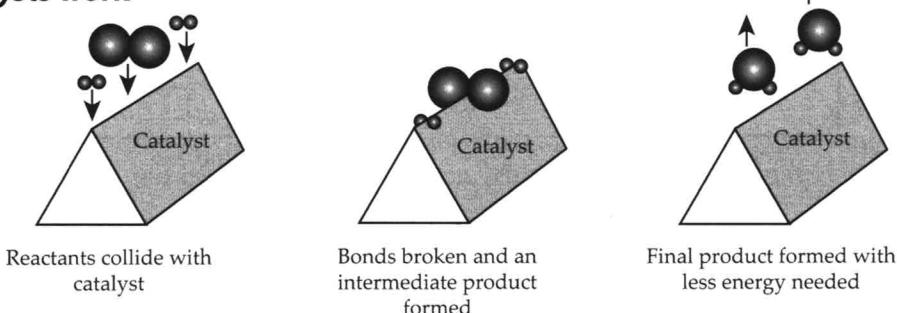
In reactions between solids and liquids (e.g. metal in acid) the reaction rate will also depend on the amount of surface area of the solid exposed.



1.4 CATALYSTS

Catalysts are substances that increase the chance of a reaction occurring without themselves being used up in the reaction. The reactants first collide with the catalyst surface, bonds are broken and an intermediate product is formed with the catalyst. This catalytic process requires less reaction energy to produce the final product than an uncatalysed reaction.

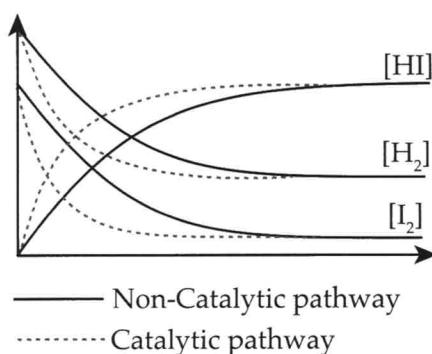
How catalysts work



Catalysts speed up the rate at which equilibrium is attained and are used in industry to make a reaction take place faster. Consider the reaction where HI is produced from reacting hydrogen and iodine: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

From the graph we can see that the catalysed reaction reaches equilibrium (horizontal line) quicker than the uncatalysed reaction.

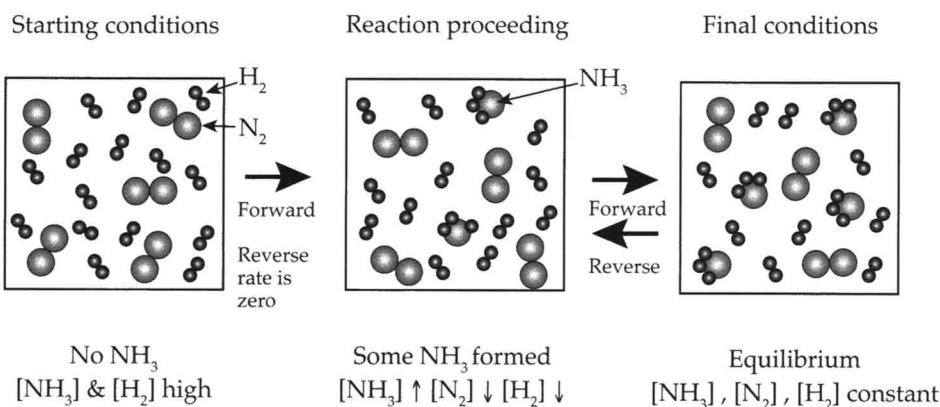
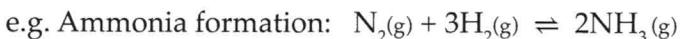
Although the rate of a reaction is increased, it is important to note that catalysts will have no effect on the yield and are not consumed in any reaction. Enzymes are nature's version of catalysts for biological reactions, e.g. the yeast enzyme converts sugar to alcohol. Enzymes are important in biological systems because temperature is often low. The human body at 37°C uses extensive enzyme systems as particles have little kinetic energy and would have a low rate of reaction.



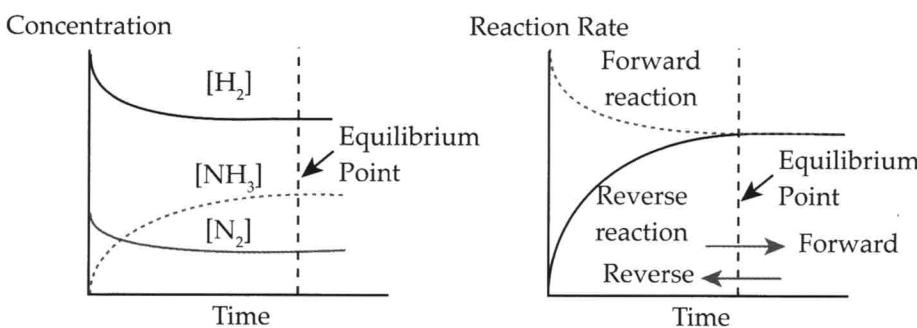
1.5 REVERSIBLE REACTIONS

Most chemical reactions are reversible (symbol \rightleftharpoons). When a reversible reaction is said to be in equilibrium it is in a stable, or balanced, state because the concentrations of the reactants and the products are constant.

Reactions can never be stationary because collisions are occurring all the time; it is just that when enough product molecules have been formed they can then collide to reform the reactants back again and then the forward rate = the reverse rate (a state of dynamic equilibrium).



As the reaction proceeds the concentrations of the reactants drop as they start to be used up and the concentration of the products rises as they become formed. Now that there are products, these can also collide and break up and will re-form the reactants back again.

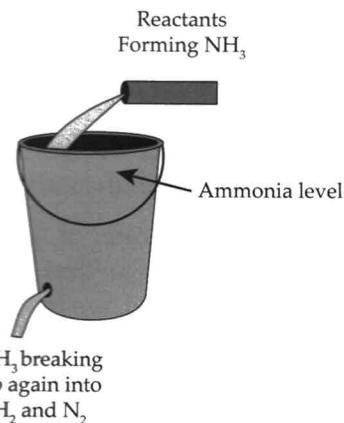


The rate at which the reactants are breaking up equals the rate at which the products are breaking up and returning to become reactants again – this stable situation is called a Dynamic Equilibrium.

Imagine a bucket with a hole in the side that was being filled with a hose. Water is lost through the hole at the bottom at the same time but starts to fill up as the rate the water coming in is greater than the rate it is being lost. However, as the water height gets greater the pressure at the bottom increases, so the rate it flows out increases (deeper water exerts more pressure). At a certain depth of water the bucket will be being filled at the same rate as it is emptying.

Here the water coming in represents the reactants (H_2 and N_2) producing the ammonia and the level of water in the bucket represents the amount of ammonia present.

The water running out through the hole represents the NH_3 breaking up again into H_2 and N_2 again.



1.6 EQUILIBRIUM CONSTANT

The equilibrium constant (K) for a particular reaction indicates the relative proportions of products and reactants, once equilibrium has been reached.

$$K = \frac{[\text{Product 1}] \times [\text{Product 2}]}{[\text{Reactant 1}] \times [\text{Reactant 2}]}$$

For the ammonia reaction above, this gives: $K = \frac{[\text{NH}_3] \times [\text{NH}_3]}{[\text{N}_2] \times [\text{H}_2] \times [\text{H}_2] \times [\text{H}_2]} = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$

Example

At a particular temperature the concentrations of the gases present in a closed vessel are: hydrogen 2.4 mol L⁻¹; nitrogen 0.25 mol L⁻¹; ammonia 0.10 mol L⁻¹. Calculate the value of the equilibrium constant for ammonia.

Solution

$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{[0.1]^2}{[0.25][2.4]^3} = 2.9 \times 10^{-3} \text{ mol}^{-2} \text{ L}^2$$

The K value for this reaction will always be the same, regardless of the starting concentration, which is about 3×10^{-3} at 300°C. This value will, however, change with temperature.

The low K value for ammonia formation shows that there is far less product than reactant once equilibrium has been reached. As a comparison, the K value for the ionisation of a strong acid is very large (about 1000), showing the acid exists almost totally as ionic products. As a rough rule if $K > 10^4$, the forward reaction is fully favoured and if $K < 10^{-4}$ the reverse reaction is fully favoured.

The K value for the reaction $2\text{NO}_{2(g)} \rightleftharpoons \text{N}_{2(g)}\text{O}_{4(g)}$ is 0.48. This means that at equilibrium there will be a roughly equal amount of both gases.

However, in the reaction $\text{SO}_{3(g)} \rightleftharpoons \text{SO}_{2(g)} + \frac{1}{2}\text{O}_{2(g)}$ the K value is 10^{-12} , meaning that the mixture would almost entirely consist of SO_3 molecules at equilibrium.

1.7 LE CHÂTELIER'S PRINCIPLE (LCP)

Le Châtelier's Principle predicts the outcome when conditions (concentration, T, P, V, etc) at equilibrium are changed in a reversible reaction. This principle states that:

If conditions are changed from equilibrium then the system will always readjust to partially compensate for those changes.

The ammonia equation will illustrate this idea: $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)} + 92 \text{ kJ}$

e.g. If we added more nitrogen, for instance, the reaction would move towards the right so that the amount of nitrogen would decrease.

Exam questions can be of 3 types – asking what effect there would be if 1) concentrations were changed, 2) vessel volume were changed and 3) temperature were changed. For each of these changes in conditions the question could ask about the change in reaction Yield (amount of products) or the new Rate of the reaction.

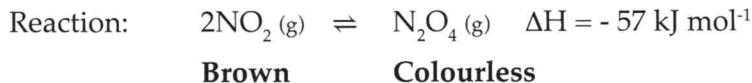
Question types

How Yield is affected	How Rate is affected
Change concentration of a reactant/product	
Change volume of the vessel	
Change temperature of the vessel	

Important note on heterogeneous equilibria: A solid cannot have a concentration as it would need to be a solution – and a solid is not dissolved in anything!

Concentration values are the number of moles of solute divided by number of moles of solvent. Similarly, a pure liquid, such as water cannot have a concentration value either and is discounted in equilibrium equations.

Example: NO_2 in equilibrium with N_2O_4 (NO_2 is brown and N_2O_4 is colourless, so an equilibrium mixture is pale brown).



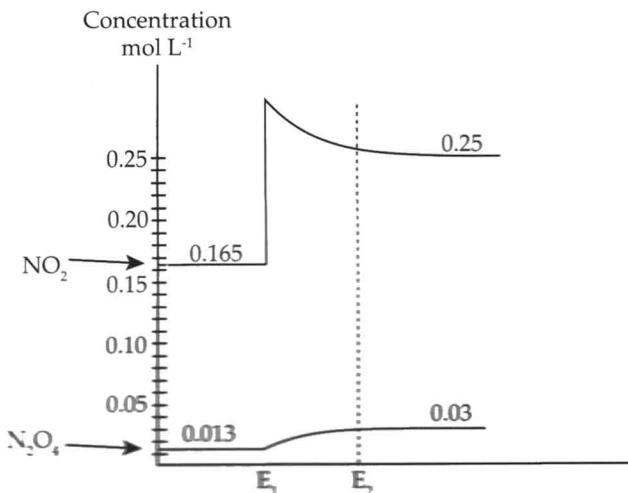
Change in conditions	Immediate effect	Change to equilibrium	Final observation	Prediction
NO_2 added	brown colour deepens	Moves to the right	Becomes paler	More N_2O_4 produced
N_2O_4 added	Becomes lighter	Moves to the left	Becomes darker	More NO_2 produced
Volume decreased	Becomes darker brown	Moves to the right	Slowly returns to paler brown	More N_2O_4 produced
Volume increased	Becomes paler	Moves to the left	Brown colour intensifies	More NO_2 produced
Temperature raised	Becomes darker	Moves to the left	Brown colour intensifies	More NO_2 is produced

1.8 THE EFFECT OF CONCENTRATION

In ammonia synthesis, if some more N_2 is added to an equilibrium mix then by LCP the system will produce more NH_3 (forward reaction) so as to use up the extra N_2 added. Why? Because with more N_2 molecules available more reactant collisions can occur than previously and so more NH_3 can be produced. The concentration values eventually settle back so that K has the same value as before.

This is predicted by Le Châtelier's Principle but it is better explained by talking about the change of Rate: At equilibrium the forward and reverse rates are equal. If we add more nitrogen the forward rate is now greater than the reverse rate and so the reaction must move to the right.

Consider the equilibrium: $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$



Initially there are equilibrium conditions (E_1) but when NO_2 is added the graph rises immediately. The forward rate now exceeds the reverse rate and so the equilibrium shifts to the right gradually, as shown by the upward slope of the graph, producing more N_2O_4 yield.

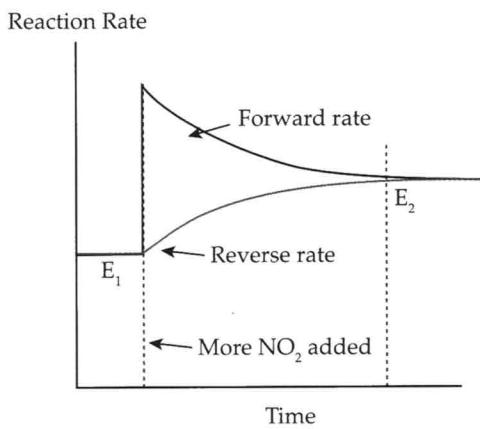
To produce more N_2O_4 the amount of NO_2 has to be gradually used up, and so its graph must gradually reduce but not to the original level as before. It will eventually level out when the new equilibrium (E_2) is reached. At E_1 the K value is given by:

$$K = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{[0.013]}{[0.165]^2} = 0.48$$

After the new equilibrium is established (E_2) the value of K is given by:

$$K = \frac{[0.03]}{[0.25]^2} = 0.48$$

Note that K attains the same value again and is unaffected by the addition of extra NO_2 . The Rates graph looks like this:



We can see here that after the extra NO_2 has been added the forward rate increases instantly which gradually increases the amount of product, but uses up the reactant. Hence the probability of successful forward collisions will gradually reduce. As more product is produced the reverse rate will gradually increase until forward and reverse rates now become equal but at a higher value because there are now more particles present overall.

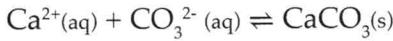
1.9 ENVIRONMENTAL ASPECTS

Due to Greenhouse Gas emission, the levels of CO_2 in our oceans is steadily rising but the carbonate ion content of the sea is important for the growth of coral reefs in Australian waters.

The formation of carbonate ions from carbon dioxide is shown by:



Coral body is built from calcium carbonate when the carbonate ions combine with calcium ions in the water:



Living coral polyps have a calcium carbonate skeleton and when they die these skeletons form part of the growing reef. Normally, sea water is slightly alkaline, with a pH of about 8.2 but as more CO_2 is absorbed its acidity rises, which affects the carbonate/hydrogen carbonate equilibrium:



Hence the effect of acidification is predicted to be to remove the carbonate ion from the water by favouring the reverse reaction in this equilibrium equation. This would cause a reduction in the ability of the coral polyp skeleton to form and thus stunt the growth of coral crops.

However, there is also a conflicting process attributable to rising sea temperatures. Higher temperatures cause the metabolism of these polyps to increase, thus increasing the growth of the coral reefs. It remains to be seen which of these two processes will become dominant.

1.10 THE EFFECT OF VOLUME CHANGE

If the size of the vessel containing a gas is decreased then the pressure of the gases is increased by decreasing the space between particles. Le Châtelier's Principle predicts that the equilibrium will move in the direction which reduces the pressure. Pressure is produced by the bombardment of particles – the larger the number of particles colliding per second, the larger the partial pressure it exerts.

Consider this gaseous production reaction: $X_2(g) + 3Y_2(g) \rightleftharpoons 2XY_3$

There are 4 particles on the left and only 2 on the right, so Le Châtelier predicts that, with a decreased vessel volume, the equilibrium will shift to the right in order to reduce the number of particles bombarding per second.

Looking at this reaction mathematically: $K = \frac{[XY_3]^2}{[X_2][Y_2]^3}$

Suppose, at equilibrium, all the reactants are contained in a 1 litre vessel and have a concentration of 1 mol L⁻¹, then. For K:

$$K = \frac{[1]^2}{[1][1]^3} = 1. \text{ The equilibrium constant for this reaction equals 1.}$$

K must remain constant after any change (except for temperature) so suppose we reduce the volume of the vessel to 0.5 litre. All the concentrations are now doubled to 2 mol L⁻¹ so, before equilibrium is reached, the equation fraction will have changed to a temporary value called Q:

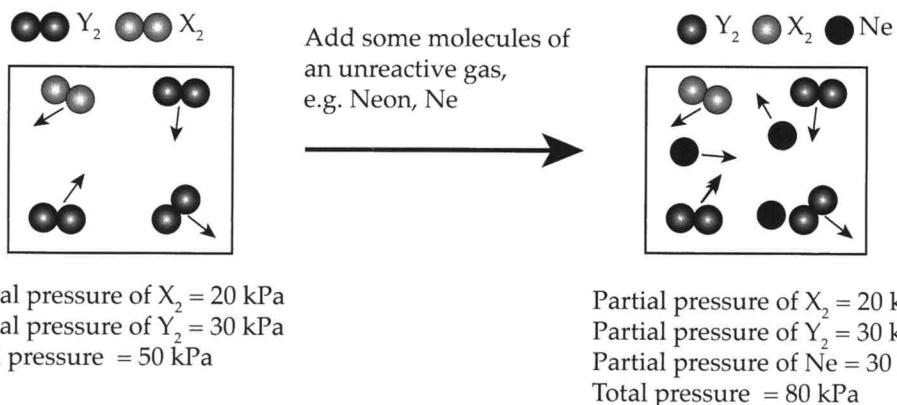
Q is now $\frac{[2]^2}{[2][2]^3} = 0.25$ which is smaller than the constant value that K must attain.

The equilibrium concentrations must now change in a direction which will increase K back up to 1 again, i.e. more products.

We can see here why Le Châtelier's Principle works - if the pressure is increased, to preserve K, the equilibrium must move to the side with least particles.

This logic only works if the pressure change is brought about by a change in volume. The total pressure could also be increased by adding another gas which does not take part in the reaction, e.g. a noble gas. Here, the pressure would increase because there are now more collisions, but the particles would actually stay at the same spacing, so this would have no effect at all!

Although the pressure is higher in the right-hand vessel, the yield and rate are unaffected.



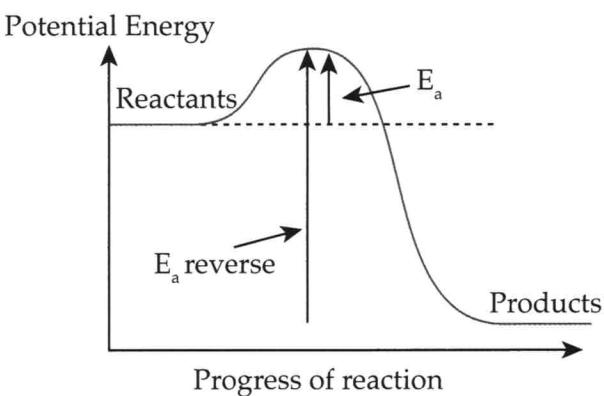
1.11 THE EFFECT OF TEMPERATURE CHANGE

According to Le Châtelier's Principle, an increase in temperature will favour the direction that removes heat from the system. In the example of ammonia synthesis, heat is given out when the stronger bonds in the hydrogen and nitrogen molecules form into weaker bonds holding the ammonia molecule together. So, when the reactants transform into products, this difference in bond energies emerges as heat energy given out to the surroundings i.e. an exothermic reaction.



This reaction is exothermic and the forward reaction will produce more heat so if the temperature is raised, the reverse reaction will be favoured (more reactants) by the LCP.

To understand this fully we must look at the energy profile for this reaction.



Interpreting this graph, we can see that, in an exothermic reaction, the activation energy forwards is much smaller than the activation energy for the reverse reaction i.e. it takes less energy for the H_2 and N_2 to jump the forward barrier than for NH_3 to jump the reverse barrier.

If more energy is supplied to the reaction the forward and the reverse rates of reaction will both increase but it will affect the reverse rate more. Imagine that it is like high jump, where the forward height to jump is 1.0 m but the reverse height is 2.5 m. Consequently 92% of people might be able to jump over the forward barrier but only 2% can jump from right to left. If we give everyone extra energy (e.g. by putting strong springs in their shoes) both the forward and reverse jumpers would be more successful, so the figures might now become 98% successful forward and 35% successful in reverse jumping.

We can see that it would benefit the reverse reaction rate proportionately more than the forward rate. Hence if heat is supplied to an exothermic reaction the equilibrium would favour the endothermic (reverse) direction. Likewise, heating will favour the forward direction in the case of an endothermic reaction.

Changes in K

Consider the ammonia production equation again: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) + 92 \text{ kJ mol}^{-1}$

We can see that if we were to cool the reaction vessel down the forward reaction would be favoured to produce more ammonia and heat. However, if more ammonia is to be produced this will affect the value of K, as the reactants must go down and products increased.

Example

Originally hydrogen = 2.4 mol, nitrogen = 0.25 mol, ammonia = 0.10 mol so $K = 2.98 \times 10^{-3}$.

Now at a lower temperature: $\text{H}_2 = 2.0$, $\text{N}_2 = 0.06$, $\text{NH}_3 = 0.15$ so $K = 0.094$.

This is larger than before – so, for a rise in temperature, K reduces for an exothermic reaction and increases for an endothermic reaction.

1.12 COMPROMISE CONDITIONS

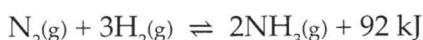
Le Châtelier's Principle suggests several ways of achieving more yield. These are:

- Add more of the reactants
- Remove the products as they form
- Set and maintain pressure as necessary to produce a greater yield
- Set and maintain temperature as necessary to produce the optimum yield
- Use a suitable catalyst.

Industrial processes need to produce the highest yield for the lowest cost in the shortest time.

The Haber process

In this process ammonia is made industrially according to the equation:



In the Haber Process N_2 and H_2 react at high pressure as this favours the forward reaction (producing more NH_3) – about 200 atmospheres is used. Being exothermic, the forward reaction would be favoured by lowering the temperature, but this would in turn reduce the reaction rate and would take too long to obtain product because ammonia decomposes more at higher temperatures.

Hence a compromise temperature of about $400\text{-}450^\circ\text{C}$ is used (less yield but produced at a higher rate), using a catalyst of iron/iron oxide to further increase reaction rate.

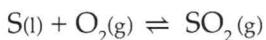
Getting less product, but in a shorter time will give more product overall in a day!

Ammonia is extracted from the mix by liquefying – thus removing the product. If NH_3 is removed in the equation above then the equilibrium must continually move to the right and produce more yield.

The Contact Process

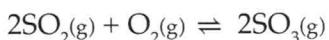
In the Contact Process sulfuric acid is produced according to these steps:

Sulfur is burnt in air:



Molten sulphur is sprayed into the gaseous O_2 increasing surface area and collisions.

SO_2 is then oxidised to SO_3 at high temperatures:

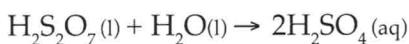
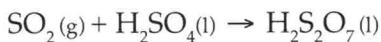


The forward reaction is favoured by high pressure and low temperature but again, compromise conditions are used in practise.

As the rate of the reaction is important economically, high temperatures (600°C) and pressures are used, with a catalyst (V_2O_5).

198 kJ of heat is released per mole.

If SO_3 is added directly to water it produces lots of heat and so these reactions are used to control the rate.



Finally, $\text{SO}_3(\text{g})$ is absorbed in concentrated $\text{H}_2\text{SO}_4(\text{l})$ to produce oleum, $\text{H}_2\text{S}_2\text{O}_7(\text{l})$ and the oleum is added to water to produce H_2SO_4 .

Acids and Bases

2.1 INTRODUCTION

Today acids and bases are part of our everyday life. Our food could not be digested without the aid of the hydrochloric acid in our stomachs and window-cleaner would not work without having a base (ammonia) as its main component. We can also find acids in lemons and oranges and use acids to dissolve metals in mining or to clean paving stones.

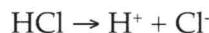
Toothpaste is slightly basic to counteract the acid formed by bacteria in our mouth. Acids have a sharp taste and bases have a soapy feel to them, but there have been different methods of defining what acids and bases are.

2.2 DIFFERENT DEFINITIONS

In 1815 Davy identified acids as substances that contained replaceable hydrogen - hydrogen that could be partly or totally replaced by metals. He saw that when acids reacted with metals they formed salts and he also defined bases as substances that reacted with acids to form salts and water. His definitions were accepted as standard during most of the 1800s.

Arrhenius

Svante Arrhenius was a Swedish Chemist who, besides developing the theory of dissociation of ions, the Greenhouse Effect and winning a Nobel Prize, also developed a theory of acids and bases in 1884. With the Arrhenius model of what an acid is, an acid was viewed as a substance which simply provided H^+ ions in solution, e.g. hydrochloric acid is an acid:



A base is a substance, which provides OH^- ions in solution, e.g potassium hydroxide is a base:



The Arrhenius model helps us to classify many of the common chemicals as acids or bases:

Some common acids are: HCl , H_2CO_3 , HNO_3 , H_2SO_4 , CH_3COOH , H_3PO_4 - all of which produce hydrogen ions in solution.

Common bases are: KOH , NaOH , $\text{Ca}(\text{OH})_2$, NH_3 , $\text{Mg}(\text{OH})_2$ - all of which produce hydroxide ions in solution.

However, the Arrhenius theory does not help to explain how some salts which do not contain H^+ ions can show acidic properties and have a low pH. These reactions are classified as hydrolysis reactions and are dealt with by a different notion of an acid, called the Brønsted-Lowry model.

Brønsted-Lowry

In 1923 the Brønsted-Lowry definition was proposed quite independently by Brønsted in Denmark and Lowry in England.

The Brønsted-Lowry (Brønsted-Lowry) model views acids as H^+ or proton donors and bases as proton acceptors. With this model, we say that a species is acting as an acid or base, rather than the species is an acid or base. Using that Brønsted-Lowry approach all the Arrhenius and Lewis acids would still be classified as acids but it now allows for the species that can act as an acid or a base.

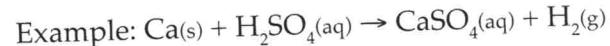
The Brønsted-Lowry model will be the main approach used in this book, as it provides the most flexible system.

2.3 ACID/ BASE REACTIONS

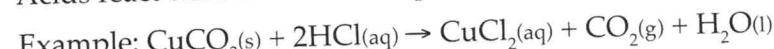
Acids and bases react with each other to produce a salt and water.



Acids react with reactive metals (Ca, Mg, Zn, Al etc.) to produce hydrogen gas.



Acids react with carbonates to produce $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O(l)}$.



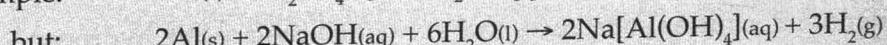
Acids react with hydrogen carbonates to produce $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O(l)}$.



Acids react with metal oxides to produce salt and water.

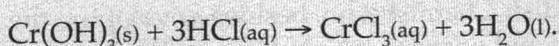


Al, Cr, Pb and Zn are called amphoteric metals as they can react with both acids and bases to produce hydrogen gas. The metals also produce complex compounds with bases.

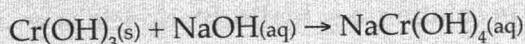


Certain metal hydroxides are also known as amphoteric because they can react with both acids and bases to produce a complex ion, e.g. aluminium, zinc and chromium hydroxides.

Chromium hydroxide, for example, reacts with acid:

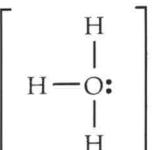
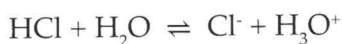


It can also react with a base:



2.4 THE BRØNSTED-LOWRY APPROACH

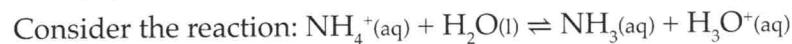
One main discovery that this model incorporates is that a single proton cannot exist on its own, but it will combine with a water molecule to form H_3O^+ (the electron-dot diagram of the hydronium ion is shown on the right). So all Brønsted-Lowry equations involve a reaction with water, e.g. the ionisation of hydrochloric acid now becomes:



According to the Brønsted-Lowry model, an acid is defined as a proton donor and a base as a proton acceptor. In an acid-base reaction, a proton (H^+) is transferred from the acid to the base. As a result, what the acid changed into can now act as base, called conjugate base, and the base has changed into a new acid called conjugate acid.

In the reaction $\text{HCl} + \text{H}_2\text{O} \rightleftharpoons \text{Cl}^- + \text{H}_3\text{O}^+$ the HCl molecule donates a proton to the water molecule and H_2O accepts this proton. Hence HCl is acting as an acid and H_2O is acting as a base. After giving up a proton, the HCl has now changed into the Cl^- ion and becomes the conjugate base of HCl. The water molecule, which acted as the original base, now becomes its conjugate acid, H_3O^+ .

HCl and Cl^- are termed "Conjugate acid/base pairs" and H_2O and H_3O^+ are also termed "Conjugate acid/base pairs"



NH_4^+ is acting as an acid, and NH_3 would be its conjugate base. H_2O is now acting as a base and H_3O^+ would be its conjugate acid.

Example

In the reaction $\text{HSO}_4^- + \text{CH}_3\text{COO}^- \rightleftharpoons \text{SO}_4^{2-} + \text{CH}_3\text{COOH}$, experimental evidence indicates that the forward reaction is dominant which makes HSO_4^- the Brønsted-Lowry acid and CH_3COO^- a Brønsted-Lowry base. SO_4^{2-} is the conjugate base of HSO_4^- and CH_3COOH the conjugate acid of CH_3COO^- .

Conjugate acid-base pairs

Following the Brønsted-Lowry concept, that an “acid minus a proton is a conjugate base”, and “base plus a proton is a conjugate acid”, we can identify the conjugate acid-base pairs for many species.

