Higher
Chemistry

HSN13000
Unit 3 – All Topics

Contents

Topic 1 – Chemical Equilibrium

Reversible Reactions

We are already familiar with reactions that are one way. They 'go to completion' and the products do not change back into the reactants.

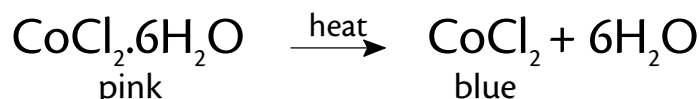eg $$Mg_{(s)} + 2H^+_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + H_{2(g)}$$
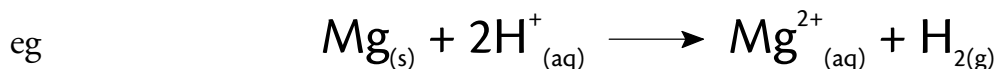
However, there are many reactions in which the products can react to reform the reactants. They are called reversible reactions.

eg heating hydrated cobalt chloride, $CoCl_2.6H_2O$

$$CoCl_2.6H_2O \xrightarrow{\text{heat}} CoCl_2 + 6H_2O$$
$$\text{pink} \qquad\qquad\qquad \text{blue}$$

The pink hydrated form returns when water is added

$$CoCl_2 + 6H_2O \longrightarrow CoCl_2.6H_2O$$
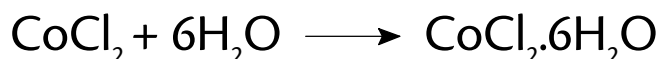
Such a reaction can be shown using reversible arrows

$$CoCl_2.6H_2O \rightleftharpoons CoCl_2 + 6H_2O$$
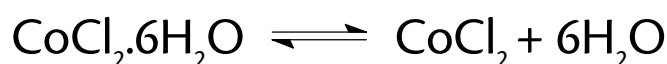
Reversible reactions give rise to a situation called equilibrium.

Consider the general reversible reaction:

$$A + B \rightleftharpoons C + D$$
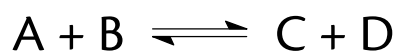
If we start with A and B an allow them to react then, initially, the rate of the forward reaction, r_f, is high because the concentrations of A and B are high. The rate of the back reaction, r_b, is zero initially because the concentrations of C and D are zero. As the reaction proceeds the concentrations of A and B decrease while the concentrations of C and D increase. This means r_f falls and r_b increases. This continues until the two rates become equal. At this point the concentration of A, B, C and D do not change and the system is in chemical equilibrium.
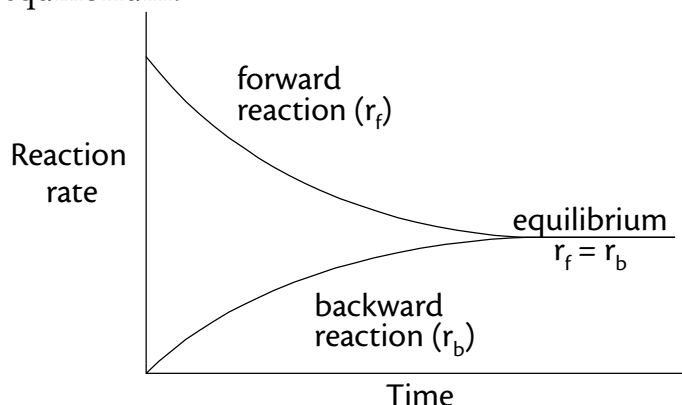
At the molecular level the forward and backward reactions are continuing but, because their rates are equal, the concentrations of the four substances remain constant. This is called dynamic equilibrium.

Note that equilibrium is reached only in a closed system. This means that no substances are added or removed.

Position of Equilibrium

It is important to realise that a system in equilibrium does not imply 50% reactants and 50% products – this would be a rare occurrence. In some cases equilibrium is established when the forward reaction is nearly complete – we say that the equilibrium lies to the right. In other cases equilibrium is reached when the forward reaction is barely started. Such an equilibrium lies to the left. The two graphs below show how the concentrations of A, B, C and D might vary with time as equilibrium is being established. In the left graph the concentrations of A and B are greater than C and D at equilibrium so this equilibrium lies to the left. In the right graph the concentrations of A and B are less than C and D at equilibrium so this equilibrium lies to the right.
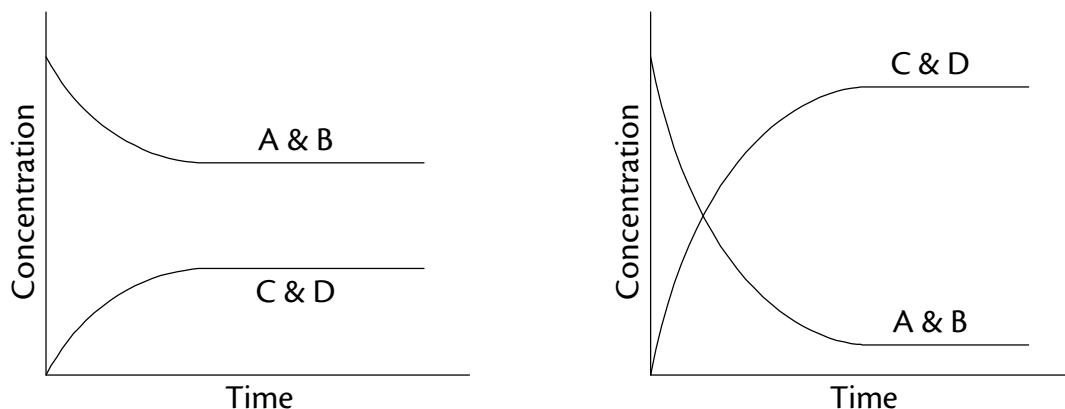
For a reaction, the same equilibrium position is reached whether we start from the 'reactants' or the 'products'. In the above example under the same conditions the same equilibrium position would have been reached if we had started with C and D. This can be shown using the fact that iodine is soluble in trichloroethane ($C_2H_3Cl_3$) and also in aqueous potassium iodide solution. Tubes X and Z represent the 2 starting positions. Tube Y represents the same equilibrium position attained from the 2 starting points.
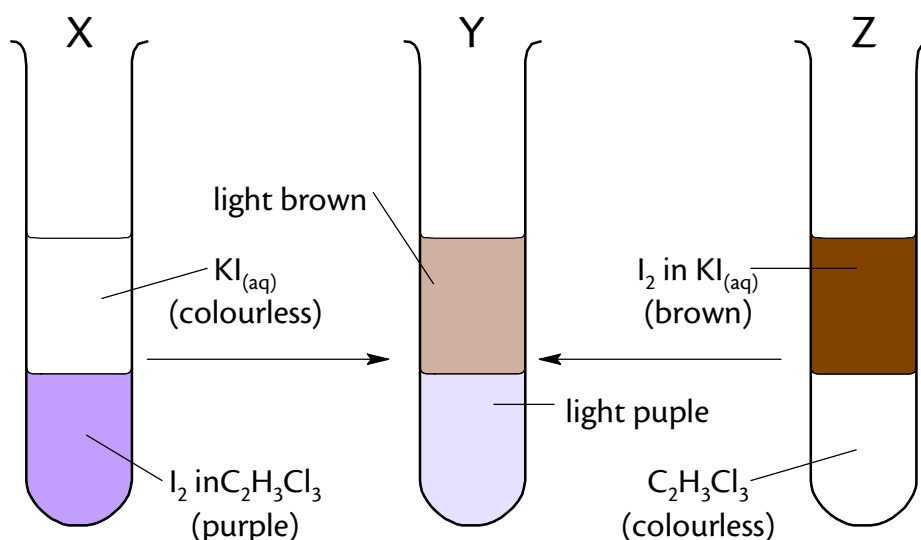
Factors that affect the Position of Equilibrium

Many reactions in the chemical industry (eg Haber Process) are equilibria. It is important to understand what factors control the position of equilibria since this clearly affects the conversion of reactants to products. Equilibrium is reached when the rates of two

opposing reactions become equal, so it seems reasonable to study the factors that we already know affect reaction rates:

a) catalysts
b) concentration
c) pressure (of gases)
d) temperature

Effect of Catalysts on Equilibrium

A catalyst has the effect of lowering the energy barrier between reactants and products by providing an alternative reaction path. From the graph we can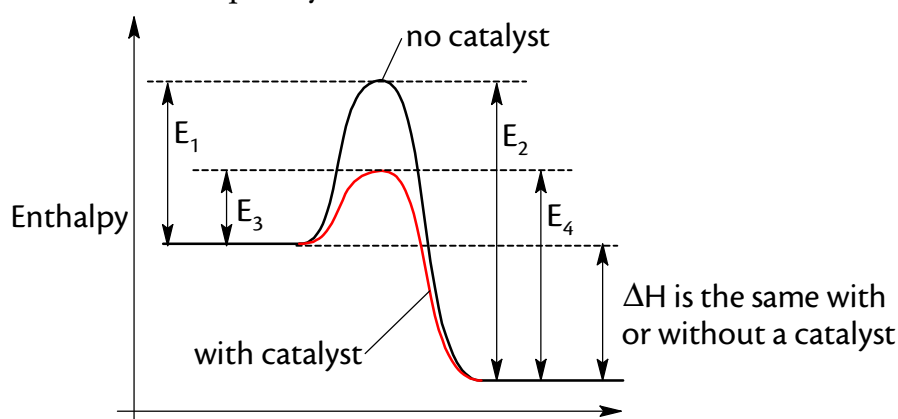 see that if the barrier is lowered for the forward reaction it is also lowered for the back reaction by the same amount. The net effect is that a catalyst does not alter the position of equilibrium. However, a catalyst speeds up both the forward and back reactions so the same equilibrium is reached more quickly.

E_1 Forward activation energy, no catalyst E_2 Back activation energy, no catalyst
E_3 Forward activation energy, with catalyst E_4 Back activation energy, with catalyst

Effect of Concentration on Position of Equilibrium

Consider the following equilibrium:

$$A + B \rightleftharpoons C + D$$
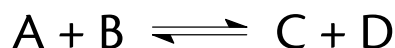
Increasing the concentration of A or B will speed up the forward reaction so producing more C and D until a new equilibrium position further to the right is established. Decreasing the concentration of C or D will slow down the back reaction which converts C and D into A and B. This means the concentration of C and D will increase again moving the equilibrium position to the right.

By a similar argument either increasing the concentration of C and D or decreasing the concentration of A and B moves the equilibrium to the left.

The two following reactions illustrate these points:

$$ICl_{(l)} + Cl_{2(g)} \rightleftharpoons ICl_{3(s)}$$
$$\text{brown liquid} \qquad\qquad\qquad \text{yellow crystals}$$
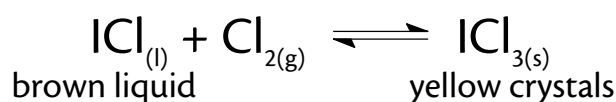
When chlorine is added we see an increase in the amount of yellow crystals and a decrease in brown liquid. This is because the increase in the concentration of chlorine has speeded up the forward reaction and moved the equilibrium to the right. Removing chlorine has the opposite effect and the equilibrium moves to the left.

$$Fe^{3+}_{(aq)} + CNS^{-}_{(aq)} \rightleftharpoons FeCNS^{2+}_{(aq)}$$

colourless   red
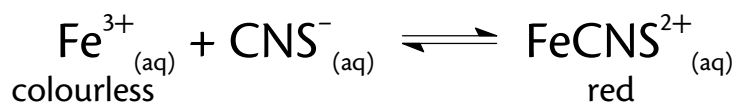
The intensity of the colour indicates the position of the equilibrium i.e. the more red the colour the further right the equilibrium lies.

