2 The specification overview

2a. Overview of A Level in Chemistry A (H432)

Learners must complete all components (01, 02, 03 and 04).

Content Overview	Assessment Overview	
Content is split into six teaching modules: • Module 1 – Development of practical skills in chemistry • Module 2 – Foundations in chemistry • Module 3 – Periodic table and energy • Module 4 – Core organic chemistry • Module 5 – Physical chemistry and transition elements • Module 6 – Organic chemistry and analysis Component 01 assesses content from modules 1, 2, 3 and 5. Component 02 assesses content from modules 1, 2, 4 and 6. Component 03 assesses content from all modules (1 to 6).	Periodic table, elements and physical chemistry (01) 100 marks 2 hours 15 minutes written paper	**37%** of total A level
	Synthesis and analytical techniques (02) 100 marks 2 hours 15 minutes written paper	**37%** of total A level
	Unified chemistry (03) 70 marks 1 hour 30 minutes written paper	**26%** of total A level
	Practical Endorsement in chemistry (04) (non exam assessment)	Reported separately (see Section 5)

All components include synoptic assessment.

Module 5: Physical chemistry and transition elements

The content within this module assumes knowledge and understanding of the chemical concepts developed in Module 2: Foundations in chemistry and Module 3: Periodic table and energy.

This module extends the study of energy, reaction rates and equilibria, and the periodic table. The main areas of physical chemistry studied include:

- rate equations, orders of reaction, the rate determining step
- equilibrium constants, Kc and Kp
- acid–base equilibria including pH, Ka and buffer solutions
- lattice enthalpy and Born–Haber cycles
- entropy and free energy
- electrochemical cells. T

he main areas of inorganic chemistry studied include:

- redox chemistry
- transition elements.

5.1 Rates, equilibrium and Ph

Key terms

i rate of reaction

During a chemical reaction, the concentration of the reactants decreases and the concentration of the products increases. The rate of a reaction is the decrease in concentration of reactants per unit time, or the increase in concentration of products per unit time. The units of rate of reaction are $\mathrm{mol dm^{-3} s^{-1}}$.

ii rate equation and order with respect to a substance

The relationship between the rate of a chemical reaction and the concentration of the reactants is shown by the rate equation of the reaction.

Consider the reaction A + 3B ⍰ 2C + 4D

The rate of this chemical reaction is given by the equation

$$\text{rate} = k[\mathrm{A}]^m[\mathrm{B}]^n\text{, where } m \text{ and } n \text{ are 0, 1 or 2}$$

[A] is the concentration of A, and [B] is the concentration of B.

m and n are the orders of reaction with respect to A and B respectively.

The order of reaction with respect to a given reactant is the power of that reactant's concentration in the rate equation.

iv overall order of reaction

The sum of these powers, in this case m + n, is known as **the overall order of reaction**:

The overall order of reaction is the sum of the powers of the reactant concentrations in the rate equation

v rate constant

k is the **rate constant** of the reaction.

The rate constant is the constant of proportionality in the rate equation.

vi half-life

The half-life of a reaction, t1/2, is the amount of time needed for a reactant concentration to decrease by half compared to its initial concentration. Its application is used in chemistry and medicine to predict the concentration of a substance over time

vii rate-determining step

The rate determining step is the slowest step of a chemical reaction that determines the speed (rate) at which the overall reaction proceeds.

viii activation energy

In chemistry, activation energy is a term introduced in 1889 by the Swedish scientist Svante Arrhenius to describe the minimum energy which must be available to a chemical system with potential reactants to result in a chemical reaction.

ix heterogeneous and homogenous catalyst

Catalysts can be divided into two main types - heterogeneous and homogeneous. In a heterogeneous reaction, the catalyst is in a different phase from the reactants. In a homogeneous reaction, the catalyst is in the same phase as the reactants.

DETERMINING ORDERS OF REACTION

The orders of reaction with respect to each reactant in the reaction can be determined by carrying out the reaction with various different initial concentrations and measuring the change in initial rate of reaction. The orders of reaction can be determined arithmetically or graphically.

If the order of reaction with respect to one reactant is being determined, the concentration of one reactant only should change; the others should remain constant so that the change in rate can be attributed to the change in concentration of that reactant alone.

If the overall order is being determined, the concentration of all reactants should change by the same factor.

1. The arithmetic method

(change in concentration)$^{\text{order of reaction}}$ = change in rate

If the reaction is first order, then if the concentration doubles the rate will also double. If the concentration triples the rate will also triple, etc.

If the reaction is second order, then if the concentration doubles the rate will quadruple. If the concentration triples the rate will increase ninefold, etc.

If the reaction is zero order, then the change in concentration will have no effect on the rate of reaction.

Example 1

Consider the reaction $RX + OH^- \rightarrow ROH + X^-$
The following rate data were obtained at constant temperature:

Initial concentration of RX/ moldm^{-3}	Initial concentration of OH/ moldm^{-3}	Initial rate/ moldm^{-3} s^{-1}
0.01	0.04	8×10^{-3}
0.01	0.02	4×10^{-3}
0.005	0.04	4×10^{-3}

From expt 2 to expt 1, the concentration of hydroxide ions doubles and the concentration of RX is unchanged. The rate also doubles, so the order of reaction with respect to OH^- is 1.

From expt 3 to expt 1, the concentration of RX doubles and the concentration of hydroxide ions is unchanged. The rate also doubles, so the order of reaction with respect to RX is also 1.

The rate equation can thus be written as follows: rate = $k[RX][OH^-]$

Having deduced the rate equation, the rate constant can be calculated using the data in one of the experiments.

Eg in expt 1, $k = \text{rate}/([RX][OH^-]) = 8 \times 10^{-3}/(0.04 \times 0.01) = 20\ \text{mol}^{-1}\text{dm}^3\text{s}^{-1}$.

Example 2

Consider the reaction $PCl_3 + Cl_2 \rightarrow PCl_5$
The following rate data were obtained at constant temperature:

Initial concentration of PCl_3/ moldm^{-3}	Initial concentration of Cl_2/ moldm^{-3}	Initial rate/ moldm^{-3} s^{-1}
0.2	0.1	0.0004
0.4	0.1	0.0008
0.8	0.2	0.0064

From expt 1 to expt 2, the concentration of PCl_3 doubles and the concentration of Cl_2 is unchanged. The rate also doubles, so the order of reaction with respect to PCl_3 is 1.

From experiment 2 to experiment 3, the concentration of both reactants doubles. The rate increases eightfold, so the overall order of reaction is three.

The order of reaction with respect to chlorine is therefore 3 – 1 = 2.

The rate equation can thus be written as follows: rate = $k[PCl][Cl]^2$

So $k = rate/[PCl_3][Cl_2]^2 = 0.0004/(0.2 \text{ x } 0.1^2) = 0.2 \text{ mol}^{-2}\text{dm}^6\text{s}^{-1}$

2. The Graphical method

If the concentrations in the different experiments are not simple whole number ratios of each other, it is not easy to compare the concentrations and rates. The order of reaction with respect to each reactant can be deduced by plotting a graph of concentration vs initial rate (an **initial rate-concentration graph**)

a) first-order reactions

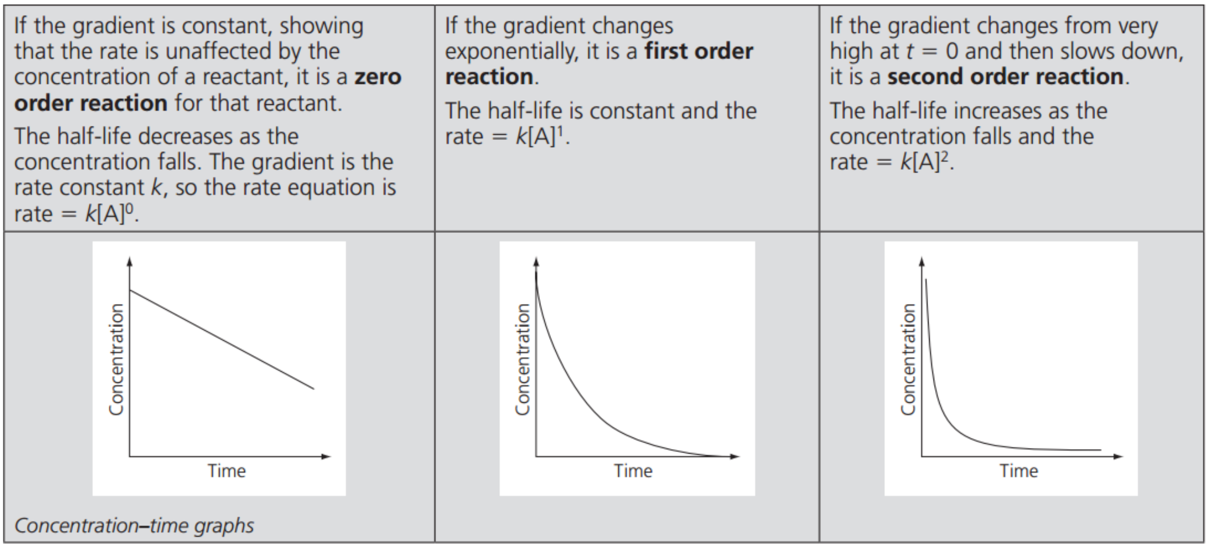
If Rate = k[A], then a plot of initial rate against initial concentration will be a staight line through the origin of gradient k:

b) second-order reactions

If rate = k[A]^{2}, then a plot of initial rate against initial concentration will be a curve through the origin.