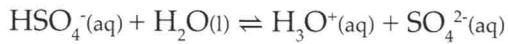
Species	Conjugate base	Conjugate acid
H_2O	OH^-	H_3O^+
HCO_3^-	CO_3^{2-}	H_2CO_3
NH_3	NH_2^-	NH_4^+
HSO_4^-	SO_4^{2-}	H_2SO_4
H_2PO_4^-	HPO_4^{2-}	H_3PO_4
HSO_3^-	SO_3^{2-}	H_2SO_3

2.5 POLYPROTIC ACIDS

Acids that donate only one proton in aqueous solutions are called **Monoprotic** acids. For example, HCl and HNO_3 are examples of monoprotic acids. Acids such as H_2SO_4 and H_3PO_4 can donate more than one proton in aqueous solutions – these two acids are termed **Diprotic** and **Triprotic** acids respectively. Polyprotic acids such as these donate their protons in stages.

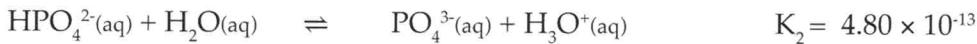
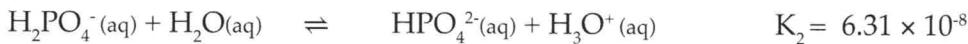
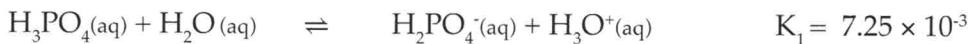
The first stage donation always has a higher ionisation constant than the following stages.

With sulfuric acid:



With the 1st, strong, ionisation this goes to completion, i.e. 100% ionisation but the 2nd stage ionisation is fairly weak as 1 mole of HSO_4^- only gives about 0.3 moles of H_3O^+ ions. Overall then, 1 mole of H_2SO_4 would give about 1.3 moles of hydrogen ions.

Phosphoric acid has 3 stages of ionisation, each with different K values:

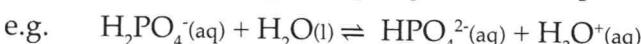


Phosphoric acid is triprotic and all the ionisations are weak, as shown by the low K values.

2.6 ACIDIC AND BASIC SALTS

Ions that react with water to form acidic solutions are called acidic ions. Ions such as:

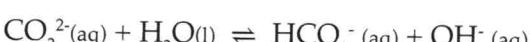
HSO_4^- , H_2PO_4^- , HCO_3^- , NH_4^+ , H_3O^+ , Al^{3+} complexes, Fe^{3+} complexes can all donate protons.



Ions which react with water to form basic solutions are called Basic Ions. For example:

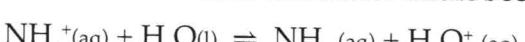
O^{2-} , OH^- , F^- , PO_4^{3-} , CO_3^{2-} , S^{2-} can gain protons.

e.g. 1. Sodium carbonate solution is basic because the carbonate ion can accept a proton:



Sodium carbonate is the salt made from a strong base (NaOH) and a weak acid (H_2CO_3)

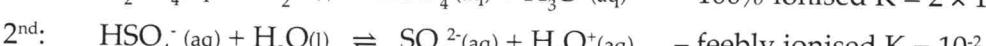
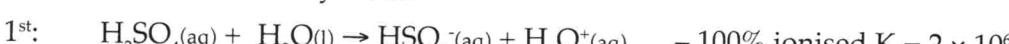
e.g. 2. Ammonium nitrate solution is acidic because the ammonium ion can donate a proton:



Ammonium nitrate is a salt made from a strong acid and a weak base.

From the examples above we could derive a principle that if the acid the salt is prepared from is strong, then the solution of the salt will be acidic, or if that acid is weak, then the salt solution will be basic.

The exception to this would be the salts made from sulfuric acid, which most people would classify as strong. Actually, only the first ionisation of H_2SO_4 is strong (100% ionised) – but the second ionisation is fairly weak:



This means that the HSO_4^- ion can only act as an acid to produce SO_4^{2-} but some of the SO_4^{2-} ions will move to the left of the equilibrium mixture, accepting a proton to produce a basic solution.

e.g. Na_2SO_4 will be basic in solution and NaHSO_4 will be acidic.

A salt made from a strong acid and a strong base (e.g. NaCl) will be neutral because neither the Na^+ nor the Cl^- ion will react with water in a Brønsted-Lowry reaction.

Nitrates, chlorides, bromides and iodides all produce neutral salt solutions.

Carbonates, sulfides and cyanides all give basic solutions.

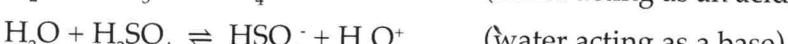
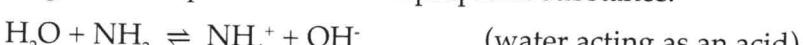
Nitrates, chlorides, bromides and iodides of the ammonium ion and some metals produce acidic solutions.

NB: weak acid / weak base salts are neutral (e.g. $\text{CH}_3\text{COONH}_4$).

Amphiprotic Species

Some species can donate or accept protons – these are called amphoteric or amphiprotic. Hence these substances can act both as acids or bases.

Water is a good example of such an amphiprotic substance:



HSO_4^- , H_2PO_4^- , HCO_3^- are other examples of amphoteric or amphiprotic substances which can both accept or donate protons.

2.7 STRENGTHS OF ACIDS AND BASES

Acids and bases are classified as either strong or weak, depending on the extent to which they become ionised.

Examples of strong acids are: HCl , HBr , HI , HNO_3 , HClO_4 , H_2SO_4 (1st ionisation) which all

have a very high equilibrium constant.

Examples of strong bases are: hydroxides and oxides of Groups 1 metals and hydroxides and oxides of Group 2 metals, except beryllium.

Examples of common weak acids are: HF, HCN, CH₃COOH, HNO₂, H₃PO₄, H₂CO₃.

Examples of common weak bases are solutions of: NH₃, Na₂CO₃, CH₃NH₂.

Concentrated acids and bases are not the same as strong acids and bases.

A concentrated solution is one which has a large number of particles per litre.

For example, 10 mol L⁻¹ solution of an acid or base is a concentrated solution. However, this may be a solution of a strong acid such as HCl or a weak acid such as CH₃COOH, or a strong base such as NaOH, or a weak base such as Na₂CO₃.

A dilute solution is one which has a low concentration of particles in it.

For example, it can be a 10⁻⁴ mol L⁻¹ solution of HCl, or CH₃COOH, or NaOH or Na₂CO₃.

Thus you can have a dilute solution of a strong acid or base in which all particles are ions, or a concentrated solution of a weak acid or base in which most of the particles are molecules and very few ions.

You can also have a concentrated solution of a weak acid in which most of the particles are molecules with very few ions, or a strong acid or base in which most of the particles are ions.

2.8 ACID DISSOCIATION CONSTANTS

Water contains a very small proportion of H⁺ and OH⁻ ions.

The equilibrium expression for the water dissociation reaction is: 2H₂O(l) ⇌ H₃O⁺(aq) + OH⁻(aq).

The product [H₃O⁺] × [OH⁻] is called the ionic product constant K_w.

For water, K_w is 1 × 10⁻¹⁴ mol² L⁻² at 25°C as one molecule of water produces one H₃O⁺ and one OH⁻ ion in solution, pure water is said to be neutral.

A solution which has a greater H⁺ ion concentration than its OH⁻ ion concentration is said to be acidic, whereas a solution which has a greater OH⁻ ion concentration than H⁺ ion concentration is said to be basic.

As there is a fixed relationship between the hydrogen and hydroxide ion concentrations, a basic solution is one in which hydroxide ion concentration varies from 10⁻⁷ to 10 mol L⁻¹, and an acid solution is one in which the hydrogen ion concentration varies from 10⁻⁷ to 10 mol L⁻¹.

2.9 THE pH SCALE

Because the concentration of ions in solution varies so greatly (from about 10 to 10⁻⁷ mol L⁻¹), it would be very difficult to display the change in concentration graphically. Hence a logarithmic variation is used which displays all concentrations as powers of 10. A logarithm of a number is the power to which 10 must be raised to produce that number.

e.g. 1000 is 10³, hence log (1000) = 3. Log (0.01) = -2 because 0.01 = 10⁻².

To find the log of number which is not a simple power of 10 we must use a calculator:

e.g log (3000) = 3.48

A conventional way to indicate the extent of acidity is to take the power to which 10 is raised to give the H⁺ ion concentration and discard the negative sign.

pH is therefore defined as the negative log of the hydrogen ion concentration.

For example, if the H⁺ ion concentration is 10⁻⁵ mol L⁻¹, then the pH is 5.

$$\text{pH} = -\log [\text{H}^+]$$

As the [H⁺] increases, the pH will decrease.

A change in pH of 1 corresponds to a 10-fold change in the concentration of the H⁺ ions e.g. If pH changes from 2 to 3 the [H⁺] changes from 10⁻² to 10⁻³.

Acid solutions can have pH values from below 0 up to 7, and basic solutions can have a pH from 7 to 14+.

Distilled water has a pH of 7 at 25°C and is neutral. The pH of human blood is normally between 7.3 and 7.5.

Hydroxide ions

K_w for water is given by [H⁺] × [OH⁻] and stays constant if temperature remains constant. From the previous chapter on equilibrium, we learnt that if [H⁺] increases then the [OH⁻] must decrease so the product always remains at a value of 10⁻¹⁴.

If a base is added to pure neutral water with a hydrogen ion concentration of 10⁻⁷ mol L⁻¹, the concentration of H⁺ ions decreases because the OH⁻ ions from the base react with the H⁺ ions in the water hence the pH value increases.

For example, a 0.1 M NaOH solution has [OH⁻] = 0.1 mol L⁻¹, the corresponding hydrogen ion concentration becomes 10⁻¹³ mol L⁻¹ and hence the pH becomes 13. The calculation is based on the fact that H⁺ ion concentration and OH⁻ ion concentration bear a constant relationship:

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

This calculation could also be done using the concept of pOH which is the negative log of the hydroxide ion concentration and the equation: pH + pOH = 14.

For the 0.1 molar NaOH, the pOH = -log (10⁻¹) → pOH = 1

Hence pH = 14 – 1 = 13.

This method is often quicker than using the equation $[\text{H}^+] \times [\text{OH}^-] = 1 \times 10^{-14}$

pH Calculation Examples

- a) If the [H]⁺ = 1 × 10⁻³ mol L⁻¹, the pH is 3.
- b) If the [OH]⁻ concentration is 1 × 10⁻⁴ mol L⁻¹, then the pOH = 4.

This gives a value for pH of 14 – 4 = 10. So the concentration of H⁺ = 1.0 × 10⁻¹⁰ mol L⁻¹

- c) To find the pH of NaOH solution with concentration 0.05 mol L⁻¹, first we find the pOH
 $\text{pOH} = -\log (0.05) = 1.30$
 $\therefore \text{pH} = 14 - 1.3 = 12.7$

When equal volumes of a strong acid and a strong base of equal concentrations are added, the pH of the resulting solution will be 7.

Mixing acid and base

If we mix an acid and a base, the resulting solution can be acidic or basic, depending on the final concentration of hydrogen ions. If the number of hydrogen ions is in excess, then the final solution will be acidic. Acid/base mixing calculations will always require you to find the limiting reagent from the number of moles of each.

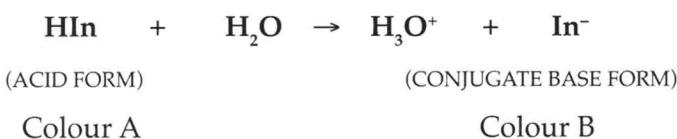
2.10 ACID/BASE INDICATORS

Commercial pH papers are able to give colours for every main pH unit. Universal Indicator, which is a solution of a mixture of indicators is able to also provide a full range of colours for the pH scale.

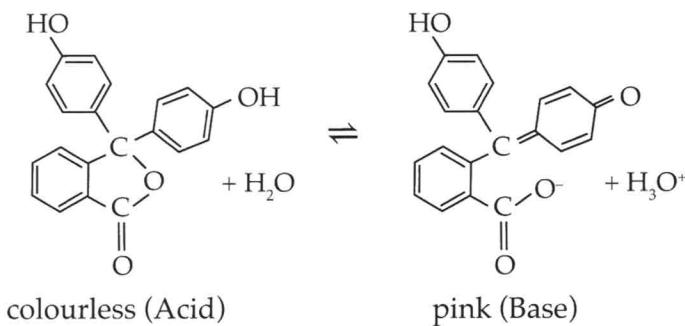
There is a variety of indicators that change colour at various pH levels. A properly selected acid-base indicator can be used to visually "indicate" the approximate pH of a solution sample by changing its colour. Indicators are usually weak organic acids or base dye obtained from plants that change colours at particular pH values.

The weak acid form of the indicator (HIn) will have one colour and its conjugate base (In^-) will have a different colour.

The weak acid equilibrium in water is:



Phenolphthalein is an example of a colourless, weak acid which dissociates in water forming pink anions. Under acidic conditions, the equilibrium is forced to the left (colourless) and in basic conditions the H_3O^+ are removed which causes the equilibrium to move to the right to produce more of the pink conjugate base species.



Some common indicators used in acid/base titrations are: Litmus, Phenolphthalein, Methyl Orange, Bromothymol Blue, etc. Each of these would be appropriate for different titration endpoints

Litmus colour changes are: pH 4.5 = red; pH 8.2 = blue

Phenolphthalein: pH 8.2 = colourless; pH 10 = pink.

Bromophenol blue: pH 6.5 = yellow; pH 7.2 = blue.

Methyl orange: pH 3.5 = red; pH 4.5 = yellow.

2.11 THE ACIDITY OF NATURAL SYSTEMS

Example

50 mL of 0.015 mol L⁻¹ solution of KOH is mixed with 30 mL of 0.021 mol L⁻¹ HNO₃.

Calculate the final pH of the mixture.

Answer

$$n(\text{OH}^-) = 0.015 \times 0.05 = 7.5 \times 10^{-4} \text{ mol}$$

$$n(\text{H}^+) = 0.021 \times 0.03 = 6.3 \times 10^{-4} \text{ mol}$$

H⁺ is the limiting reagent and the excess n(OH⁻) = 7.5 × 10⁻⁴ - 6.3 × 10⁻⁴ = 1.2 × 10⁻⁴ mol.

Total volume of solution is now 50 + 30 = 80 mL = 0.08 L

$$\text{Concentration of OH}^- = \frac{1.2 \times 10^{-4}}{0.08} = 1.5 \times 10^{-3} \text{ mol L}^{-1}$$

$$\text{pOH} = -\log(1.5 \times 10^{-3}) = 2.82$$

$$\text{So pH} = 14 - 2.82 = 11.2.$$

The internal, physiological functions of many organisms are pH-dependent. Body enzymes, protein digestion, blood and body cells all require different pH environments to function. If these are not controlled then enzymes can often cease to work and the organic system might fail.

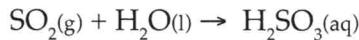
The gastric juice in the stomach has a pH of 1.0 to 2.0. Blood has a pH of 7.3 to 7.5 and the pancreas can only function in a slightly alkaline environment.

Soil pH determines the kind of plants that will grow in that environment. For example, strawberries need a soil pH of about 7.5, and ferns need to grow in a soil pH of around 5.

Normal rain has a pH of about 6 because it dissolves atmospheric carbon dioxide and nitrogen oxides produced during lightning strikes.

However, acid rain has a pH of about 3 which is often produced in heavy industrial areas where SO₂ and NO₂ dissolve in rain water.

The reactions are as follows:



Acids like citric acid and ethanoic acid are used in food preservation. Food is pickled in vinegar (5% ethanoic acid) to prevent bacterial and fungal growth and has been used like this for thousands of years.

Many cleaning agents are slightly basic, so household ammonia can easily remove oil stains from clothes and skin as most oils tend to be acidic. Most soaps and detergents are slightly basic as they are actually salts of long-chain weak organic acids.

The approximate pH values of some well-known substances are shown below:

0.1 M HCl (1); gastric juice (1.4); lemon juice (2.3); vinegar (2.9); orange juice (3.5); tomatoes (4.2); coffee (5.0); rain water (6.2); pure water (7); blood (7.4); seawater (8.2); soap (11.0); household ammonia (11.5); 0.1 M NaOH oven-cleaner (13.0).

2.12 VOLUMETRIC ANALYSIS

Volumetric analysis is the process of calculating the concentration of an unknown solution using another solution whose exact concentration is known. This latter solution is known as a Primary Standard and must be prepared carefully.

With liquid acids, the concentrations, when purchased, are not accurately known and cannot be used as primary standards. Their concentration must be standardised against a standard solution with a known concentration as a reference.

The criteria for selecting a primary standard substance for use are that

It must:

- be a very pure soluble solid,
- be stable in air,
- have a fairly high relative formula mass.

Two compounds commonly used are sodium carbonate (Na_2CO_3) for acid/base titrations and oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) for redox titrations.

To produce a primary standard solution, an accurately weighed mass of the compound is made up to an accurately known volume in a volumetric flask. The concentration of the solution to be standardised can then be found by titration against this standard.

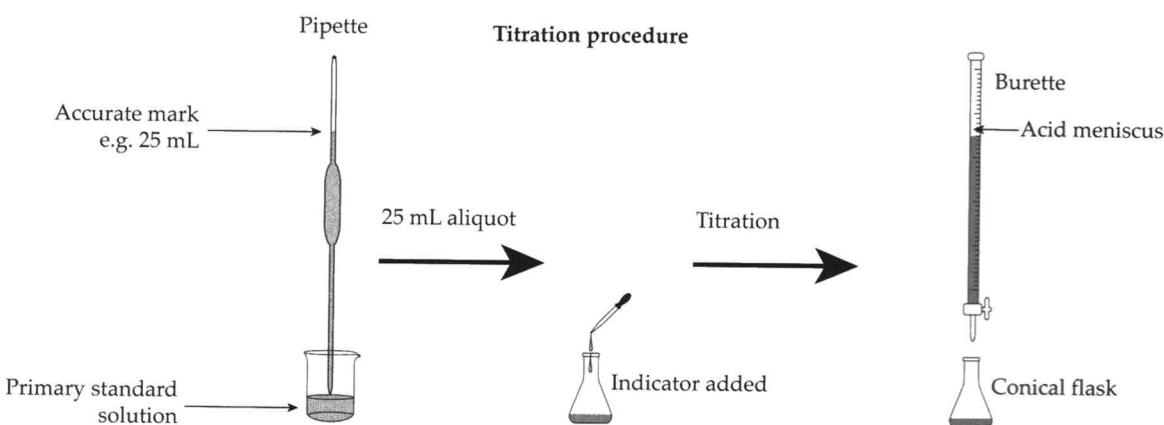
Example: To make up a standard solution of sodium carbonate solution

1.254 g of Na_2CO_3 powder was dissolved in water and then made up to exactly 250 mL of primary standard in a volumetric flask. To find the exact concentration of the solution, the following calculation is made:

Relative formula mass of $\text{Na}_2\text{CO}_3 = 105.99$

so $n(\text{Na}_2\text{CO}_3) = 1.254 / 105.99 = 0.01183$ moles.

$[\text{Na}_2\text{CO}_3] = 0.01183 / 0.25 = 0.0473 \text{ mol L}^{-1}$.



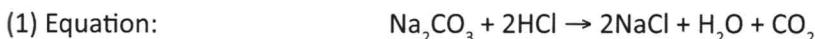
Procedure: An **Aliquot** (accurate volume – typically 25 mL) of primary standard solution is drawn up into the pipette using a pipette filler bulb and is then transferred to a clean, conical flask. A few drops of a suitable indicator are added. The burette is initially rinsed with the acid of unknown concentration before finally filling. It is then zeroed by running some into a beaker until the meniscus reaches the zero mark. Acid is then run carefully into the conical flask containing the standard aliquot until the endpoint is reached (indicator colour change) and the volume of acid used is noted. This volume is called the **Titre**.

This procedure should be repeated three times for precision, with the first (rough) reading discarded and all other readings averaged. The three titre values should be concordant, which means they are within 0.1 mL of each other.

Example

A hydrochloric acid solution is required to be standardised. 25.00 mL of standard sodium carbonate solution was pipetted into a conical flask and the hydrochloric acid run into it from a burette until an endpoint was reached for three concordant readings, shown by an indicator.

The burette readings were: 17.0 mL, 16.75 mL, 16.77 mL and 16.73 mL.

Answer

(2) Mole ratio: 2HCl: 1 Na₂CO₃

Average titre = 16.75 mL (excluding the 1st rough reading)

(3) Moles taken: $n(\text{Na}_2\text{CO}_3) = cV = 0.0473 \times 0.025 = 1.183 \times 10^{-3} \text{ mol}$.

(4) Moles used: $n(\text{HCl}) = 2 \times n(\text{Na}_2\text{CO}_3) = 2.366 \times 10^{-3} \text{ mol}$.

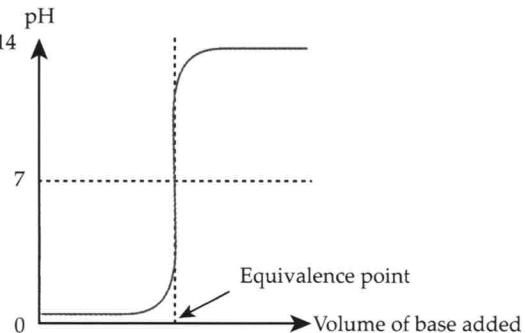
(5) Concentration of HCl: $c = n/V = 2.366 \times 10^{-3} / 0.01675 = 0.141 \text{ mol L}^{-1}$.

2.13 TITRATIONS

Strong acid versus strong base

With a strong acid/strong base titration the equivalence point occurs at a pH of 7. The equivalence point is when the stoichiometrically equivalent number of moles of acid and base have been added. 1 mole of strong acid will exactly neutralise 1 mole of strong base.

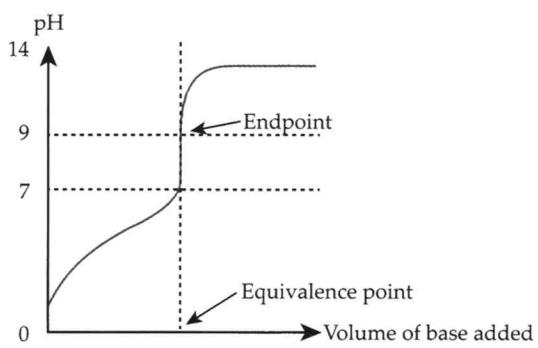
The titration curve is shown here which will be vertical at the equivalence point (25 mL of base). Because of this almost any indicator can be used that changes colour between pH 5 and pH 9. The titre value at which the colour changes is called the Endpoint.



Weak acid versus strong base

When a strong base is titrated against a weak acid at the equivalence point, the pH will be above 7 as the acid is providing less than one mole of H⁺ ions per mole of base.

It is the equivalence point, determined by stoichiometry, which is important in calculating the concentration and so the Endpoint colour change must occur at the Equivalence Point. This can be arranged by a suitable choice of indicator.



For example, suppose we titrated 0.10 mole L⁻¹ NaOH solution in the burette against a 25.00 mL aliquot of 0.1 mol L⁻¹ acetic acid solution in the conical flask. Because the stoichiometric ratio for acid to base is 1:1, the correct reading on the burette at equivalence point should be 25.00 mL (number of moles of acid = number of moles of base).

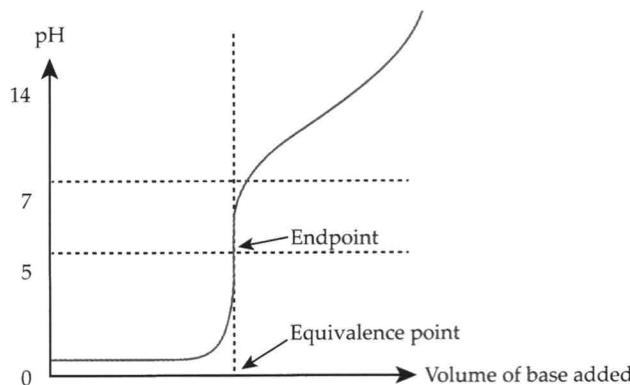
However, at this point the solution will not be neutral at pH 7. It will be basic because the CH₃COO⁻ ion reacts with water to produce OH⁻ ions. Therefore, to obtain the correct reading of 25 mL, the indicator colour needs to change at a pH of around 9. A suitable indicator that changes at pH 9 is called phenolphthalein, which changes from colourless to pink at a pH of around 9.

Weak base versus strong acid

When a weak base is titrated against a strong acid however, at the equivalence point, the pH will be below 7 as the base is providing less than one mole of OH^- ions per mole of acid.

To arrange for the Endpoint to be the same as the Equivalence Point an indicator must be chosen which changes colour at pH 5.

A suitable indicator for strong acid/weak base titrations is methyl orange. This changes from orange to yellow as base is added at around pH 5.



Weak acid versus weak base

There will be no sharp endpoint for this type of titration so the only way the equivalence point can be assessed is by using a pH meter to monitor the solution.

2.14 BACK TITRATIONS

Back titrations are used if the unknown acid or base is insoluble or cannot be titrated for some reason, e.g. to find the mass of a particular metal in an alloy or % purity of an insoluble metallic compound.

Method:

Weigh the compound X

Add a large, measured amount of reagent (call this n_1) that will totally dissolve compound X (e.g. acid)

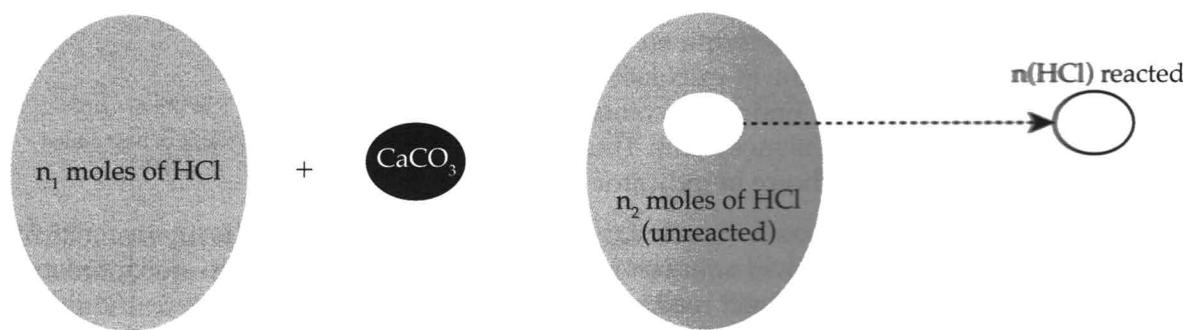
Titrate the excess reagent to find how much of it is left after reacting (call this n_2)

Calculate the number of moles n_R of reagent that reacted by subtracting, i.e. $n_R = n_1 - n_2$

Use the reaction equation to find the stoichiometric ratio and hence the number of moles of X present.

Graphic representation

e.g. To find the mass of CaCO_3 in limestone



n_1 moles of acid were added and n_2 left over, so the number of moles reacted must equal $n_1 - n_2$ from which $n(\text{CaCO}_3)$ can be found.

Example

A 4.432 g sample of a limestone containing CaCO_3 was reacted with 25.0 mL of 1.020 M HCl and it all dissolved, leaving a sandy residue. The excess acid was reacted with 0.275 M NaOH and the average titre value for the volume of NaOH (aq) was found to be 27.93 mL.

Determine the % of CaCO_3 in the limestone.

Answer

A flow-chart is often useful to hold all the information here:

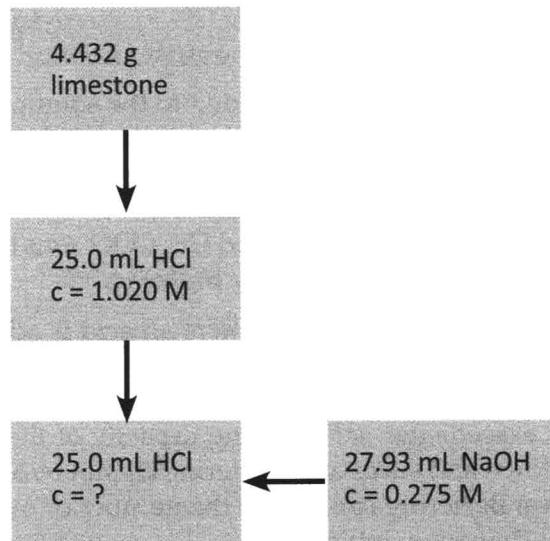
Rules for flowchart are:

Substances are shown in boxes

Processes are shown by arrows
("is added to")

n_1 is the original moles of HCl

n_2 is the remaining moles of HCl

**Calculation**

$$\text{Number of moles of HCl added } (n_1) = cv = 1.020 \times 0.025 = 0.0255 \text{ mol}$$

$$n(\text{NaOH}) \text{ titre} = cv = 0.275 \times 0.02793 = 7.680 \times 10^{-3} \text{ mol}$$

$$1:1 \text{ ratio of NaOH with HCl, so } n(\text{HCl}) \text{ remaining } (n_2) = 7.680 \times 10^{-3} \text{ mol}$$

$$n(\text{HCl}) \text{ used in reaction with } \text{CaCO}_3 = n_1 - n_2 = 0.0255 - 7.680 \times 10^{-3} = 0.01782 \text{ mol.}$$



$$\text{So } n(\text{CaCO}_3) = \frac{1}{2} \times n(\text{HCl}) = 0.5 \times 0.01782 = 0.00891 \text{ mol}$$

$$m(\text{CaCO}_3) = nM_r = 0.00891 \times 100.09 = 0.892 \text{ g.}$$

$$\% \text{ CaCO}_3 = \frac{0.892}{4.432} \times 100 = 20.1\%$$

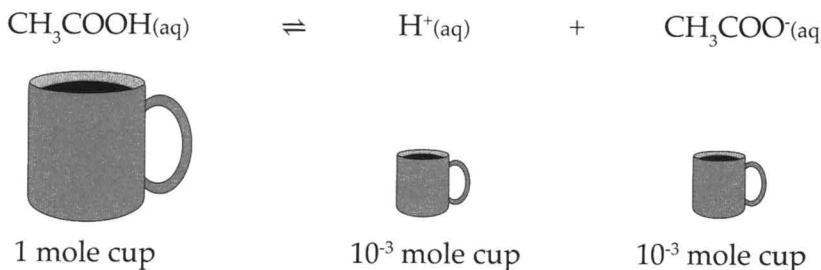
2.15 THE CHEMISTRY OF BUFFER SOLUTIONS

Many aqueous solutions can resist a change in pH when small amounts of acid or base are added. Such solutions are called Buffer Solutions – but they are limited in the extent to which they can resist change by their **Buffering Capacity**. Human blood, for example, is a complex aqueous solution with a pH buffered at about 7.4. Any large deviation from the pH can be serious and even be fatal, as vital enzymes cannot survive the large pH changes which would occur if too much H^+ or OH^- ions were present, i.e. the Buffering Capacity is exceeded.