Some of the equilibrium mixture is put in 4 test tubes and A is kept as a control. The diagram shows what was added to the others and the resulting change in appearance.

A	B	C	D
orange	blood red	blood red	very pale orange
control	FeCl$_3$ added	KCNS added	NaCl added
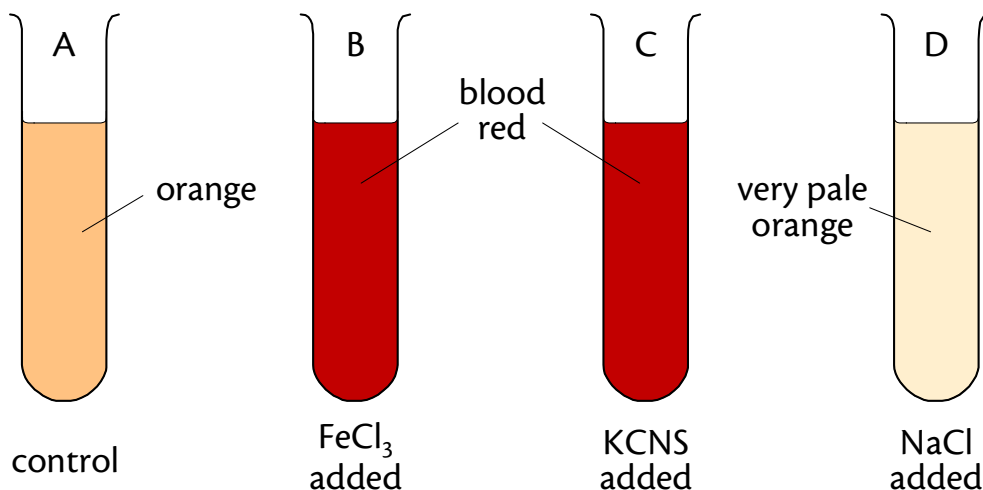
The addition of either Fe^{3+} ions or CNS^{-} ions shifts the equilibrium to the right and results in the formation of more of the red complex ion.

When NaCl is added the Cl^{-} ions form a complex with Fe^{3+} so the concentration of $Fe^{3+}_{(aq)}$ falls. This moves the equilibrium to the left and the colour pales.

Effect of Pressure on the Position of Equilibrium
A change in pressure can only affect equilibria in which gases are involved.

The pressure exerted by a gas is caused by the freely moving gas molecules colliding with the walls of the containing vessel. An increase in the number of molecules in the vessel will cause an increase in pressure, the size of the container being kept constant. Similarly a decrease in the number of molecules causes a decrease in pressure. The effect of changes in pressure on an equilibrium involving gases is equivalent to changes in concentration on a system involving solutions. Increasing the pressure favours whichever reaction brings about a reduction in the total number of gas molecules. Decreasing the pressure favours the reaction that increases the total number of gas molecules.

We can observe the effect of pressure using the brown gas nitrogen dioxide. Nitrogen dioxide (NO_2) exists as an equilibrium mixture with its colourless dimer, dinitrogen tetroxide (N_2O_4).

$$N_2O_4 \rightleftharpoons 2NO_2$$

1 mole   2 moles
colourless   brown

N_2O_4/NO_2

strong clip   gas syringe
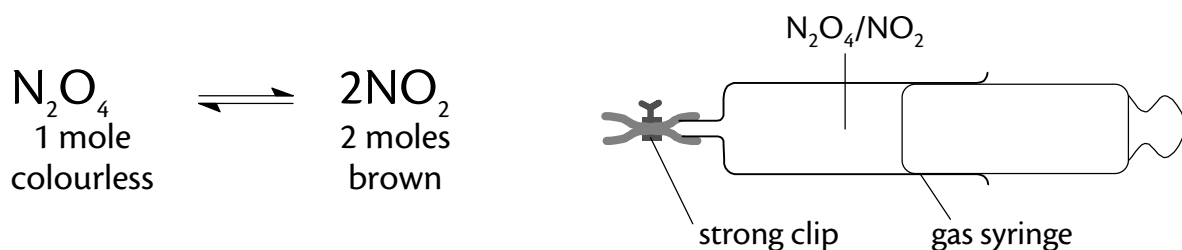
When the plunger is pushed in the pressure is increased so the equilibrium shifts to the left to reduce the number of molecules and so reduce the pressure. The full results of this experiment are in the table:

Applied pressure change	Initial colour change	Final colour change
Increase (plunger in)	Darkens due to compression	Lightens as equilibrium shifts to the left
Decrease (plunger out)	Lightens due to expansion	Darkens as equilibrium shifts to the right

If an equilibrium system has the same number of gas molecules on both sides of the arrow, a change in pressure will have no effect on the position of equilibrium. However an increase in pressure (i.e. concentration) will increase the rates of both forward and back reactions and so reduce the time for equilibrium to be established.

Industrial Preparation of Methanol
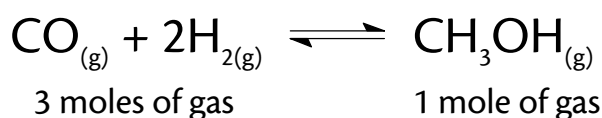We met this reaction in Unit 2

$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$$
3 moles of gas   1 mole of gas

High pressure favours the forward reaction because it gives a reduction in the number of gas molecules. So high pressure increases the yield of methanol. In the original industrial process (1923) the mixture was compressed to 300 atmospheres. In 1966, development of a more efficient catalyst allowed the process to be run at 50 to 100 atmospheres. As we saw earlier a catalyst has no effect on equilibrium position so the more efficient catalyst did not increase the yield of methanol and the lower pressure actually gives a lower yield of methanol. The advantage is that the lower pressure plant is cheaper to build and safer to run. The carbon monoxide/hydrogen mixture (called synthesis gas or syngas) in the above process is generated as follows:

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$$
2 moles of gas   4 moles of gas
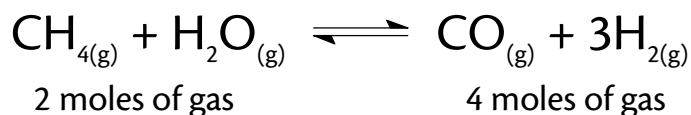
In this reaction raising the pressure would favour the back reaction so reducing the yield of syngas. As a result this process is run at normal pressure.

Effect of Temperature on the Position of Equilibrium
In a system at equilibrium, if the forward reaction is exothermic the back reaction must be endothermic, and vice versa.

If the temperature is raised, then the rate of both reactions increases but not equally. A rise in temperature favours the reaction that needs to have heat supplied, i.e. the endothermic reaction. A decrease in temperature has the opposite effect and favours the exothermic reaction.

We can observe the effects of temperature using again the N_2O_4 / NO_2 system

$$N_2O_4 \rightleftharpoons 2NO_2 \qquad \Delta H = +ve$$
colourless   brown
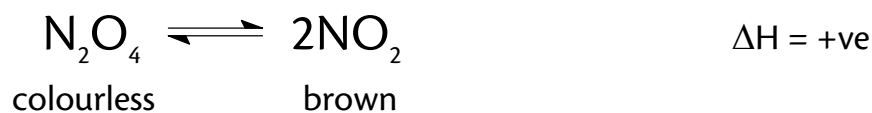
Samples of this mixture in 3 test tubes at different temperatures are shown:
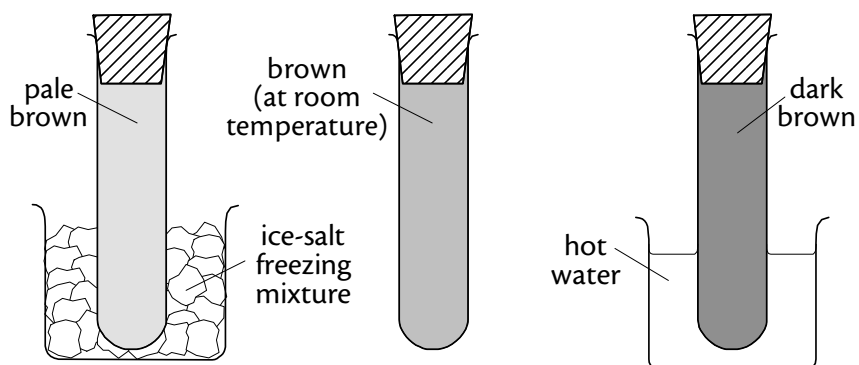
When the temperature is raised the forward reaction, which is endothermic, is favoured so the equilibrium shifts to the right. The concentration of NO_2 increases and so the colour darkens. Lowering the temperature favours the exothermic reaction which is the back reaction. The equilibrium shifts to the left and the colour lightens as the concentration of N_2O_4 increases.

Industrial preparation of Methanol

This is an exothermic reaction:

$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)} \qquad \Delta H = -91 \text{ kJ mol}^{-1}$$
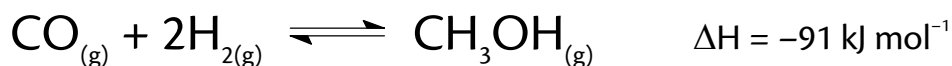
(The ΔH value is given for the forward reaction)

An increase in temperature favours the back reaction and so decreases the equilibrium concentration of methanol. This suggests that to get a high yield of methanol we should carry out the reaction at low temperature. However, low temperature means a low rate and a long time to establish equilibrium. A compromise is reached at a moderately high temperature (200 to 300°C) which gives a worthwhile rate but a reduced yield of methanol.

The carbon monoxide/hydrogen mixture called syngas is produced in an endothermic reaction.

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)} \quad \Delta H = +206 \text{ kJ mol}^{-1}$$
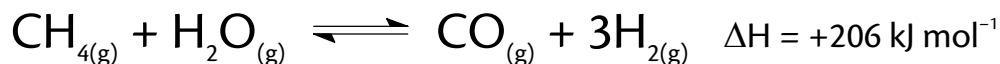
This reaction is carried out at 800°C which both gives a high rate and favours the forward endothermic reaction. This shifts the equilibrium to the right and increases the yield of syngas.

Le Chatelier's Principle

The effect of changes in concentration, pressure and temperature on an equilibrium can be predicted using Le Chatelier's Principle:

> If a system at equilibrium is subjected to a change, the system will adjust to oppose the effect of the change

The Haber Process for Ammonia

This is a good example of the application of chemical principles to an industrial process.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = -92 \text{ kJ mol}^{-1}$$
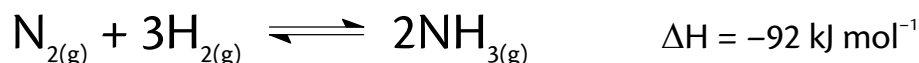
Catalyst

In the absence of a catalyst the nitrogen and hydrogen hardly combine. Anyway, the high temperature needed to make the nitrogen and hydrogen combine would force the equilibrium to the left so little ammonia would be formed. An iron catalyst is used in the Haber process; this allows a fast reaction rate at lower temperature and gives a reasonable yield of ammonia.

Pressure

The formation of ammonia gives a decrease in the number of molecules of gas, so a high pressure favours ammonia production. However, plants that operate at high pressure are costly to build and require expensive compressors.

Temperature

A low temperature would give a high equilibrium yield of ammonia. However a low temperature means a slow rate and a long time to come to equilibrium. A higher temperature increases the rate but gives a reduced yield of ammonia. Clearly compromises must be reached between the competing factors which are summarised below.