c) zero order reactions

If rate = k, then a plot of initial rate against initial concentration will be a horizontal line:



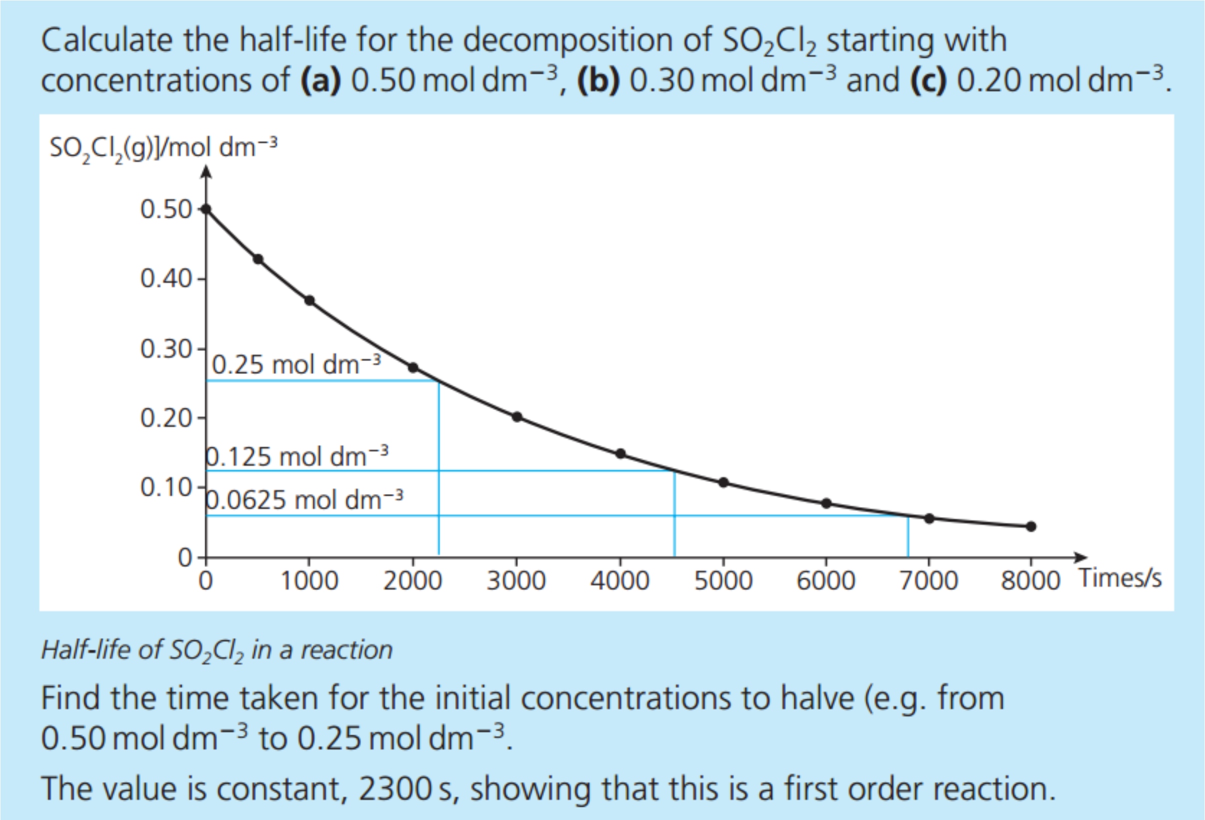
If the gradient is constant, showing that the rate is unaffected by the concentration of a reactant, it is a **zero order reaction** for that reactant. The half-life decreases as the concentration falls. The gradient is the rate constant k, so the rate equation is rate = $k[A]^0$.	If the gradient changes exponentially, it is a **first order reaction**. The half-life is constant and the rate = $k[A]^1$.	If the gradient changes from very high at $t = 0$ and then slows down, it is a **second order reaction**. The half-life increases as the concentration falls and the rate = $k[A]^2$.

Concentration–time graphs

How the reaction rate varies with time for zero, first and second order reactions

An even better method is to plot log (rate of reaction) against log (concentration). This should always give a straight line, the gradient of which is the order of reaction.

Half lives
The half-life is the time needed for any reactant concentration to fall to half of its initial value.



Calculate the half-life for the decomposition of SO_2Cl_2 starting with concentrations of **(a)** 0.50 mol dm^{-3}, **(b)** 0.30 mol dm^{-3} and **(c)** 0.20 mol dm^{-3}.

Half-life of SO_2Cl_2 in a reaction

Find the time taken for the initial concentrations to halve (e.g. from 0.50 mol dm^{-3} to 0.25 mol dm^{-3}.

The value is constant, 2300 s, showing that this is a first order reaction.

3. Measuring initial rates of reaction

In some reactions, it is not easy to measure the rate of reaction directly, and easier to mention the time taken for a particular stage in the reaction to be reached.

Since rate is the change in concentration per unit time, it follows that the rate is inversely proportional to time taken. **A graph of 1/t against initial concentration will give curves like those shown above.**

Examples of such measurements could be:

- time taken for fixed amount of gas to be produced

- time taken for absorbance to change by a certain amount

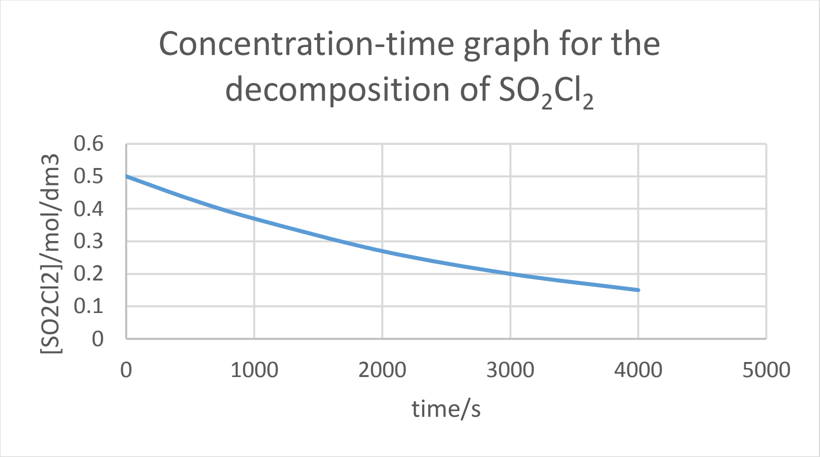
- use of a **clock reaction**: the appearance of a certain coloured product is delayed by adding a fixed amount of another species.
  Eg $S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$
  Iodine is produced in this reaction. If starch was added to the original mixture, a blue-black colour would appear immediately. However if a fixed amount (ie 0.02 moles) of sodium thiosulphate is also added to the mixture, it reacts with the iodine and a blue-black colour is only seen when all the thiosulphate has been used up.
  It is possible to measure the time taken for the blue-black colour to appear.

CONCENTRATION-TIME GRAPHS

It is not always possible to carry out several different experiments. It is possible to obtain much useful information about the kinetics of a reaction by monitoring how the concentration of a reaction changes over time in a single reaction, and then plotting a graph of concentration against time (a **concentration-time graph**).