Buffers generally require two species: an acidic one (to react with the added OH^-) and a basic one (to react with the added H^+). This requirement is fulfilled by having a weak acid-base conjugate pair such as $\text{CH}_3\text{COOH} / \text{CH}_3\text{COO}^-$, or $\text{NH}_4^+ / \text{NH}_3$. The former (acidic buffer) can be prepared by adding CH_3COONa to a solution of acetic acid (CH_3COOH). The latter (basic buffer) can be prepared by adding ammonium chloride (NH_4Cl) to a solution of ammonia, NH_3 . In general, a buffer mixture consists of an aqueous solution of an acid-base conjugate pair prepared by mixing a weak acid or base with a salt of that acid or base.

How do buffers work?

Consider the ionisation of ethanoic acid, which has a small value of K_a so that, for a 1 mol L⁻¹ solution, there will only be about 10^{-3} of each product in 1 litre of solution:



Imagine that a base is now added to the solution so that OH⁻ ions are present to interact. The H⁺ ions will be reduced by their reaction with the OH⁻ ions to form water and therefore their concentration will be reduced. The pH will momentarily go up, but by Le Châtelier's Principle, more CH₃COOH must ionise and replace them – to a large extent. By the analogy above, the large cup can pour more H⁺ and CH₃COO⁻ ions back into the smaller cups. Hence the excess of OH⁻ ions has been successfully **buffered**.

Now consider the situation where an acid is added to the equilibrium solution above. By Le Châtelier's Principle, the equilibrium will move to the left so as to reduce the amount of H⁺ ions. However, the capacity of the small cups is very low – 10⁻³ moles, so if the amount of acid added exceeds the 10⁻³ buffering capacity of the right side of the equation then the pH must drop down and successful buffering cannot be achieved. The CH₃COO⁻ ions will have all been used up! Buffering capacity is the number of moles of acid/base that can be absorbed before the pH changes significantly.

How can this problem be overcome? Simply by replacing the small cups on the right with large, 1 mole cups, i.e. add some more of the conjugate base to equal the number of moles of acid – there will now be a reservoir 1 mole of CH₃COO⁻ ions.

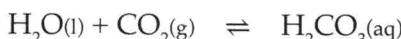
An acidic buffer solution is an equal mix of acid and conjugate base (CH₃COOH/CH₃COO⁻) and a basic buffer solution would be an equal mix of base and its conjugate acid (NH₃/NH₄⁺).

The Buffering Capacity is the maximum amount of acid/base that can be absorbed without a significant change in the pH of the solution. In this case, it is now 1 mole, rather than 10⁻³ moles.

2.16 BUFFER ACTION IN BLOOD

The pH of the human blood varies from 7.38 to 7.42. There are two buffer systems that help the pH levels to be maintained at a near constant value. One is the carbonic acid/hydrogen carbonate ion equilibrium. The other is the hydrogenated and dehydrogenated forms of haemoglobin, the component of blood that transports oxygen.

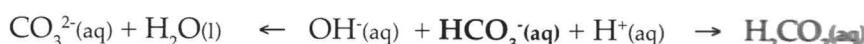
Carbonic acid forms in blood due to the reaction between water and the carbon dioxide gas from the inhaled air and that which is produced from respiration in the cells:



The aqueous carbonic acid, then, gives away a proton to form hydrogen carbonate ion:



The HCO₃⁻ ion is amphiprotic and so can absorb or donate a proton on its own. This means that it can act as a buffer for the blood without the need for the addition of another species:



Homeostasis is the term used for the ability of an organism to **counteract environmental changes with physiological responses**.

For example, the concentration of carbonic acid is controlled by **respiration**. When we exhale air CO₂ is released from the system and the concentration of H₂CO₃ decreases. This raises the

pH of the blood. When we inhale air, CO_2 and H_2CO_3 in the system increase and this lowers the pH of the blood.

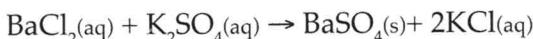
The function of the kidneys also helps maintain the pH balance. The ammonia formed by the release of nitrogen from some amino acids combines with excess H^+ ions to form ammonium ions which are removed by urination.

When the pH of the blood rises above 7.45 a condition known as *alkalosis* occurs which may produce a stroke in a patient. When a person hyperventilates or has excessive respiration, the result is an increase in the pH. To rectify this, people are asked to breathe into a paper bag. This shifts the equilibrium backward to increase the levels of CO_2 and H_2CO_3 in the blood which lowers the blood pH again. So the chemical buffering system in humans is a crucial part of our bodily make-up.

Redox Reactions

Older ideas of oxidation and reduction usually involved a notion of gaining or losing oxygen or hydrogen, e.g. iron oxidising to iron oxide. Oxidation and reduction reactions are involved in the rusting of metals, in cellular respiration, photosynthesis, in batteries, in the combustion of fuels, in the extraction of metals, in photography and in explosions.

In the definition of oxidation and reduction we think of electrons being transferred from one species to another. The following is not a redox reaction as there is no interchange of electrons:

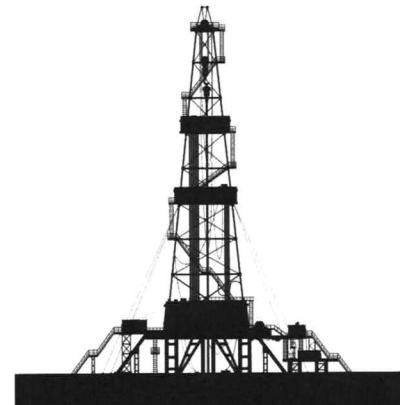


However, the majority of chemical reactions take place because of this transfer of electrons from one species to another. This chapter concentrates on these so-called Redox reactions.

3.1 KEY IDEAS IN REDOX REACTIONS

Electron Transfer

- Oxidation is a chemical process which involves the loss of electrons by a species.
- Reduction is a chemical process which involves the gain of electrons by a species.
- A way of remembering this is to use the word OIL RIG – Oxidation is Loss and Reduction is Gain.
- Oxidation is caused by oxidising agents, or oxidants, and reduction is caused by reducing agents, or reductants.
- Oxidants will always be reduced and reductants will always be oxidised.



OIL RIG

Oxidation is Loss and Reduction is Gain

Oxidation Numbers

Oxidation numbers can be assigned to reacting species before and after the reaction to identify those species that are oxidised and those that are reduced. Oxidation numbers (ON) indicate how many electrons the species appears to have lost. A positive value of ON means electrons have been lost and a negative value shows how many electrons have been gained, e.g. Fe^{3+} has an ON of +3 and N^{3-} has an ON of -3. The rules for assigning oxidation numbers are shown below.

- The oxidation number of any free element is zero, whether they are monatomic, diatomic or polyatomic, e.g. Ag , O_2 , P_4 .
- The oxidation number of monatomic ions is equal to the charge on the ion, e.g. K^+ , Na^+ , Cl^- , Br^- etc.
- Oxygen generally has an oxidation number of -2. OF_2 is an exception where it has an oxidation number of +2 and in peroxides the ON of oxygen is -1, as in H_2O_2 .
- Hydrogen, when bonded to non-metals, has an oxidation number of +1. When bonded to the active metals (alkali and alkaline earth metals) as a hydride, like NaH or CaH_2 , it is -1.

The sum total of all the oxidation numbers in a molecule or a formula unit is zero, e.g. H_2SO_4

The sum total of all the oxidation numbers in a polyatomic ion is equal to the charge of that ion, e.g. $\text{Cr}_2\text{O}_7^{2-} = -2$.

In compounds, the group 1 elements e.g. Li, Na, K, Rb, Cs and Fr always have an oxidation number of +1, and the group 2 elements, e.g. Be, Mg, Ca, Sr and Ba always have an oxidation number of +2.

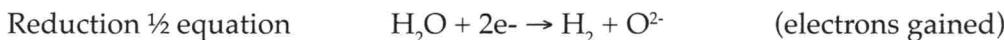
Examples of Oxidation Numbers in Compounds

FeO	Fe = +2,	O = -2
N_2O_3	N = +3	O = -2
NO_3^-	N = +5	O = -2
NH_4^+	N = -3	H = +1
SO_4^{2-}	S = +6	O = -2
H_2S	S = -2	H = +1
$\text{S}_2\text{O}_3^{2-}$	S = +2	O = -2
MnO_4^-	Mn = +7	O = -2
CH_4	C = -4	H = +1
CrO_4^{2-}	Cr = +6	O = -2
NH_4NO_3	N = -3, and	N = +5
		O = -2

Half Equations

In the reaction $\text{Mg(s)} + \text{H}_2\text{O(l)} \rightarrow \text{MgO(s)} + \text{H}_2\text{g}$, magnesium is oxidised to MgO, but water is reduced to H₂.

There are two half-reactions occurring here:



Here, magnesium is the reductant and hydrogen is the oxidant. Removal of electrons from the magnesium releases energy and this energy is used to push electrons onto the hydrogen ion in water. We can find the relative energies needed for redox reactions to occur in the Standard Reduction Potentials table (see later in this chapter).

Two metals can compete for the role of pushing electrons onto the other metal in Metal Displacement Reactions. The competition winner is the metal which is the most reactive – which, again, is shown in the Standard Reduction Potentials table.

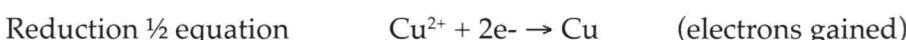
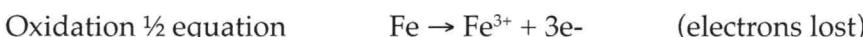
Consider a piece of iron placed into a copper sulfate solution. The redox reaction is:



Here, the iron wins the competition, as it pushes its electrons off onto the copper ion, thus reducing it to copper metal. The iron, itself, becomes oxidised in the process to Fe³⁺.

Copper is said to be *displaced* from the solution and will be precipitated as a salmon pink solid.

Fe is the reductant and Cu²⁺ is the oxidant.



The number of electrons the Fe supplies must equal the number that the Cu²⁺ receives and so the two half equations must be balanced for electrons. Reaction (i) is multiplied by 2 and equation (ii) multiplied by 3. This will give the overall balanced redox equation:



Balancing Half Equations

The rules and order of balancing for an equation that does not appear in the Standard Reduction Tables are summarised in the phrase. An aid to memory is: **Breakfast We Have Eggs: B W H E**.

B – Add coefficients to balance all species except for H and O.

W – Add water to the side of the equation with less oxygen.

H – Add H⁺ ions to the side of the equation with least hydrogen.

E – Add electrons to the side of the equation which is most positive **overall**.

Example: Balance this ½ equation: $\text{SO}_2 \rightarrow \text{H}_2\text{S}_2\text{O}_3$

B Balance the sulfur atoms: $2\text{SO}_2 \rightarrow \text{H}_2\text{S}_2\text{O}_3$

W Add water to the right: $2\text{SO}_2 \rightarrow \text{H}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}$
(4 O on both sides now)

H Add H⁺ to the left: $2\text{SO}_2 + 4\text{H}^+ \rightarrow \text{H}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}$
(4 H on both sides now)

E Add electrons to the left: $2\text{SO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{H}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}$
(zero charge on both sides now)

Final balanced reduction $\frac{1}{2}$ equation:

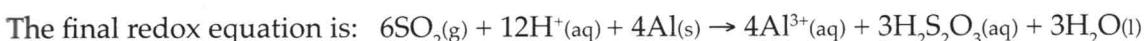


Suppose the reductant in this case was aluminium, then the oxidation $\frac{1}{2}$ equation would be:



The overall redox equation is formed by amalgamating these two equations which makes the number of electrons given out by the aluminium the same as those taken in by the SO_2 .

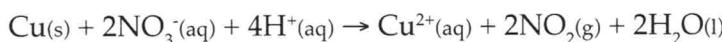
Equation (i) must be multiplied by 3 and equation (ii) multiplied by 4 to make the number of electrons the same (12).



(NB: the equation will not proceed without the H^+ ions on the left, so this reaction must occur in acidic conditions. If no H^+ is present then it will not occur).

Splitting Equations

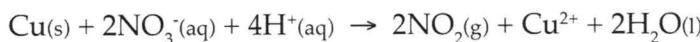
There may be a reaction where the simple balancing process seems very hard to do, such as this one:



This clearly is made up from two separate $\frac{1}{2}$ equations and so separating them would make the balancing much easier:



Multiply (i) by 2 and add to (ii) to obtain the fully balanced equation:



3.2 REDUCTANT STRENGTHS

If a substance gives up electrons readily it is said to be a strong reducing agent. Its oxidised form will be a poor oxidising agent, e.g. Zn is a good reductant but Zn^{2+} is a very poor oxidant.

If a substance gains electrons readily it is said to be a strong oxidising agent. Its reduced form is a poor reducing agent, e.g. Cl_2 is a good oxidant but Cl^- is a very poor reductant.

Though the strength of oxidising agents and reducing agents are relative, certain common substances in industry are known to be strong oxidising agents or strong reducing agents.

Carbon, carbon monoxide and hydrogen are used as strong reducing agents in industry, whereas nitric acid and sulfuric acid are used as strong oxidising agents. Acidified potassium permanganate and potassium dichromate are strong oxidising agents, used in redox volumetric analysis.

Other examples of strong oxidising agents are H_2O_2 , ozone, halogens and active non-metals. Most reactive metals are strong reducing agents.

The table supplied on the Chemistry Data Sheet shows the relative strengths of species – all compared with hydrogen which is a standard and is defined as being zero on the scale.

Part of this table is shown below as Table 1.

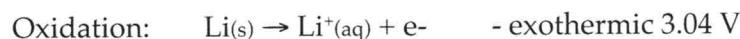
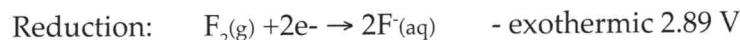
3.3 SPONTANEOUS REACTIONS

The table below shows the energy that is given out by a particular reaction. If energy needs to be absorbed to make the reaction work, this is shown as a negative value.

For instance: Fluorine has seven electrons in its outer shell, so if it can gain an electron it will attain a full shell and reach a more stable state of F^- (full shell). Hence, the reaction $F + e^- \rightarrow F^-$ will give out energy (similar to exothermic reactions). The reduction of fluorine to F^- is a very energetic reaction, giving out 2.89 units of energy (measured in volts). It is therefore the best oxidant in the table.

The lithium ion Li^+ is the worst oxidant, requiring an **input** of 3.04 units of energy to reduce it to lithium metal. This makes it the best reductant because, if we look at the reverse reaction $Li \rightarrow Li^+$ we see that 3.04 units of energy would be released (going from right to left of the table, reverse the voltage sign).

In the reaction where fluorine is mixed with lithium, the two half equations would be



The total energy evolved would be found by adding the energy values = 5.93 V (very large!)

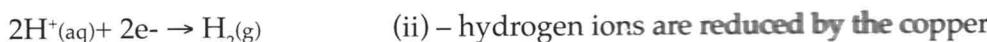
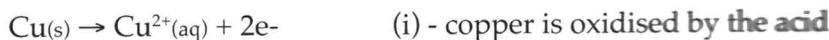
From table 1 below we can also find out whether a proposed reaction would be spontaneous or not, i.e. occur without an input of energy.

Table 1

Reduction Half-Reaction	Standard Reduction Potential (E°) at 25°C
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	+2.89
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	+1.08
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	+0.54
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	-0.14
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	-0.44
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	-0.74
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.76
$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$	-1.18
$Na^+(aq) + e^- \rightarrow Na(s)$	-2.71
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.04

E° is the relative energy output, in volts, compared to hydrogen. An example of a reaction that could not occur from energy considerations is copper metal reacting with an acid.

Looking at the redox reactions required from the table above:



However, if we add the E° values for the two equations, we get $-0.34 + 0.00 = -0.34$ V

The negative value of overall E° shows this reaction is **not** spontaneous and will not occur – so copper will not react with acids.

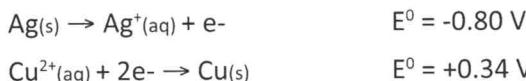
Of the two half reactions, the reduction reaction must always go from left to right and the oxidation reaction must be reversed (from right to left). If the energy given out by one reaction is less than the energy needed to make the other reaction proceed then the overall reaction will not occur spontaneously, i.e. energy must be supplied to make it work.

Example

Will silver metal react when placed into copper sulfate solution?

Answer

The half reactions that need to occur are:



However, adding the E° values, we see the total energy value here is -0.46 – a negative value. Hence, this reaction cannot occur spontaneously. The answer then is no, they will not react.

As a rule, if the reduction equation in the table is on the left and above the oxidation equation going from right to left, then the reaction will proceed – because the E° values beneath are always lower than the ones above.

So zinc will be able to dissolve in acid because the reactions are:



Strong oxidants usually contain an element in its highest oxidation state. For example, in MnO_4^- manganese is in an oxidation state of $+7$. In $\text{Cr}_2\text{O}_7^{2-}$, chromium is in an oxidation state of $+6$.

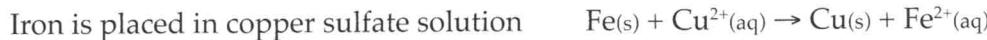
Strong reductants usually contain an element in its lower oxidation state. For example, the reactive metals such as potassium and sodium always have an oxidation state of zero.

3.4 DISPLACEMENT REACTIONS

A special type of redox reaction is where precipitation takes place of one ionic species A (usually a metal ion) by an elemental reductant B. The reductant metal then replaces species A in solution, e.g. $\text{A}^{2+}(\text{aq}) + \text{B(s)} \rightarrow \text{A(s)} + \text{B}^{2+}(\text{aq})$

This type of reaction is called a **Displacement Reaction**. Metal B would have to be a stronger reductant than metal A for this to be energetically viable.

For instance:



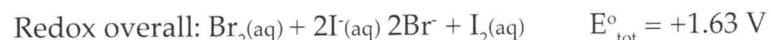
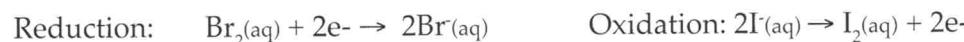
Cu^{2+} is above iron in the table and on the left.

Fe is to the right in the table and below so the total E° values will be positive and allow a spontaneous reaction. Total $E^\circ = +0.34 + 0.44 = 0.78 \text{ V}$

Any acid is shown as the H^+ reaction on the E° table and so any metal that is below H^+ and on the right will be dissolved.

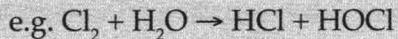


Displacement reactions can also occur with non-metals. Bromine water will displace iodine from sodium iodide solution:



3.5 DISPROPORTIONATION REACTIONS

In a disproportionation reaction an element in a certain oxidation state is both oxidised and reduced at the same time. For this to occur, a reactant must contain an element that is capable of having at least three oxidation states. The halogens and transition metals, with their many common oxidation states, undergo disproportionation in many ways:

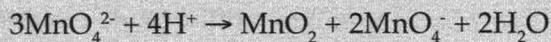
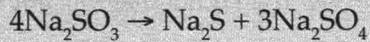


Chlorine has gone from an oxidation number of zero up to +1 (oxidation to HOCl) and down to -1 (reduction to Cl⁻)

A common reaction often asked about is the disproportionation of hydrogen peroxide as it is used to prepare oxygen in the lab, using a catalyst:



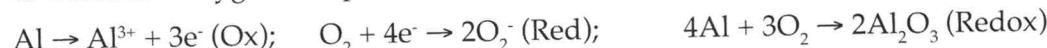
Other examples of disproportionation are:



3.7 CORROSION

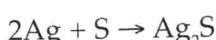
Corrosion of metals is a redox reaction. Many metals such as copper, iron, aluminium and silver corrode by reaction with air to form their oxides or sulfides.

Aluminium does not appear to corrode although aluminium is a more reactive metal than iron. This is because the aluminium oxide layer prevents any exposure of the underlying metal to water and oxygen and prevents further corrosion:

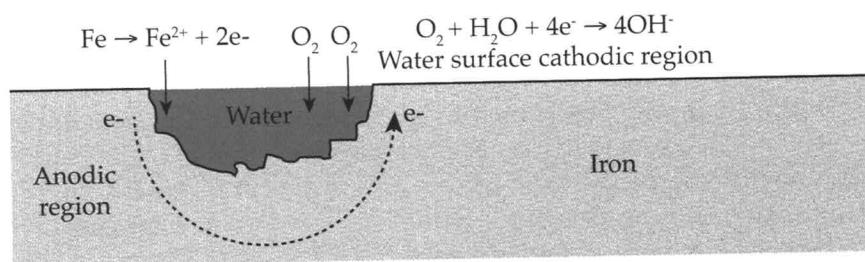


Hence aluminium can be used for window frames, boats and wheels without any apparent corrosion.

Silver reacts with the sulfur in the air or the hydrogen sulfide gas in the environment to become black silver sulfide. This is called *Tarnishing* and happens with silver spoons and trophies.



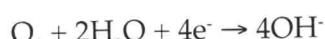
The rusting of iron is an oxidation – reduction process. Where the iron surface is cracked or has a weakness in structure exposed to water, oxidation will take place:



Iron oxidises and donates the electrons:



Oxygen dissolves in the water and absorbs these electrons, producing a basic solution:



Iron reacts with oxygen: $4\text{Fe}^{2+} + \text{O}_2 \rightarrow 4\text{Fe}^{3+} + 2\text{O}^{2-}$

Iron III reacts with water: $\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3 + 3\text{H}^+$

Iron hydroxide decomposes: $\text{Fe}(\text{OH})_3 \rightarrow \text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ (Rust)

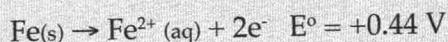
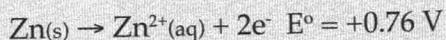
3.8 CORROSION PREVENTION

Corrosion can be minimised by protecting the surface from the environment. Painting, varnishing, greasing, plating with less reactive metals tin and coating with a thick oxidised layer of the metal which is non-porous are some of the usual measures taken to minimize corrosion.

Metals like chromium, when used as plating, will provide a non-porous, shiny layer that increases the value of the article and makes it last longer.

Galvanising

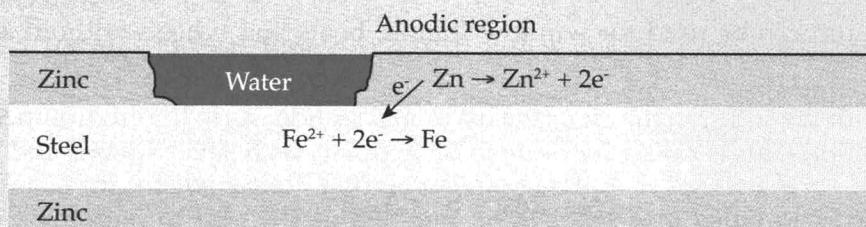
Covering iron in a thin layer of a more reactive metal produces a cell with a reverse voltage which pushes the electrons back onto the iron when it starts to oxidise. Suppose an iron sheet is coated with zinc. In wet conditions the following aqueous reactions can take place:



For these two metals to work as a cell, the iron reaction must be reversed to give a positive overall voltage ($0.76 \text{ V} - 0.44 \text{ V}$). Hence the overall reaction would be:



In other words, the zinc, being more reactive, would push the electrons back on to the iron should it begin to lose electrons and become ions. Instead of the iron dissolving, the zinc will dissolve, leaving the iron un-corroded. This method of cathodic protection is called Galvanising after the famous Italian scientist Galvani. Steel poles, sheets, etc. are dipped into molten zinc to coat them which protects the steel even where there are gaps in the coating.



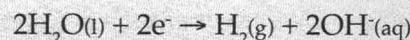
Sacrificial anodes

With large structures, such as ships, steel piles, water tanks or floating oil rigs, blocks of zinc or aluminium are actually bolted onto the outside steel area, ensuring a good electrical contact. The principle is the same, with the zinc forming a cell with the steel and feeding electrons back to sites of potential oxidation of the iron. The zinc is sacrificed for the sake of the steel and will gradually dissolve. After some months or years the zinc block would be unbolted and replaced with a new one and the protective process would continue.

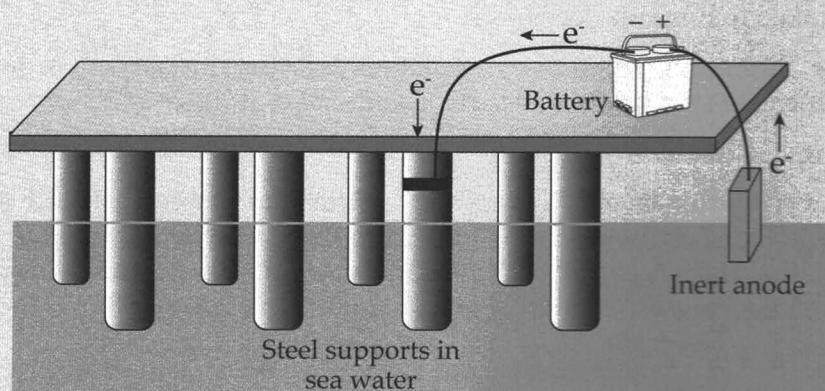
Cathodic Protection

Electrons can actually be “pushed back” onto rusting iron directly by using a cell, instead of making use of a more reactive metal to do this. This method connects an electron source, such as a battery or a transformer, directly to the exposed piece of iron or steel using a connecting wire.

The battery supplies the energy to reverse the reaction: $2\text{e}^- + \text{Fe}^{2+} \rightarrow \text{Fe}_{(\text{s})}$ at the pipe support (cathode) and at the anode negative charge returns through the seawater from the reduction reaction carried by the OH^- ion.



For the circuit to be complete a large piece of scrap iron is used as an inert anode, just hanging in the water and returning the electrons to the battery.



3.9 GALVANIC CELLS

We can make use of the different reactivities of metals in solution to drive electrons from one metal to another around an external circuit. In this way the chemical energy differences shown in the Standard Reduction Table can provide energy to an external source, e.g. light a lamp.

When this happens, the metal losing electrons is oxidised and the metal gaining electrons is reduced.

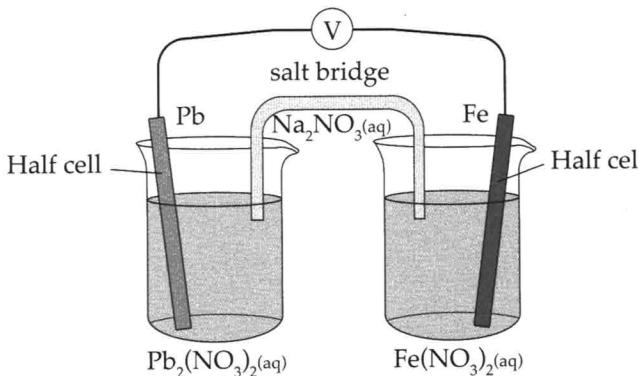
Solutions do not conduct by means of electron flow, as with metals, but use ions. To allow ions to flow in a cell and complete the circuit, the metals must be linked with a conducting liquid — an ionic salt solution — contained in a tube. This ion-filled tube is called a *salt bridge*.

Example Question

- Show an galvanic cell using lead and iron as electrodes.
- What is the output voltage of the cell?
- Identify which metal is the anode and which is the cathode.
- Which way do the electrons flow?
- Which way do the ions flow in the salt bridge?

Answers

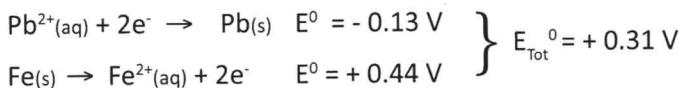
This cell is represented by the symbols: Fe/Fe²⁺//Pb²⁺/Pb (Convention is Oxidation//Reduction)



Here we have two competing reactions for reduction:



The lead reaction shows that it is a better reductant than iron and so the iron reaction must be reversed in order to gain a positive value of energy (E°) overall. Hence the $\frac{1}{2}$ equations must be:



Output voltage of the cell is 0.31 volts which will be the voltmeter reading in this case.

Note: The anode is where oxidation takes place and the cathode is where reduction takes place (Remember by: ANOX and REDCAT). Hence the **anode** is the iron, as it is oxidised to Fe^{2+} and lead will be the **cathode** as Pb^{2+} ions are reduced to Pb solid.

- From the equations above we can see that electrons are coming out from the iron reaction:
 $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$
Hence the electrons will flow from the iron electrode through the voltmeter and back to the lead where they are used to reduce the Pb^{2+} ions to Pb solid.
- Negative charge flows out from the iron and must flow back to the right hand half-cell to complete the circuit through the salt bridge. So it must be the negative SO_4^{2-} ions that move from left to right through the salt bridge tubing.

The voltage of a cell and the electrode names can be found using the Standard Reduction Table. We just use the principle that, with two dissimilar metals and their ions, the species which is top left in the table will be the one reduced and therefore the cathode (REDCAT). The species on the bottom right in the table will be where the equation is reversed and will be the anode as it will be oxidised (ANOX).

e.g. Suppose a cell is made up from the metals silver and manganese.

Top left in the Table is the Ag^+ ion and bottom right will be Mn metal. So the half equations will be:



Total output cell voltage will be $0.80 + 2.36 = 3.16 \text{ V}$.

3.10 USEFUL GALVANIC CELLS

Voltaic cells provide portable energy sources and are very important in today's technological world. There are basically three types of voltaic cells: The common Dry Cell, Alkaline battery cells and the Lithium iodide cell. These cells, called Primary Cells, as they are non-rechargeable – so once used, they must be disposed of in a safe manner. The car battery and the nickel-cadmium cell are examples of Secondary Cells, i.e. they are rechargeable for repeated discharge and recharging. Cells which do not store the chemicals, such as the fuel cells, form the third type of cell.

PRIMARY CELLS

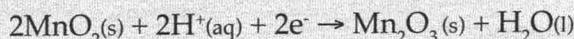
The Common Dry Cell

The electrolyte used is NH_4Cl and ZnCl_2 paste - so there is no liquid to spill.