Condition	Pro (Advantages)	Con (Disadvantages)
high pressure	good equilibrium yield of NH_3	costly to build and operate
low temperature	good equilibrium yield of NH_3 and easy on catalyst	reaction slow to reach equilibrium

The percentage yield of ammonia at various temperatures and pressures is shown on the graph below.
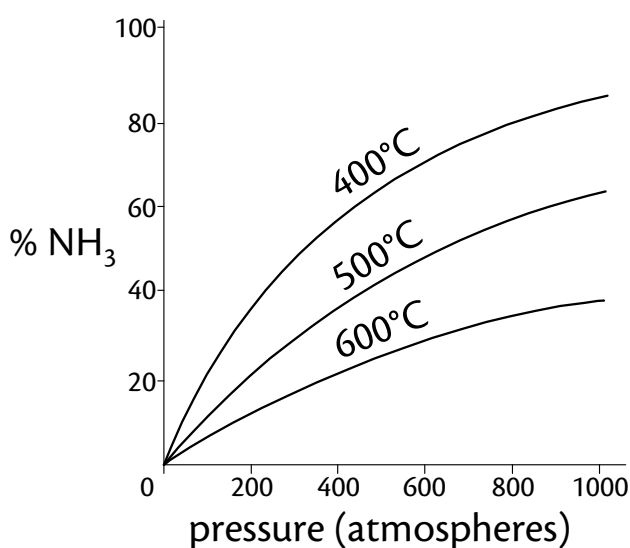
A modern ammonia plant operates at about 80 atmospheres and a temperature of 500K. From the graph we would expect a yield of about 25% ammonia. However, the yield obtained in practice is only about 14%. This is because the time the gases spend in the catalytic converter is too short for equilibrium to be established. It is more economical to remove the ammonia that has formed by cooling it to liquid ammonia and recycling the unreacted nitrogen and hydrogen. Repeated recycling gives a conversion rate of about 98%.

Raw Materials for the Haber Process

The nitrogen comes from the air. The hydrogen comes from syngas manufactured from natural gas and steam.

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$$
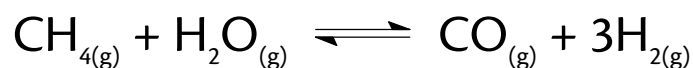
An industrial process is obviously more economic if the raw materials are readily available.

Marketability of Ammonia

This is clearly important for any industrial product. There is a large market for ammonia because it is further converted into fertilisers, nitric acid and nylon.

Equilibrium in aqueous solutions

We learned in fourth year that pure water conducts electricity to a slight extent. This is due to the slight dissociation of water molecules as shown by the equilibrium.

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$
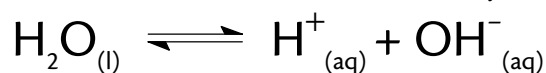
The equilibrium lies very much to the left; only 1 in every 555 million water molecules dissociates.

The pH scale

Dilution of 1 mol l^{-1} HCl

With a pH meter we found that 1 mol l^{-1} HCl had a pH of 0. We took 10 ml of this acid solution and made the volume up to 100ml with distilled water – this is a ten fold dilution and gave us 0.1 mol l^{-1} HCl which had a pH of 1. This dilution was repeated several times.

It is worth remembering that for dilutions such as this, $C_1V_1 = C_2V_2$ where C is the concentration and V is the volume.

Before we look at the full results, note that square brackets are used in chemistry to denote concentration. So $[H^+]$ means "the concentration of H^+ ions" usually measured in mol l^{-1}.

For   0.1 mol l^{-1} HCl $[H^+] = 10^{-1}$ mol l^{-1}
and for   0.01 mol l^{-1} HCl $[H^+] = 10^{-2}$ mol l^{-1} and so on

Results

HCl concentration (mol l^{-1})	$[H^+]$ (mol l^{-1})	pH
1.0	10^0	0
0.1	10^{-1}	1
0.01	10^{-2}	2
0.001	10^{-3}	3
0.0001	10^{-4}	4
0.00001	10^{-5}	5
0.000001	10^{-6}	6
0.0000001	10^{-7}	7

Dilution of 1 mol l^{-1} NaOH

This similar experiment gave these results:

NaOH concentration (mol l^{-1})	[OH$^-$] (mol l^{-1})	pH
1.0	10^{0}	14
0.1	10^{-1}	13
0.01	10^{-2}	12
0.001	10^{-3}	11
0.0001	10^{-4}	10
0.00001	10^{-5}	9
0.000001	10^{-6}	8
0.0000001	10^{-7}	7

Ionic Product for Water

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$
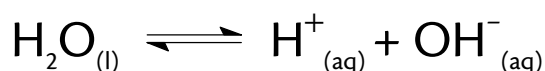
When pure water dissociates one H$^+$ ion is produced for every OH$^-$ ion, so

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

From the two previous tables above we can see that at pH 7

$$[H^+] = [OH^-] = 10^{-7} \text{ mol l}^{-1}$$

The ionic product of water, $K_W = [H^+][OH^-] = 10^{-7} \times 10^{-7} \text{ mol}^2 \text{ l}^{-2}$
$$= 10^{-14} \text{ mol}^2 \text{ l}^{-2}$$

This is a very important relationship. Although we have worked it out for water at pH7, it is true at all pH values.

The crucial fact to remember is that the relationship

$$[H^+][OH^-] = 10^{-14} \text{ mol}^2 \text{ l}^{-2}$$

must be true at all times in aqueous solutions.

The table below (which incorporates the two previous tables) shows the relationship between [H$^+$], [OH$^-$] and pH.

Concentration of H$^+_{(aq)}$ (mol l^{-1})	[H$^+$]	pH	[OH$^-$]	Concentration of OH$^-_{(aq)}$ (mol l^{-1})
10	1×10^{1}	−1	1×10^{-15}	
1	1×10^{0}	0	1×10^{-14}	
0.1	1×10^{-1}	1	1×10^{-13}	
0.01	1×10^{-2}	2	1×10^{-12}	
0.001	1×10^{-3}	3	1×10^{-11}	
0.000 1	1×10^{-4}	4	1×10^{-10}	
0.000 01	1×10^{-5}	5	1×10^{-9}	
0.000 001	1×10^{-6}	6	1×10^{-8}	
0.000 000 1	**1×10^{-7}**	**7**	**1×10^{-7}**	**0.000 000 1**
	1×10^{-8}	8	1×10^{-6}	0.000 001
	1×10^{-9}	9	1×10^{-5}	0.000 01
	1×10^{-10}	10	1×10^{-4}	0.000 1
	1×10^{-11}	11	1×10^{-3}	0.001
	1×10^{-12}	12	1×10^{-2}	0.01
	1×10^{-13}	13	1×10^{-1}	0.1
	1×10^{-14}	14	1×10^{0}	1
	1×10^{-15}	15	1×10^{1}	10

Calculating the pH of Solutions

Example 1

What is the pH of a 0.01 mol l^{-1} solution of hydrochloric acid?

$$HCl_{(g)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

1 mole   1 mole

$[H^+] = 0.01$ mol l^{-1}

$ = 10^{-2}$ mol l^{-1}
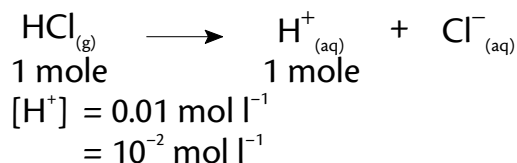
So the pH = 2

Example 2

What is the pH of a 0.001 mol l^{-1} solution of sodium hydroxide?

$$NaOH \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

1 mole   1 mole

$[OH^-] = 0.001$ mol l^{-1}

$ = 10^{-3}$ mol l^{-1}
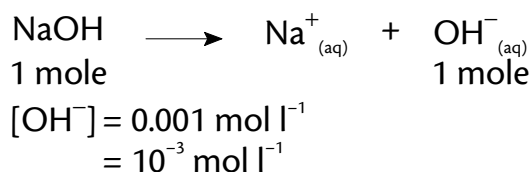
In any aqueous solution:

$[H^+][OH^-] \quad = \quad 10^{-14}$ mol^2 l^{-2}

So $\qquad [H^+] = \dfrac{10^{-14}}{[OH^-]}$

$ = \dfrac{10^{-14}}{10^{-3}}$

$ = 10^{-11}$ mol l^{-1}

So the pH = 11

Both the examples we have done have shown integral pH values.

In fact the pH scale is continuous running from less than 0 to more than 14, and pH values can be non integral (although you will not do calculations with such values).

Strong and Weak Acids

The pH of a 0.1 mol l^{-1} solution of hydrochloric acid is 1. Hydrochloric acid is a strong acid and is fully dissociated into ions in aqueous solution.

$$HCl_{(g)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

1 mole   1 mole
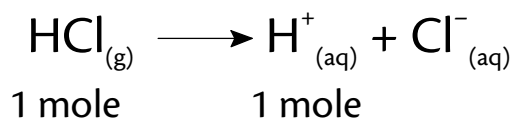
So if the HCl concentration is 0.1 mol l^{-1} then $[H^+]$ is also 0.1 mol l^{-1}

ie $[H^+]$ 0.1 $= 10^{-1}$ mol l^{-1}

So the pH $= 1$

When the pH of 0.1 mol l^{-1} ethanoic acid is measured it is found to be 3. This indicates a lower hydrogen ion concentration. Ethanoic acid is a weak acid because it is not fully dissociated into ions in aqueous solution.

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$
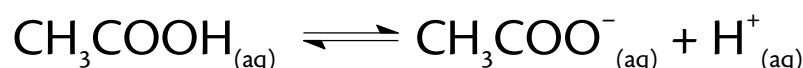
Comparison of Strong and Weak Acids

Equimolar (0.1 mol l^{-1}) solution of hydrochloric and ethanoic acids were compared in a number of experiments. The results were:

	Hydrochloric acid	Ethanoic acid
pH	1	3
Conductivity	High	Low
Reaction with Mg	Fast	Slow
Reaction with $CaCO_3$	Fast	Slow

The higher concentration of $H^+_{(aq)}$ ions in hydrochloric acid accounts for the lower pH, the high conductivity and the faster reaction rates.

The experiments above can be used to distinguish strong and weak acids.

Amount of Alkali Neutralised by Strong and Weak Acids

Neutralisation is the joining of H^+ and OH^- ions to form water.

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)}$$

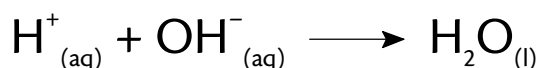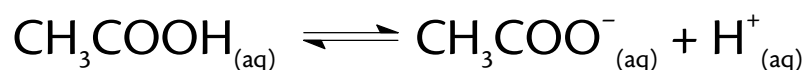We might expect that weak acids with their lower concentration of $H^+_{(aq)}$ ions would neutralise a smaller amount of alkali than a strong acid. However 0.1 mol l^{-1} ethanoic acid neutralises exactly the same volume of sodium hydroxide solution as 0.1 mol l^{-1} hydrochloric acid.

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$

removed by $OH^-_{(aq)}$ to form water

Ethanoic acid is a weak acid so at any one time there is a small concentration of $H^+_{(aq)}$ ions. As these are removed from the equilibrium mixture by joining with $OH^-_{(aq)}$ ions to form water, the equilibrium shifts to the right. More CH_3COOH molecules dissociate to produce more $H^+_{(aq)}$ ions which are in turn neutralised by $OH^-_{(aq)}$ ions. This continues until all the weak acid molecules have dissociated and so the same amount of alkali is neutralised by a weak acid as a strong acid.