A typical concentration-time graph would look like this:

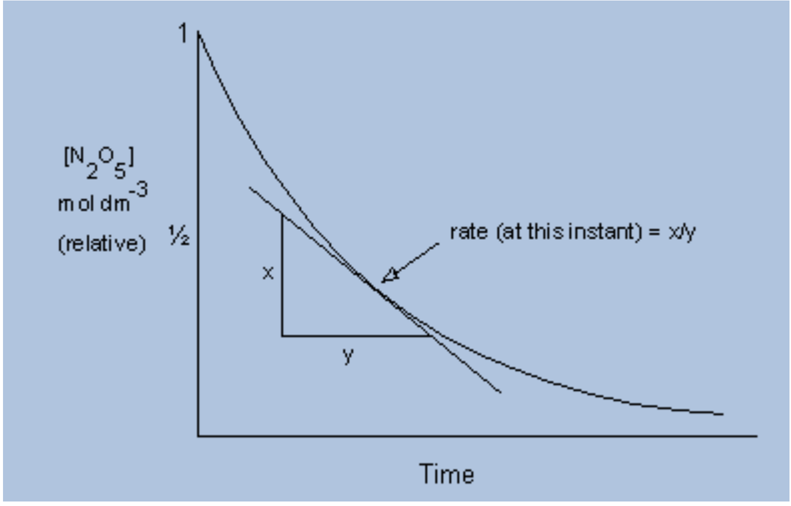
Eg for the reaction $SO_2Cl_2 \rightarrow SO_2 + Cl_2$



a) finding the rate of reaction from the graph

The rate of reaction is the change in concentration per unit time and can therefore be calculated from the gradient of the line at a particular time.

As the graph is a curve (its gradient is steadily decreasing with time), the gradient of the line at a particular point must be calculated by drawing a tangent to that line at a particular point and calculating the gradient of that tangent.



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The initial rate of reaction is the gradient of the tangent to the curve at t = 0.

The rate of reaction at a particular time is the gradient of the tangent to the curve at that particular time.

b) Deducing the order of reaction and the rate constant from the graph

By measuring the gradients of the tangents at different points on the curve, it is possible to deduce the order of reaction by the arithmetic method:

Taking the concentration-time graph for the decomposition of SO_2Cl_2 (above):

Start by measuring the initial rate of reaction:
The initial concentration of SO_2Cl_2 is 0.5 $moldm^{-3}$.
The gradient of the tangent to the curve at this point is 1.6×10^{-4} $moldm^{-3}s^{-1}$

Then measure the rate of reaction after the concentration of SO_2Cl_2 has fallen to half of its initial value:
After 2200 s, the concentration of SO_2Cl_2 is 0.25 $moldm^{-3}$.
The gradient of the tangent to the curve at this point is 8.0×10^{-5} $moldm^{-3}s^{-1}$

It is clear that when the concentration of SO_2Cl_2 halves, the rate of reaction also halves. This shows that the order of reaction with respect to of SO_2Cl_2 is 1 and that the rate equation is therefore rate = $k[SO_2Cl_2]$.

If the rate of reaction has fallen by a factor of 4 when the concentration had halved, it would show that the reaction was **second order.**
If the rate of reaction had not fallen at all when the concentration had halved, it would show that the reaction was **zero order.**

The rate constant can be determined by rearranging the rate equation: $k = rate/[SO_2Cl_2]$

EXPLAINING ORDERS OF REACTION

The orders of reaction for a chemical equation are not always the same as the reaction coefficients:

Eg the reaction $NO_2 + H_2 \rightarrow NO + H_2O$ has the following rate equation:
rate = $k[NO_2]^2$
It is therefore not possible to predict the rate equation of a reaction simply by looking at the reaction coefficients.

Many reactions consist of a series of different steps, some of which are slow and some of which are very fast.
It is the slowest step in a chemical reaction which determines how fast a reaction is. For this reason the slowest step in a chemical reaction is called the **rate-determining step**. Changing the rate of this step will affect the overall rate of reaction; changing the rate of fast steps won't.

Eg consider the reaction $NO_2 + H_2 \rightarrow NO + H_2O$
This reaction happens in two steps:
Step 1: $NO_2 + NO_2 \rightarrow NO_3 + NO$ this step is slow
Step 2: $NO_3 + H_2 \rightarrow NO_2 + H_2O$ this step is fast
Step 1 is the slowest step and is therefore the rate-determining step. This involves two molecules of NO_2, and so doubling the concentration of NO_2 will make collisions in this step four times more likely. So the reaction is second order with respect to NO_2. H_2 is not involved in this step; it is only involved in the second, fast step. Changing the concentration of H_2 therefore has no effect on the rate of reaction, and the reaction is zero order with respect to H_2.

The rate equation of a chemical reaction is determined by the number of each species involved in the rate-determining step of that reaction.

EFFECT OF CHANGING CONDITIONS ON THE RATE CONSTANT

1. Effect of concentration, pressure and temperature on the rate constant

The rate equation shows the relationship between the concentration of reactants and the rate of reaction.

If the concentration of one of the reactants increases, the rate of reaction will also increase, the rate constant, k will not change.

If the pressure increases, the concentration of all the reactants will increase and so the rate of reaction will also increases. Again the rate constant will not change.

The rate constant k is thus independent of concentration and pressure.

If the temperature increases, however, or a catalyst is added, the rate of reaction increases without a change in concentration, and so it must be the rate constant, k, that is changing.

The rate constant k thus varies with temperature, and is also affected by the addition of a catalyst.

If the temperature is increased, the rate constant k will increase.

If the temperature is decreased, the rate constant k will decrease.

If the concentration or pressure is changed at constant temperature, the rate constant will not change.

Kinetics of the reaction between propanone and iodine in acid solution

$$I_2 + CH_3COCH_3 \rightarrow CH_2ICOCH_3 + HI$$

Hydrogen ions catalyse this reaction.

- The rate equation has the form of rate = k[CH3COCH3] x [I2] y [H1] z
- Varying the concentration of each species in turn gives the order of each species – x, y and z.
- The reaction can be followed by titrating the remaining unreacted iodine with standard sodium thiosulfate using starch indicator. Alternatively, a colorimeter can be used to monitor the brown colour of the iodine.
- Experimental data shows the reaction to be first order with respect to both propanone and hydrogen ions, but zero order for iodine.
- The reactant iodine is not in the rate equation at all but hydrogen ions are present, despite not being reactants.

Example calculation

Experiment	Iodine/ mol dm^{-3}	Propanone/ mol dm^{-3}	Hydrogen ions/mol dm^{-3}	Relative rate of reaction
1	0.006	0.6	0.6	1
2	0.006	0.12	0.6	1.9
3	0.006	1.8	0.6	3.1
4	0.006	0.6	1.2	2.1
5	0.012	0.6	0.6	0.9

Use this data to establish which species are involved in the rate determining step.

Answer:

In experiments 1and 2, doubling concentration of propanone doubles the rate initially. **(First order)**

In experiments 1 and 4 doubling hydrogen ions doubles the rate. **(First order)**

In experiments 1 and 5, doubling the concentration of iodine has no effect on rate. **(Zero order)**

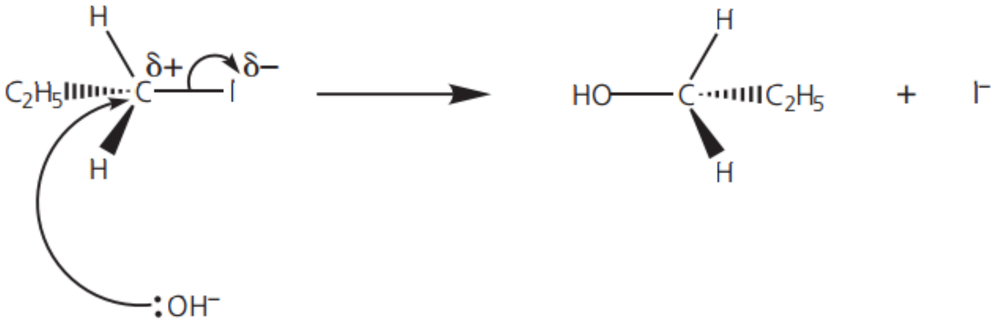
The rate determining step therefor involves both hydrogen and propanone but not iodine.

Rate equations as evidence for SN1 and SN2 mechanisms for tertiary and primary halogenoalkane hydrolysis

Nucleophilic substitution mechanisms of halogenoalkanes- Two substitution mechanisms are possible when an iodoalkane reacts with aqueous alkali:

$$R{-}I + OH^- \rightarrow R{-}OH + I^-$$

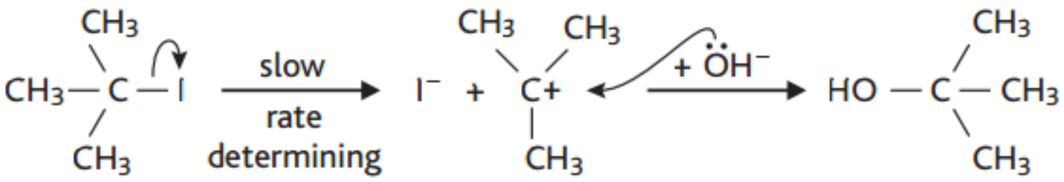
Only the experimental rate data can show which mechanism actually takes place.