The zinc container is the anode and a carbon rod and MnO_2 powder are the cathodes.

The anode reaction is: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$

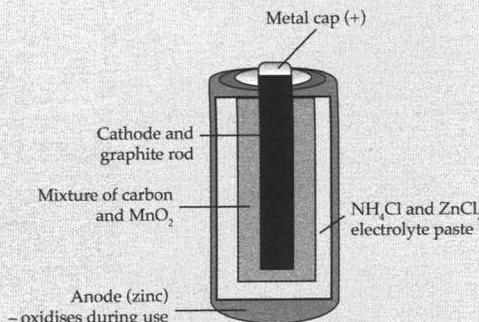
The cathode reaction is:



The H^+ ions needed for this reaction are provided by the ammonium ion in NH_4Cl : $\text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}^+$

Dry cells are mainly used for torches, children's electrical toys and TV remote controls. They give an output of 1.50 volts.

Advantages: cheap.

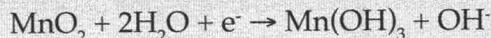


The Alkaline Cell

The electrolyte used is KOH solution with a zinc container is the anode. Carbon and MnO_2 are the cathodes.

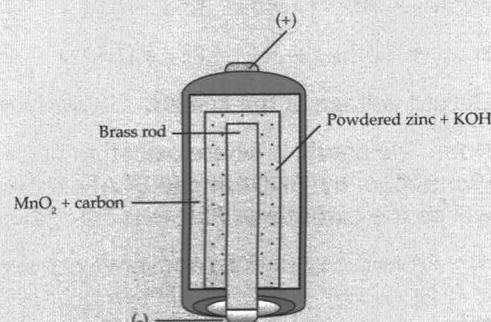
The anode reaction is: $\text{Zn} + 2\text{OH}^- \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{e}^-$

The cathode reaction is:



Mainly used for portable radios and CD players. They give an output of between 1.50 and 1.65 volts.

Advantages: they have a higher energy density and shelf-life than the dry cell.

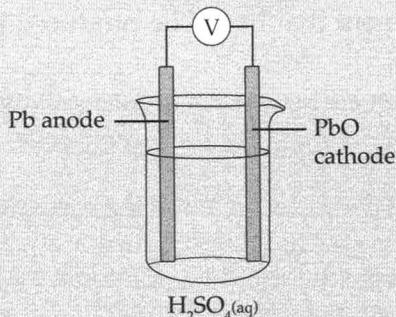


Rechargeable Cells

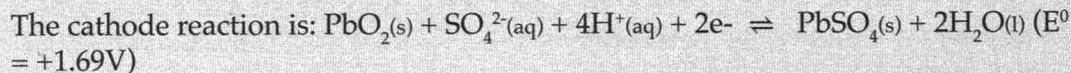
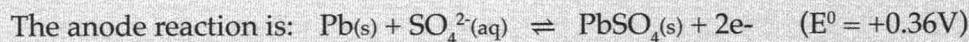
All the Galvanic cells referred to so far have been what are termed Primary Cells. This means that, once the chemicals or metals have reacted then the cell is discarded; they cannot be charged up again. Secondary Cells, however, have the advantage of being able to be recharged and hence can save money on components.

One very common rechargeable battery in use is the one under the bonnet of most cars – used to start the car. This particular Secondary Cell is called the Lead-Acid Accumulator.

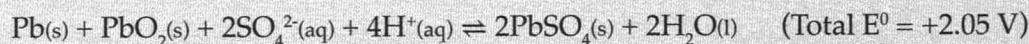
Lead-Acid Accumulator



Discharging



So the overall reaction for discharging the cell is:

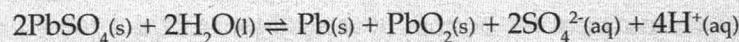


Normally, for car batteries, six of these cells are placed in series to give a voltage of 12.3 V overall.

The lead-acid battery is able to supply the very large current required to start the car. As the battery discharges both plates become “sulfated” so, when the battery is completely flat the anode and cathode have both become lead sulfate and the sulfuric acid pH has risen considerably. One way of telling that the battery is flat is by looking at the density of the electrolyte. Normally the density of the acid in the battery is around 1.2 g cm^{-3} but, as it loses its acid concentration, the density would become closer to 1.0 g cm^{-3} .

Charging

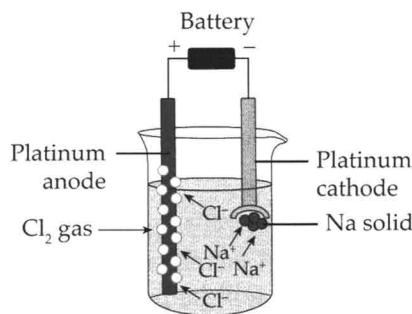
The Lead-acid battery can be recharged by connection to a 12 volts electrical supply so that the reactions above are reversed when the anode and cathode revert to their original components of lead and lead oxide.



Galvanic Cells

Galvanic cells generate a voltage by utilising the different reactivities of species to produce a spontaneous reaction. However, by supplying energy in the form of an applied external voltage reactions can be forced to reverse and produce a metallic or non-metallic product.

Cells where a voltage is applied to produce a redox reaction are called Electrolytic Cells, e.g. sodium and chlorine can be produced by the electrolysis of molten (fused) sodium chloride crystals using inert electrodes.



The anode reaction is $2\text{Cl}^-(l) \rightleftharpoons \text{Cl}_2(g) + 2\text{e}^-$ (chlorine gas is evolved) E° here is -1.36 V

The cathode reaction is $\text{Na}^{+}(l) + \text{e}^- \rightleftharpoons \text{Na}(s)$ (sodium metal is produced) E° here is -2.71 V

The required voltage to reduce the Cl^- and oxidise the Na^+ would be $1.36 + 2.71 = 4.07$ V.

Note: This redox reaction would not occur in an aqueous solution because the water would be electrolysed in preference to the NaCl . Reducing water at the cathode to hydrogen would only require a voltage of only 0.83 volts and oxidising water to oxygen at the anode would only require 1.23 volts. Hence a total applied voltage of only $0.83 + 1.23 = 2.06$ volts would be needed. Compounds composed of highly reactive elements like sodium and chlorine can only be oxidised or reduced when they are in the fused, liquid form – not a solution.

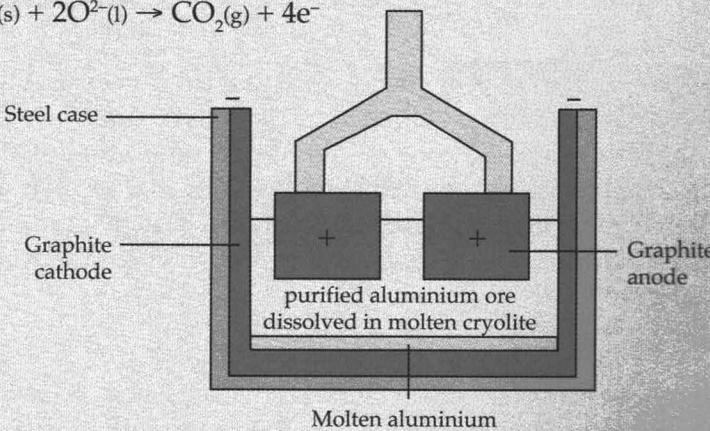
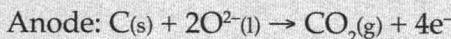
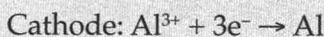
An example of another vital element that has to be produced by the electrolysis of the fused compound is Aluminium.

Electrolysis of alumina

Alumina (Al_2O_3) is plentiful in Australia, but it has an extremely high melting point (over 2040°C) which makes the reduction process energy intensive. By adding Cryolite (Na_3AlF_6) to the mix the melting point can be brought down to about 900°C which makes the process more economically viable.

A steel container lined with graphite serves as the cathode and the anodes are a set of carbon rods. The temperature is kept over 900°C throughout and aluminium is collected as a liquid while the liberated oxygen oxidises the carbon anode to CO and CO_2 .

The reactions are:



Molten aluminium is run off from the outlet at the bottom of the cell and CO_2 is evolved at the anode.

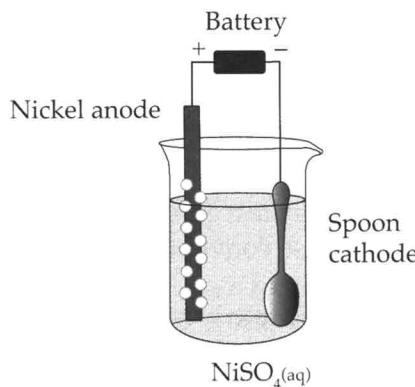
Electroplating

The electrolysis of some solutions of cations can be used to deposit a layer of metal onto another metal providing the reduction E° value is energetically lower than that of water. Zinc, cadmium, nickel, copper and tin, for instance, can all be deposited onto a steel substrate by electrolysing a solution of the cation.

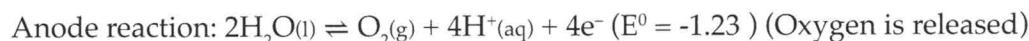
An example of how electroplating works is shown below, where a brass spoon is to be plated with nickel.

For the reaction $\text{Ni}^{2+}(aq) + 2\text{e}^- \rightleftharpoons \text{Ni}(s)$ the E° value is -0.24 V which means the reaction is endothermic. Hence if energy is supplied by connecting to a battery supplying at least +0.24 V the nickel ions will be precipitated as nickel metal. This is the basis of electroplating.

Nickel plating a spoon



A solution of nickel sulfate form the electrolyte and nickel metal acts as the anode.



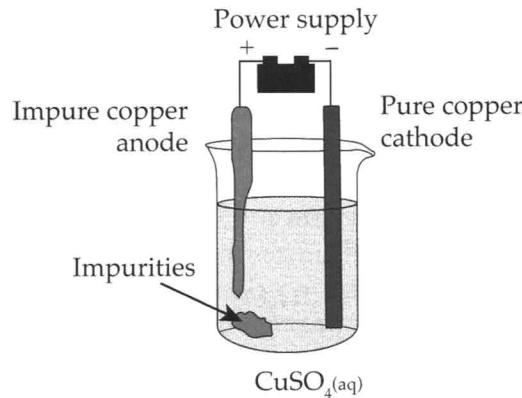
Total voltage that must be applied is $0.24 + 1.23 = 1.47 \text{ V}$.

(Note that the sulphate ion is non-reactive so it is water that becomes oxidised)

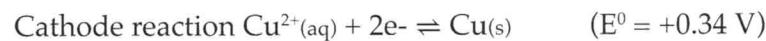
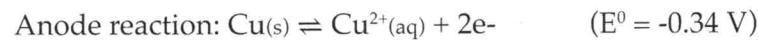
Electrowinning

Electrowinning or electro refining is a process by which a pure metal can be produced from an impure sample. This electrowinning is used to produce pure samples of metals such as copper, lead and cadmium as well as being used to recycle uranium metal from spent fuel rods. An example of the electrowinning process is shown below for the refining of copper from a metal sample which may have impurities of carbon, silver, etc. mixed with it.

Copper purification process



The impure copper sample is used as the anode and a purified (or pure copper plated) rod of copper is used as the cathode, with an electrolyte of copper sulfate solution. The copper ions dissolve from the anode into solution, leaving the impurities behind.



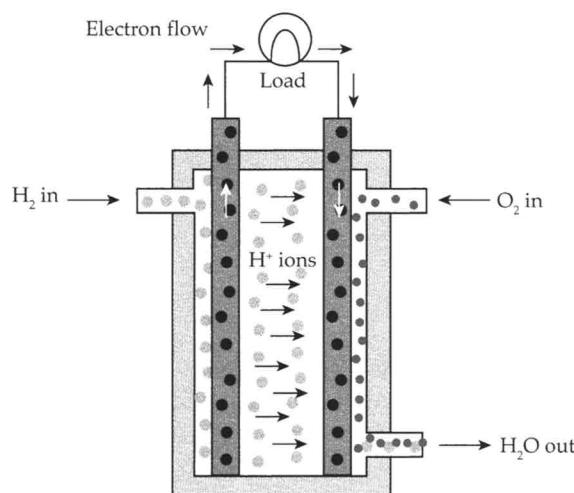
It seems that the total voltage required for this reaction would be zero ($+0.34 + (-0.34 \text{ V}) = 0.00 \text{ V}$) but some small voltage would actually be required to overcome the activation energy of the reactions.

Fuel cells

Many substances such as H₂ or CH₄ can also be used as fuels even though there are no ions present. The source of the electrical voltage is the energy released in the breaking of the bonds in the gases and forming new ones in water molecules – the same as in combustion. Because combustion reactions are redox reactions, with fuel cells we can obtain a flow of current directly from the fuels being fed in.

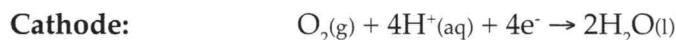
Direct production of electricity from fuels via a galvanic cell yields a rate of energy conversion higher than 40%. Galvanic cells that utilise conventional fuels are known as fuel cells.

O₂/H₂ Fuel cells (e.g. Proton exchange membrane fuel cell)



Fuel cells tend to operate at high temperatures, using hydrogen which has to be stored and oxygen drawn in from the air. Some cars have now been designed to work using fuel cells and a battery such as the one shown above was used on the Apollo moon flights for electrical power. The electrodes are composed of hollow tubes of porous, compressed carbon, impregnated with a catalyst and an electrolyte of KOH solution. Because the reactants are supplied continuously, the fuel cell cannot go "dead" or "flat".

The reactions in the fuel cell are:



The key advantage of this type of cell is that there are no metallic waste products and emit no toxic gases – just water. However, gases do need to be fed continuously to the cell and there are concerns about the storage of hydrogen for use in the fuel cell as it is very inflammable, or even explosive. NB: It currently takes 40% of the energy available from hydrogen gas to compress it for storage.

Cars running on fuel cells would offer a good alternative to petrol-engined cars.

The Energy Future – The International Partnership for Hydrogen and Fuel Cells in the Economy (IPHE)

With the universal concern about the growth of CO₂ emissions and its link to Global Warming, governments around the world have set targets for the reduction of Greenhouse Gases (mainly CH₄, CO₂ and N₂O). Hence, the aim is to reduce a reliance on the burning of fossil fuels and to increase the use of Renewable Energies, such as wind, solar, geothermal and biomass which release no gases harmful to the environment. The use of fuel cells is a very promising new direction for generating electricity directly from gas oxidation in galvanic cells.

The IPHE was established in 2003 and is a forum for member governments to share information and policy experiences with the priority of accelerating the integration of hydrogen and fuel cell technologies into their economy. Many governments are now signed up to IPHE, including Australia, USA and UK, allocating research funding of more than \$1 billion per year.

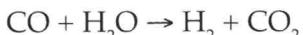
Hydrogen fuel cells can now be purchased off-the-shelf for houses and businesses requiring power outputs of up to 5 kW but are not in commercial use in vehicles due to concerns over safety and production costs of hydrogen. A tank of compressed hydrogen is highly explosive and to produce hydrogen it has been traditional to electrolyse water, which requires a large energy input. However, hydrogen is a by-product in some industries.

The NG fuel cell is a promising innovation in this field because, apart from hydrogen, it can also run on the methanol and methane contained in compressed natural gas (CNG). The advantage of this kind of cell is that it can generate electricity directly from the gas connections existing in most houses so as to charge an inboard battery.

The NG Fuel Cell works on a 2-stage process where the CNG is first broken down into hydrogen and then uses the hydrogen and oxygen to generate a voltage. The reaction occurs at quite high temperatures and uses steam mixed with CNG in stage 1:



CO is poisonous and so a second stage reaction converts this into CO₂ thus:



Hence the NG fuel cell does produce some CO₂, but the amount is about 30% lower than that emitted by power stations that generate the electricity needed to charge up battery-powered vehicles. An NG fuel cell powered car has efficiencies that are double that of similar cars charged from mains electricity and requires a much smaller battery. Using hydrogen in fuel cells at the moment is prohibitive in terms of safety and size of tank required, but an innovative storage technique has evolved recently where the low pressure CNG is adsorbed onto "Carbon sponges" inside the tank. These "sponges" can be manufactured simply and easily from charred common corn cobs which contain a kind of network of carbon nanotubes. 1 gram of the carbon substrate has an adsorption area equal to a football field! This would allow the storage tanks for the current 5 million vehicles around the world that run directly on CNG to be reduced to one third of their previous size.

Most CNG supplies presently come from non-renewable sources in the ground but methane can also be generated from waste organic material in bio-digesters and then compressed for use in a vehicle.

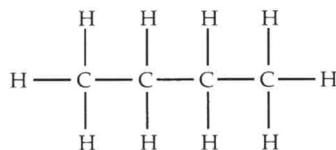
Using existing electric vehicle recharging technology, in order to travel a 600 km round trip the battery cost would be around \$50,000 whereas, if the same vehicle were powered by an NG fuel cell, the battery cost would be very small in comparison.

Hence there are many problems to solve if we are to switch entirely to a fuel cell energy world but, with current research, the cost per kilowatt generated by fuel cells has reduced about 10-fold in the last 10 years!

Organic Chemistry

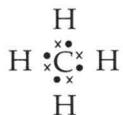
4.1 HYDROCARBONS

Organic chemistry is the chemistry of carbon compounds (other than metallic carbonates, hydrogencarbonates and the oxides of carbon). These compounds are called **hydrocarbons**.



The electron configuration of carbon is $1s^2 2s^2 2p^2$, or 2, 4, and as such, carbon atoms form four very strong covalent bonds in order to obtain a stable electron configuration.

Example



In methane,
carbon has four
single bonds



In carbon dioxide,
carbon has two
double bonds

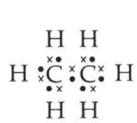


In hydrogen cyanide,
carbon has a triple bond
and a single bond

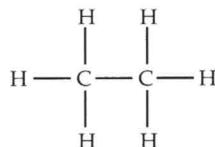
The central role of carbon in organic chemistry depends on the fact that carbon atoms can form a virtually unlimited number of straight chain, branched chain and ring molecules with a succession of strong covalent carbon-carbon bonds.

Saturated hydrocarbons are those which contain carbon and hydrogen atoms with only single bonds between carbon atoms. There are several ways to show the molecule.

Example ethane, C_2H_6



electron dot
diagram



structural formula

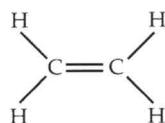


condensed formula
(semi structural)

Unsaturated hydrocarbons contain one or more double or triple bonds between carbon atoms.

Example ethene, C_2H_4

ethyne, C_2H_2



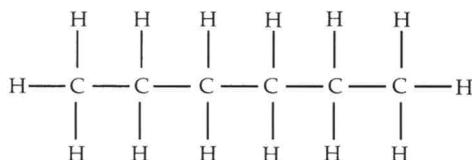
Aliphatic, alicyclic and aromatic hydrocarbons are the different types of hydrocarbons.

Aliphatic hydrocarbons

Aliphatic hydrocarbons are those with open chains of carbon atoms.

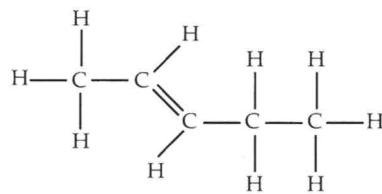
Alkanes are saturated aliphatic hydrocarbons with chain-like molecules.

Example hexane, C_6H_{14}



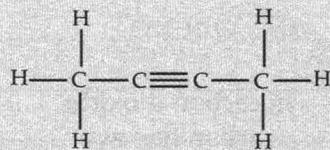
Alkenes are unsaturated and contain at least one double bond between carbon atoms.

Example pent-2-ene



Alkynes contain at least one triple bond between carbon atoms.

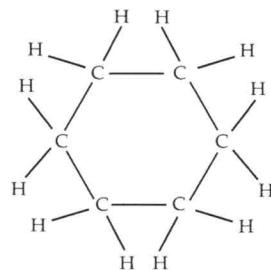
Example but-2-yne



Alicyclic hydrocarbons are formed when the ends of a chain are bonded to each other in a ring.

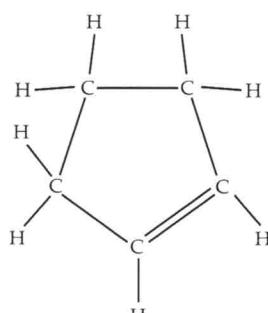
Cycloalkanes are saturated and have ring-like molecules.

Example cyclohexane, C_6H_{12}



Cycloalkenes are unsaturated and have ring like molecules.

Example cyclopentene, C_5H_8



Margarine is a butter substitute that contains both saturated and unsaturated hydrocarbons.



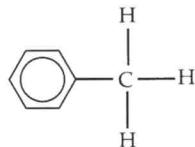
Aromatic hydrocarbons are hydrocarbons which contain a benzene ring.

Example

Benzene



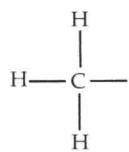
methyl benzene



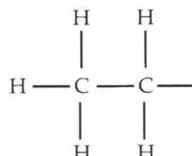
An alkyl group, or hydrocarbon radical, is one which has lost one hydrogen atom with its associated electrons. It acts as a substituent to a carbon chain or ring.

Example

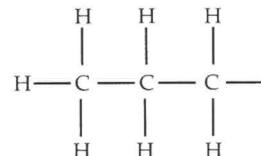
methyl



ethyl



propyl



Valence electrons not involved in bonding within the carbon-carbon chains are often used in forming bonds with other atoms, i.e. H, N and O or even in multiple bonds with other carbon atoms.

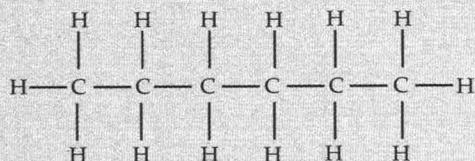
The principal classes of oxygen-containing organic compounds are alcohols, aldehydes, ketones, carboxylic acids and esters. The principal classes of nitrogen containing organic compounds are amines and amides. α -amino acids contain both the amine and carboxylic acid functional groups.

Line structures, or skeletal structures (not examinable)

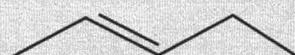
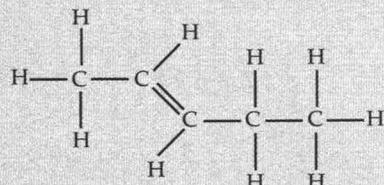
In addition to structural and condensed formulae it is possible to depict hydrocarbons using line structures. Here, a line represents a single bond. Junctions between lines are carbon atoms and it is assumed that each carbon atom has sufficient hydrogen atoms attached to it to give it four bonds. NB: These structures are not accepted in the examination. You should show all atoms and bonds.

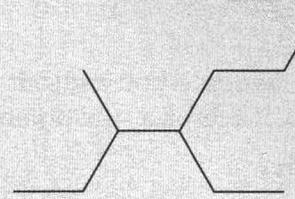
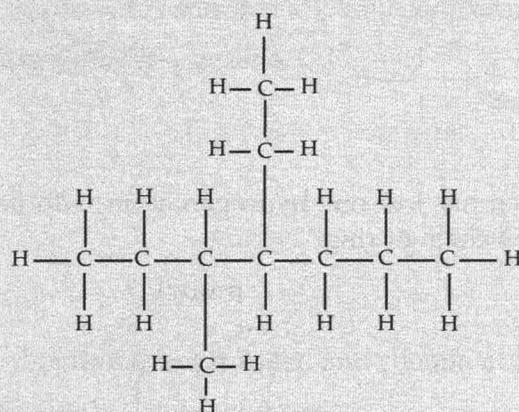
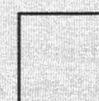
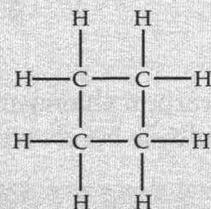
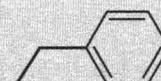
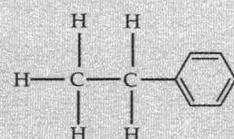
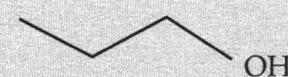
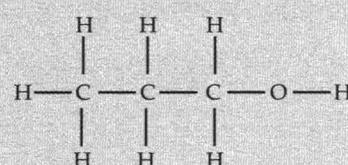
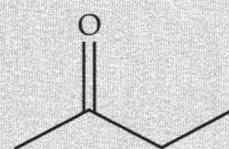
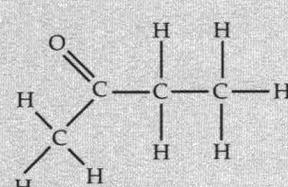
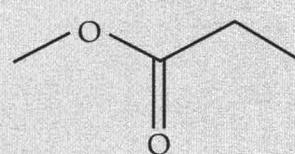
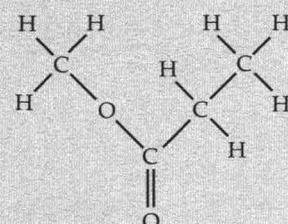
Examples

hexane



2-pentene (pent-2-ene)



4-ethyl-3-methylheptane**cyclobutane****ethylbenzene****propan-1-ol****butanone****methylpropanoate**

4.2 HOMOLOGOUS SERIES

A group or class of compounds related to each other by a general molecular formula constitutes an homologous series.

Each member of the series differs from the next member in the series by having an extra CH_2 in their formula and is called a Homologue.

All the members of the series, or homologues, have the same general molecular formula. For example alkanes, $\text{C}_n\text{H}_{2n+2}$ which refers to the alkane chain.

	Full structural formulae	Semi-structural formulae and condensed formulae
Methane	<pre> H H—C—H H </pre>	CH_4
Ethane	<pre> H H H—C—C—H H H </pre>	CH_3CH_3
Propane	<pre> H H H H—C—C—C—H H H H </pre>	$\text{CH}_3\text{CH}_2\text{CH}_3$
Butane	<pre> H H H H H—C—C—C—C—H H H H </pre>	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ or $\text{CH}_3(\text{CH}_2)_2\text{CH}_3$
Pentane	<pre> H H H H H H—C—C—C—C—C—H H H H </pre>	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ or $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$
Hexane	<pre> H H H H H H H—C—C—C—C—C—C—H H H H </pre>	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ or $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$
Heptane	<pre> H H H H H H H H—C—C—C—C—C—C—C—H H H H </pre>	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ or $\text{CH}_3(\text{CH}_2)_5\text{CH}_3$
Octane	<pre> H H H H H H H H H—C—C—C—C—C—C—C—C—H H H H </pre>	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ or $\text{CH}_3(\text{CH}_2)_6\text{CH}_3$

Homologues have the same functional group(s) and similar chemical properties

There is a regular trend in their physical properties, such as the increase in melting points and boiling points. This is due to increased dispersion forces as the molar mass increases.

Example

	methanol	ethanol	propan-1-ol	butan-1-ol
Boiling point (°C)	64.7	78.3	97.2	117.7

Alcohols have hydrogen bonding as their predominant intermolecular forces, but increasing chain length increases dispersion forces so their boiling points increase accordingly.

They also become less soluble in water as the proportion of the molecule that is non-polar increases with increasing chain length, i.e. butan-1-ol is less soluble than methanol.

4.3 FUNCTIONAL GROUPS

Each homologous series is characterised by a particular group which is specific to that particular series only. This characteristic is known as the Functional Group.

A functional group is a non-hydrocarbon part of an organic molecule or an alkyl group. These functional groups can contribute to the organic molecule's characteristic chemical properties. In addition they can influence physical properties, since they dictate the intermolecular forces present.

	General formulae	Naming suffix (prefix)	Example	Structural formula (showing bonds)
Alkanes	$C_n H_{2n+2}$	-ane	propane $CH_3CH_2CH_3$	
Alkyl group	$C_n H_{2n+1}$	-yl	propyl $CH_3CH_2CH_2-$	
Alicyclic cycloalkanes cycloalkenes	$C_n H_{2n}$ $C_n H_{2n-2}$	cyclo- -ane cyclo- -ene	cyclobutane cyclobutene 	
Halogenoalkanes (alkyl halides)	R-X X is a halogen	halo-	2-chloropropane $CH_3CHClCH_3$	
Alkenes	$C_n H_{2n}$	-ene	propene CH_2CHCH_3	
Alcohols	R-OH	-ol (hydroxy)	propan-1-ol $CH_3CH_2CH_2OH$	

	General formulae	Naming suffix (prefix)	Example	Structural formula (showing bonds)
Aldehydes	R-CHO	-al (formyl-)	propanal $\text{CH}_3\text{CH}_2\text{CHO}$	<pre> H H H—C—C—C=O H H </pre>
Ketones	R-COR'	-one (oxo-)	propanone CH_3COCH_3	<pre> O C C—H H </pre>
Carboxylic acids	R-COOH	-oic acid	propanoic acid $\text{CH}_3\text{CH}_2\text{COOH}$	<pre> H H H H C—C—C=O O </pre>
Esters	R-COOR'	-yl -oate	methyl propanoate $\text{CH}_3\text{CH}_2\text{COOCH}_3$	<pre> H H H H C—C—C=O O H </pre>
Amines	R-NH ₂	-amine (amino-)	1-propanamine $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	<pre> H H H H H H C—C—C—N H </pre>
α -amino acids	R(NH ₂)COOH	amino- -oic acid	2-amino-propanoic acid $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$	<pre> H H H H C—C—C=O O H </pre>
Amides	R-CONH ₂	-amide (amido)	propanamide $\text{CH}_3\text{CH}_2\text{CONH}_2$	<pre> H H H H C—C—C=O N—H </pre>
Nitro	R-NO ₂	nitro-	nitrobenzene $\text{C}_6\text{H}_5\text{NO}_2$	

4.4 NOMENCLATURE (NAMING OF ORGANIC COMPOUNDS)

Many organic compounds have names derived from the names of their corresponding alkanes.

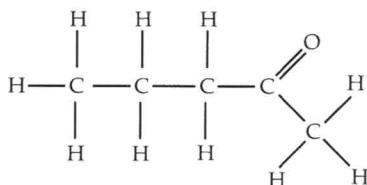
The Rules

- Count the longest continuous chain of carbon atoms that contains the main functional group. This give you the stem name:

No of C's	1	2	3	4	5	6	7	8
Stem	meth-	eth-	prop-	but-	pent-	hex-	hept-	oct-

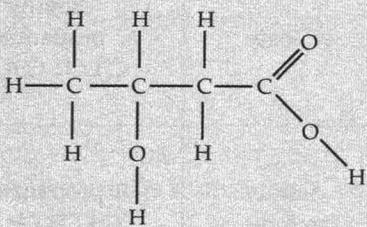
2. The main functional group of the molecule provides the end of the name, or the suffix.
3. Number the longest carbon chain so that it gives the functional group the lowest number.