This all means that the amount of alkali neutralised cannot be used to distinguish strong and weak acids.

Examples of Strong Acids

Hydrochloric acid $\qquad HCl \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$

Nitric Acid $\qquad HNO_3 \longrightarrow H^+_{(aq)} + NO_3^-{}_{(aq)}$

Sulphuric Acid $\qquad H_2SO_4 \longrightarrow 2H^+_{(aq)} + SO_4^{2-}{}_{(aq)}$
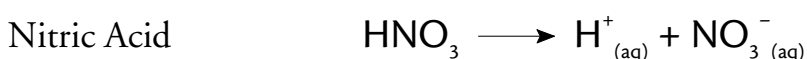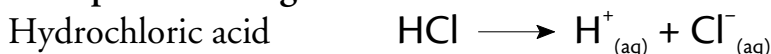
Examples of Weak Acids

Carboxylic acids
We have used ethanoic acid as an example of a weak acid, but the carboxylic acids in general are weak acids.

Note that the hydrogen atoms bonded to carbon have no tendency to ionise. The hydrogen atom bonded to the oxygen has a limited tendency to ionise.

The polarisation of the covalent bonds makes the hydrogen δ+ and assists in its removal as an H^+ ion.

Carbonic Acid
Carbon dioxide is slightly soluble in water giving the weak acid, carbonic acid, H_2CO_3

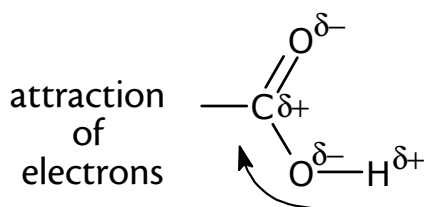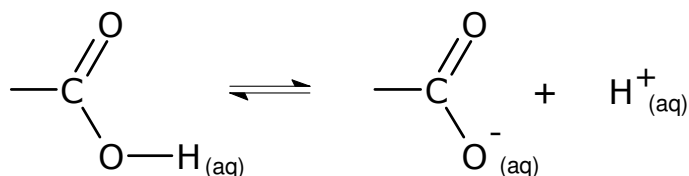$$CO_{2(g)} + H_2O_{(l)} \longrightarrow H_2CO_{3(aq)} \rightleftharpoons 2H^+_{(aq)} + CO_3^{2-}_{(aq)}$$
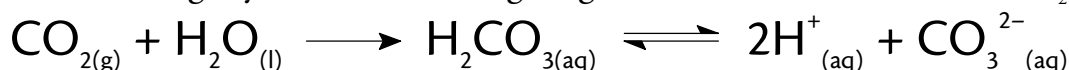
Sulphurous acid
Sulphur dioxide is very soluble in water forming the weak acid, sulphurous acid, H_2SO_3

$$SO_{2(g)} + H_2O_{(l)} \longrightarrow H_2SO_{3(aq)} \rightleftharpoons 2H^+_{(aq)} + SO_3^{2-}_{(aq)}$$
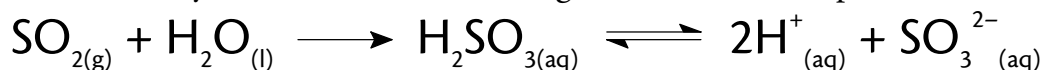
Sulphur dioxide is released into the atmosphere by the combustion of fossil fuels. It dissolves in atmospheric moisture to give sulphurous acid, one of the main constituents of acid rain.

Strong and Weak Alkalis

A strong alkali like NaOH or KOH is fully dissociated into ions in aqueous solution.

$$NaOH_{(s)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

Ammonia gas is very soluble in water. The solution is a weak alkali because it is not fully dissociated into its ions in aqueous solution.

$$NH_{3(g)} + H_2O_{(l)} \longrightarrow NH_4OH_{(aq)} \rightleftharpoons NH_4^+_{(aq)} + OH^-_{(aq)}$$

The equation below shows why an ammonia solution is alkaline – the lone pair of electrons on the nitrogen attract the δ+ hydrogen on the water molecules.

ammonia   ammonium ion
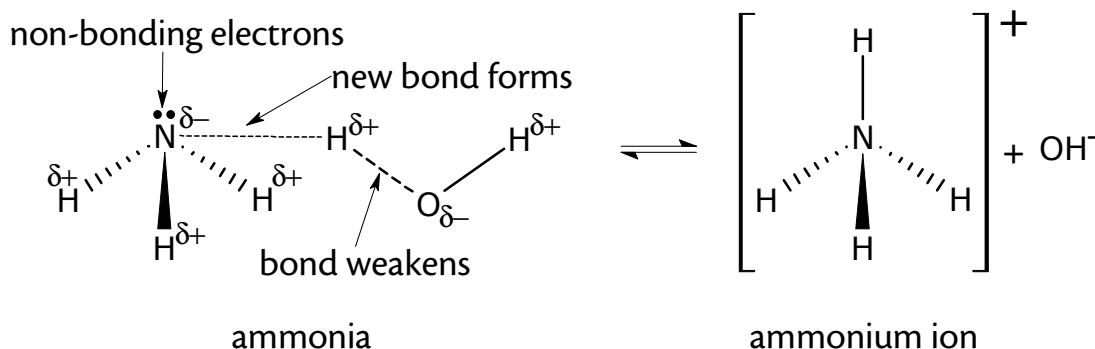
Comparison of Strong and Weak Alkalis

The table below shows the results of comparing 0.1 mol l^{-1} sodium hydroxide and 0.1 mol l^{-1} ammonia solutions

	Sodium hydroxide	Ammonia
pH	13	11–12
Conductivity	High	Low

Strong and weak alkalis cannot be distinguished by comparing the amount of acid they neutralise. (This is exactly the same as we observed earlier with strong and weak acids.)

A weak base like ammonia is only slightly ionised so initially the [OH$^-$] is low.

$$NH_4OH_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

$$\downarrow$$
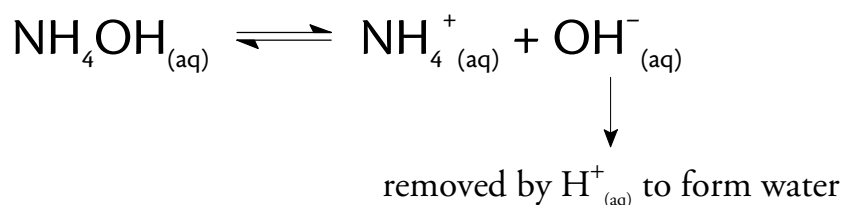
removed by H$^+$$_{(aq)}$ to form water

As acid is added, the H$^+$ ions join with OH$^-$ ions to form water. The equilibrium shifts to the right producing more OH$^-$ ions which are in turn neutralised. Eventually all the ammonia solution dissociates and so neutralises the same amount of acid as a strong alkali.

Confusion of Strength and Concentration

Don't confuse strong and weak with concentrated and dilute.

| Strong	Weak
fully dissociated in aqueous solution	not fully dissociated in aqueous solution

Concentrated	Dilute
a lot of solute in a little water eg 2 mol l^{-1}	a little solute in a lot of water eg 0.1 mol l^{-1}

Hydrolysis of Salts

When salts dissolve in water they become fully ionised. Sometimes these ions can disturb the water equilibrium giving an acidic or alkaline solution.

$$H_2O_{(l)} \rightleftharpoons H^+{}_{(aq)} + OH^-{}_{(aq)}$$

When there is an interaction between the water equilibrium and the ions from the salt we say that salt hydrolysis has taken place. Let's look at some examples.

Ammonium chloride solution

We have $$H_2O_{(l)} \rightleftharpoons H^+{}_{(aq)} + OH^-{}_{(aq)} \rightleftharpoons NH_4OH$$

and $$NH_4Cl_{(s)} \longrightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$

The H$^+$ and Cl$^-$ ions have no tendency to join because HCl is a strong acid and so is fully ionised. However NH$^{4+}{}_{(aq)}$ and OH$^-{}_{(aq)}$ are the ions of a weak base – they cannot remain totally free of each other. Some must associate to form NH$_4$OH molecules. This removes OH$^-$ from the water equilibrium which shifts to the right to replace them; this results in an excess of H$^+$ ions. The solution is therefore acidic, with a pH less than 7.

Sodium ethanoate solution

We have

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

and

$$CH_3COONa_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

$$CH_3COOH$$

The Na^+ and OH^- ions have no tendency to associate as NaOH is a strong alkali. However CH_3COO^- and H^+ are the ions of a weak acid and so cannot remain totally dissociated. Some must join to give CH_3COOH molecules. This of course removes H^+ ions from the water equilibrium which shifts to the right to replace those removed. This results in an excess of OH^- ions giving an alkaline solution, with pH greater than 7.

Potassium nitrate solution

We have

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

and

$$KNO_{3(s)} \longrightarrow K^+_{(aq)} + NO^-_{3\ (aq)}$$

The H^+ and NO_3^- are the ions of a strong acid and the K^+ and OH^- are the ions of a strong alkali. Therefore none of the ions has any tendency to associate so the water equilibrium is not disturbed and the solution is neutral, with a pH of 7.

Soaps

Soaps, as we saw in Unit 2, are salts of long chain fatty acids

eg sodium stearate $C_{17}H_{35}COO^-Na^+$

Like sodium ethanoate, they are salts of a carboxylic acid. So they are salts of a weak acid and a strong alkali. As a result, their solutions in water will be alkaline.
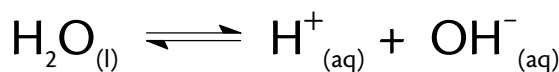
To summarise

a. The salt of a weak acid and strong alkali gives an alkaline solution
    eg CH_3COONa, Na_2CO_3, Na_2SO_3, sodium stearate

b. The salt of a strong acid and a weak alkali gives an acidic solution.
    eg NH_4Cl, $FeCl_3$

c. The salt of a strong acid and a strong alkali gives a neutral solution
    eg $NaCl$, KNO_3, Na_2SO_4, $MgCl_2$, $CaCl_2$

Equilibrium in saturated solutions

A saturated solution in contact with undissolved solute is an example of a system in equilibrium

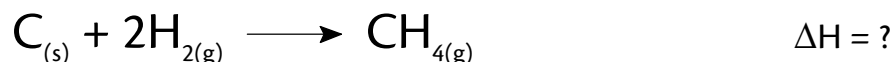$$NaCl_{(s)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$

No further overall change occurs once saturation is reached. However solute continues to dissolve at a rate just balanced by the rate at which solid crystallises from the solution.

Topic 2 – Hess's Law, Redox and Electrolysis

Hess's Law

In Unit 1 we used experimental results to calculate enthalpy changes for the Heat of Combustion of ethanol and the Heat of Solution of potassium nitrate. Sometimes we want to find the enthalpy change for a reaction that is difficult or even impossible to carry out. An example is the formation of 1 mole of methane from its elements.

$$C_{(s)} + 2H_{2(g)} \longrightarrow CH_{4(g)} \qquad \Delta H = ?$$

The heat of reaction cannot be measured directly as the reaction does not occur under normal conditions. The enthalpy can, however, be calculated using an alternative route from the reactants to the products. This uses a form of the Law of Conservation of Energy which states energy cannot be created or destroyed. Hess's Law states that:
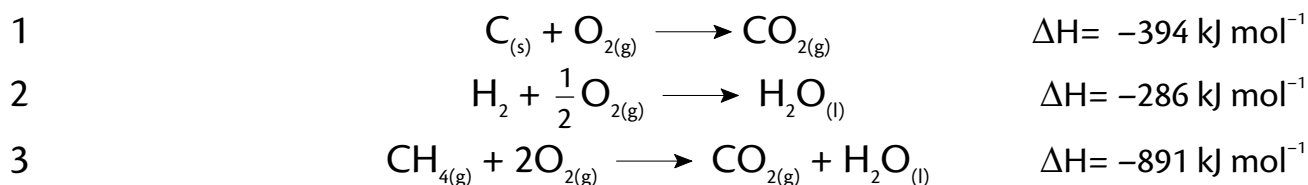
> The enthalpy change in a chemical reaction depends only on the reactants and products and is independent of the route taken between them.