Nucleophilic substitution of a primary halogenoalkane

The single step illustrated for the substitution of 1-iodopropane, a primary halogenoalkane, involves two different species – both the hydroxide ion and the primary halogenoalkane. • The reaction will be second order – it depends on the concentration of both the hydroxide ion and the primary halogenoalkane. So, rate $= k[\mathrm{RI}][\mathrm{OH}^-]$

We call this an SN2 mechanism, meaning substitution/nucleophilic/second order. Tertiary halogenoalkanes hydrolyse by the alternative SN1mechanism, meaning substitution/nucleophilic/first order.



Nucleophilic substitution of a tertiary halogenoalkane

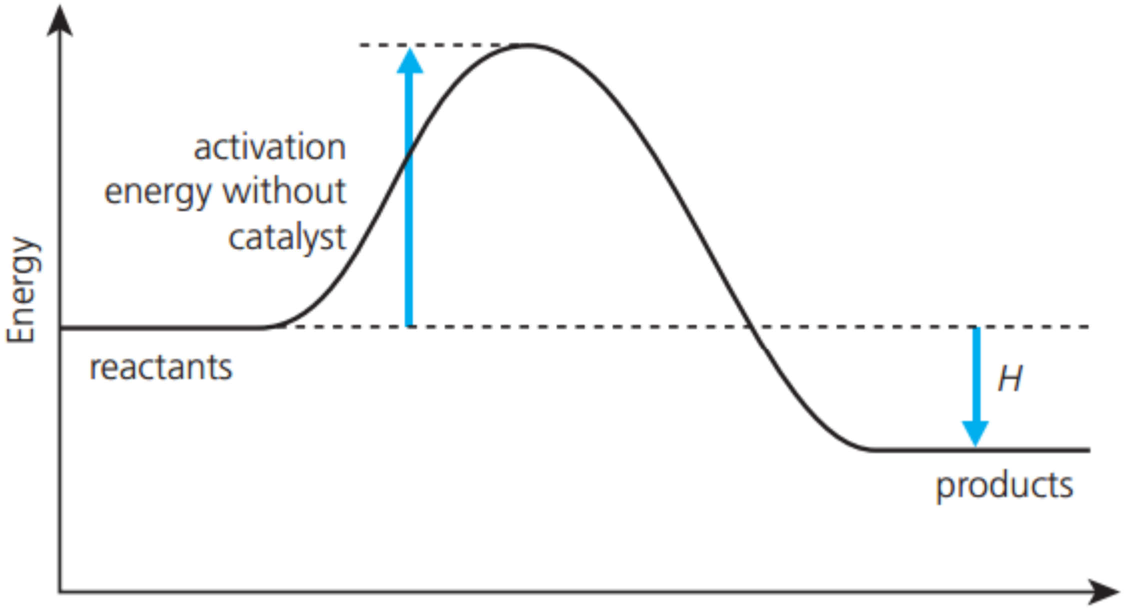
The C-halogen bond breaks first (slow step) followed by attack by the hydroxide ion (fast step).

- The slow step involves only one species and does not depend on the concentration of hydroxide ions. Hence the reaction is first order overall: rate = k[RI]

The mechanism must be consistent with the evidence:

- if the reaction is second order overall it must involve two different species
- if the reaction is first order overall (only one species in the rate equation) then this is the rate-determining step and it must be a two-step reaction.

2. The Arrhenius Equation and activation energy determination



Activation energy is the smallest amount of energy needed by reactants for products to form. The relationship between the rate constant of a reaction and the temperature can be quantified using the **Arrhenius** equation:

$$k = Ae^{(-Ea/(RT))}$$

In this equation, Ea is the activation energy for the reaction (in $Jmol^{-1}$), T is the temperature (in K), R is the molar gas constant (in $Jmol^{-1}K^{-1}$) and A is the Arrhenius constant (which varies from reaction to reaction)

Taking the logarithm of both sides of this equation gives you:

$$\log k = \log A - Ea/(RT)$$

A graph of logk against 1/T should therefore give a straight line of gradient Ea/R. This gradient can be used to determine the activation energy of the reaction.

The activation energy of a reaction can therefore be determined experimentally by comparing the rate of reaction at different temperatures, by plotting a graph of log (rate of reaction) against 1/T and finding the gradient of the line.

For example, the initial rate of reaction between HCl and $Na_2S_2O_3$ can be monitored at different temperatures by measuring how long it takes for the Sulphur produced during this reaction to prevent an X on a piece of paper under the reaction flask from being visible.

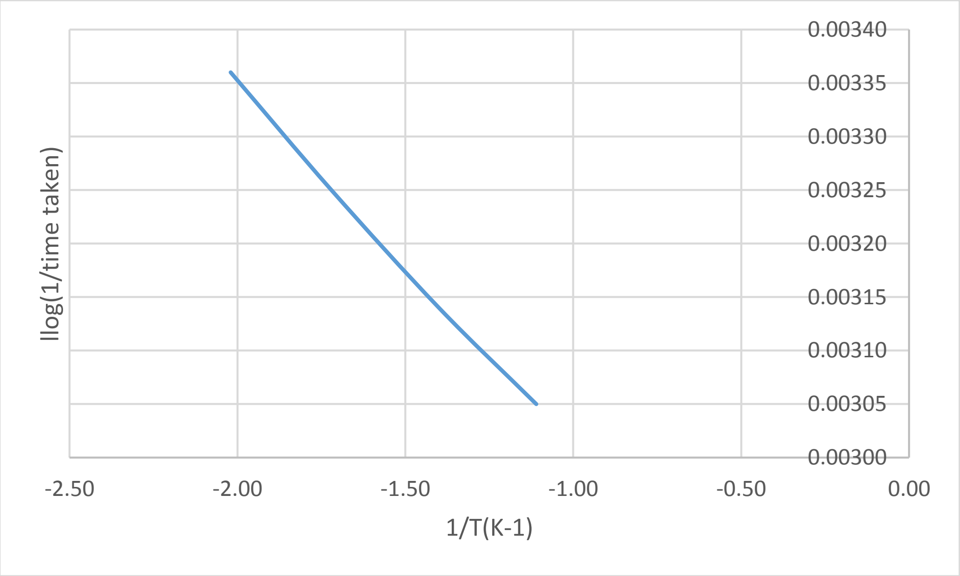
A value proportional to k can be found by calculating (1/time taken)

T (K)	Time taken for X to cease to be visible (s)	(1/time taken)/s^{-1}
298	105	9.5×10^{-3}
308	52	1.9×10^{-2}
318	25	4.0×10^{-2}
328	13	7.7×10^{-2}

Then logk and 1/T can be calculated:

T (K)	1/T (K^{-1})	(1/time taken)/s^{-1}	Log (1/time taken)
298	3.36×10^{-3}	9.5×10^{-3}	-2.02
308	3.25×10^{-3}	1.9×10^{-2}	-1.72
318	3.14×10^{-3}	4.0×10^{-2}	-1.40
328	3.05×10^{-3}	7.7×10^{-2}	-1.11

A graph of log(1/time taken) against 1/T can then be plotted:



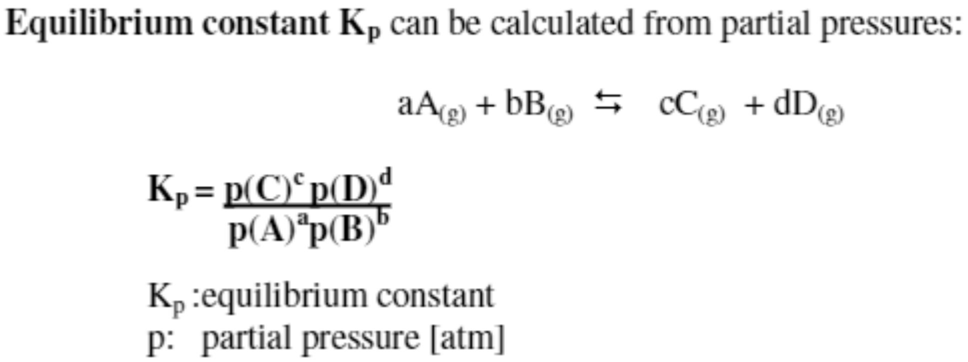
The gradient of this line can then be taken and it is approximately -2900K

According to the Arrhenius equation, this gradient = -Ea/R
So Ea = -2900 x R = 24000Jmol^{-1} = 24kJmol^{-1}

Equilibrium

When a reaction is at equilibrium, the forward reaction and reverse reaction have the same rate. The concentrations of the reaction components stay constant at equilibrium, even though the forward and backward reactions are still occurring.