Example pentan-2-one rather than pentan-4-one

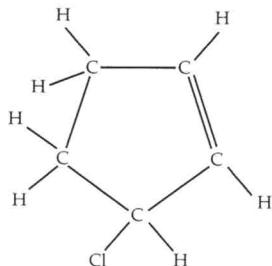


4. Any side chains (alkyl groups) or less important functional groups are included alphabetically as prefixes at the start of the name and given numbers corresponding to the carbon to which they are attached.

Example 3-hydroxybutanoic acid, since, -COOH take precedence over -OH



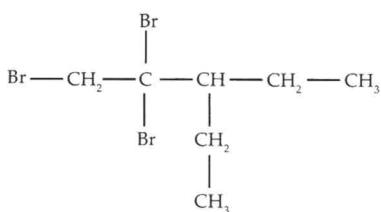
Example 3-chlorocyclopentene



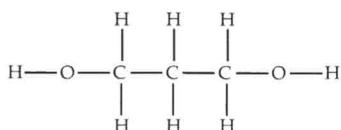
N.B. With unsaturated cyclic compounds counting starts before the double or triple bond.

5. If there is more than one of the same side chains or functional groups use di-, tri-, tetra- etc.. before their part of the name. These do not count towards the alphabetical order.

Example 1,2,2-tribromo-3-ethylpentane

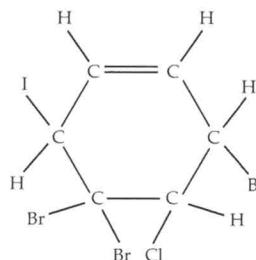


Example propane-1,3-diol



Example

4,4,6-tribromo-5-chloro-3-iodocyclohexene



IUPAC priority of functional groups

most important

carboxylic acids
esters
amides
aldehydes
ketones
alcohols
amines
alkenes
alkynes
alkanes

**4.5 ISOMERS**

Isomers are substances that have the same molecular formula, but a different structural formula.

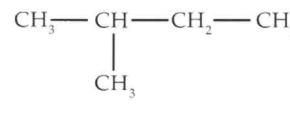
4.5.1 Structural isomers

There are two main types of structural isomers.

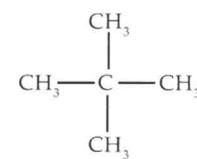
Chain structural isomers have the same molecular formula but different chain length.

Example

pentane



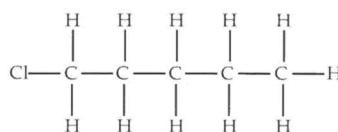
methylbutane



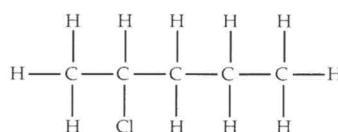
dimethylpropane

These have similar chemical properties but different physical properties because their molecules are a different shape.

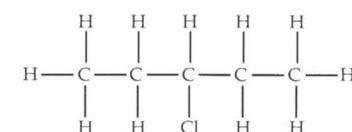
Position structural isomers have the same molecular formula but with functional groups attached at different parts of the chain.

Examples

1-chloropentane



2-chloropentane



3-chloropentane

These have different physical properties and their chemical properties are often different too.

4.5.2 Cis-trans isomerism (Geometric isomers)

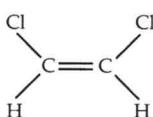
Geometric isomers have the same molecular formula and the atoms are connected in the same way but they are arranged differently in space.

They can only exist where there is a carbon to carbon double bond (as this restricts rotation) and where there are two different radicals attached to each of the double bonded carbon atoms.

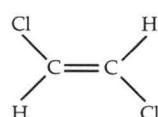
cis isomers have similar groups on the same side of the double bond.

trans isomers have similar groups attached diagonally opposite across the double bond.

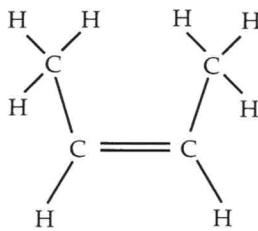
Example



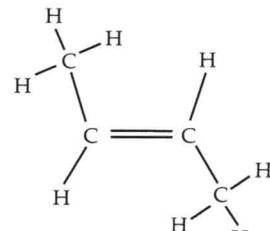
cis-1,2-dichloroethene



trans-1,2-dichloroethene



cis-but-2-ene



trans-but-2-ene

Geometric isomers have different physical properties because the different positions of the groups affect the shape and hence the intermolecular forces present.

Their chemical properties are usually similar, but this depends upon the relative position of the groups present.

4.6 PROPERTIES, PREPARATION AND REACTIONS OF THE HYDROCARBONS

4.6.1 Alkanes

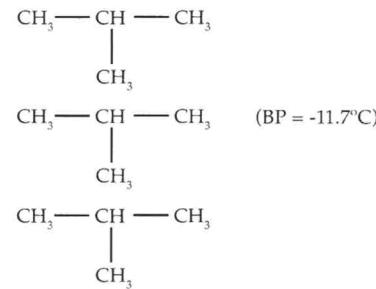
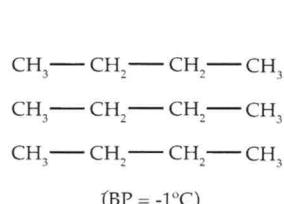
Alkanes are hydrocarbons with the general formula C_nH_{2n+2} .

Every carbon atom has four single bonds connected to other atoms.

The melting and boiling points of alkanes increases as their molecular mass increases since dispersion forces become greater with increasing chain length.

Their melting and boiling points decrease as their chains become more branched. There is less opportunity for dispersion forces to have an effect as the molecules aren't able to get close enough together.

Example butane versus methylpropane



Dispersion forces are most effective when molecules can get close together

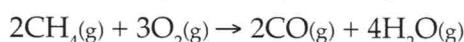
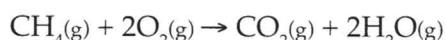
Branching prevents molecules from getting close together so dispersion forces are less effective

Reactions of alkanes

Combustion

Alkanes combust in air to produce water and carbon dioxide (or carbon monoxide in limited oxygen).

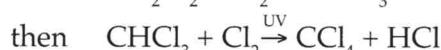
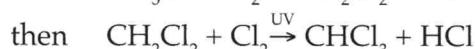
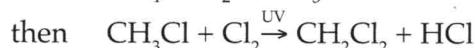
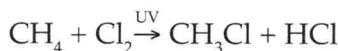
Example complete and incomplete combustion of methane



Halogenation

Alkanes undergo substitution reactions with halogens in the presence of UV light.

Example substitution of methane by chlorine

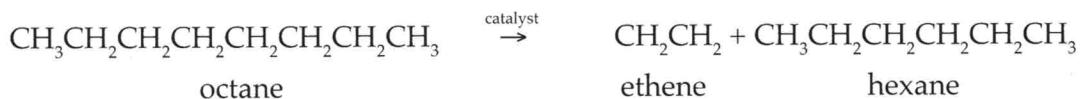


With plenty of Cl_2 and UV light the reaction is very difficult to stop and will proceed until all hydrogens have been substituted. So products are fairly unpredictable.

Cracking

The larger alkanes obtained from the distillation of petroleum can be split (or 'cracked') into smaller, more useful ones by thermal and catalytic cracking. This also produces unsaturated hydrocarbons like alkenes, used to make polymers.

Example



4.6.2 Alkenes

Alkenes are unsaturated hydrocarbons with the general formula C_nH_{2n} :

Their names are based on alkanes, but with the suffix -ene.

They possess at least one carbon-to-carbon double bond.

Alkenes have physical properties similar to alkanes.

Their chemical properties are largely influenced by the double bond, so they are more reactive than alkanes.

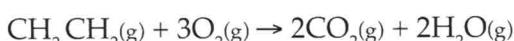
The presence of the double bond also gives rise to the possibility of geometric (cis-trans) isomerism.

Reactions of alkenes

Combustion

Alkenes combust in air to produce water and carbon dioxide (or carbon monoxide in limited oxygen).

Example

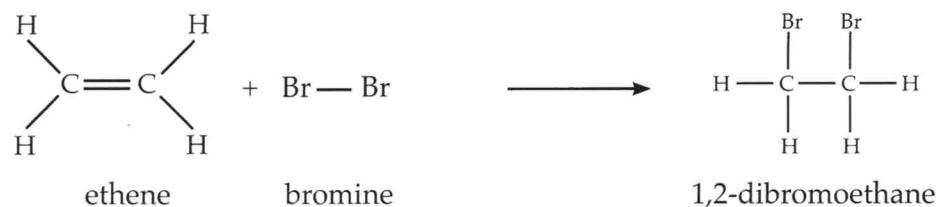


Addition reactions

Alkenes can undergo a variety of addition reactions, where two new atoms are added across the double bond, converting unsaturated compounds into saturated compounds.

Halogenation

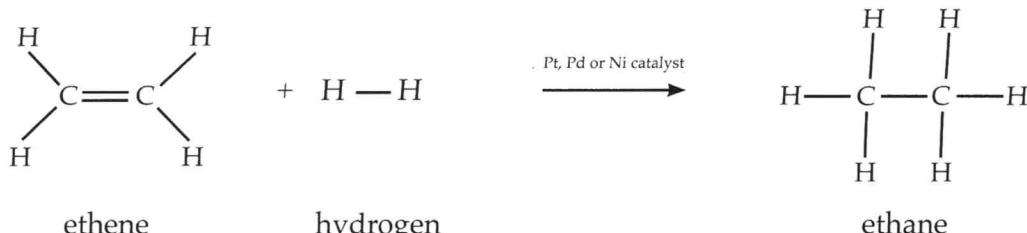
Example



N.B. Bromine water will be decolourised when shaken with an alkene (Br_2 is absorbed). This is a test for unsaturation.

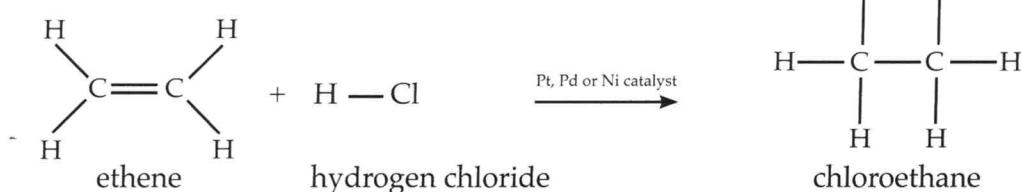
Hydrogenation (catalysts Pt, Pd, Ni)

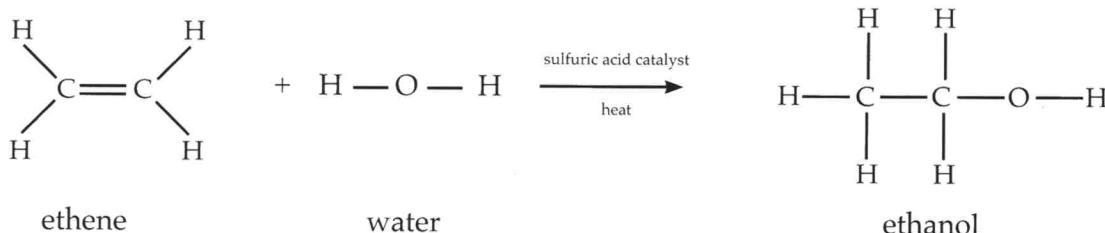
Example



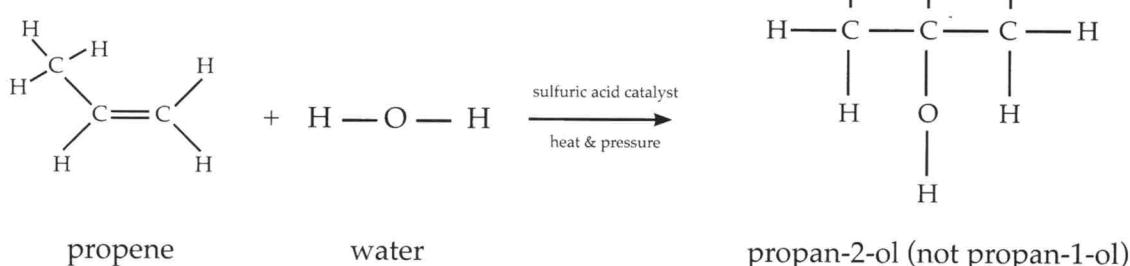
Hydrohalogenation

Example



Hydration (heat and conc. H_2SO_4 or H_3PO_4)**Example**

N.B. When hydrohalogens and water are added to asymmetrical alkenes, Markovnikov's rule is applied to predict the predominant product. The hydrogen atom of the added molecule will attach to the carbon with the greater number of hydrogens.

Example

In nature, unsaturated fatty acids in vegetable oils generally consist of hydrocarbon chains with cis double bonding. These unsaturated fatty acids are often hydrogenated to produce saturated fatty acids which are softer and have lower melting points. Unfortunately, this process can result in cis double bonds becoming trans double bonds which are thought to contribute to heart disease.

4.6.3 Halogenoalkanes (alkyl halides/haloalkanes)

Halogenoalkanes are hydrocarbons which contain one or more halogen atoms attached in place of hydrogen.

Example

chloromethane dichloromethane trichloromethane tetrachloromethane

The presence of halogen atoms can produce polar or non-polar molecules, depending upon their position and the molecule's shape. Chloromethane, dichloromethane and trichloromethane are polar since they have polar bonds and are asymmetrical. Tetrachloromethane is symmetrical, so its four polar bonds do not contribute to an overall polarity.

Some halogenoalkanes can have dipole-dipole bonding in addition to dispersion forces. These generally exhibit low melting and boiling points and make good solvents.

Preparation of halogenoalkanes**Halogenation of alkanes (see 4.6.1)**

This substitution is difficult to control and multiple substitutions often occur.

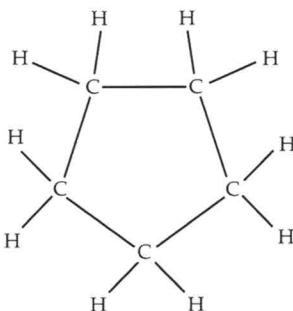
Hydrohalogenation of alkenes (see 4.6.2)

4.6.4 Alicyclic hydrocarbons

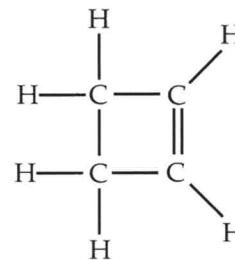
Alicyclic hydrocarbons form closed rings with as few as 3 carbon atoms.

They can be saturated cycloalkanes or unsaturated cycloalkenes.

Example



cyclopentane



cyclobutene

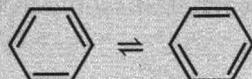
Alicyclic hydrocarbons have similar physical properties to their corresponding straight chain and branched hydrocarbons.

They undergo similar chemical reactions to those of their corresponding straight chain and branched chain hydrocarbons.

4.6.5 Aromatic hydrocarbons (arenes)

Aromatic hydrocarbons are cyclic hydrocarbons containing the characteristic benzene ring.

Benzene is a planar molecule of six carbon atoms in a ring. Kekulé's original structure below suggested that there must be alternating single and double bonds, but he found each of the carbon to carbon bonds to be equivalent. He later proposed that benzene resonates between two structures, with the bonds being single half the time and double half the time.



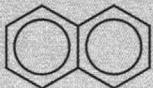
Benzene's stability and inability to readily undergo addition reactions indicates a different bonding arrangement. It is thought to be a structure with six identical carbon to carbon bonds having a bond length somewhere between that of a single bond and a double bond, with an additional six delocalised electrons not linked to any particular carbon atom.

We represent it in equations as C_6H_6 or structurally as:



Aromatic compounds have relatively low melting and boiling points due to their predominantly weak dispersion forces. They tend to be insoluble in water as the benzene ring is non-polar.

Naphthalene is a benzene derivative consisting of two joined benzene rings.



Moth balls contain naphthalene which is toxic to insects. It sublimes directly from solid to gas due to its having weak dispersion forces.

Reactions of aromatic hydrocarbons

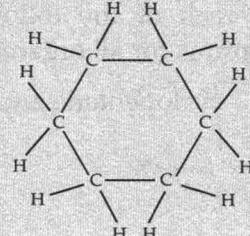
Benzene and molecules containing the benzene ring do not readily undergo the addition reactions characteristic of alkenes.

Benzene and its derivatives undergo substitution reactions.

Hydrogenation



benzene

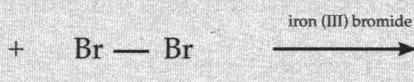


cyclohexane

Halogenation



benzene



bromine



bromobenzene

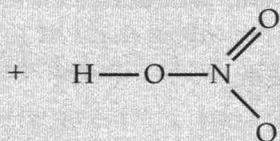


hydrogen bromide

Nitration

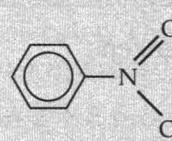


benzene



nitric acid

sulfuric acid



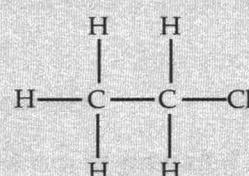
nitrobenzene

water

Alkylation

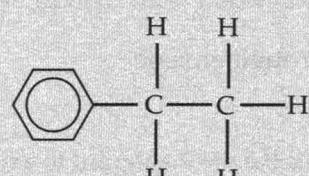


benzene

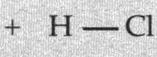


chloroethane

aluminium chloride

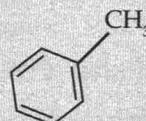


ethylbenzene

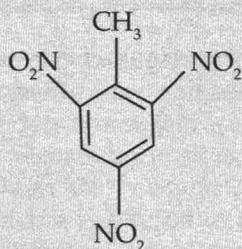


hydrogen chloride

Methyl benzene is also known as toluene, commonly used as a paint thinner.



Trinitrotoluene, or TNT, is methylbenzene with three NO_2 functional groups substituted onto the benzene ring. Its IUPAC name is 2-methyl-1,3,5-trinitrobenzene and it is an explosive.



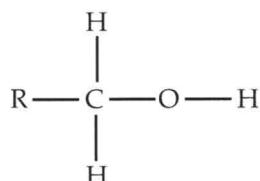
4.7 PROPERTIES, PREPARATION AND REACTIONS OF ALCOHOLS

Alcohols are alkanes containing the hydroxyl group, -OH.

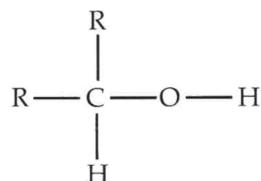
The homologous series has the general formula $C_nH_{2n+1}OH$

Alcohols are classified as primary (1°), secondary (2°) or tertiary (3°) depending upon how many alkyl groups (R) are attached to the carbon atom the hydroxyl group -OH is bonded to.

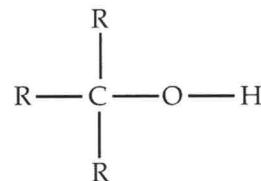
Example



1° has one alkyl group attached



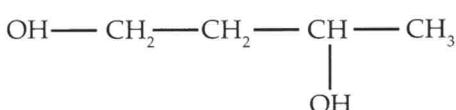
2° has two alkyl groups



3° has three alkyl groups

Alcohols may contain more than one hydroxyl group.

Example



butan-1,3-diol

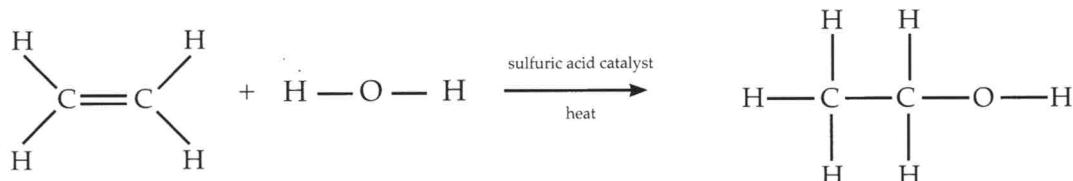
The physical properties of alcohols are influenced by the presence of the polar -OH group which allows them to form hydrogen bonds between molecules. The presence of hydrogen bonding gives alcohols higher boiling points than non-polar hydrocarbons.

Alcohols with a smaller carbon chain (e.g. methanol, ethanol and propanol) are miscible with water since hydrogen bonds can form between the -OH and H_2O , allowing them to mix.

Larger alcohols are mainly non-polar due to the long carbon chain and so form mainly dispersion forces with water. So as alcohols increase in size they become less miscible with H_2O .

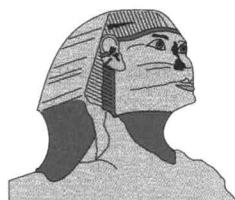
Preparation of alcohols

In industry, alcohols can be prepared by the hydration of alkenes. (see 4.6.2)



Ethanol is also made by the fermentation of carbohydrates, catalysed by enzymes from yeast.

Example Glucose fermenting to form ethanol and carbon dioxide.



The fermentation of plant sugars to form ethanol is utilised in the production of alcoholic drinks like beer and spirits, where the sugars are from grain. With wine and ciders, the sugars are from fruits. The oldest documentation referring to the fermentation of alcohol for human consumption can be traced back at least six thousand years! In Egyptian times workers were paid in beer which was offered to the gods and consumed several times per day by men, women and children.

Reactions of alcohols

Combustion

All alcohols can undergo complete combustion in excess oxygen to produce carbon dioxide and water.

Example Ethanol burning in oxygen



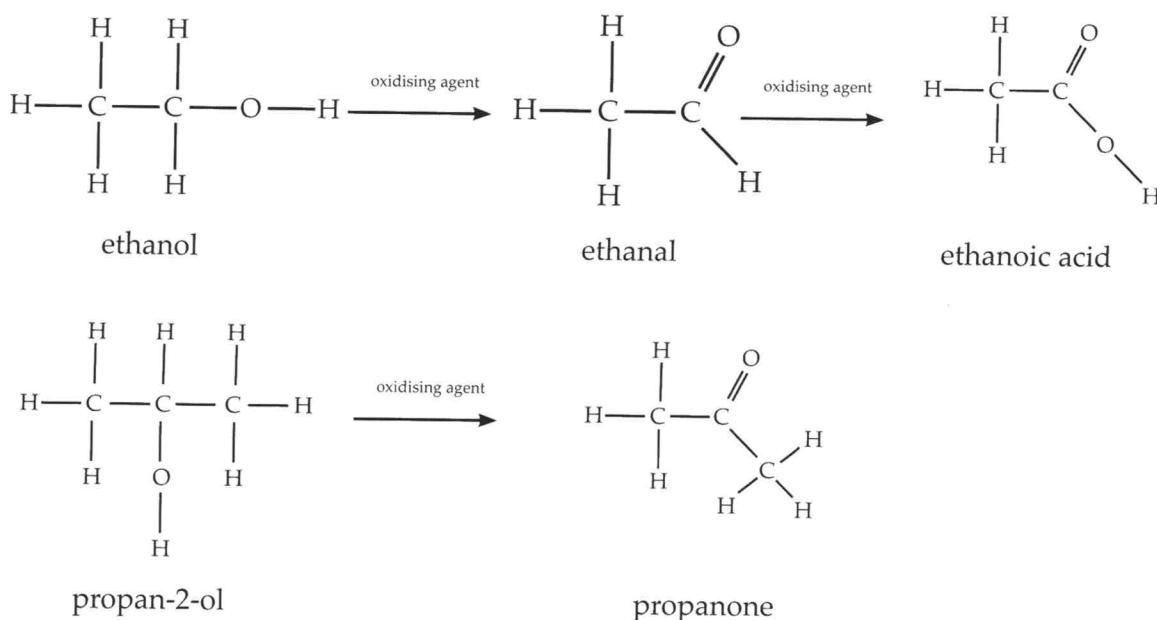
Oxidation

Primary and secondary alcohols can be oxidised by oxidising agents, including acidified MnO_4^- and $\text{Cr}_2\text{O}_7^{2-}$. Oxidation of primary alcohols firstly produces aldehydes and further oxidation results in the formation of carboxylic acids. The oxidation of secondary alcohols produces ketones. Remember oxidation is defined as a rise in oxidation number, addition of oxygen or loss of hydrogen. Reduction is the lowering of oxidation number, loss of oxygen or gain in hydrogen. In this section we will make extensive use of these full definitions.

With primary and secondary alcohols there is at least one hydrogen atom attached to the carbon atom attached to the $-\text{OH}$. The oxidising agent can remove this hydrogen and the hydrogen from the $-\text{OH}$ group which enables oxidation to occur. It allows the carbon-to-oxygen double bond, or a carbonyl group, to form.

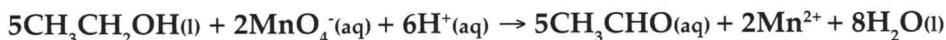
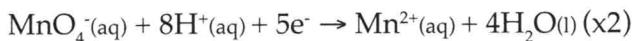
Tertiary alcohols do not have any hydrogen atoms attached to the carbon so they are not oxidised at all. The carbonyl group cannot form.

Examples



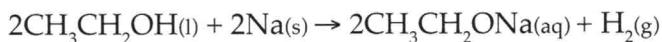
Vinegar is a solution of roughly 3-5% ethanoic acid in water. It is commonly used nowadays as a cooking ingredient but is making a resurgence as a mild household cleaning agent as people look to use less harsh chemicals in their homes. The ethanol in wines, ciders and even beer can be fermented to produce a great variety of flavoured vinegars, like white wine vinegar, red wine vinegar, apple cider vinegar and balsamic vinegar.

To write full balanced ionic equations for the oxidation of alcohols first write and balance the oxidation and reduction half equations (see Redox section) and then combine them in order to balance the number of electrons given out with those received.

Example**Reaction with sodium**

Alcohols can react with sodium to produce hydrogen gas and a sodium alkoxide.

Example sodium added to ethanol produces sodium ethoxide and hydrogen

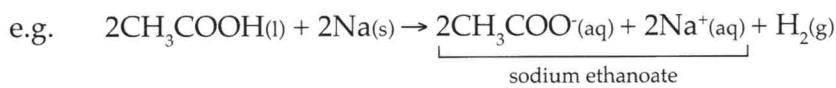


This reaction can be used to test for the presence of the hydroxy group in alcohols.

The order of reactivity of alcohols with sodium metal is primary > secondary > tertiary.

This is due to the decreased exposure of the hydroxy group for reaction as more alkyl groups are attached to the carbon bearing the hydroxy group.

Sodium also reacts with carboxylic acids to give the sodium salt.

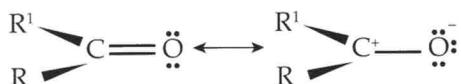


4.8 PROPERTIES, PREPARATION AND REACTIONS OF ALDEHYDES AND KETONES

The carbonyl group

The carbonyl group is a functional group with a carbon atom double bonded to an oxygen atom. Carboxylic acids, aldehydes, ketones, esters and amides contain the carbonyl group and it largely influences the properties of these compounds.

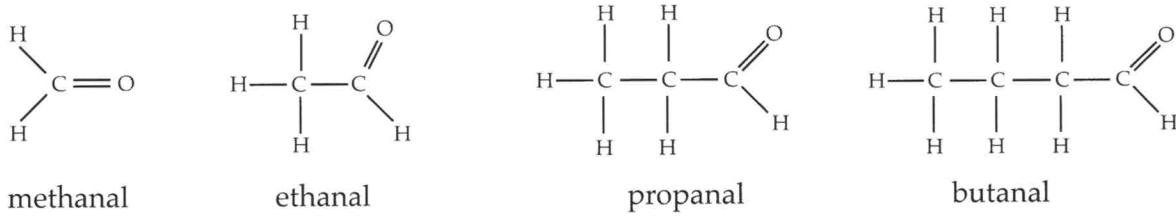
The oxygen atom is more electronegative than the carbon atom and produces a polar bond so dipole-dipole interactions between molecules can occur. Molecules that have a hydrogen atom bonded directly to a nitrogen, oxygen or fluorine atom can form hydrogen bonds with the oxygen of the carbonyl group.



4.8.1 Aldehydes

Aldehydes are oxidised products of primary alcohols and have a carbonyl group ($\text{C}=\text{O}$) at their terminal (end) carbon atom. They have the general formula $\text{R}-\text{CHO}$.

Examples



Lower molar mass aldehydes are typically gases at room temperature but larger ones are liquids due to increased dispersion forces from longer chains.

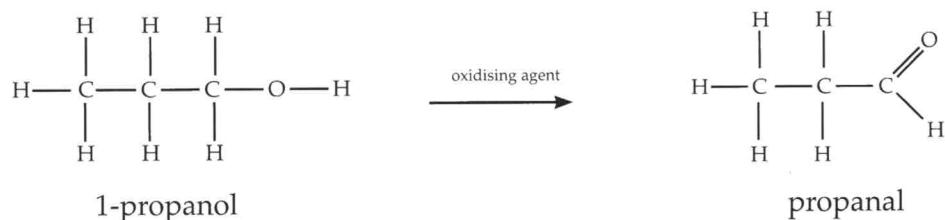
Aldehydes are polar molecules due to the presence of the carbonyl group. In addition to dispersion forces they can have dipole-dipole interactions with neighbouring molecules. Their melting and boiling points are low but still higher than similarly-sized hydrocarbons due to their polarity. Since they cannot hydrogen bond with each other they have lower melting and boiling points than corresponding alcohols.

Smaller aldehydes are soluble in water but, as the chain gets longer, their miscibility decreases. Their carbonyl group enables them to hydrogen bond with water molecules. As the hydrocarbon portion of the molecule increases in length it can only form dispersion forces with water, which do not provide enough energy on formation to break the hydrogen bonds between water molecules.

Preparation of aldehydes

Aldehydes are prepared in the laboratory by oxidation of primary alcohols, but they must be isolated once produced so that they do not oxidise further to carboxylic acids.

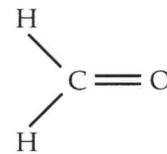
Example



Methanal is the simplest aldehyde commonly known as formaldehyde.