Its use is best illustrated by using the above example; calculate the enthalpy change for the formation of 1 mole of methane from its elements using the enthalpies of combustion of carbon, hydrogen and methane from the data book.

First write the equation for the reaction whose heat we require:

$$C_{(s)} + 2H_{2(g)} \longrightarrow CH_{4(g)} \qquad \Delta H = ?$$

Now write equations for the information given in the data book:

1	$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$	$\Delta H = -394 \text{ kJ mol}^{-1}$
2	$H_2 + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$	$\Delta H = -286 \text{ kJ mol}^{-1}$
3	$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + H_2O_{(l)}$	$\Delta H = -891 \text{ kJ mol}^{-1}$

Now use the given information to build up the required equation:

1	$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$	$\Delta H = -394 \text{ kJ mol}^{-1}$
2 × 2	$2H_2 + O_{2(g)} \longrightarrow 2H_2O_{(l)}$	$\Delta H = -572 \text{ kJ mol}^{-1}$
3 rev	$CO_{2(g)} + H_2O_{(l)} \longrightarrow CH_{4(g)} + 2O_{2(g)}$	$\Delta H = -891 \text{ kJ mol}^{-1}$
adding	$C_{(s)} + 2H_{2(g)} \longrightarrow CH_{4(g)}$	$\Delta H = -75 \text{ kJ mol}^{-1}$

Plenty of practice is needed to gain confidence in Hess's Law Problems. There is also a Prescribed Practical which verifies Hess's Law experimentally.

Redox Reactions

Reactions involving oxidation and reduction are called Redox Reactions. We met some redox reactions in Standard Grade Chemistry.

Displacement Reactions
eg zinc metal displaces silver from silver (I) nitrate solution.

We can look at this in terms of these two ion-electron half equations:

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e \qquad \text{Oxidation}$$

$$Ag^{+}_{(aq)} + e \longrightarrow Ag_{(s)} \qquad \text{Reduction}$$
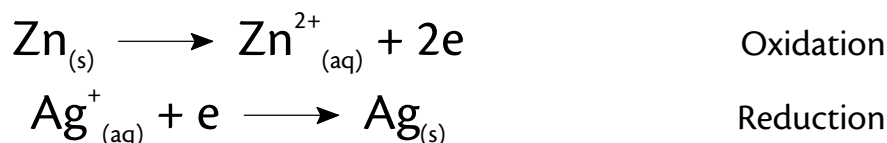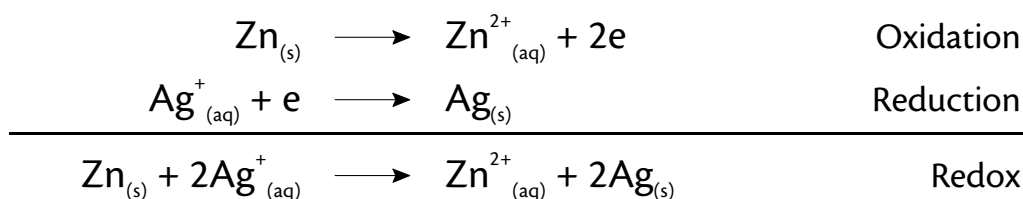
Note
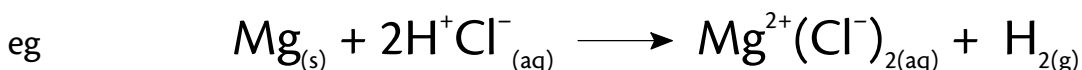The zinc metal is the reducing agent. It donates electrons and is oxidised.
The silver ion is the oxidising agent. It accepts electrons and is reduced.

The number of electrons lost in the oxidation must balance the number of electrons gained in the reduction. To achieve this we must multiply the second equation by 2. When this is done we can add the 2 half-equations to get the Redox Equation:

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e \qquad \text{Oxidation}$$

$$Ag^{+}_{(aq)} + e \longrightarrow Ag_{(s)} \qquad \text{Reduction}$$

$$\overline{Zn_{(s)} + 2Ag^{+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}} \qquad \text{Redox}$$
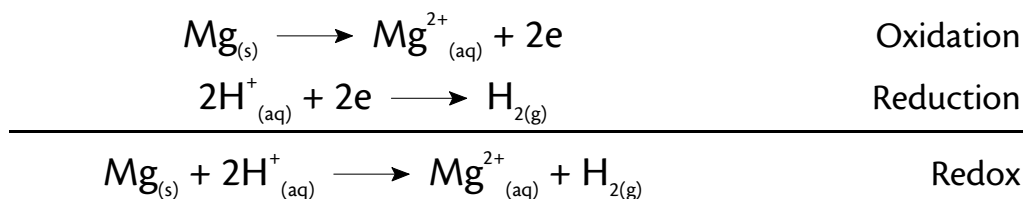
Note that the nitrate ions do not appear in the redox equation. This is because they are spectator ions and are not directly involved in the electron transfer.

Reaction of MAZIT metals with dilute acid.

$$\text{eg} \qquad Mg_{(s)} + 2H^{+}Cl^{-}_{(aq)} \longrightarrow Mg^{2+}(Cl^{-})_{2(aq)} + H_{2(g)}$$

Again we can write ion electron equations for the oxidation and reduction reactions:

$$Mg_{(s)} \longrightarrow Mg^{2+}_{(aq)} + 2e \qquad \text{Oxidation}$$

$$2H^{+}_{(aq)} + 2e \longrightarrow H_{2(g)} \qquad \text{Reduction}$$

$$\overline{Mg_{(s)} + 2H^{+}_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + H_{2(g)}} \qquad \text{Redox}$$

The magnesium metal is the reducing agent and the hydrogen ions are the oxidising agent.

Balancing ion electron half equations

Potassium permanganate ($KMnO_4$) oxidises Fe^{2+} ions to Fe^{3+} ions. During this reaction the MnO_4^{-} ions are reduced to Mn^{2+} ions.

$$Fe^{2+} \longrightarrow Fe^{3+} + e \qquad \text{This is balanced}$$

$$MnO_4^{-} \longrightarrow Mn^{2+} \qquad \text{This is not so simple to balance and needs some rules}$$

1. Write down the main chemical in its two forms (oxidised and reduced) and balance the main atom(s)

$$MnO_4^- \longrightarrow Mn^{2+}$$

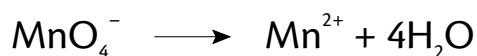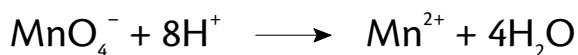2. Balance oxygen by adding water molecules

$$MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$$

3. Balance hydrogen by adding hydrogen ions

$$MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$$

4. Balance the charge by adding electrons

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$$

To get the redox equation we must multiply the iron half equation by 5 before adding.

$$5Fe^{2+} \longrightarrow 5Fe^{3+} + 5e \qquad \text{Oxidation}$$
$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O \qquad \text{Reduction}$$
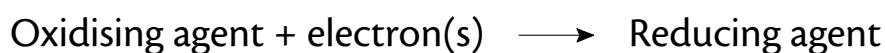$$\overline{MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O} \qquad \text{Redox}$$

Note that in the previous example the Fe^{2+} ions were the reducing agent and were themselves oxidised to Fe^{3+} ions by donating electrons.

In a different reaction Iodide (I^-) ions can be oxidised to iodine by Fe^{3+} ions. The Fe^{3+} ions are reduced to Fe^{2+} ions.

$$2I^-_{(aq)} \longrightarrow I_{2(aq)} + 2e \qquad \text{Oxidation}$$
$$Fe^{3+}_{(aq)} + e \longrightarrow Fe^{2+}_{(aq)} \qquad \text{Reduction}$$

So in the previous example, Fe^{2+} was a reducing agent and in this example Fe^{3+} is an oxidising agent. This can be summed up as:

$$\text{Oxidising agent + electron(s)} \longrightarrow \text{Reducing agent}$$

or

$$\text{Reducing agent} \longrightarrow \text{Oxidising agent + electron(s)}$$

Redox Titrations

You are familiar with acid base titrations. Redox titrations are similar but involve solutions of oxidising agents reacting with reducing agents. You will do a Prescribed Practical in which the mass of Vitamin C in a tablet is determined by a redox titration. Another common redox titration uses acidified potassium permanganate as an oxidiser; for example it can be used to oxidise Fe^{2+} ions to Fe^{3+} ions. The end point uses the fact that MnO_4^- is purple and Mn^{2+} is colourless.

In this reaction, the acidified potassium permanganate is added from a burette to the solution of iron(II) ions. The iron ions are oxidised and the purple permanganate ions (MnO_4^-) are reduced to colourless Mn^{2+} ions. The equations for this follow the example of balancing half-equations above. The end point is the first permanent pink colour; this indicates the permanganate ions have oxidised all the Fe^{2+} ions and are just in excess.

From the results, the concentration of iron ions in the solution can be calculated as the following example shows.

It takes 20 ml of 0.1 mol l^{-1} permanganate solution to react completely with 25 ml of an iron (II) solution. What is the concentration of the iron (II) ions?

Method A
Let the concentration of iron (II) ions be x. We worked out this equation earlier:

$$MnO_4^- \;\; + \;\; 5Fe^{2+} \;\; + \;\; 8H^+ \;\; \longrightarrow \;\; Mn^{2+} + 5Fe^{3+} + 4H_2O$$

1 mole   5 moles

20 ml; 0.1 mol l^{-1} 25 ml; x mol l^{-1}

$$\frac{20 \times 0.1}{25 \times x} = \frac{1}{5}$$

$$x = 0.4$$

So the concentration of iron(II) ions is 0.4 mol l^{-1}

Method B
This is an alternative fuller answer which leads you through the problem in steps:

First calculate the number of moles of permanganate used

0.1 mol l^{-1} permanganate means

1000ml contains   0.1 moles of permanganate ions

so   20.0 ml contains $\dfrac{0.1}{1} \times \dfrac{20}{1000}$ moles permanganate ions

= 0.002 moles permanganate

Now calculate the moles of iron reacting with the permanganate

The equation tells us that 1 mole of permanganate reacts with 5 moles of iron ions,

so   the moles of iron we have   = 0.002 x 5 moles iron ions
                                        = 0.01 moles iron ions

so   25 ml Fe^{2+} solution contains   0.01 moles iron(II) ions

so   1000 ml Fe^{2+} solution contains $\dfrac{0.01}{1} \times \dfrac{1000}{25}$ moles iron(II) ions

=0.4 moles iron(II) ions

This means that the concentration of the iron(II) ions is 0.4 mol l^{-1}

Electrolysis

We met electrolysis in Standard Grade but only in a qualitative way; in other words we were only interested in what the products were but not how much was formed.

eg we electrolysed copper(II) chloride solution using carbon electrodes. The ions present are $Cu^{2+}_{(aq)}$ and $Cl^-_{(aq)}$.