Equilibrium constants are used to define the ratio of concentrations at equilibrium for a reaction at a certain temperature. In general, we use the symbol K or K_c, to represent equilibrium constants. When we use the symbol K_c, the superscript c means that all concentrations are being expressed in terms of molar concentration, or $\frac{\text{mol solute}}{\text{L of solution}}$. When a reaction component is a gas, we can also express the amount of that chemical at equilibrium in terms of its partial pressure. When the equilibrium constant is written with the gases in terms of partial pressure, the equilibrium constant is written as the symbol K_p.



Equilibrium constant K_p can be calculated from partial pressures:

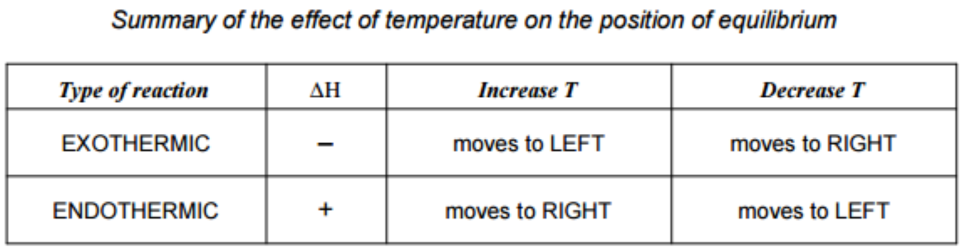
$$aA_{(g)} + bB_{(g)} \leftrightarrows cC_{(g)} + dD_{(g)}$$

$$K_p = \frac{p(C)^c p(D)^d}{p(A)^a p(B)^b}$$

K_p :equilibrium constant
p: partial pressure [atm]

Points to remember:

Equilibrium constant values are only changed by temperature changes



Summary of the effect of temperature on the position of equilibrium

Type of reaction	ΔH	*Increase T*	*Decrease T*
EXOTHERMIC	–	moves to LEFT	moves to RIGHT
ENDOTHERMIC	+	moves to RIGHT	moves to LEFT

Liquids and solids do not appear in the equilibrium equation.

All the partial pressures should have the same unit

Make sure the reaction is balanced otherwise the stoichiometric coefficients will be incorrect

Calculating Kp

Example 1 *A mixture of 16g of O_2 and 42g of N_2, exerts a total pressure of 20000 Nm^{-2}.*
What is the partial pressure of each gas ?

moles of O_2 = mass / molar mass = 16g / 32g = 0.5 moles
moles of N_2 = mass / molar mass = 42g / 28g = 1.5 moles *total moles = 2*

mole fraction of O_2 = 0.5 / 2 = 0.25
mole fraction of N_2 = 1.5 / 2 = 0.75 *sum of mole fractions (0.75 + 0.25) = 1*

partial pressure of O_2 = mole fraction x total pressure
= 0.25 x 20000 Nm^{-2} = ***5000 Nm^{-2}***

partial pressure of N_2 = mole fraction x total pressure
= 0.75 x 20000 Nm^{-2} = ***15000 Nm^{-2}***

Example 2 *When nitrogen (1 mole) and hydrogen (3 moles) react at constant temperature at a pressure of 8 x 10^6 Pa, the equilibrium mixture was found to contain 0.7 moles of ammonia. Calculate K_p .*

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

moles (initially)	1	3	0	
moles (equilibrium)	1 - x	3 - 3x	2x	(x moles of N_2 reacted)
mole fractions	(1-x)/(4-2x)	(3-3x)/(4-2x)	2x/(4-2x)	(total moles = 4 - 2x)
partial pressures	P.(1-x)/(4-2x)	P.(3-3x)/(4-2x)	P.2x/(4-2x)	(total pressure = P)

At equilibrium there are 0.7 moles of ammonia, so 2x = 0.7 (therefore x = 0.35)
and the total pressure, (P) = 8 x 10^6 Pa.

applying the equilibrium law $K_p = \dfrac{(PNH_3)^2}{(PN_2)\,.\,(PH_2)^3}$ Pa^{-2}

Substituting in the expression gives **ANS. K_p = 1.73 x 10^{-14} Pa^{-2}**

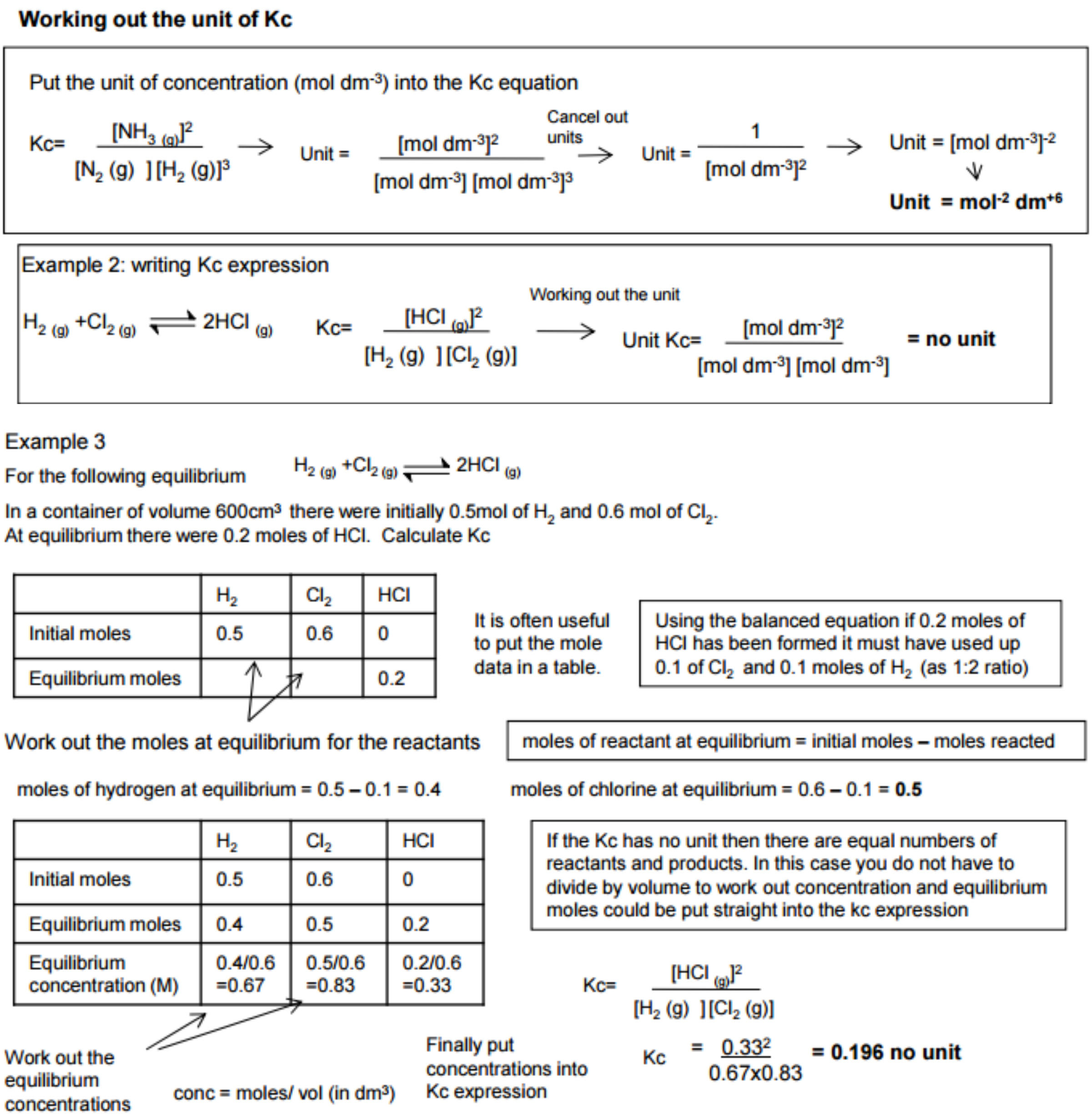
Calculating Kc

For a generalised reaction
$mA + nB \rightleftharpoons pC + qD$
m,n,p,q are the stoichiometric balancing numbers
A,B,C,D stand for the chemical formula