Formalin is a solution of formaldehyde in water used as a disinfectant and for the preservation of biological specimens.

It is also used in nail varnish as a solvent, but it is a known carcinogen.

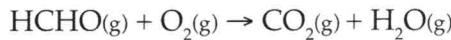


Reactions of aldehydes

Combustion

Aldehydes can burn completely in oxygen to produce carbon dioxide and water.

Example



Oxidation

Aldehydes can be oxidised to form carboxylic acids.

Example



N.B. No numbering is required to place the aldehyde and carboxylic acid groups as they must be on the end.

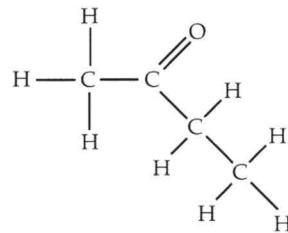
Reduction

Aldehydes can also be reduced to form primary alcohols using reducing agents such as LiAlH_4 and NaBH_4 .

4.8.2 Ketones

Ketones are oxidation products of secondary alcohols which have a carbonyl group within their carbon chain. They have the general formula $\text{R}-\text{COR}'$.

Example



butan-2-one

N.B. Numbering is required for ketones longer than three carbon atoms.

Ketones are liquids at room temperature with boiling points that increase with increasing chain length due to increased dispersion forces as the chains get longer.

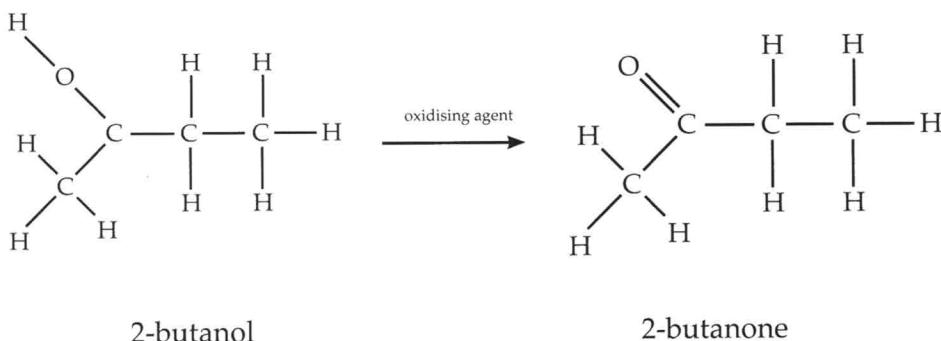
Ketones are polar molecules due to the presence of the carbonyl group (C=O). Like aldehydes, they can have dipole-dipole interactions with neighbouring molecules and have melting and boiling points higher than similarly-sized hydrocarbons. They have lower melting and boiling points than corresponding alcohols.

Like aldehydes, smaller ketones are soluble in water but as the chain gets longer their miscibility decreases. The smallest ketone is propanone (nail-varnish remover) which is an important solvent for organic compounds and is also miscible with water.

Preparation of ketones

Ketones are prepared in the laboratory by the oxidation of secondary alcohols. Unlike aldehydes, they are very difficult to oxidise further.

Example



Reactions of ketones

Combustion

Ketones can burn completely in oxygen to produce carbon dioxide and water.

Example



Reduction

Ketones can be reduced to secondary alcohols using reducing agents such as LiAlH_4 and NaBH_4 .

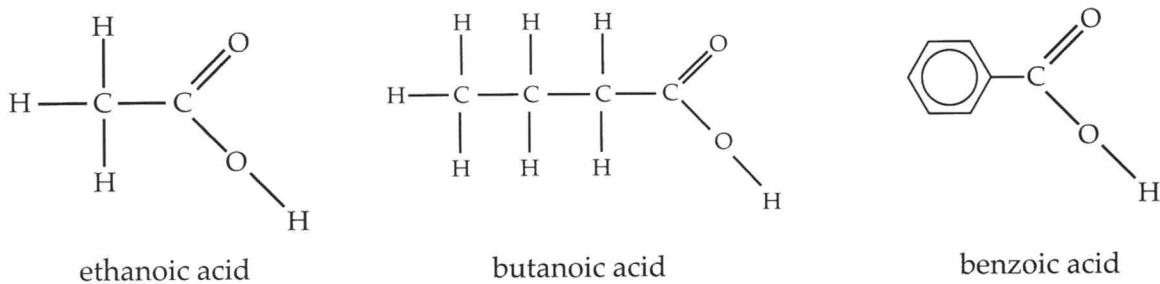
Ketones and oxoacids (carboxylic acids with an additional carbonyl group within the chain) are produced in the liver when the body burns fats for energy. This can occur in people who have diabetes when there is not enough insulin in their bodies to obtain energy from sugar. A build-up of ketones can lead to ketoacidosis which can be fatal if not treated.

4.9 PROPERTIES, PREPARATION AND REACTIONS OF CARBOXYLIC ACIDS AND ESTERS

4.9.1 Carboxylic acids

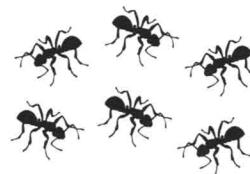
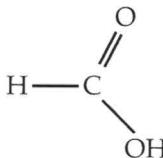
Carboxylic acids are formed by the replacement of a hydrogen atom with a carboxyl functional group -COOH group. The carboxyl group is always at the end of the molecule and it is the most important of the functional groups, so takes precedence when naming.

Example



Carboxylic acids are polar molecules due to the presence of the carbonyl group ($\text{C}=\text{O}$) and can form hydrogen bonds with water. They are typically soluble in water. Once again their solubility decreases with the increasing length of their carbon chain. If the strength of the dispersion forces between these larger carboxylic acid molecules is greater than that of the possible hydrogen bonds that could form with water then the carboxylic acid will not dissolve. They have high melting and boiling points due to hydrogen bonding.

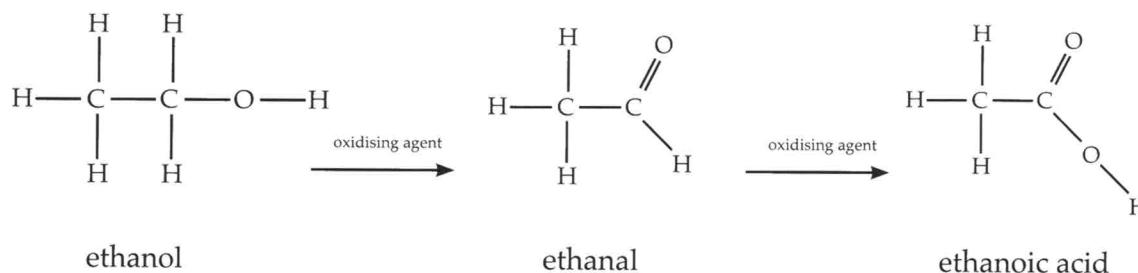
Methanoic acid, commonly called formic acid, is a pungent, clear liquid which was originally distilled from ants since it occurs naturally in their venom. 'Formica' is the Latin word for ant.



Preparation of carboxylic acids

Carboxylic acids can be prepared by the oxidation of primary alcohols or aldehydes.

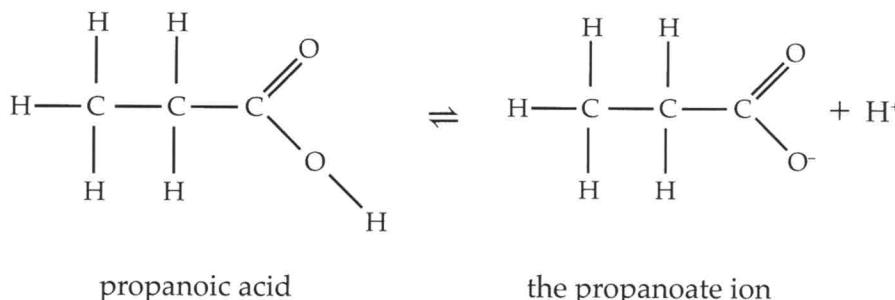
Example



Reactions of carboxylic acids

Carboxylic acids are weak acids and dissociate to a small extent into the H^+ ion and a carboxylate ion. They have the chemical properties of weak acids.

Example

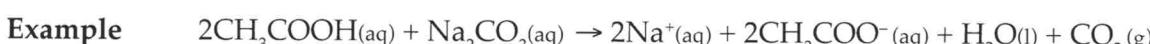


Neutralisation

Carboxylic acids undergo neutralisation reactions with alkalis to produce a salt and water.



They react with carbonates and hydrogencarbonates to produce a salt, water and carbon dioxide.



With reactive metals

They react with reactive metals to produce a soluble salt and hydrogen gas.

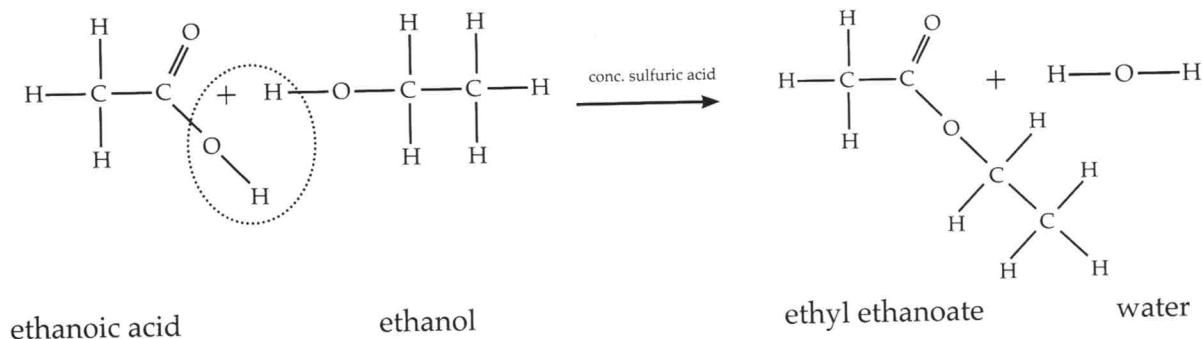
Example



Esterification

Carboxylic acids react with alcohols to produce esters. This reaction is called esterification. Concentrated sulfuric acid is used to link the alcohol and the carboxylic acid together by removing a water molecule. The H comes from the alcohol and the OH from the carboxylic acid.

Example



Reduction

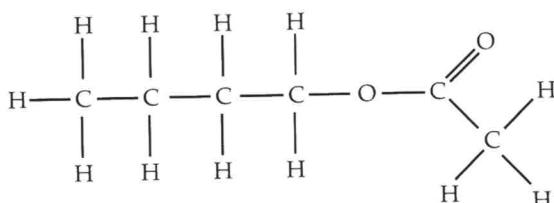
Carboxylic acids can be reduced back to alcohols using a very strong reducing agent like LiAlH_4 .

4.9.2 Esters

Esters have a sweet fruity smell and are found in nature in fruits and flowers. As such, they are used in perfumes and cosmetics and to flavour foods.

Esters contain the functional group $-\text{COO}-$ and have the general formula $\text{R}-\text{COOR}'$.

Example



butyl ethanoate

N.B. the alkyl prefix comes from the alcohol and the carboxylate suffix comes from the carboxylic acid.
Butyl ethanoate is prepared by reacting butanol and ethanoic acid.

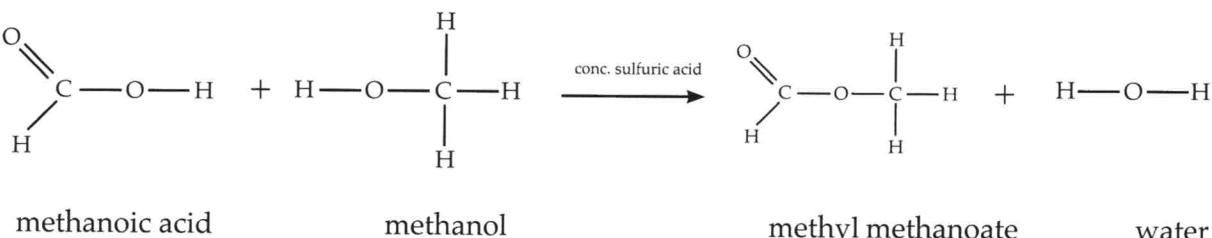
Esters are polar molecules though their melting and boiling points are quite low due to their having considerable non-polar chains. Dispersion and dipole-dipole forces exist between molecules. They tend to be liquids at room temperature but evaporate easily.

They are typically insoluble in water because their long non-polar chains overcome any hydrogen bonding. However, being polar, they are powerful solvents for many polar organic compounds. This makes them good solvents in paints and lacquers.

The ester functional group is also used in condensation polymerisation in the formation of polyesters.

Preparation of esters

Example



Esters are sweet smelling and are used in perfumery for their characteristic aromas.

pentyl ethanoate	pears
octyl ethanoate	oranges
pentyl butanoate	apricots / strawberries
3-methyl butyl ethanoate	bananas
methyl propyl methanoate	raspberry
ethyl butanoate	pineapple
methyl butanoate	apple
methyl salicylate	oil of wintergreen (Dencorub)

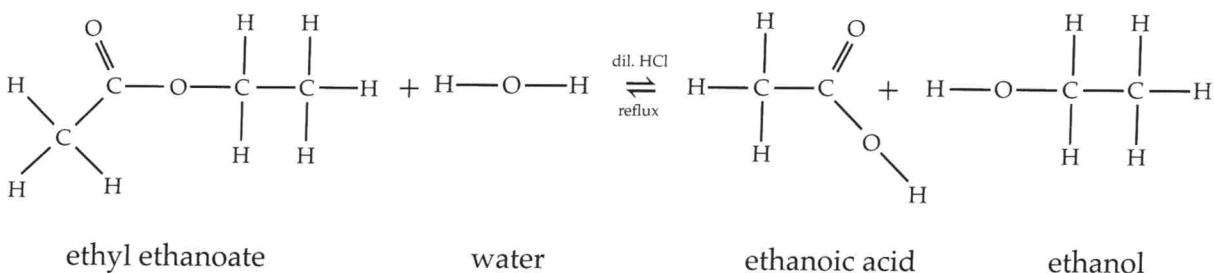
Reactions of esters

Hydrolysis

Esters can be hydrolysed to form alcohols and carboxylic acids.

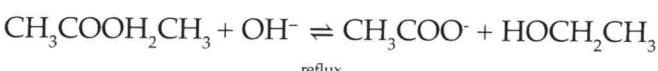
Acid hydrolysis splits the ester into an acid and an alcohol which is the reverse of the esterification reaction. The ester is refluxed with a dilute acid like hydrochloric or sulfuric acid.

Example



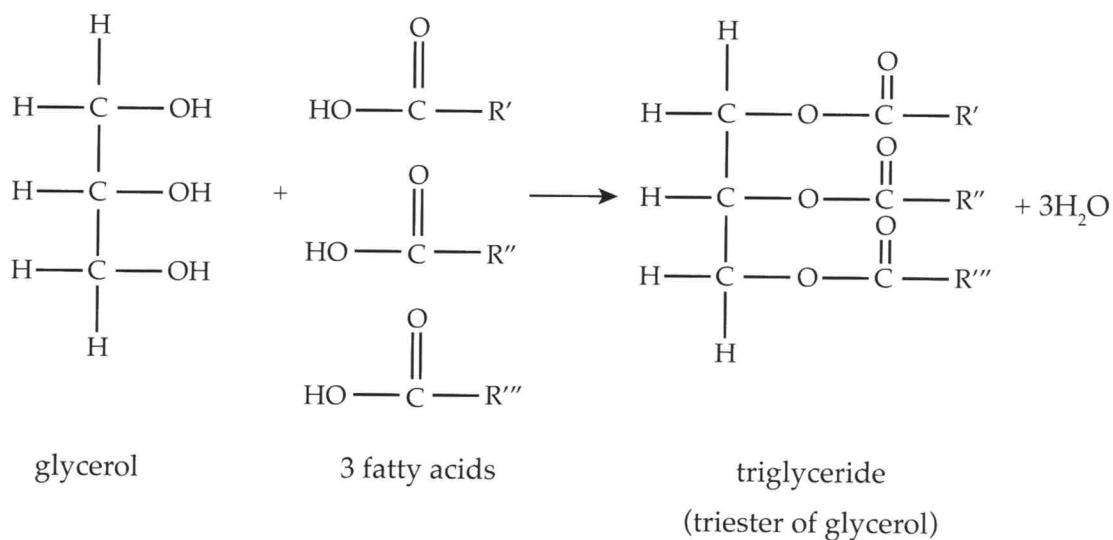
Alkaline hydrolysis splits the ester into an alcohol and a carboxylate ion. The ester is refluxed with a dilute alkali like sodium hydroxide.

Example



Fats and oils

Fats and oils (triglycerides) are esters of glycerol and fatty acids. Triglycerides can be made into soaps (see Soap Making).

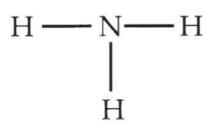


4.10 PROPERTIES, PREPARATION AND REACTIONS OF AMINES, AMIDES AND α -AMINO ACIDS.

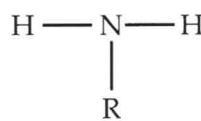
4.10.1 Amines

Amines are organic derivatives of ammonia, where one or more hydrogens are replaced by an organic group. They have the general formula R-NH₂.

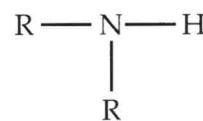
They are classified by the number of carbons attached to the nitrogen atom. R represents an alkyl group.



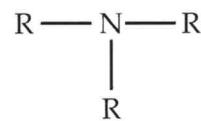
ammonia



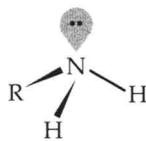
1° primary amine



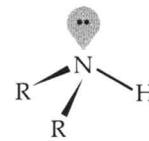
2° secondary amine



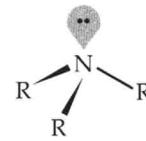
3° tertiary amine



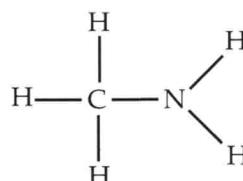
1° primary amine



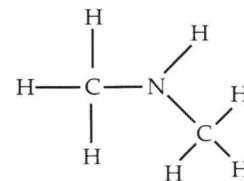
2° secondary amine



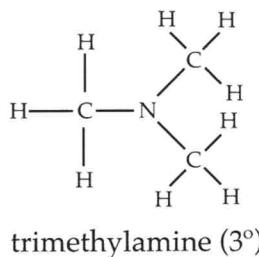
3° tertiary amine



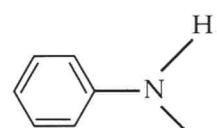
methylamine (1°)



dimethylamine (2°)

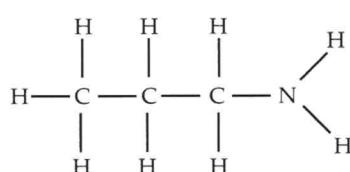
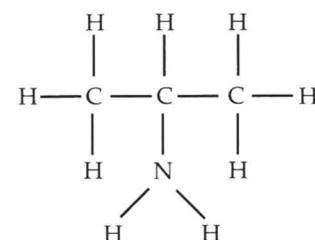


trimethylamine (3°)

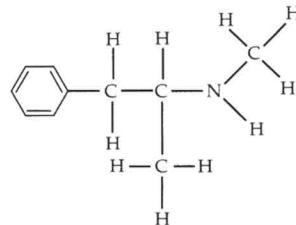


phenylamine (1°)

Alternative nomenclature

1-propanamine, propylamine
or amino propane2-propanamine, 2-propylamine
or 2-amino propane

Methylamine is used in the synthesis of many compounds including herbicides, fungicides and insecticides. It is also a precursor for the manufacture of the extremely dangerous addictive drug, methamphetamine or crystal meth shown.



Amines have relatively high melting and boiling points since they can form hydrogen bonds with each other, as well as dispersion forces and dipole-dipole interactions.

The boiling points of secondary amines are lower than the corresponding primary amines. Secondary amines form hydrogen bonds but have the nitrogen atom in the middle of the chain rather than at the end, which decreases dipole-dipole interactions and dispersion forces.

Tertiary amines do not have any hydrogen atoms attached directly to the nitrogen. They cannot form hydrogen bonds with each other and so their boiling points are much lower than both primary and secondary amines of similar size.

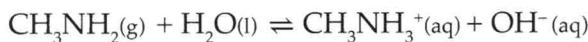
Small amines are soluble in water since the amine group can form hydrogen bonds with water molecules. Solubility decreases with increasing chain length, since the strength of the dispersion forces between these larger amine molecules is greater than that of the possible hydrogen bonds that could form with water.

Amines are found in nature as amino acids. Many are used as catalysts and solvents or in the manufacture of dyes, medicines and polymers.

Reactions of amines

Amines that are able to dissolve act as weak bases. They form alkaline solutions by accepting a proton from water, leaving hydroxide ions.

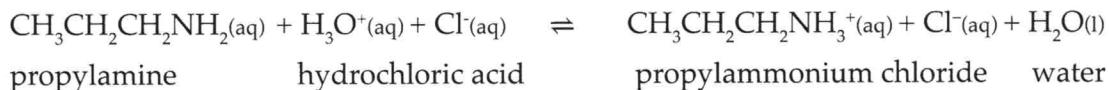
Example Hydrolysis of methylamine



Neutralisation

Amines react with acids to produce a salt and water.

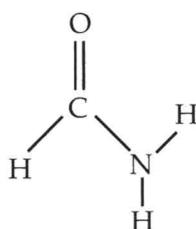
Example



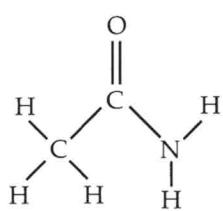
4.10.2 Amides

Amides are carboxylic acid derivatives, where the hydroxy group (-OH) is replaced by an amine group (-NH₂). They contain the functional group -CONH₂ and have the general formula R-CONH₂.

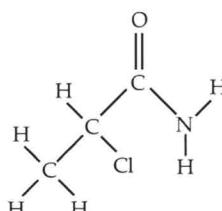
Examples



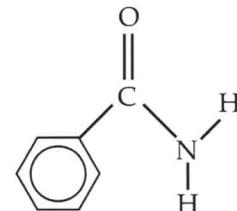
methanamide



ethanamide



2-chloropropanamide

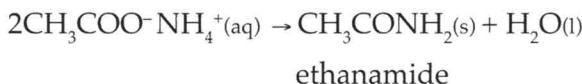
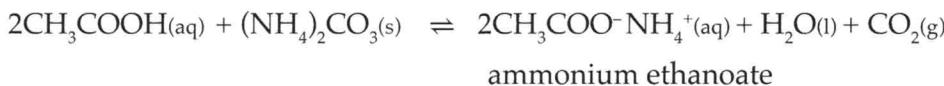


benzamide

Preparation of amides

Amides can be prepared in the laboratory by reacting carboxylic acids with ammonium carbonate to produce an ammonium salt and then heating it to remove water. Excess acid is required to stop any dissociation of the ammonium salt as it is heated.

Example Preparation of ethanamide



Reactions of amides

Amides do not behave as bases since proximity to the carbonyl group causes the lone pair of electrons on the nitrogen to become delocalised and not attractive to protons.

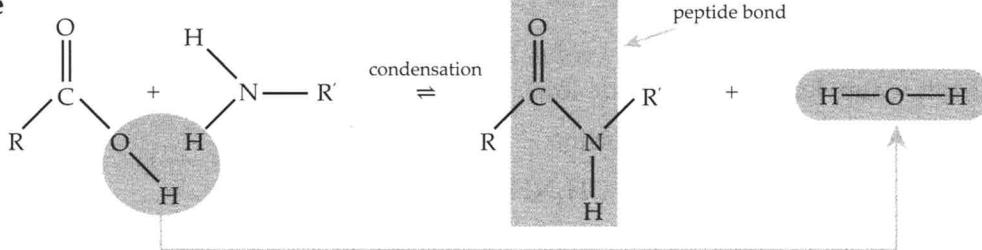
Reduction

Amides can be reduced to amines using reducing agents such as LiAlH_4 and NaBH_4 .

The amide bond

The amide bond occurs when the amine functional group reacts with the carboxylic acid functional group.

Example



When dicarboxylic acids or diamines react they can form polymers with long chains held together by amide bonds. They are called polyamides. Nylons and Kevlar are synthetic polyamides. (see 4.11.2)

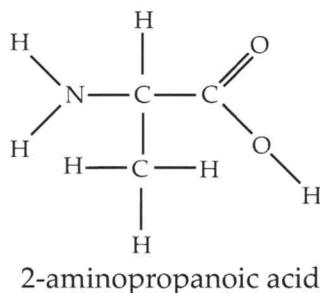
The amide bond can also form between amino acid molecules since they contain both amine and carboxylic acid functional groups at different ends of the molecule. In this case it is called a peptide bond and it produces proteins, which are natural polyamides. (see 4.11.3)

4.10.3 α -amino acids

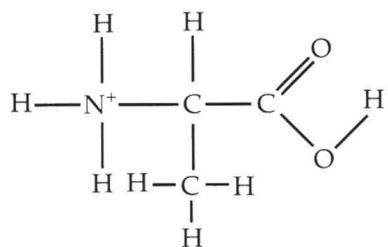
Amino acids are naturally occurring and are molecules that contain both the basic amine group $-\text{NH}_2$ and the acidic carboxyl group $-\text{COOH}$. This makes them amphoteric, i.e. they can both accept and donate protons.

If both the amino and the carboxyl groups are attached to the first or alpha (α) carbon atom they are called α -amino acids.

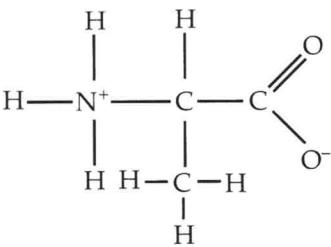
Example



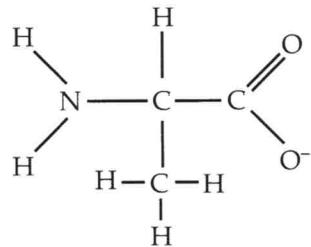
When solid and in solution they can exist as 'zwitterions' which are dipolar ions (have a positive and negative end). This explains their high melting and boiling points and their solubility in water.



acidic conditions
(proton accepted)



the zwitterion

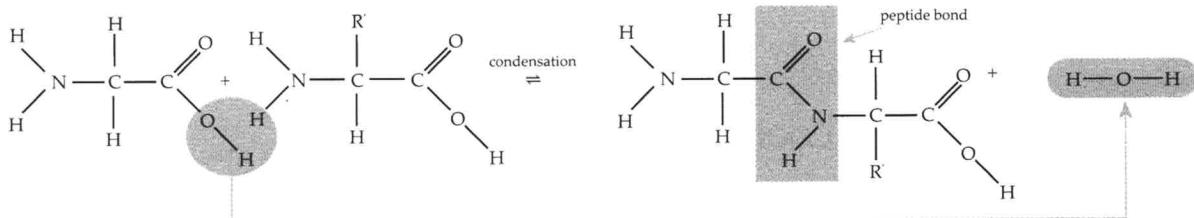


alkaline conditions
(proton donated)

α -amino acids are the building blocks of proteins

About 20 α -amino acids occur naturally and it is these that produce proteins essential to life. Amino acids join to make dipeptides in condensation reactions as shown below. Many amino acids produce polypeptides and these form proteins. (see 4.11.3).

Example

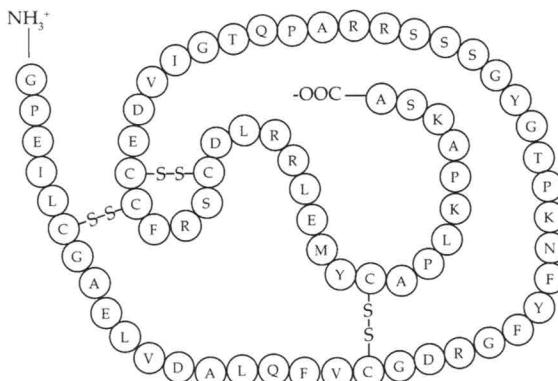


Peptides in sport

Peptides are small chains of amino acids not long enough to be considered full proteins. They are the building blocks that produce proteins.

In recent times athletes and body builders (and footballers) have been taking peptides as supplements. They enable the athlete to build muscle mass quickly and also assist in recovery from injuries. Peptides don't come with the side effects of steroids but many haven't yet been cleared for human use. They are difficult to detect in urine tests.

IGF, MGF and SARMs are some of the commonly used peptides. IGF is a chain of amino acids including isoleucine (I), glycine (G), alanine (A) and glutamic acid (E) shown using their one letter symbols below.



4.11 POLYMERS

Polymers are large organic molecules with very long chains, formed by joining up smaller units called monomers. This process is called polymerisation.

Natural polymers include proteins and starch. The synthetic polymers (often called plastics) include Teflon, polyethene, Nylon and polystyrene.

The physical properties of polymers can be explained from the type of bonding between the large polymer molecules.

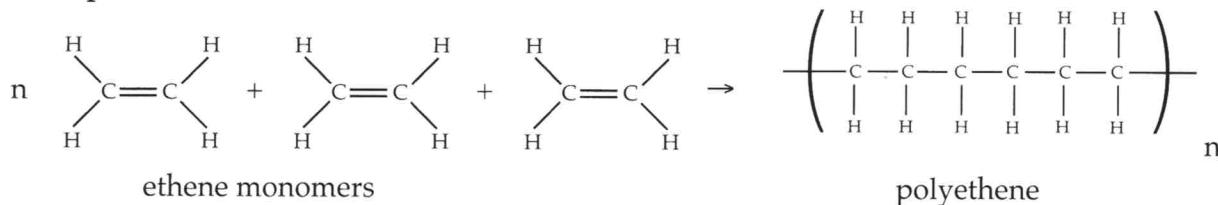
There are two main types of polymers: Addition polymers and Condensation polymers

4.11.1 Addition polymers

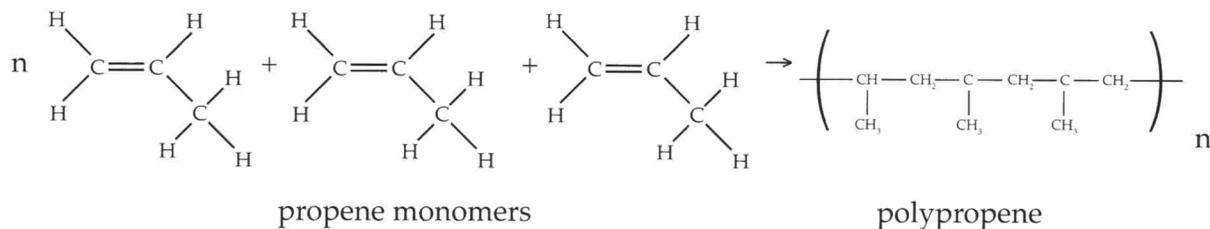
Addition polymers are formed from addition reactions, where the double bonds in alkenes open up to form long chains of carbon atoms. The structure of the alkene monomer contributes to the final structure and, therefore, the properties of the polymer.