Negative electrode (the cathode)
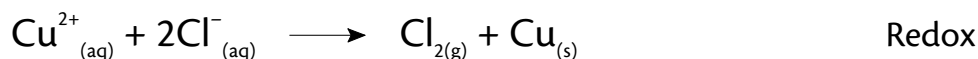This attracts Cu^{2+} which gains electrons to become copper metal:

$$Cu^{2+}_{(aq)} + 2e \longrightarrow Cu_{(s)} \qquad\qquad \text{Reduction}$$

Positive electrode (the anode)
This attracts the Cl^- ions which lose electrons to become chlorine gas

$$2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2e \qquad\qquad \text{Oxidation}$$

As before the oxidation and reduction ion electron half equations can be added to give the redox equation

$$Cu^{2+}_{(aq)} + 2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + Cu_{(s)} \qquad\qquad \text{Redox}$$

We return to electrolysis now but we will be studying it in a quantitative way. In other words we will be interested in how much product is made.

You will carry out a Prescribed Practical in which dilute sulphuric acid will be electrolysed. The aim is to find out what quantity of electricity is required to produce 1 mole of hydrogen gas at the negative electrode. The total quantity of electricity passing in an electrolysis depends on the size of the current and the time the current was passing. The following formula is used:
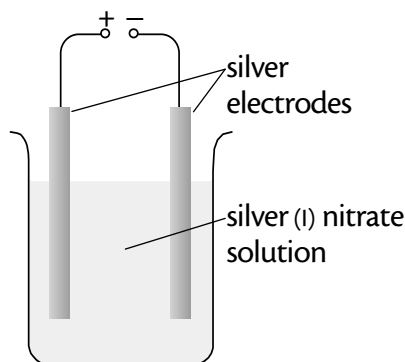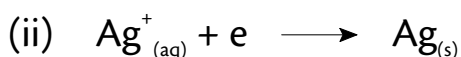
$$\text{quantity of electricity (coulombs)} = \text{current (amps)} \times \text{time (seconds)}$$

$$Q = I \times t$$

The following are some typical results from similar quantitative electrolyses.

1. Electrolysis of silver (I) nitrate solution
Using silver electrodes the positive electrode dissolves (i) and silver ions are discharged and deposited as silver metal on the negative electrode (ii).

(i) $\qquad Ag_{(s)} \longrightarrow Ag^+_{(aq)} + e$

(ii) $\quad Ag^+_{(aq)} + e \longrightarrow Ag_{(s)}$

The negative electrode is weighed before and after the experiment.

The current, in amps, and the time, in seconds, for which it passed are also noted.

Typical results

Mass of silver deposited   = 0.7167 g

Current passed   =   0.5 A

Time   =   1282 s
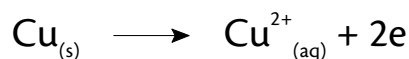
$$Q = I \times t$$
$$= 0.5 \times 1282$$
$$= 641 \text{ C}$$

    0.7167g of silver are deposited by   641 C

So 107.9g (1 mole) of silver would be deposited by $\dfrac{641}{1} \times \dfrac{107.9}{0.7167}$
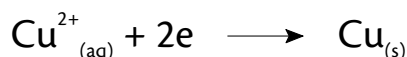
$$= 96\,500 \text{ C}$$

This quantity of electricity, 96 500 C, is called 1 Faraday (1 F).

So 1 Faraday discharges 1 mole of silver ions (Ag^+)

2. Electrolysis of Copper (II) Sulphate

Using copper electrodes, the positive electrode dissolves

$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e$$

and copper ions are discharged and deposited as copper metal on the negative electrode

$$Cu^{2+}_{(aq)} + 2e \longrightarrow Cu_{(s)}$$

The same measurements are made as in the previous experiment.

Typical results

Mass of copper deposited = 0.1184 g

Current passed   =   0.2 A

Time   =   1800 s

$$Q = I \times t$$
$$= 0.2 \times 1800$$
$$= 360 \text{ C}$$

    0.1184g of copper are deposited by   360 C

So 63.5g (1 mole) of copper would be deposited by $\dfrac{360}{1} \times \dfrac{63.5}{0.1184}$

$$= 193\,000 \text{ C}$$

This quantity of electricity is 2 Faradays (2 F).

So 2 Faradays are required to deposit 1 mole of copper (II) ions (Cu^{2+})

Electrolysis in General

1 mole of silver ions	$Ag^+ + e \longrightarrow Ag$	requires 1 Faraday
1 mole of copper (II) ions	$Cu^{2+} + 2e \longrightarrow Cu$	requires 2 Faradays
1 mole of aluminium ions	$Al^{3+} + 3e \longrightarrow Al$	requires 3 Faradays
1 mole of hydrogen ions	$H^+ + e \longrightarrow \frac{1}{2}H_2$	requires 1 Faraday
1 mole of bromide ions	$Br^- \longrightarrow \frac{1}{2}Br_2 + e$	requires 1 Faraday

In general, one mole of ions is discharged by nF Coulombs where n is the charge on the ion and F is the Faraday.

Here is a worked example of a typical electrolysis problem.

What mass of nickel is deposited at the negative electrode when a solution of nickel (II) chloride is electrolysed for 25min 30s using a current of 0.4A?

Calculate the total quantity of electricity using

$$Q = I \times t$$

Remember time must be in seconds; 25min 30 s = 1530s

So   Q = 0.4 × 1530
         = 612 C

Treat this as a calculation from an equation; so start with a balanced equation:

$$Ni^{2+}_{(aq)} \quad + \quad 2e \quad \longrightarrow \quad Ni_{(s)}$$

	2 moles	1 mole
so	2 × 96 500 C	58.7g
therefore	612 C	$\frac{58.7}{1} \times \frac{612}{2 \times 96500}$
		= 0.186g

So mass of nickel deposited = 0.186g

Topic 3 − Nuclear Chemistry

Radioactivity

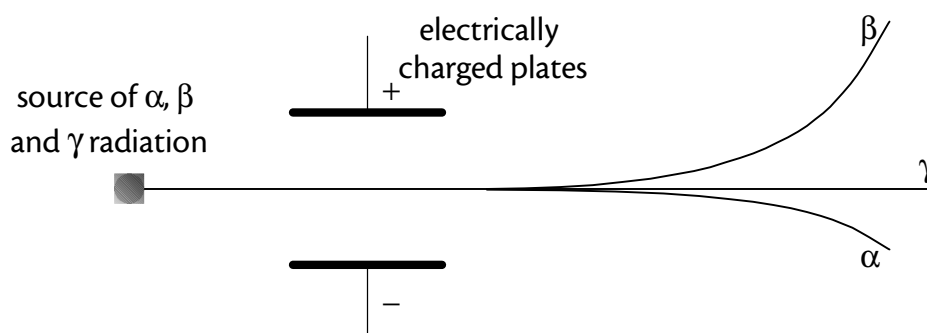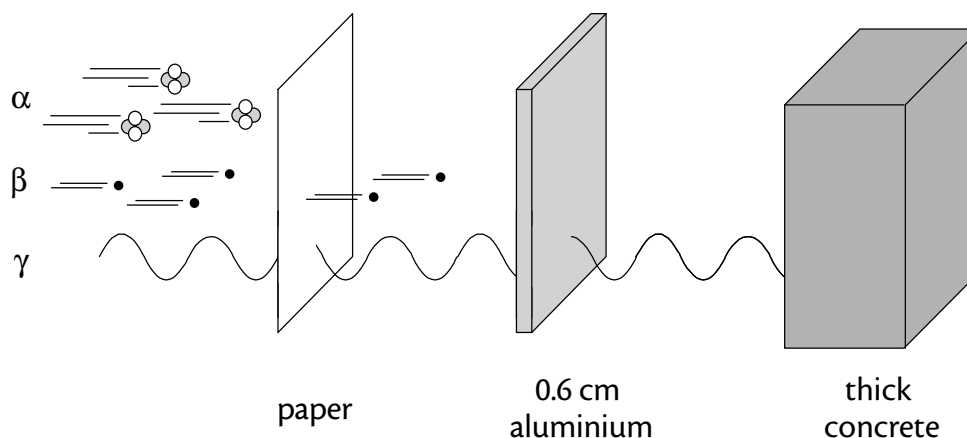As the title suggests this topic is about the chemistry of the nucleus and not about the orbitting electrons which have had an influence on the chemical reactions we have studied so far. In 1896, Becquerel discovered that compounds of uranium could 'fog' photographic plates which had been kept in the dark. The phenomenon became known as radioactivity and such substances were said to be radioactive. They emit radiation which can be of 3 types: α-, β- and γ-radiation. The radiation was affected by electric fields as shown:

This shows that α-radiation is positively charged, β-radiation is negative and γ-radiation has no charge.

α-, β- and γ-radiations also have different penetrating powers:

Some of the properties of these radiations are summarised in the table:

Name	Penetration	Nature	Charge	Mass (amu)
α (alpha)	few cm in air	He nucleus	2+	4
β (beta)	thin metal foil	electron	1−	1/2000 (approx)
γ (gamma)	thick concrete	emr*	none	None

*electromagnetic radiation

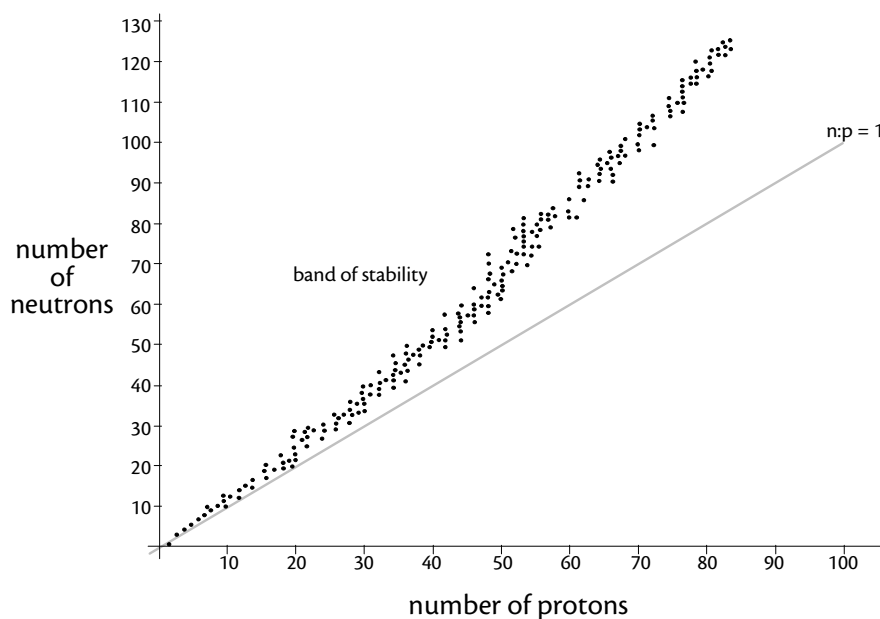α-particles are identical to helium nuclei, $^{4}_{2}\text{He}^{2+}$. They are positively charged.

β-particles are electrons, $^{0}_{-1}\text{e}$. They are negatively charged.

γ-rays are very high energy electromagnetic radiation, similar to X-rays, hence the great penetrative powers. They have no charge.