Kc = equilibrium constant

$$\boxed{Kc = \frac{[C]^p\,[D]^q}{[A]^m\,[B]^n}}$$

[ ] means the equilibrium concentration



Working out the unit of Kc

Put the unit of concentration (mol dm^{-3}) into the Kc equation

$$Kc = \frac{[NH_{3\,(g)}]^2}{[N_2\,(g)\,]\,[H_2\,(g)]^3} \rightarrow \text{Unit} = \frac{[mol\,dm^{-3}]^2}{[mol\,dm^{-3}]\,[mol\,dm^{-3}]^3} \xrightarrow{\text{Cancel out units}} \text{Unit} = \frac{1}{[mol\,dm^{-3}]^2} \rightarrow \text{Unit} = [mol\,dm^{-3}]^{-2}$$

$\downarrow$ **Unit = mol^{-2} dm^{+6}**

Example 2: writing Kc expression

$$H_{2\,(g)} + Cl_{2\,(g)} \rightleftharpoons 2HCl_{\,(g)} \qquad Kc = \frac{[HCl_{\,(g)}]^2}{[H_2\,(g)\,]\,[Cl_2\,(g)]} \xrightarrow{\text{Working out the unit}} \text{Unit } Kc = \frac{[mol\,dm^{-3}]^2}{[mol\,dm^{-3}]\,[mol\,dm^{-3}]} \quad \textbf{= no unit}$$

Example 3

For the following equilibrium $H_{2\,(g)} + Cl_{2\,(g)} \rightleftharpoons 2HCl_{\,(g)}$

In a container of volume 600cm^3 there were initially 0.5mol of H_2 and 0.6 mol of Cl_2. At equilibrium there were 0.2 moles of HCl. Calculate Kc

	H_2	Cl_2	HCl
Initial moles	0.5	0.6	0
Equilibrium moles			0.2

It is often useful to put the mole data in a table.

Using the balanced equation if 0.2 moles of HCl has been formed it must have used up 0.1 of Cl_2 and 0.1 moles of H_2 (as 1:2 ratio)

Work out the moles at equilibrium for the reactants

moles of reactant at equilibrium = initial moles – moles reacted

moles of hydrogen at equilibrium = 0.5 – 0.1 = 0.4

moles of chlorine at equilibrium = 0.6 – 0.1 = **0.5**

	H_2	Cl_2	HCl
Initial moles	0.5	0.6	0
Equilibrium moles	0.4	0.5	0.2
Equilibrium concentration (M)	0.4/0.6 =0.67	0.5/0.6 =0.83	0.2/0.6 =0.33

If the Kc has no unit then there are equal numbers of reactants and products. In this case you do not have to divide by volume to work out concentration and equilibrium moles could be put straight into the kc expression

$$Kc = \frac{[HCl_{\,(g)}]^2}{[H_2\,(g)\,]\,[Cl_2\,(g)]}$$

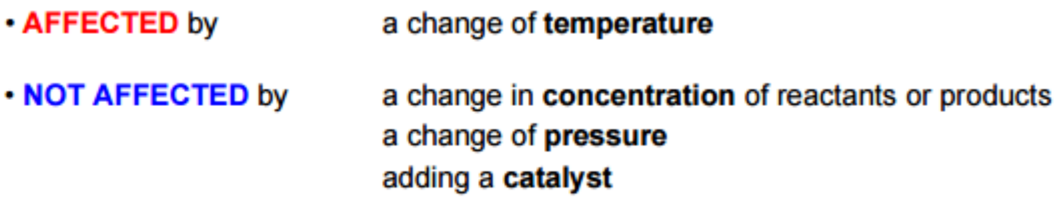
Work out the equilibrium concentrations

conc = moles/ vol (in dm^3)

Finally put concentrations into Kc expression

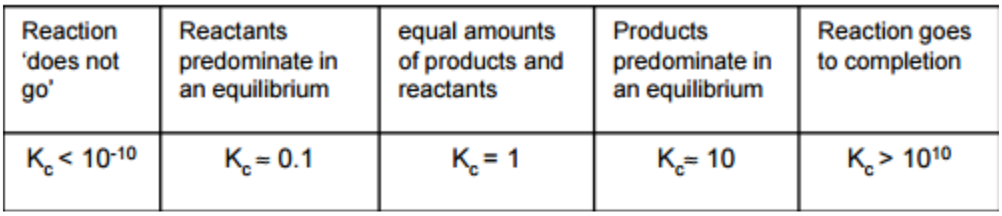
$$Kc \;=\; \frac{0.33^2}{0.67 \times 0.83} \quad \textbf{= 0.196 no unit}$$

Value of Kc or Kp :



- **AFFECTED** by a change of **temperature**
- **NOT AFFECTED** by a change in **concentration** of reactants or products
  a change of **pressure**
  adding a **catalyst**

Predicting extent of reactions using Kc values



Reaction 'does not go'	Reactants predominate in an equilibrium	equal amounts of products and reactants	Products predominate in an equilibrium	Reaction goes to completion
$K_c < 10^{-10}$	$K_c = 0.1$	$K_c = 1$	$K_c = 10$	$K_c > 10^{10}$

5.1.3 Acids bases and buffers

The Bronsted-Lowry Theory of acids and bases

The theory states that:

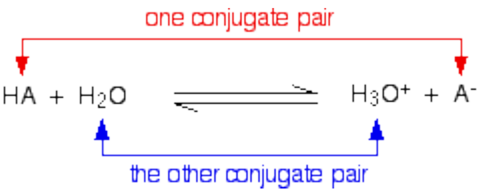
An acid is a proton (hydrogen ion) donor.

A base is a proton (hydrogen ion) acceptor

Acid base reactions involve transfer of electrons.

Brønsted–Lowry conjugate acid-base pairs

Consider an acid HA, and think of the reaction as being reversible.



In the forward reaction:

The HA is an acid because it is donating a proton (hydrogen ion) to the water.

The water is a base because it is accepting a proton from the HA.

In the back reaction between the hydroxonium ion and the A- ion:

The H3O+ is an acid because it is donating a proton (hydrogen ion) to the A- ion.

The A- ion is a base because it is accepting a proton from the H3O+.

The reversible reaction contains two acids and two bases. We think of them in pairs, called **conjugate pairs.**

pH

pH is a measure of the dissociation of an acid or base, and also of the concentration of that acid / base (and is related to the concentration of H_3O^+ ions).

Calculating pH from hydrogen ion concentration

Logarithmic scale is used when dealing with pH calculations as the concentration of hydrogen ions at room temperature is very small.

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

Examples:

Example 1:
Calculate the pH of a 0.01 moles dm^{-3}solution of a strong acid HCl.

As the acid only contains one hydrogen atom it will only produce one hydrogen ion per molecule when dissolved in water.
Therefore the H+ concentration is = 0.01 moles dm^{-3}
log 0.01 = -2
pH = 2

Example 2:

Calculate the pH of a 0.01 moles dm-3 solution of a strong base NaOH
As the base only contains one OH group it will only produce one hydroxide ion per molecule when dissolved in water.
Therefore the OH- concentration is = 0.01 moles dm-3
As the ionic product of water at 25ºC [H+] x [OH-] = 1 x 10^{-14}
Then [H+] = 1 x 10^{-12}
log 1 x 10^{-12} = -12
pH = 12

Calculating concentration of hydrogen ions in mol dm-3 from pH

Expression used:

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

Example for pH 3.5:

$$[H+] = 10^{-3.5} = 3.162 \times 10^{-4} mol/$$
dm3

Strong Acids & Bases

A strong acid is one which is 100% ionised in solution

pH of strong acid:

pH = -log$_{10}$[H$^+$]

=> **[H$^+$] equals concentration of the acid e.g. HCl**, unless it is a diprotic acid, like H_2SO_4, which has double the H$^+$ concentration

Monoprotic (monobasic): $HCl \rightarrow H^+ + Cl^-$

Diprotic (dibasic): $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$

The stronger the ability of an acid to donate protons, the stronger the acid

An acid can become a base if paired with a stronger acid, forming new **conjugated acid-base pairs**:

$$HNO_{3(l)} + H_2SO_{4(l)} \rightleftharpoons H_2NO_3{}^+{}_{(l)} + HSO_4{}^-{}_{(l)}$$

base1	**acid2**	**acid1**	**base2**

H_2SO_4/HSO_4^- are a **conjugated acid-base pair**

pH of a weak acid

A weak acid is one that is only partially ionised e.g Ethanoic acid

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Acid dissociation constant, Ka, for a weak acid

Weak acid are only about 1% ionised in most cases so a new equilibrium constant Ka is calculated. To work out Ka for a weak acid the formula below is used.

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$$ which can also be written as $$K_a = \frac{[H^+]\,[A^-]}{[HA]}$$

To make the calculation easier two assumptions are made to simplify the Ka expression:

1) $[H^+{}_{(aq)}]_{eqm} = [A^-{}_{(aq)}]_{eqm}$ because they have dissociated according to a 1:1 ratio.