In the example 'n' represents the number of monomers and the chain will be 'n' units long.

Example

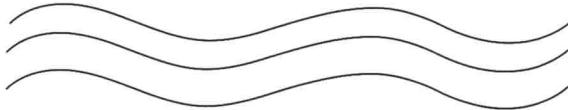


Branched chains

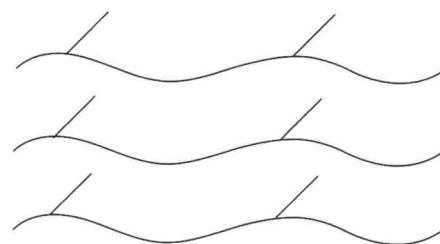


If the addition polymer is regular and unbranched the chains can get close together providing a larger surface area for dispersion forces between chains to occur. This contributes to higher melting points and greater strength.

If the polymer chains have branching along the chain this decreases the strength of dispersion forces, as the chains can't get closer together.

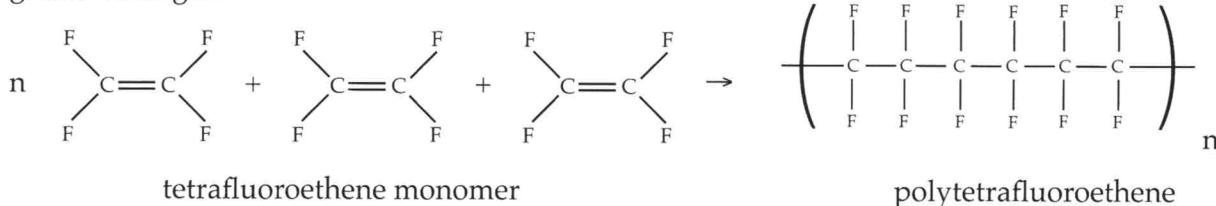


Unbranched chains can get closer which increases dispersion forces

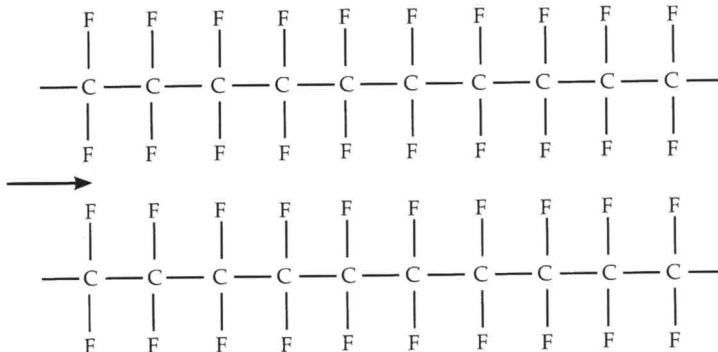


Branched chains are further apart so dispersion forces are decreased

If there are groups like halogens attached to the chains this can allow dispersion forces of even greater strength.



Dispersion forces
are possible between
polymer chains



Examples and uses of addition polymers

Name	Structure & bonding	Properties	Uses
Polyethene (polythene)	$\left(\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{C} & -\text{C}- \\ & \\ \text{H} & \text{H} \end{array} \right)_n$	Low density polyethene has random branched chains and low dispersion forces. High density polyethene is more regularly arranged and larger dispersion forces.	LDPE's have low melting points, and are weak and flexible. HDPE's have higher melting points and are stronger.
Polychloroethene (polyvinylchloride) PVC	$\left(\begin{array}{c} \text{H} & \text{Cl} \\ & \\ \text{C} & -\text{C}- \\ & \\ \text{H} & \text{H} \end{array} \right)_n$	Polar C-Cl bonds allow for dipole-dipole interactions.	Hard and rigid. Can be made softer with plasticisers.
Polytetrafluoroethene PTFE	$\left(\begin{array}{c} \text{F} & \text{F} \\ & \\ \text{C} & -\text{C}- \\ & \\ \text{F} & \text{F} \end{array} \right)_n$	Highly polar C-F bonds cause increased dispersion forces.	Non-stick, high melting point and very strong.
Polyphenylethene (polystyrene)	$\left(\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{C} & -\text{C}- \\ & \\ \text{H} & \text{C}_6\text{H}_5 \end{array} \right)_n$	Benzene rings along the chains keep chains apart but contribute to dispersion forces.	Can be expanded on production to low density. Brittle.

4.11.2 Condensation polymers

Condensation polymerisation usually occurs between two different types of monomers that contain two functional groups. Water is eliminated through a condensation reaction and bonds are formed to join monomers together.

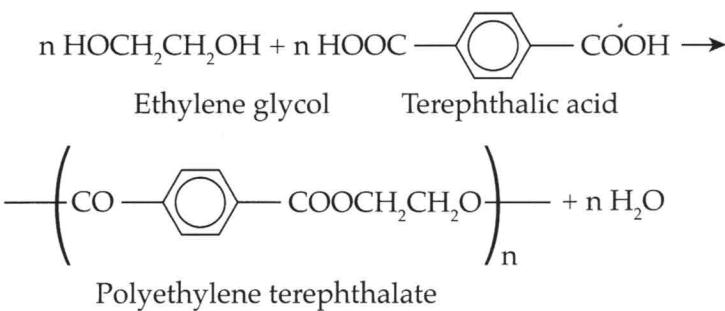
Condensation reactions can be used to produce polyesters and polyamides.

Polyesters

Polyesters result from condensation reactions between diols (alcohols with two hydroxyl groups) and dicarboxylic acids (carboxylic acids with two carboxyl groups). The carboxyl groups and the hydroxyl groups form ester links to produce the polymer chain.

Example

Polyethylene terephthalate [PET] is a strong polyester used in fibres for clothing, transparent drink bottles and food containers.

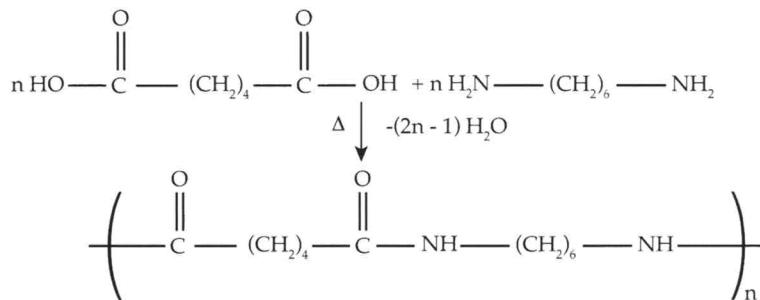


Like addition polymers, the properties of a condensation polymers are determined by the structure of the polymer. Polyester chains contain the carbonyl group, C=O, at regular intervals along the chain which allows dipole-dipole interactions between chains. These contribute to the strength of the polymer.

Polyamides

Polyamides result from the condensation reactions between dicarboxylic acids and diamines (amines with two amino groups). The amino groups and the carboxyl groups form amide links to produce the polymer chain.

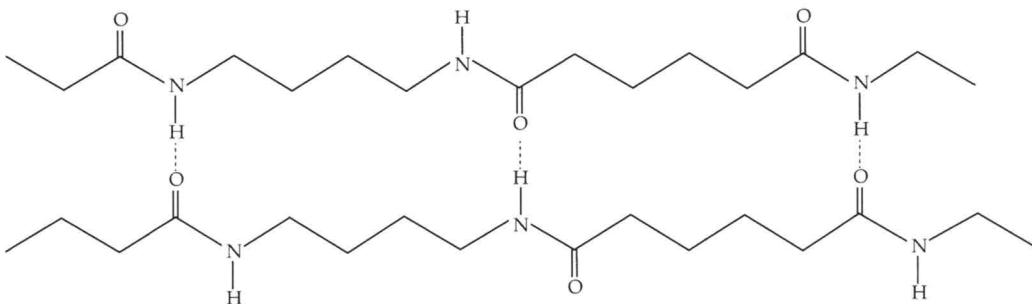
Example Nylon 6,6



Nylon

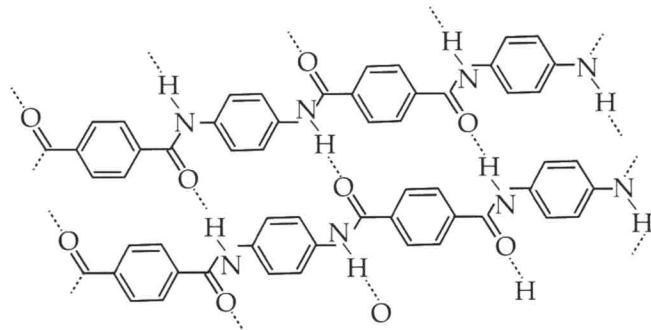
In the 1930's women's silk stockings were very popular, but in the depression years the price became prohibitive. Nylon was invented at around the same time and nylon stockings were marketed as a cheaper replacement. It is thought that the name nylon was coined because ladies from New York to London were wearing these fashionable modern items. Hence NY-LON.

Polyamide chains contain the C=O and N-H groups and so can form hydrogen bonds and dipole-dipole interactions between chains.



Generally the smaller the monomers the greater the proportion of C=O and / or N-H there are in the polymer. This increases the polymer's strength as these enable more hydrogen bonding and dipole-dipole interactions.

Kevlar is a very strong polyamide used to make sails and body armour. The amide bond enables the polymer chains to form hydrogen bonds with one another.



4.11.3 Polypeptides and proteins from a bonding perspective

Polypeptides and proteins are natural polyamide condensation polymers that form when amino acids (which contain both the amino and carboxyl groups) form amide links to produce the polymer chain.

The α -amino acid monomers are joined by peptide bonds (amide links) to form polypeptides. Each protein contains at least one long polypeptide. Polypeptides are said to contain amino acid residues.

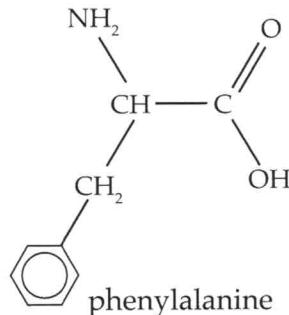
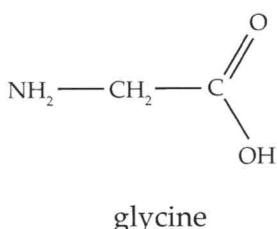
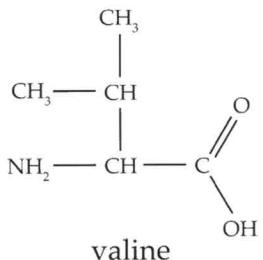
Proteins have four levels of structure. These levels are called primary, secondary, tertiary and quaternary. Quaternary structure is beyond the scope of this course.

The hydrogen bonds and dipole-dipole interactions that protein chains exhibit contribute to the structure of the protein.

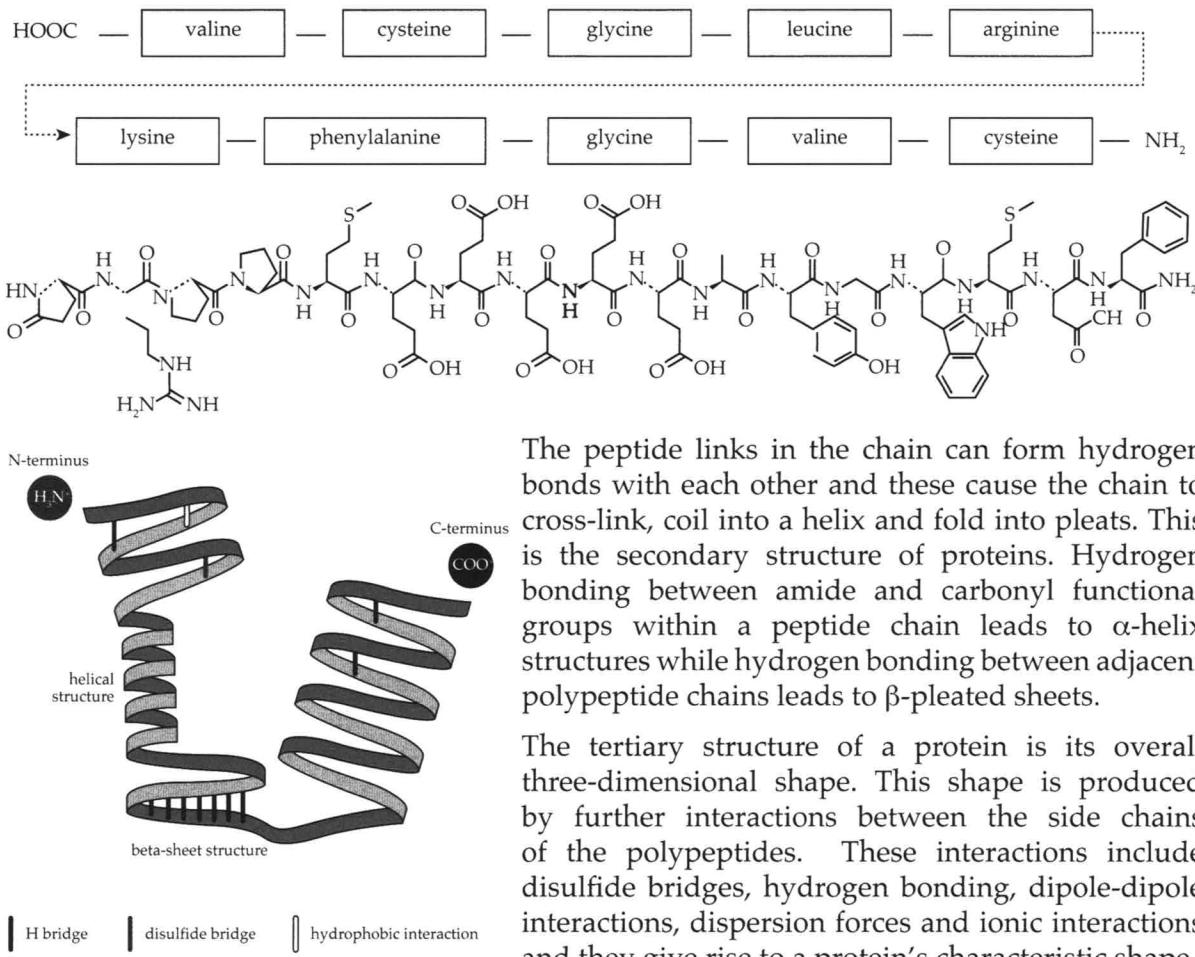
In addition, there are dispersion forces between polymer chains which increase with the increasing molecular mass of attached groups.

The specific sequence of α -amino acids that makes up a protein is called its **primary structure**.

Examples



These amino acids form peptide links with each other to form polypeptides.



The peptide links in the chain can form hydrogen bonds with each other and these cause the chain to cross-link, coil into a helix and fold into pleats. This is the secondary structure of proteins. Hydrogen bonding between amide and carbonyl functional groups within a peptide chain leads to α -helix structures while hydrogen bonding between adjacent polypeptide chains leads to β -pleated sheets.

The tertiary structure of a protein is its overall three-dimensional shape. This shape is produced by further interactions between the side chains of the polypeptides. These interactions include disulfide bridges, hydrogen bonding, dipole-dipole interactions, dispersion forces and ionic interactions and they give rise to a protein's characteristic shape.

- Disulfide bridges are covalent bonds between two sulfur-containing side groups. This forms a very strong bond.
- Hydrogen bonding occurs between groups like –OH and –NH₂.
- Dipole-dipole interactions occur between polar side groups.
- Dispersion forces are weak interactions between non-polar side groups like methyl, CH₃.
- Ionic interactions are between charged side groups like CO₃²⁻ and NH₃⁺.

The Protein Data Bank (PDB)

The Protein Data Bank (PDB) houses an international repository of the structural data of known proteins. Most of the data has been determined by X-ray crystallography which provides the 3-D coordinates of the atoms within a protein. Other methods including nuclear magnetic resonance (NMR), vibrational spectroscopy and cryo-electron microscopy have enabled more structures and many of higher resolution to be recorded. When a new protein is discovered, comparison to other proteins through databases like the PDB can help to predict its function.

The function of a protein is dependent on its 3-D structure. Proteins contain a wide range of functional groups. When combined in various sequences, these functional groups determine the structure and can account for the protein's function.

Structural proteins are proteins that are more rigid than others and can form structural parts of cells, e.g. collagens provide support for connective tissues such as tendons and ligaments.

Contractile proteins have more flexibility and their function is due to their ability to act as springs, levers or hinges, e.g. myosin which is involved in muscle contraction and movement.

Hormonal proteins are messenger proteins which help to coordinate certain bodily activities, e.g. insulin which controls blood-sugar concentration.

Transport proteins move molecules from one place to another around the body, e.g. haemoglobin

transports oxygen through the blood via red blood cells.

Storage proteins store metals ions and amino acids, e.g. ferritin stores iron in the body.

Enzymes are proteins that have functional groups and shapes that are essential to their function of catalysing specific chemical reactions in biological systems. (See 4.11.4 below)

Antibodies are proteins used by the immune system to identify and defend against antigens like bacteria and viruses, e.g. Immunoglobulin A (IgA) prevents colonization of mucosal areas by pathogens.

4.11.4 Enzymes

Enzymes are biological catalysts that accelerate chemical reactions. They are required to catalyse most of the metabolic processes that occur in cells. Most enzymes are proteins and their 3D structure makes them specific to certain biological reactions. They allow substrates to react and form products at the rate necessary for the cell to survive. Being catalysts, they aren't used up in the reaction and work by providing an alternative pathway to lower activation energy.

Enzyme activity can be affected by inhibitors, like drugs and poisons, which decrease their activity. There are also enzyme activators that increase their activity.

Enzymes activity is also affected by changes in temperature and pH.

Examples of Enzymes

Proteases break down or hydrolyse peptide bonds of proteins. They aid digestion. Lipases hydrolyse fats or lipids. Amylase hydrolyses dietary starch into disaccharides and trisaccharides, enabling them to be converted by other enzymes into glucose. Catalase catalyses the decomposition of hydrogen peroxide into water and oxygen.

Commercially, enzymes are used in biological washing powders to remove protein, fat or starch stains on clothing. Enzymes are also used to make antibiotics.

4.11.4 Empirical and molecular formulae of organic compounds

The empirical formula of a compound is the formula which shows the simplest ratio of the atoms of different elements present in the molecule. Quantitative information about the elements in the compound is collected empirically by experiment.

In simple empirical formula calculations the percentages or masses of elements in a sample of a compound are provided. These can be converted to moles and then the simplest ratio of moles of the elements found.

When finding empirical formulae of organic compounds, products of reactions of the compound provide information about the quantities of elements present. Typically the organic compound will contain carbon, hydrogen and oxygen. Other elements like nitrogen, sulfur or even halogens like chlorine may also be present.

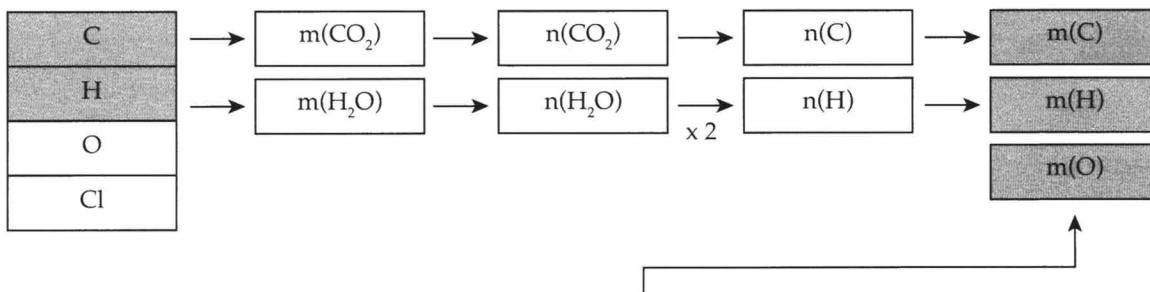
The masses of carbon and hydrogen in the compound can be found using combustion analysis, where the compound is burned completely in excess oxygen. The mass of carbon dioxide produced provides information about the mass of carbon in the compound. The mass of water produced tells us the mass of hydrogen in the compound.

Separate samples of the compound can then be subjected to other reactions to collect products containing any other elements present. Often these include products like ammonia, sulfur dioxide and silver chloride. These masses can provide information about the masses of the other elements contained in the compound.

Oxygen is often present, but the mass of this in the compound can only be determined by subtracting the masses of all other elements, once determined, from the original mass of the analysed sample.

Once the masses of all elements in the sample are known the empirical formula can be determined.

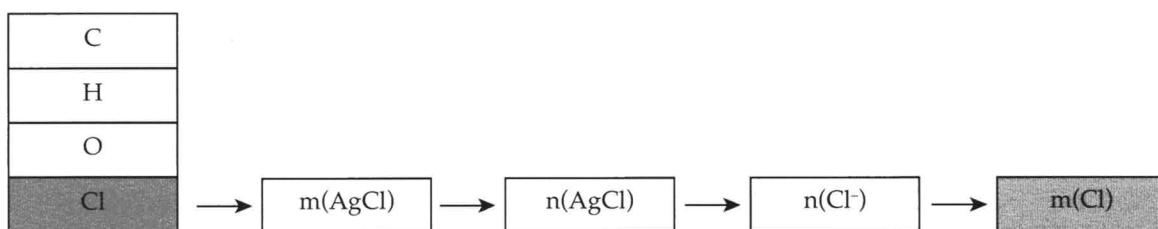
Sample 1



Once the masses of carbon and hydrogen in Sample 1 are known, and the mass of chlorine in Sample 2 is adjusted to determine its mass in Sample 1, these can be subtracted from the original mass of sample to determine the mass of oxygen.

$$m(\text{Cl})_{\text{Sample 1}} = \frac{m(\text{Sample 1})}{m(\text{Sample 2})} \times m(\text{Cl})_{\text{Sample 2}}$$

Sample 2



Then determine the simplest ratio of moles for each element:

Example

		C	H	O	Cl
Mass (g)	m	14.92	3.130	9.935	22.01
Molar mass (g mol ⁻¹)	M	12.01	1.008	16.00	35.45
Moles (mol)	n = m/M	$\frac{14.92}{12.01}$ = 1.242	$\frac{3.130}{1.008}$ = 3.105	$\frac{9.935}{16.00}$ = 0.6209	$\frac{22.01}{35.45}$ = 0.6209
Simplest ratio of moles	Divide by smallest	$\frac{1.242}{0.6209}$ = 2	$\frac{3.105}{0.6209}$ = 5	$\frac{0.6209}{0.6209}$ = 1	$\frac{0.6209}{0.6209}$ = 1

The empirical formula is C₂H₅OCl.

The molecular formula of a compound shows its actual formula so if E.F. is CH₂O, M.F. could be C₂H₄O₂, C₃H₆O₃ etc. It will either be the same as the empirical formula, or a whole number multiple of it. To determine the molecular formula from the empirical formula one must be provided with the molar mass of the compound, or be given information to calculate it. Then the molar mass of the empirical formula can be compared with the molar mass of the molecular formula.

Empirical determination of the molar mass of the compound is often done by weighing a sample of the compound, turning it into a gas, and then measuring its pressure, temperature and volume. From PV = nRT, the number of moles of sample can be obtained, and then using the mass of sample the molar mass can be calculated.

$$n(\text{sample}) = \frac{P \times V}{R \times T} \quad \text{where } P = \text{pressure in kPa}$$

V = volume in L

R = gas constant, 8.314

T = temperature in Kelvin

$$M(\text{sample}) = \frac{m}{n}$$

Example

A 1.622 g of an organic compound X containing only carbon, hydrogen and bromine was analysed in the laboratory. The compound was divided into equal samples for testing. The first sample was combusted in plenty of oxygen and produced 0.535 g carbon dioxide. The water produced in the reaction escaped as steam and was unable to be measured. The second sample was reacted with concentrated nitric acid and then treated with silver nitrate to yield 1.525 g of silver bromide.

- (a) Determine the empirical formula of compound X.

Sample 1:

$$\begin{aligned} n(\text{CO}_2) \text{ in sample 1} &= m(\text{CO}_2) / M(\text{CO}_2) \\ &= 0.535 / 44.01 \\ &= 0.01216 \text{ mol} \end{aligned}$$

$$\begin{aligned} n(\text{C}) \text{ in sample 1} &= n(\text{CO}_2) \\ &= 0.01216 \text{ mol} \end{aligned}$$

$$\begin{aligned} m(\text{C}) \text{ in sample 1} &= n(\text{C}) \times M(\text{C}) \\ &= 0.01216 \times 12.01 \\ &= 0.1460 \text{ g} \end{aligned}$$

Sample 2:

$$\begin{aligned}
 n(\text{AgBr})_{\text{in sample 2}} &= m(\text{AgBr}) / M(\text{AgBr}) & M(\text{AgBr}) = 107.9 + 79.90 \\
 &= 1.525 / 187.8 \\
 &= 8.12 \times 10^{-3} \text{ mol} \\
 n(\text{Br})_{\text{in sample 2}} &= n(\text{AgBr}) \\
 &= 8.12 \times 10^{-3} \text{ mol} \\
 m(\text{Br})_{\text{in sample 2}} &= n(\text{Br}) \times M(\text{Br}) \\
 &= 8.12 \times 10^{-3} \times 79.90 \\
 &= 0.6488 \text{ g}
 \end{aligned}$$

Since samples are the same size, 0.811g

$$\begin{aligned}
 m(\text{H}) &= 0.8110 - m(\text{C}) - m(\text{Br}) \\
 &= 0.8110 - 0.1460 - 0.6488 \\
 &= 0.01619 \text{ g}
 \end{aligned}$$

		C	H	Br
Mass (g)	m	0.1460	0.01619	0.6488
Molar mass (g mol ⁻¹)	M	12.01	1.008	79.90
Moles (mol)	n = m/M	0.01216	0.01606	0.00812
Simplest ratio of moles	Divide by smallest	$\frac{0.01216}{0.00812} = 1.497$	$\frac{0.01606}{0.00812} = 1.993$	$\frac{0.00812}{0.00812} = 1$
		3	4	2

The empirical formula is C₃H₄Br₂.

- (b) A further 0.500 g sample of compound X was heated to above its boiling point and turned into a gas. At 135.0°C and a pressure of 101.3 kPa its volume was measured to be 83.7 mL. What is its molecular formula?

$$\begin{aligned}
 n(X) &= \frac{PV}{RT} \\
 &= \frac{101.3 \times 0.0837}{8.314 \times (135.0 + 273.15)} \\
 &= 2.499 \times 10^{-3} \text{ mol}
 \end{aligned}$$

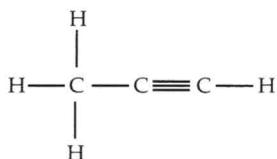
$$\begin{aligned}
 M(X) &= m(X) / n(X) \\
 &= 0.500 / 2.499 \times 10^{-3} \\
 &= 200.11 \text{ g mol}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 M(\text{C}_3\text{H}_4\text{Br}_2) &= (3 \times \text{C}) + (4 \times \text{H}) + (2 \times \text{Br}) \\
 &= 199.862 \text{ g mol}^{-1}
 \end{aligned}$$

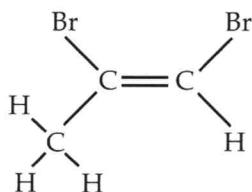
Since the molar mass of the molecular formula is essentially the same as the molar mass of the empirical formula, the molecular formula is also C₃H₄Br₂.

- (c) It is discovered that compound X was the product of the addition of bromine to an alkyne. Draw the structure of both compound X and the original alkyne from which it was prepared.

An alkyne with three carbon atoms will be propyne.

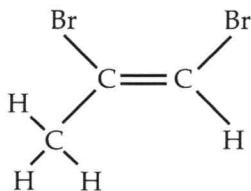


The addition of bromine to propyne produces 1,2-dibromopropene.

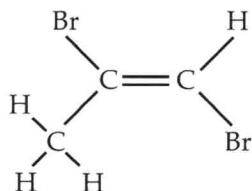


- (d) Give the two possible IUPAC names for compound X.

1,2-dibromopropene has two geometric isomers.



cis-1,2-dibromopropene



trans-1,2-dibromopropene

Chemical synthesis

In industry companies employ scientists to design chemical synthesis pathways in order to make or synthesise new substances, and to refine existing substances.

Chemical synthesis often requires a sequence of chemical reactions and chemists select reagents and reaction conditions in order to optimise the rate and yield of the product. Collision theory, the use of catalysts and the careful manipulation of systems in equilibrium are utilised. For example the production of ammonia via the Haber process and the production of sulphuric acid via the Contact process (See Chapter 1 section 1.12).

Chemists begin by researching in the laboratory with small quantities in order to determine most efficient way to turn a raw material into the desired product. Small scale pilot plants are often built to test the process and once optimised then large scale production can commence.

5.1 ENVIRONMENTAL AND ECONOMIC CONSIDERATIONS

Chemists designing chemical synthesis pathways must take into account the sustainability of the process. They should aim to meet current demand and production requirements whilst ensuring that the process does not prevent future needs being met. Use of renewable resources, both for raw materials and for the energy requirements of the process would be ideal but is often difficult to achieve. This is a challenge for chemists catering for the modern consumer world and an increasing population.

For both economic and environmental reasons, which go hand in hand, chemists look to the availability of **local resources** to meet their raw material and energy requirements. This minimises transport costs and also the use of fuels.

Minimising waste is very important and chemists work to ensure that raw materials are used fully and energy losses are avoided. Unused reactants can be recycled back into the process to achieve greater conversion to products.

Energy recycling should be employed wherever practicable. Here energy that might leave the system is recovered and reused in the process e.g. excess heat can be used to generate electrical energy or simply be returned to the process where required. This reduces energy costs and also minimises greenhouse gas pollution by reducing fuel consumption.