Radioactivity is connected solely with the nucleus of the element concerned. This means that its chemical state is totally unimportant! Uranium compounds are as radioactive as the element.
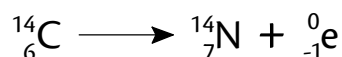
Radioactivity is a feature of unstable nuclei and emitting radiation is a means by which the nuclei can become stable. So what makes a nucleus unstable? Protons are positively charged and it is thought that the neutrons prevent the protons repelling each other. The proton:neutron ratio is an important factor in deciding whether a nucleus is stable or not. For small stable atoms, the number of protons and neutrons are approximately the same but as the atoms become larger, the number of neutrons needs to be greater than the number of protons if the atom is to be stable. Look at the graph below:

If an atom has too many or too few neutrons for the number of protons, the atom will not lie on the belt of stability and will be unstable and so, radioactive. Very large atoms (>83 protons) are always unstable, irrespective of the number of neutrons in the nucleus. It is generally found that where a nucleus has too many neutrons, it changes a neutron into a proton and an electron and ejects the electron as β-radiation.
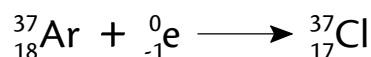
$$\,^{1}_{0}n \longrightarrow \,^{1}_{1}p + \,^{0}_{-1}e \qquad\qquad \text{β-emission}$$

This extra proton results in an increase in atomic number.

eg ^{14}C emits a β-particle and becomes a stable isotope of nitrogen

$$\,^{14}_{6}C \longrightarrow \,^{14}_{7}N + \,^{0}_{-1}e$$

The opposite might happen if the neutron:proton ratio is too low – electron capture happens from the first 'shell'. This combines with a proton to form a neutron and the other electrons rearrange themselves to fill the first shell.

$$\,^{37}_{18}Ar + \,^{0}_{-1}e \longrightarrow \,^{37}_{17}Cl$$

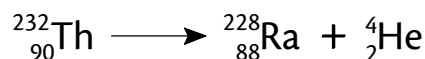It is found that very large nuclei (generally those with atomic number beyond 83) can become more stable by becoming smaller ie decreasing mass – this can be done by emitting α-particles. An α-particle consists of a helium nucleus ($^{4}_{2}He$) so its emission means a loss in mass of 4. These radiations come from the nucleus and as a result the nucleus is changed. We must look at this in more detail.

α-emission

The nucleus loses 2 protons and 2 neutrons; this decreases the charge on the nucleus by 2 and the mass of the nucleus by 4.
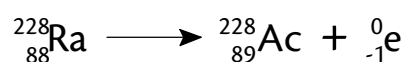
eg thorium 232 is an α-emitter. We can show this in a nuclear equation. Note: both the mass (top number) and the charge (bottom number) must be balanced in a nuclear equation.

$$^{232}_{90}\text{Th} \longrightarrow {}^{228}_{88}\text{Ra} + {}^{4}_{2}\text{He}$$

Since the emission also involves the loss of two protons the atomic number must decrease by 2 and we have made a new element. This is called transmutation.
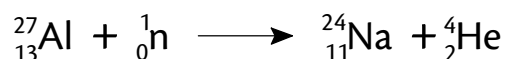
β-emission

A β-particle is an electron, yet the nucleus does not contain any electrons. It is thought that a neutron changes into a proton and an electron and this electron is emitted as β-radiation. The other result is that the nucleus contanins an extra proton and the atomic number increases by 1. This another example of transmutation.

$$^{228}_{88}\text{Ra} \longrightarrow {}^{228}_{89}\text{Ac} + {}^{0}_{-1}\text{e}$$
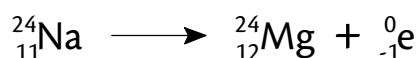
γ-emission

Emission of γ-radiation often occurs along with the other types of radiation. It is a means by which nuclei can lose energy but, as it is not particle in nature and so has no mass or charge it does not affect mass number or atomic number.

Artificial Radioactivity

The examples above are natural radioisotopes but it is possible to make radioactive isotopes, and many are made for special purposes. They can be made by bombarding stable isotopes with neutrons in a nuclear reactor. Since neutrons are uncharged they are not repelled by the nucleus.

$$^{27}_{13}\text{Al} + {}^{1}_{0}\text{n} \longrightarrow {}^{24}_{11}\text{Na} + {}^{4}_{2}\text{He}$$

The sodium isotope produced by the above can decay by β-emission to produce magnesium:

$$^{24}_{11}\text{Na} \longrightarrow {}^{24}_{12}\text{Mg} + {}^{0}_{-1}\text{e}$$

This source of radioactive isotopes is employed for making some of the useful radioisotopes which we will meet later. Very high energy particle accelerators have now been developed which allow positively charged particles to be used for bombardment.

Predictability of Radioactive Decay

When unstable nuclei emit radiation they are said to be decaying. It is impossible to predict exactly when one particular nuclide will in fact decay – this is a purely random event. However, with the massive numbers of radioactive nuclides in any measurable quantity, the laws of probability allow us to determine when a certain defined fraction of them will have decayed – the fraction is in fact ½ of the original. The time that this takes to happen is called the 'half-life'.

Half-life for any radioactive isotope is a constant, irrespective of how much of the isotope is left. It is also independent of the form (element, mixture or compound), temperature or applied pressure – it is fixed! However the intensity of the radiation will depend on the quantity of the radioisotope present. The graph below shows the decay of ^{32}P.

It is an example of an exponential decay curve. The percentage of the original left after n half-lives is $(\frac{1}{2})^n$. Here are some examples of half life calculations:

Example 1

A radioisotope of phosphorus has a mass of 80g and a half-life of 14 days. Calculate the mass of the isotope remaining after 56 days.

56 days = 4 half-lives

$$80g \xrightarrow{t_{1/2}} 40g \xrightarrow{t_{1/2}} 20g \xrightarrow{t_{1/2}} 10g \xrightarrow{t_{1/2}} 5g$$

So the mass remaining after 56 days is 5g

Example 2

The initial radioactivity of a radioisotope was 100 counts/minute. If the activity fell to 25 counts/minute in 24 days, what is the half-life of the radioisotope?

$$100 \xrightarrow{t_{1/2}} 50 \xrightarrow{t_{1/2}} 25$$

2 half-lives have elapsed in 24 days, so the half-life of the radioisotope is 12 days.

Example 3

A radioisotope has a half life of 7×10^3 years. How long will it take for 48g of the radioisotope to decay to leave 6g?

$$48g \xrightarrow{t_{1/2}} 24g \xrightarrow{t_{1/2}} 12g \xrightarrow{t_{1/2}} 6g$$

3 half-lives = $3 \times 7 \times 10^3$ = 2.1×10^4 years

Uses of radioisotopes

1. Medical Uses

For many years now, radiotherapy has been used for the treatment of some cancers.

^{60}Co is often used for the treatment of deep seated tumours – it is a γ-emitter so is able to penetrate to the site of the tumour. Skin cancers can be treated with less penetrating radiation from ^{32}P which is a β-emitter. It is also possible to monitor biological processes in the body. For example, radioactive iodine, ^{132}I or ^{123}I, is used to investigate possible disease of the thyroid gland. After injection of a solution containing some of the isotope its uptake in the thyroid gland can be determined – this allows diseased areas to be traced.

2. Industrial uses

Measurements and monitoring of various industrial processes can be made using radioactive isotopes. For example, imperfections in metal castings and welded joints can be examined using very penetrating radiation (γ-radiation from ^{60}Co or ^{192}Ir). Photographic film can be used as the detector. Continuous measurements and control of continuous processes can be made such as in the monitoring of thickness of paper, plastic and thin metal sheets. β- or γ-sources can be used to pass radiation through the sheets – one beam goes through a reference sheet of correct thickness. Any difference in signals between the two sources shows difference in thickness and this can trigger a response to make a correction.

3. Agricultural uses

Isotopes ^{32}P and ^{14}C can be used to determine the uptake of phosphates and carbon dioxide in plants. This is called 'isotopic labelling'.

γ-radiation can be used to kill bacteria and moulds in crops and this helps to increase the storage life.
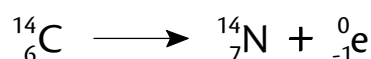
4. Dating

The age of materials can be determined from the half life of certain isotopes. Carbon dating is probably the most familiar form of this technique.

^{14}C is a radioactive isotope which exists naturally due to its formation in the upper atmosphere from nitrogen bombarded by neutrons.

$$^{14}_{7}N + {}^{1}_{0}n \longrightarrow {}^{14}_{6}C + {}^{1}_{1}p$$

Carbon-14 has a half-life of 5600 years and decays by β-emission.

$$^{14}_{6}C \longrightarrow {}^{14}_{7}N + {}^{0}_{-1}e$$

The rate of formation is equal to the rare of decay so there is a constant level of carbon-14 in the atmosphere. So carbon in the atmosphere is mostly the common isotope carbon-12 but with a small fixed proportion of carbon-14. Carbon-14 is absorbed by plants during photosynthesis so all living plants and animals contain the radioisotope. The level of carbon-14 in living materials is also constant since the rate of decay equals the rate of uptake from the atmosphere. When the plant or animal dies it no longer absorbs carbon-14 so the level of radioactivity will decrease. By comparing the activity of plant or animal remains with that of living material and knowing that the half life of carbon-14 is 5600 years, it is possible to calculate the age of the remains.
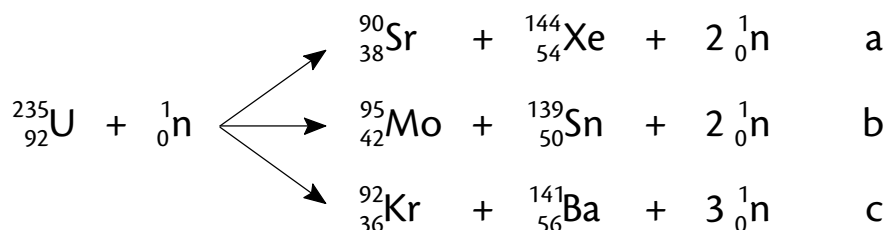
Example

Carbon from a wooden beam in a tomb has an activity of 3.75 counts per minute per gram of carbon. New wood has an activity of 15 counts per minute. What is the age of the beam?

$$15 \xrightarrow{\ t_{1/2}\ } 7.5 \xrightarrow{\ t_{1/2}\ } 3.75$$

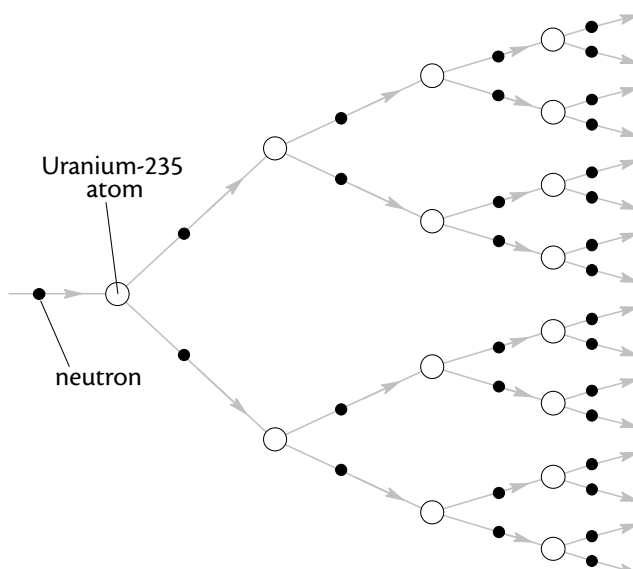$$2 \text{ half-lives } = 2\times 5600 = 11200 \text{ years}$$

5. Production of energy

Nuclear Fission involves the splitting of atoms by slow moving neutrons. The resulting nuclei are more stable than the original so energy is liberated in the process. The pattern of fragmentation varies. Here are three possible ways in which ^{235}U undergoes fission:

$$^{235}_{92}U + {}^{1}_{0}n \begin{cases} {}^{90}_{38}Sr + {}^{144}_{54}Xe + 2\,{}^{1}_{0}n & \text{a} \\[4pt] {}^{95}_{42}Mo + {}^{139}_{50}Sn + 2\,{}^{1}_{0}n & \text{b} \\[4pt] {}^{92}_{36}Kr + {}^{141}_{56}Ba + 3\,{}^{1}_{0}n & \text{c} \end{cases}$$
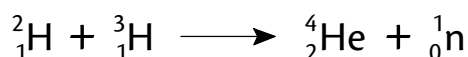
The fission process emits further neutrons. These can cause fission in other ^{235}U atoms and a chain reaction develops. The diagram on the right show what happens when two neutrons are released, as in reactions **a** and **b** above.