2) As the amount of dissociation is small we assume that the initial concentration of the undissociated acid has remained constant.

So $[HA_{(aq)}]_{eqm} = [HA_{(aq)}]_{initial}$

$$Ka = \frac{[H^+{}_{(aq)}][A^-{}_{(aq)}]}{[HA\ (aq)]}$$

Simplifies to ↓

$$Ka = \frac{[H^+{}_{(aq)}]^2}{[HA_{(aq)}]_{initial}}$$

Example:

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$K_a = \frac{[CH_3COO^-]\,[H_3O^+]}{[CH_3COOH]}$$

or

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$K_a = \frac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]}$$

Example

Example 5 What is the pH of a solution of 0.01M ethanoic acid (ka is 1.7×10^{-5} mol dm^{-3})?

$$CH_3CO_2H_{(aq)} \rightleftharpoons H^+{}_{(aq)} + CH_3CO_2^-{}_{(aq)}$$

$$Ka = \frac{[H^+{}_{(aq)}][CH_3CO_2^-{}_{(aq)}]}{[CH_3CO_2H_{(aq)}]} \longrightarrow Ka = \frac{[H^+{}_{(aq)}]^2}{[CH_3CO_2H_{(aq)}]_{initial}} \longrightarrow 1.7 \times 10^{-5} = \frac{[H^+{}_{(aq)}]^2}{0.01}$$

$[H^+{}_{(aq)}]^2 = 1.7 \times 10^{-5} \times 0.01$

$[H^+{}_{(aq)}] = \sqrt{1.7 \times 10^{-7}} = 4.12 \times 10^{-4}$

$pH = -\log [H^+] = -\log (4.12 \times 10^{-4})$

$pH = 3.38$

Ka for some simple acids

Acid	**Ka (mol dm-3)**
Hydrofluoric acid	5.6 x 10-4
Methanoic acid	1.6 x 10-4
Ethanoic acid	1.7 x 10-5
Hydrogen sulphide	8.9 x 10-8

The smaller the Ka value the weaker the acid

pKa

This is the acid dissociation constant

Formula: $\mathrm{p}K_\mathrm{a} = -\log_{10}(K_\mathrm{a})$

the pKa value is directly proportional to the standard Gibbs free energy change for the reaction. The value of the pKa changes with temperature and can be understood qualitatively based on Le Châtelier's principle: when the reaction is endothermic, Ka increases and pKa decreases with increasing temperature; the opposite is true for exothermic reactions.

Ionic product of water Kw:

$H_2O \leftrightarrows H^+ + OH^-$ (slightly dissociated)

At room temperature $k_w = [H^+] \times [OH^-] = 10^{-14}$ mol^2 dm^{-6}

pk_w = -log k_w = 14

-> increase of temperature increases k_w => more dissociation

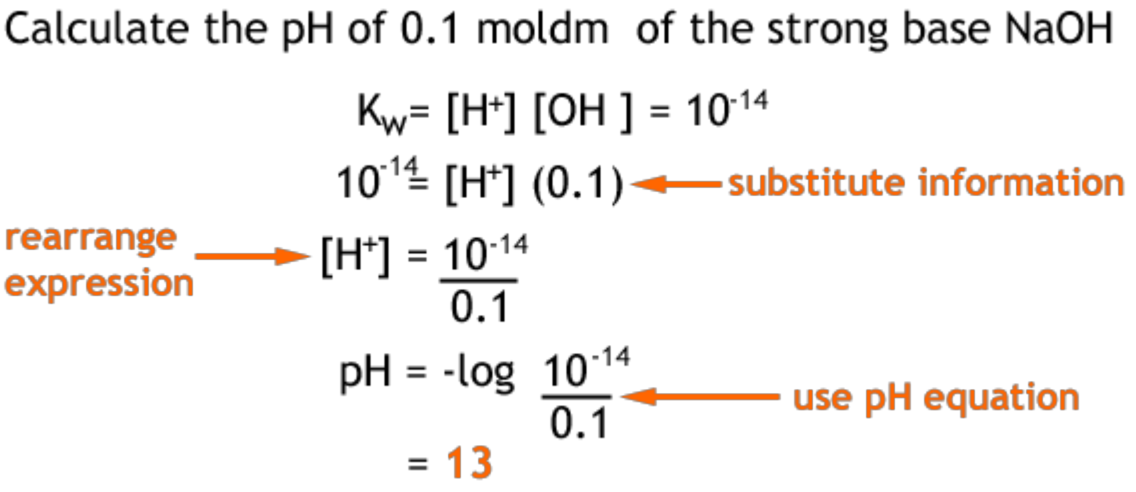
Knowledge of Kw enables us to calculate the pH of strong bases.

pH of strong base:

pH = 14 + log[OH^-]

[OH^-] equals concentration of the base, unless the chemical formula of the base contains more than one mole of OH^- ions (e.g. $Ca(OH)_2$ -> double [OH^-])

H^+ forms H_3O^+ (hydronium ions) with water



Calculate the pH of 0.1 moldm of the strong base NaOH

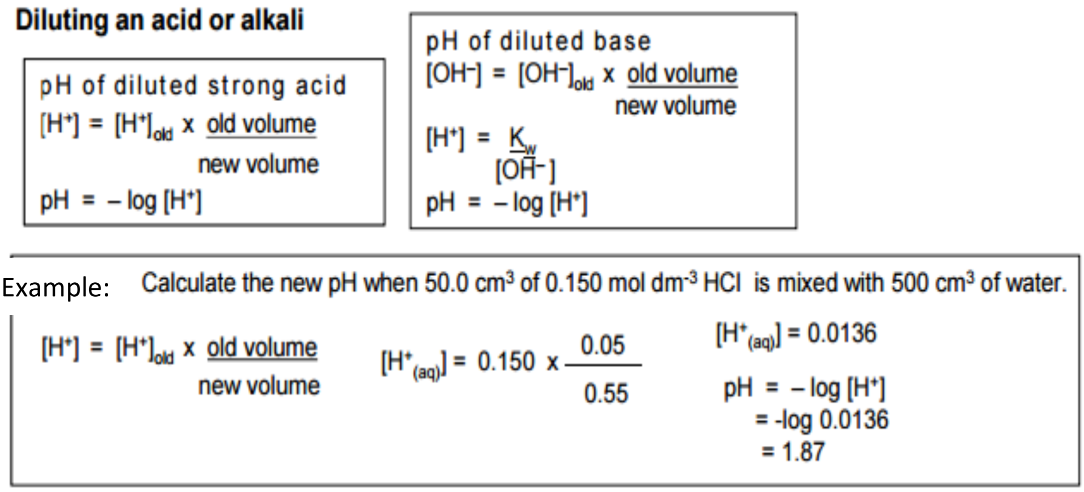
$$K_W = [H^+] [OH\ ] = 10^{-14}$$

$$10^{-14} = [H^+]\ (0.1) \longleftarrow \text{substitute information}$$

$$\text{rearrange expression} \longrightarrow [H^+] = \frac{10^{-14}}{0.1}$$

$$\text{pH} = -\log \frac{10^{-14}}{0.1} \longleftarrow \text{use pH equation}$$

$$= 13$$



Diluting an acid or alkali

pH of diluted strong acid

$$[H^+] = [H^+]_{old} \times \frac{\text{old volume}}{\text{new volume}}$$

$$pH = -\log [H^+]$$

pH of diluted base

$$[OH^-] = [OH^-]_{old} \times \frac{\text{old volume}}{\text{new volume}}$$

$$[H^+] = \frac{K_w}{[OH^-]}$$

$$pH = -\log [H^+]$$

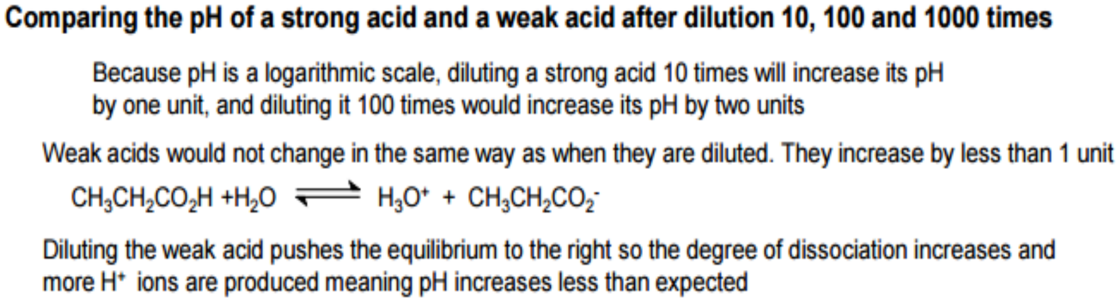
Example: Calculate the new pH when 50.0 cm^3 of 0.150 mol dm^{-3} HCl is mixed with 500 cm^3 of water.