The **Atom economy** can be used in green chemistry as an alternative to yield. It is given as a percentage and represents the proportion of reactant atoms that make their way into the final product. It is a measure of

$$\text{Atom economy \%} = \frac{\text{Relative molecular/formula mass of desired products} \times 100}{\text{Relative molecular/formula mass of all reactants}}$$

Catalysts can be used to decrease energy requirements whilst maintaining a sufficient rate.

Often processes involve toxic reactants or by-products. These should be kept from entering the natural environment. Processes should be designed with safety in mind.

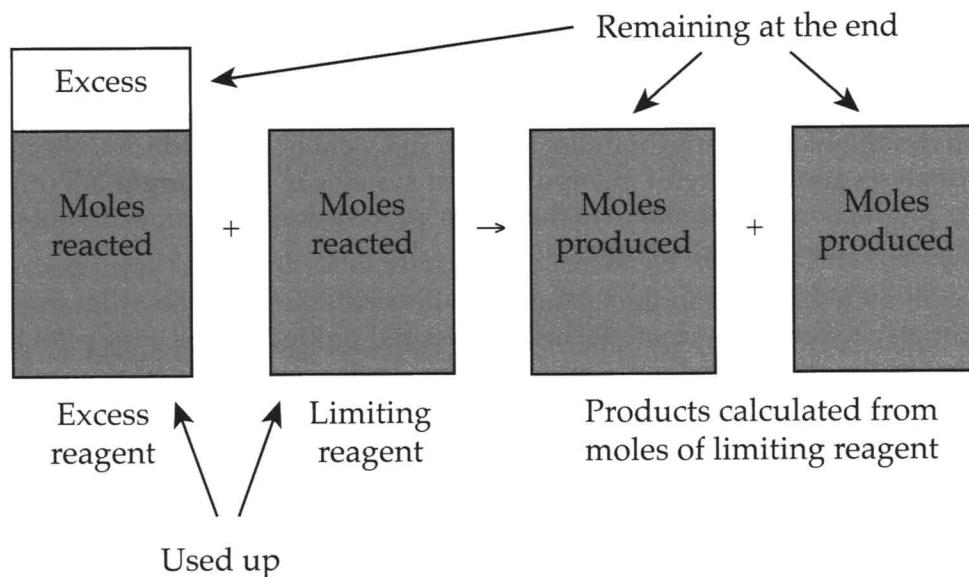
5.2 CALCULATIONS IN CHEMICAL SYNTHESIS

5.2.1 Limiting reagent calculations

Quantities of products required in a chemical synthesis reaction can be calculated by comparing stoichiometric quantities with actual quantities and by determining the limiting reagent.

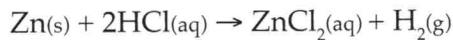
In a typical calculation, using a chemical equation, information is provided about one of the reactants or products. It could be the mass, moles, concentration or gaseous volume of this species. In a limiting reagent problem information is provided about two of the reactants. The chemist must then determine which reactant is the limiting reagent (the one that runs out) and which is the excess reagent. The limiting reagent is always all used up.

Once the limiting reagent is determined it can be used to calculate the mass, moles, concentration or gaseous volume of any of the other species in the chemical equation, including the amount of the excess reactant that actually reacted.



Example

Hydrogen gas is produced by the reaction between zinc and hydrochloric acid, according to the equation below.



If 10.94 g of hydrochloric acid is added to 13.08 g of zinc, calculate the limiting reagent, the mass of hydrogen gas produced and also the mass of excess reactant.

Step 1. Determine the limiting reagent.

Calculate the number of moles of each reactant.

$$\begin{aligned} n(\text{Zn}) &= m/M \\ &= 13.08 / 65.38 \\ &= 0.2000 \text{ mol of Zn} \\ n(\text{HCl}) &= m/M \\ &= 10.94 / 36.458 \\ &= 0.3000 \text{ mol of HCl} \end{aligned}$$

Step 2. Compare the stoichiometric and actual amounts

Stoichiometric	$n(\text{Zn})$:	$n(\text{HCl})$
	1	:	2
Actual	$n(\text{Zn})$:	$n(\text{HCl})$
	0.2000	:	0.300
or	1	:	1.50

← not enough as it needs to be 2

Therefore HCl is the limiting reagent!

Chapter 5

Now you can use the limiting reagent to work out product produced and excess reagent.

Step 3. Calculate moles of H₂ produced

$$\begin{aligned} n(H_2) &= \frac{1}{2} \times n(HCl) \\ &= \frac{1}{2} \times 0.3000 \\ &= 0.1500 \text{ mol} \end{aligned}$$

Step 4. Calculate mass of H₂ produced

$$\begin{aligned} m(H_2) &= n \times M & M(H_2) &= 2 \times 1.008 \\ &= 0.150 \times 2.016 & &= 2.016 \text{ g mol}^{-1} \\ &= 0.3024 \text{ g} \end{aligned}$$

Step 5. Calculate the moles of excess reactant that reacted.

$$\begin{aligned} n(Zn) &= \frac{1}{2} \times n(HCl) \\ &= \frac{1}{2} \times 0.300 \\ &= 0.1500 \text{ mol} \end{aligned}$$

Step 6. Calculate the mass of excess reactant that reacted.

$$\begin{aligned} m(Zn) &= n \times M & M(Zn) &= 65.38 \text{ g mol}^{-1} \\ &= 0.1500 \times 65.38 \\ &= 9.809 \text{ g} \end{aligned}$$

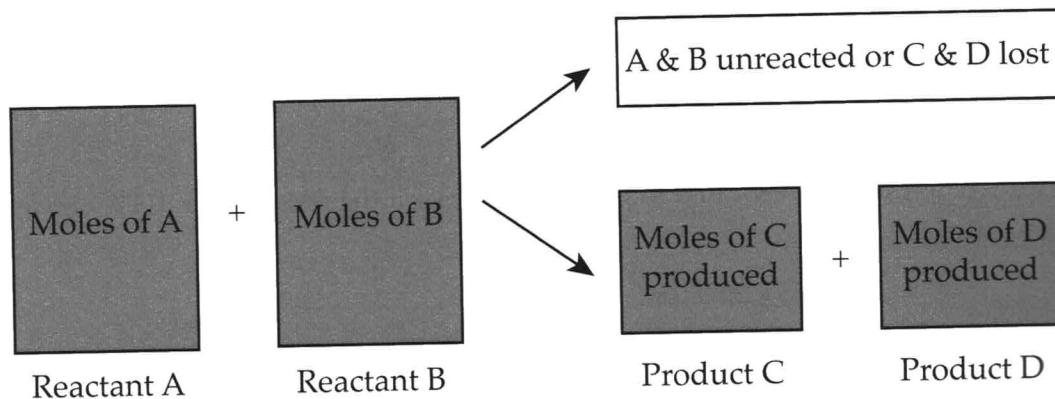
Step 7. Calculate the mass of excess reactant remaining.

$$\begin{aligned} m(Zn)_{\text{remaining}} &= m(Zn)_{\text{initial}} - m(Zn)_{\text{reacted}} \\ &= 13.08 - 9.809 \\ &= 3.371 \text{ g} \end{aligned}$$

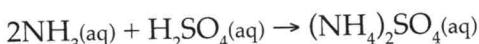
5.2.2 Percentage yield calculations

Chemists calculate the percentage yield of a chemical synthesis reaction by comparing theoretical versus actual product quantities.

In most industrial examples the process is not 100% efficient. If this is the case, the mass of products will be less than that predicted by stoichiometric calculations, as some is lost in production. It is important for chemists to be able to calculate losses for economic reasons.

**Example**

The fertiliser, ammonium sulfate, is produced by the following reaction:



What mass of ammonium sulfate could be produced from 30.0 kg of ammonia, assuming that the sulfuric acid is in excess and the process is 75.0% efficient?

This problem is solved as with other mass to moles to moles to mass problems.

$$\begin{aligned}
 n(\text{NH}_3) &= m(\text{NH}_3) / M(\text{NH}_3) & M(\text{NH}_3) &= 17.034 \text{ g mol}^{-1} \\
 &= 30000 / 17.034 \\
 &= 1761.18 \text{ mol} \\
 n((\text{NH}_4)_2\text{SO}_4) &= \frac{1}{2} \times n(\text{NH}_3) \\
 &= 880.59 \text{ mol} \\
 m((\text{NH}_4)_2\text{SO}_4) &= n(\text{NH}_3) \times M((\text{NH}_4)_2\text{SO}_4) & M((\text{NH}_4)_2\text{SO}_4) &= 132.144 \text{ g mol}^{-1} \\
 &= 880.59 \times 132.144 \\
 &= 116364.92 \text{ g}
 \end{aligned}$$

If the process is only 75% efficient then,

$$\begin{aligned}
 m((\text{NH}_4)_2\text{SO}_4) &= 75 / 100 \times 116364.92 \\
 &= 87273.69 \text{ g} \\
 &= 87.3 \text{ kg produced}
 \end{aligned}$$

It is also possible for chemists to alter the reactant amounts for an inefficient process to ensure that a maximum quantity of product is obtained.

Example

With the previous example, assume that the chemist needs to obtain 100.0 kg of ammonium sulfate.

What mass of ammonia is required to ensure that 100.0 kg of ammonium sulfate is obtained assuming that the process is 75.0% efficient?

This problem is solved as with other mass to moles to moles to mass problems.

$$\begin{aligned}
 n((\text{NH}_4)_2\text{SO}_4) &= m((\text{NH}_4)_2\text{SO}_4) / M((\text{NH}_4)_2\text{SO}_4) \\
 &= 100000 / 132.144 \\
 &= 756.75 \text{ mol} \\
 n(\text{NH}_3) &= 2 \times n((\text{NH}_4)_2\text{SO}_4) \\
 &= 2 \times 756.75 \\
 &= 1513.50 \text{ mol} \\
 m(\text{NH}_3) &= n(\text{NH}_3) \times M(\text{NH}_3) \\
 &= 1513.50 \times 17.034 \\
 &= 25780.97 \text{ g}
 \end{aligned}$$

So 25780.97 g of ammonia is required to produce 100.0 kg if the process was 100% efficient

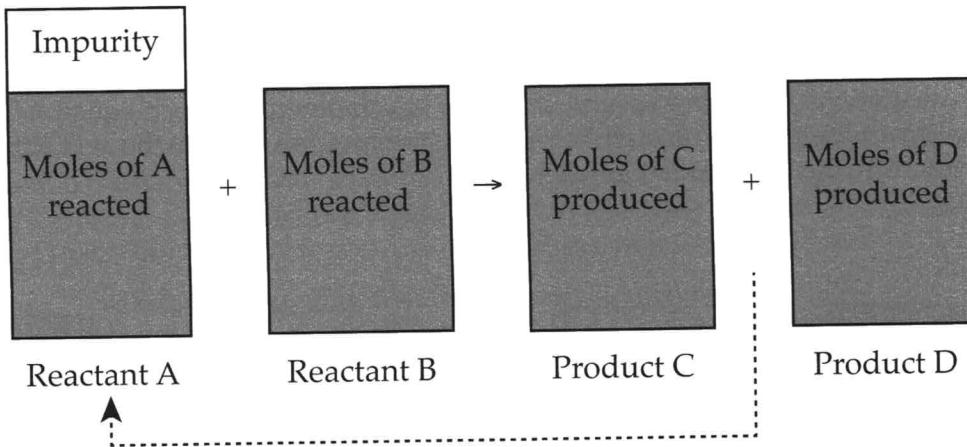
Since it is only 75% efficient,

$$\begin{aligned}
 m(\text{NH}_3)_{\text{required}} &= 100 / 75 \times 25780.97 \\
 &= 34374.62 \text{ g}
 \end{aligned}$$

Mass of NH_3 required is 34.4 kg (to 3 s.f.)

5.2.3 Percentage purity calculations

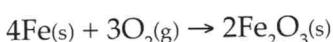
Often one of the reactants in a chemical synthesis is impure. If an impure reactant is used, it is possible to calculate the percentage purity of the reactant using stoichiometry and information about the products of the reaction.

**Example**

A sample of iron wire is oxidised to iron (III) oxide by reaction with oxygen. If 5.70 g of iron wire produces 8.00 g of iron (III) oxide, calculate the percentage purity of the iron wire.

Here the iron (III) oxide product is the known and the original impure iron wire is the unknown.

Step 1: Write the balanced equation.



Step 2: Calculate the number of moles of product.

$$\begin{aligned} n(\text{Fe}_2\text{O}_3) &= m(\text{Fe}_2\text{O}_3) / M(\text{Fe}_2\text{O}_3) & M(\text{Fe}_2\text{O}_3) &= (2 \times \text{Fe}) + (3 \times \text{O}) \\ &= 8.00 / 159.7 & &= 159.7 \text{ g mol}^{-1} \\ &= 0.0501 \text{ mol} & & \end{aligned}$$

Step 3: Calculate the moles of iron in the impure reactant.

$$\begin{aligned} n(\text{Fe}) &= 4/2 \times n(\text{Fe}_2\text{O}_3) \\ &= 0.1002 \text{ mol} \end{aligned}$$

Step 4: Calculate the mass of iron in the impure reactant.

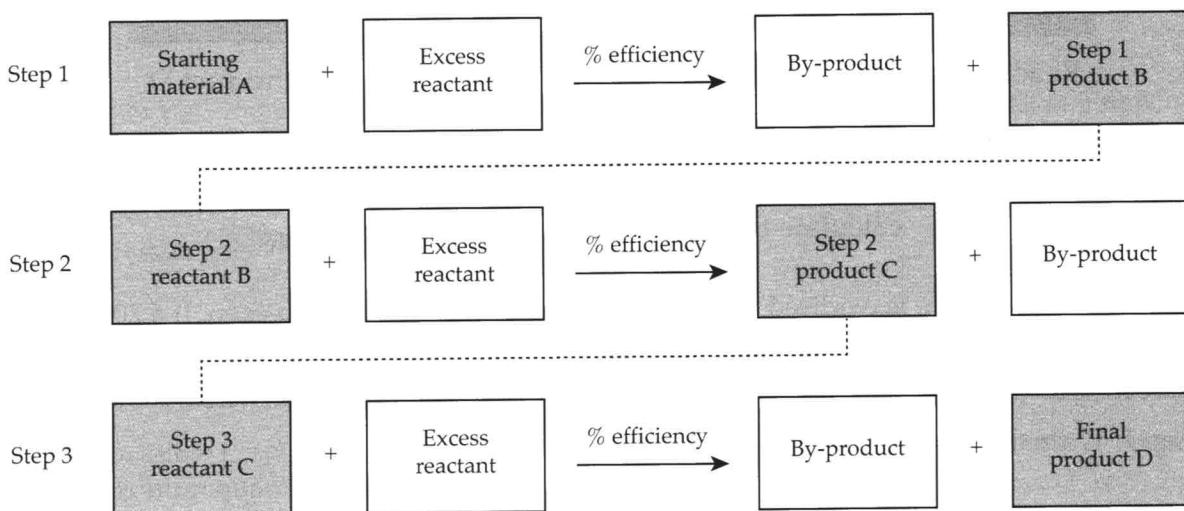
$$\begin{aligned} m(\text{Fe}) &= n(\text{Fe}) \times M(\text{Fe}) & M(\text{Fe}) &= 55.85 \text{ g mol}^{-1} \\ &= 0.1002 \times 55.85 \\ &= 5.60 \text{ g} \end{aligned}$$

Step 5: calculate the percentage purity

$$\begin{aligned} \% \text{ purity} &= m(\text{Fe}) / m(\text{impure sample}) \times 100 \\ &= \frac{5.595}{5.70} \times 100 \\ &= 98.2\% \end{aligned}$$

5.2.4 Multiple step stoichiometry calculations

Many industrial processes involve a series of reactions to produce the final product. When attempting calculations involving several steps the stoichiometry of each equation must be taken into account. One product of an earlier reaction becomes a reactant in the next. Efficiencies of each reaction can also be included for each step.



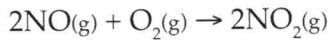
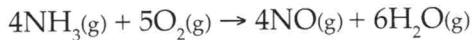
$$n(B) = \text{stoichiometric ratio} \times n(A) \times \% \text{ efficiency}$$

$$n(C) = \text{stoichiometric ratio} \times n(B) \times \% \text{ efficiency}$$

$$n(D) = \text{stoichiometric ratio} \times n(C) \times \% \text{ efficiency}$$

Example

The Ostwald Process for the production of nitric acid is an example of a multiple step process. Calculate the mass of nitric acid produced when 300.0 kg of ammonia is reacted with excess oxygen. The first reaction is 96.0% efficient and the second reaction is 87.0% efficient. Assume that the final reaction is 100% efficient.



$$\begin{aligned} n(\text{NH}_3) &= m(\text{NH}_3) / M(\text{NH}_3) \\ &= 300000 / 17.034 \\ &= 17611.84 \text{ mol} \end{aligned}$$

$$\begin{aligned} n(\text{NO}) &= 4/4 \times n(\text{NH}_3) \times 96/100 \\ &= 16907.36 \text{ mol} \end{aligned}$$

$$\begin{aligned} n(\text{NO}_2) &= 2/2 \times n(\text{NO}) \times 87/100 \\ &= 14709.40 \text{ mol} \end{aligned}$$

$$\begin{aligned} n(\text{HNO}_3) &= 4/4 \times n(\text{NO}_2) \\ &= 14709.40 \text{ mol} \end{aligned}$$

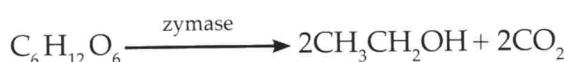
$$\begin{aligned} m(\text{HNO}_3) &= n(\text{HNO}_3) \times M(\text{HNO}_3) & M(\text{HNO}_3) &= (1 \times \text{H}) + (1 \times \text{N}) + (3 \times \text{O}) \\ &= 14709.40 \times 63.018 & &= 63.018 \text{ g mol}^{-1} \\ &= 926957.27 \text{ g} \\ &= 927 \text{ kg (3 sfs)} \end{aligned}$$

5.3 EXAMPLES OF CHEMICAL SYNTHESIS

Industrial production of ethanol

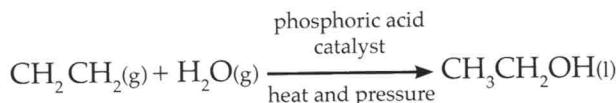
Ethanol can be produced via the fermentation of carbohydrates like sugar from sugar cane. This reaction is catalysed by enzymes from yeast. Biological catalysts are often used to provide cheaper, lower energy, chemical synthesis pathways which are an alternative to more expensive pathways that require high temperature or pressure conditions.

Example Glucose fermenting to form ethanol and carbon dioxide.



Ethanol can also be produced by the direct hydration of ethene. Here, high temperatures and pressures are required. Conditions of 70 atm, 300°C and the use of a phosphoric acid catalyst are chosen to maximise yield.

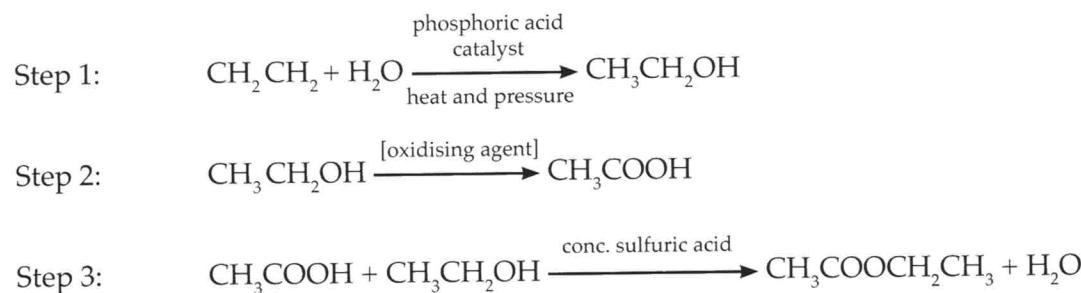
Example



Multiple step chemical synthesis

The production of ethyl ethanoate is an example of a multiple-step chemical synthesis.

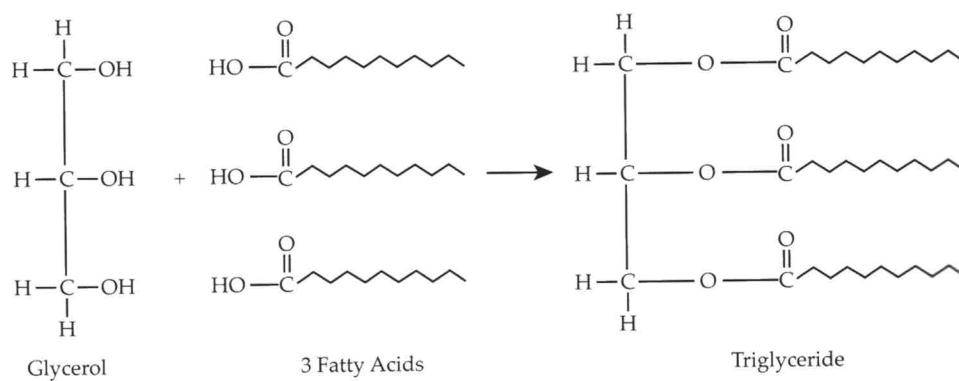
Ethanol, once produced, can be oxidised to ethanoic acid as described in the Carboxylic Acid section. This ethanoic acid can then be reacted with more ethanol to produce the ester, ethyl ethanoate, as described in the Ester section.



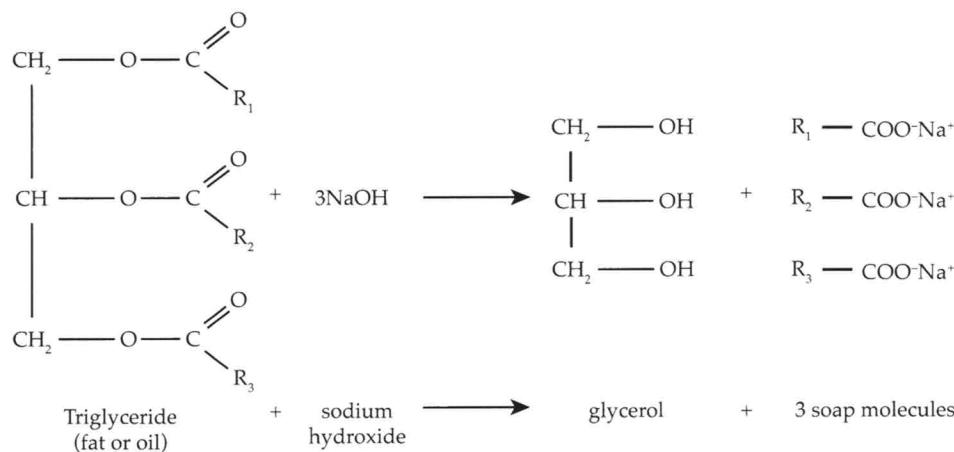
Soap making or saponification

Fatty acids are long chain carboxylic acids. If the chain contains no double bonds it is called a saturated fatty acid. If it contains double bonds it is called an unsaturated fatty acid. If it contains many double bonds it is called polyunsaturated.

Typical fats are triglycerides or lipids and these are formed when three fatty acids react with glycerol in a condensation reaction. Triglycerides contain ester linkages and so the reaction is an example of an esterification reaction.



Soap-making, or saponification, involves the basic hydrolysis of fats. It produces glycerol and soap, which is a sodium or potassium salt of a long chain fatty acid.

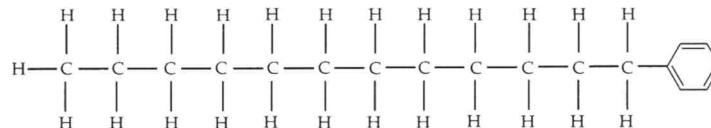


Detergents

Detergents are typically alkylbenzene sulfonates.

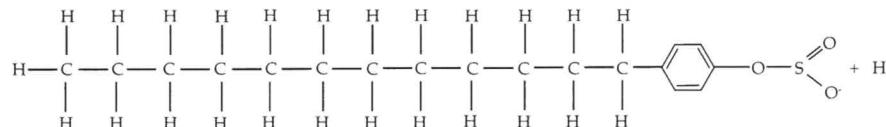
They are produced in a three-step process:

- Alkylbenzenes are produced from the reaction between benzene and a halogenoalkane.



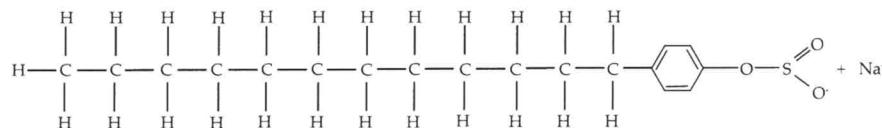
dodecylbenzene

- The alkylbenzene is reacted with concentrated sulfuric acid to produce an alkylbenzene sulfonic acid.



dodecylbenzenesulfonic acid

- The alkylbenzene sulfonic acid is neutralised with sodium hydroxide to produce the detergent, sodium alkylbenzene sulfonate.



sodium dodecylbenzenesulfonate – the Detergent

How do soaps and detergents work?

Soaps and detergents are surfactants or wetting agents. They enable water to wash away oils, grease and dirt.

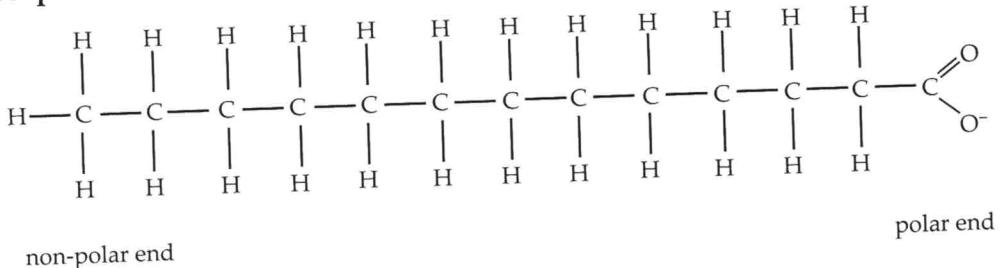
Oil and grease are non-polar and do not dissolve in water.

Once soaps and detergents dissolve they have a hydrophobic non-polar, hydrocarbon end which will bond with oil and grease, and a hydrophilic, polar charged end which will bond with water.

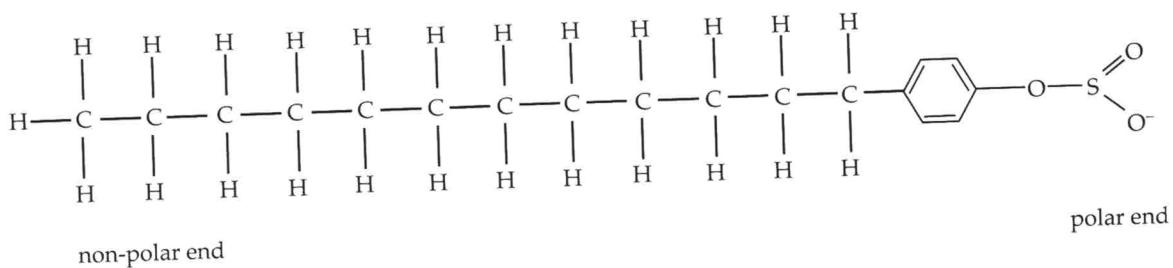
With soaps, the non-polar end is a hydrocarbon chain and the polar end is the carboxylate group.

With anionic detergents the non-polar end is a hydrocarbon chain containing a benzene ring (often dodecylbenzene) and the polar end is the sulfonate group.

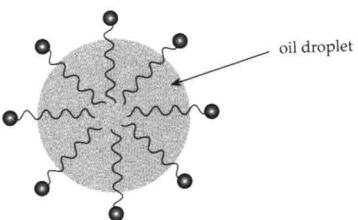
Typical soap



Typical detergent



On agitation in water, the surfactant molecules can surround small droplets of oil and grease forming micelles. The hydrophobic end dissolves in the oil and the hydrophilic end in water. These small droplets can now be washed away as they are effectively dissolved in water.



Soaps are not effective in hard water as it contains calcium and magnesium ions and these form a precipitate, or scum, with the soap ions, removing them from solution.



Detergents in contrast do not form scum with calcium or magnesium ions and so can be used in hard water.

Biodiesel

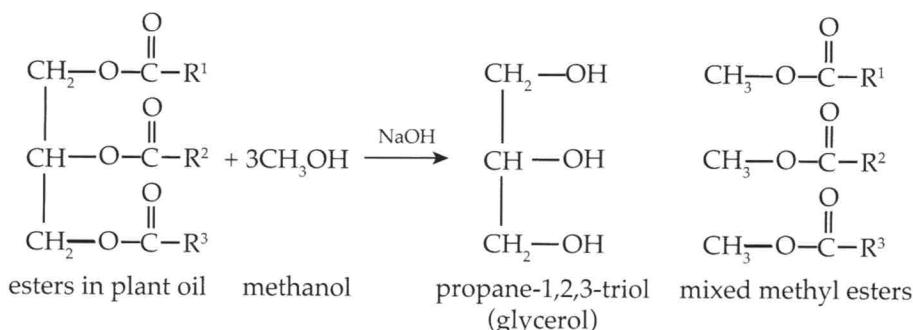
Biodiesel is non-toxic, biodegradable and a renewable fuel source. It is considered a carbon-neutral fuel as the carbon dioxide produced in its combustion is equivalent to that which was absorbed by the plant from which it was made.

Diesel or petrodiesel is different from biodiesel in that it is a mixture of alkenes rather than methyl esters.

Biodiesel can be manufactured by converting the triglycerides obtained from animal fats or vegetable oils into methyl esters. The fatty acids are subjected to a process of condensation called transesterification.

Base-catalysed transesterification

Transesterification is similar to the saponification reaction for soap making. If this base catalysed reaction is performed in the presence of methanol it transforms the triglycerides into biodiesel rather than soap.



Lipase catalysed transesterification

Biodiesel can also be prepared by a lipase-catalysed process. Lipase is an enzyme that catalyses the hydrolysis of fats (lipids). Enzymatic transesterification has advantages over the chemical catalysis of transesterification as it is less energy intensive and allows easy recovery of glycerol. Limitations of the enzyme-catalysed reactions include high cost of enzyme, low yield and long reaction time.