In a nuclear reactor the rate of this chain reaction must be controlled by lowering boron rods into the reactor. This nuclear reaction yields a huge amount of energy in the form of heat and this can be used to generate electricity.

Nuclear Fusion is when two nuclei join ('fuse'), causing energy to be released. This is another possible source of energy for the future. One such possibility is:

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

The above reaction creates even more energy than can be obtained from any fission reaction – only one ton ^{2}H and ^{3}H per year would be required for a 1000 MW power station. However it is very difficult to make 2 nuclei fuse because they are positively charged and the repulsion between them has to be overcome. It can only be achieved at exceptionally high temperatures, as found in our sun and stars. A great deal of research into this possibility is being conducted and it may well be a power source for the future.

Nuclear or Fossil Fuels for Generation of Electricity?

Calculations of energy released from the above equation show that 1 mole (235g) of ^{235}U would yield the equivalent energy of 60 tonnes of high quality coal (which would deliver 220 tonnes of CO_2 to the atmosphere)! This is of extreme environmental importance as nuclear reactors would reduce the consequences of the greenhouse effect and also reduce a contribution to acid rain. There are, however, some serious drawbacks of energy production from nuclear reactors. Serious accidents at nuclear plants would result in immensely catastrophic problems (probability of this is claimed to be low but accidents have happened – such as Chernobyl, 1986). The waste from some fission reactions is still very radioactive and needs to be re-processed or stored, perhaps for thousands of years, until the radioactivity has decayed to a safe level. Its disposal is a matter of great concern and debate.
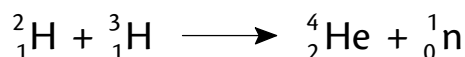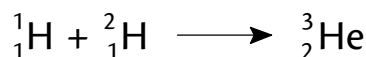
Background Radiation

Many people think that the radiation surrounding us (in the air etc) comes purely from man's work with radioactive materials – eg from nuclear reactors, fallout from nuclear explosions etc. However, much of our surrounding radiation is natural, from atmospheric radon and cosmic radiation. The pie chart below shows the relative contributions to our 'background radiation'.

The Origin of the Elements

Nuclear fusion reactions occur in our sun:

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

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

In the heaviest stars with the hottest and most compressed centres, further fusion can take place:

$$3\,^{4}_{2}He \longrightarrow ^{12}_{6}C$$

$$^{12}_{6}C + ^{4}_{2}He \longrightarrow ^{16}_{8}O$$
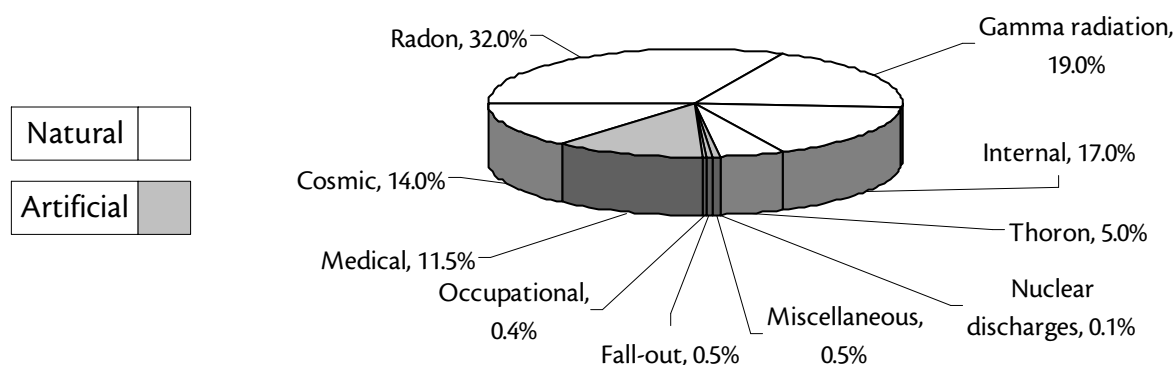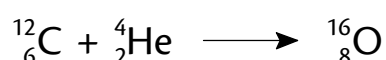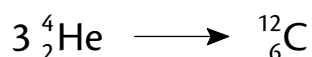
All the naturally occurring elements have been formed in stars in this way.

Topic 4 – Chemical Industry

Note: these are brief notes and must be supplemented by other sources.

Importance of the Chemical Industry

- the Chemical Industry is one of the largest British industries.
- its products are indispensable to many aspects of modern life and many are used for the benefit of society
- it is the only manufacturing industry to export more than it imports and so earns a trade balance surplus from these exports for Britain
- also invisible trade balance surplus from selling licences to use British processes abroad
- the chemical industry involves the investment of large sums of money but employs relatively few people making it a capital intensive and not a labour intensive industry.

What products does it make?

The 5 main categories of product that the industry makes are:
- basic inorganics and fertilisers
- dyestuffs, paint and pigments
- petrochemicals and polymers
- pharmaceuticals
- specialities

Stages in the manufacture of a new product

The manufacture of a new product is a step-wise process from its discovery, probably on a very small scale, to its production, on a large scale. The steps are:

research and development	a new potentially useful chemical is prepared and patented. Some products are discovered by accident but others as a result of long and expensive research.
laboratory process	small scale to review the production route
pilot study	the product is now required in larger amounts and will be manufactured in a pilot study using the route identified by the research group but in kilogramme quantities. Product quality, health hazards, and production costs will be discussed.
scaling up	planning the scaling up from lab quantities to full scale production will have been going on from the pilot study stage.
production	plant design, planning considerations, commissioning and start up
review	this will occur at each stage. All processes are reviewed and modifications are made.

Raw Materials and Feedstocks

A feedstock is a chemical from which other chemicals are manufactured. Feedstocks are made from raw materials; the basic resources that the earth supplies to us. They are:

- fossil fuels – coal, oil and natural gas
- metallic ores – eg aluminium extracted from bauxite (Al_2O_3)
- minerals – chlorine from sodium chloride
- water and air – water in hydration of ethene to ethanol and nitrogen in the Haber Process, oxygen in the catalytic oxidation of ammonia
- organic materials – of plant and animal origin eg vegetable oils and starch

Crude oil is a raw material from which naphtha is obtained by fractional distillation. Naphtha is a feedstock that can be cracked to produce ethene.

Batch and Continuous Processes

In a batch process the chemicals are loaded into the reaction vessel. The reaction is monitored and at the end of the reaction the product is separated and the reaction vessel cleaned out ready for the next batch. In a continuous process the reactants are continuously loaded at one end of the reaction vessel and the products are removed at the other end. Each process has advantages and disadvantages.

Batch Process

pros
- suited to smaller scale production up to 100 tons per annum
- more versatile than continuous as they can be used for more than one reaction
- more suited for multi step reactions or when reaction time is long

cons
- possibility of contamination from one batch to the next
- filling and emptying takes time during which no product, and hence no money, is being made
- safety – relatively large amounts of reactants may not be controllable in the event of an exothermic reaction going wrong

Continuous Process

pros
- suited to large scale production >1000 tons per annum
- suitable for fast single step processes
- more easily automated using computer control
- smaller workforce operates round the clock, 365 days per year
- greatest safety risk is at start up but this may be only every few months or years
- tend to operate with relatively low volumes of reactants allowing easy removal of excess heat energy

cons
- very much higher capital cost before any production can occur
- not versatile, can make only one product
- not cost effective when run below full capacity

In general products that are made on a very large scale will use a continuous process
eg. sulphuric acid, ammonia, iron, ethene, poly(ethene)

Products made on a smaller scale or when a continuous process would be difficult to devise or operate will use a batch process
eg. pharmaceuticals, dyes, copper refining by electrolysis

Factors Influencing the Choice of Synthetic Route

- cost, availability of feedstocks
- the yield of the reaction
- can unreacted starting materials be recycled?
- can by-products be sold?
- difficulty and cost of waste disposal
- energy consumption
- emissions to the atmosphere

Economic Aspects

Operating Conditions

The conditions under which a chemical process operates are chosen to maximise economic efficiency. We have considered these in other topics but examples are:

- raising the temperature may increase the rate of a reaction but it will increase energy costs so may not be economic
- increasing the pressure may shift an equilibrium in favour of the product but will mean using stronger reaction vessels and more powerful compressors and may not be economic.

Costs in the Chemical Industry

Costs come under 3 main categories – capital, fixed and variable costs.

The amount of money paid by the chemical industry for raw materials, energy, labour, research and development, plant design and construction, waste disposal, warehousing, packaging, distribution, marketing and sales must all be covered by the selling price of the product. Sales must also produce a profit to invest in new research and to pay off loans.

Capital Costs
These are incurred when building the plant. The life of a plant is assumed to be only about 10 years after which it is written off. The cost of this depreciation is recovered under fixed costs.

Fixed Costs
These are costs that are the same whether 1 ton or 1000 tons of product are made. The effect of the fixed cost decreases as the amount of product increases. They include:
- depreciation of the plant
- labour
- land purchase

Variable Costs
These are directly related to output and include
- raw materials and energy
- packaging
- waste disposal and effluent treatment

Use of Energy

As we have just seen, energy is an important variable cost and steps are taken to keep it to a minimum. This involves

- choosing processes which use less energy
- using the heat from exothermic reactions elsewhere in the plant, for example to supply heat to an endothermic reaction
- using waste heat to generate electricity to use in the plant or sell for district heating

Location of the Chemical Industry

Many locations are for historical and practical reasons. They had to be near
- raw materials
- water supply
- good communications; near ports, roads and rail
- reliable energy supplies
- available skilled labour

Safety and the Environment

The chemical industry is well aware of its environmental responsibilities and is acting accordingly.

- power stations that burn fossil fuels must remove the sulphur dioxide from the flue gases before release to the atmosphere. The SO_2 is converted to H_2SO_4 which is sold.
- waste used to be dumped in quarries, rivers, the sea or stored in containers from which it could leak into streams. These methods are no longer acceptable and are increasingly becoming illegal. Waste must be treated and discharged only when it is not harmful to the environment – it must meet requirements of pH and metal ion content.
- water containing organic waste must not be discharged into rivers or canals if it will reduce significantly the oxygen content of the water, causing fish to die.
- between 1990 and 1996 discharge of potentially harmful chemicals into UK rivers was reduced by 91 %.
- plants have reduced accidents by 50% in the last decade.
- road and rail tankers that carry chemicals are constructed to withstand impact in accidents.
- plants have their own fire fighting teams on site.
- plants are designed with safety in mind.

Chemicals are hazardous so the accident rate will never be zero but the aim is to learn from mistakes and reduce the rate to a minimum.