$$[H^+] = [H^+]_{old} \times \frac{\text{old volume}}{\text{new volume}}$$

$$[H^+_{(aq)}] = 0.150 \times \frac{0.05}{0.55}$$

$$[H^+_{(aq)}] = 0.0136$$

$$pH = -\log [H^+]$$
$$= -\log 0.0136$$
$$= 1.87$$



Comparing the pH of a strong acid and a weak acid after dilution 10, 100 and 1000 times

Because pH is a logarithmic scale, diluting a strong acid 10 times will increase its pH by one unit, and diluting it 100 times would increase its pH by two units

Weak acids would not change in the same way as when they are diluted. They increase by less than 1 unit

$$CH_3CH_2CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CH_2CO_2^-$$

Diluting the weak acid pushes the equilibrium to the right so the degree of dissociation increases and more H^+ ions are produced meaning pH increases less than expected

Titration curves

Key definitions of terms

End point: When indicator changes colour

Equivalence point: When colour change occurs after solutions are mixed in exact equation proportions

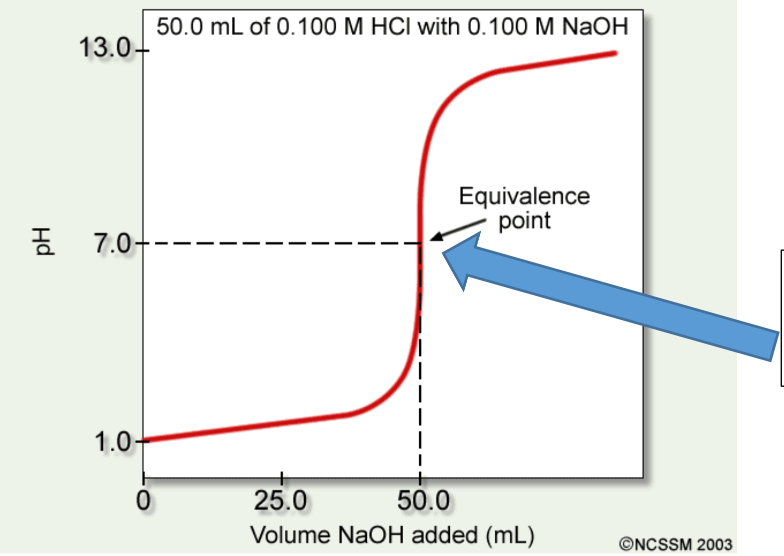
Types of curves

- Strong acid and strong base
- Weak acid and strong base
- Strong acid and weak base
- Weak acid and weak base

When constructing curves,

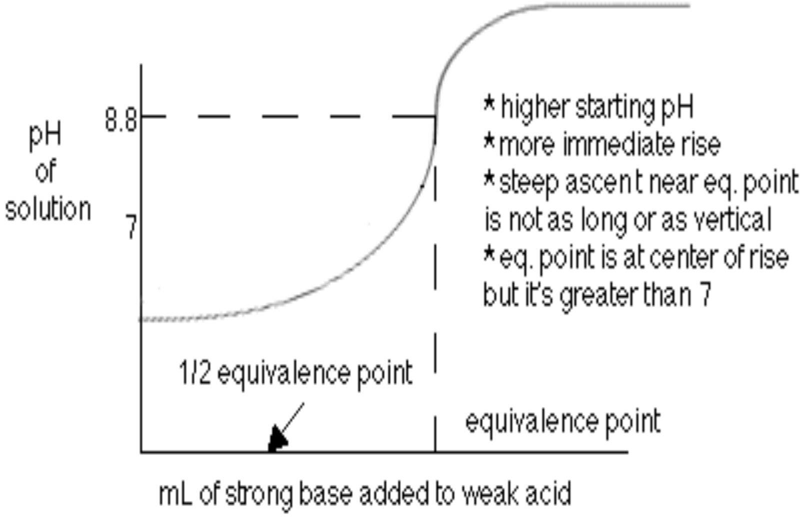
1. Measure initial pH of acid
2. Add alkali in small amounts and record volume added
3. Stir mixture to equalise pH
4. Add even smaller volumes when close to end point
5. Alkali is added in excess

Strong acid versus strong base titrations



Equivalence point lies at mid point of the extrapolated vertical part of curve.

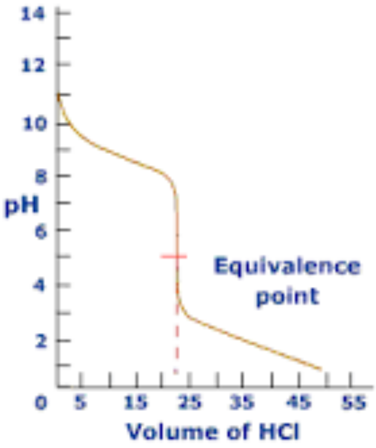
Weak acid versus strong base titration



Strong acid versus weak base titration

Rapid fall at start but rate of fall slows down . This is due to a buffer solution being set up.

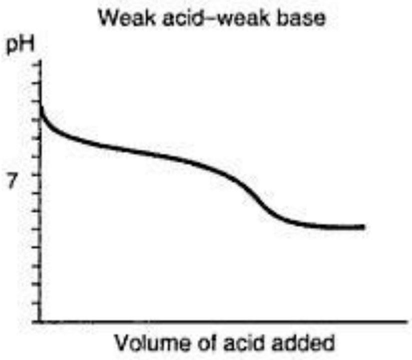
Equivalence point is now in the acidic range



The pH titration curve of weak base(NH_4OH) and strong acid (HCl)

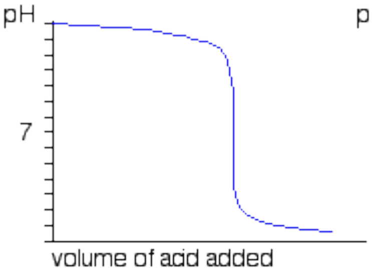
Equivalence point is about 7. This is a difficult titration as there isn't a steep part of the graph.

Weak acid and weak base

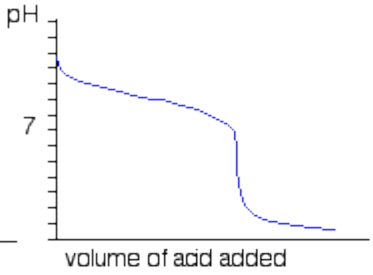


Summary of titration curves

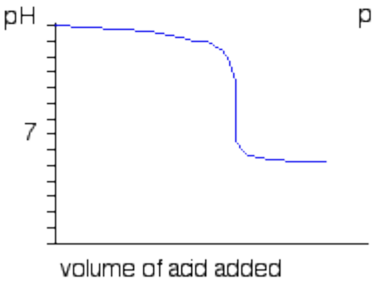
strong acid - strong base



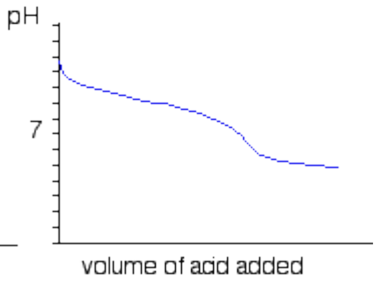
strong acid - weak base



weak acid - strong base



weak acid - weak base



Summary of equivalence points

Type of titration	pH at equivalence point	pH change at equivalence point
Strong acid - strong alkali	7.0	4 to 10
Weak acid - strong alkali	Approx 8.5	7 to 10
Strong acid - weak alkali	Approx 5.5	4 to 7
Weak acid - weak alkali	Approx 7	No sudden change

Choosing indicators for titrations

Indicators are considered to be weak acids therefore must have a different colour to their conjugate bases. The end-point of a titration is reached when [HIn] =[In-]. To choose a correct indicator for a titration one should pick an indicator whose end-point coincides with the equivalence point for the titration.

$$HIn_{(aq)} \rightleftharpoons In^-_{(aq)} + H^+_{(aq)}$$

colour A colour B

Applying Le Chatelier will give us the colour. In an acid solution the H+ ions present will push this equilibrium towards the reactants. Therefore colour A is the acidic colour. In an alkaline solution the OH ions will react and remove H+ ions causing the equilibrium to shift to the products. Colour B is the alkaline colour.

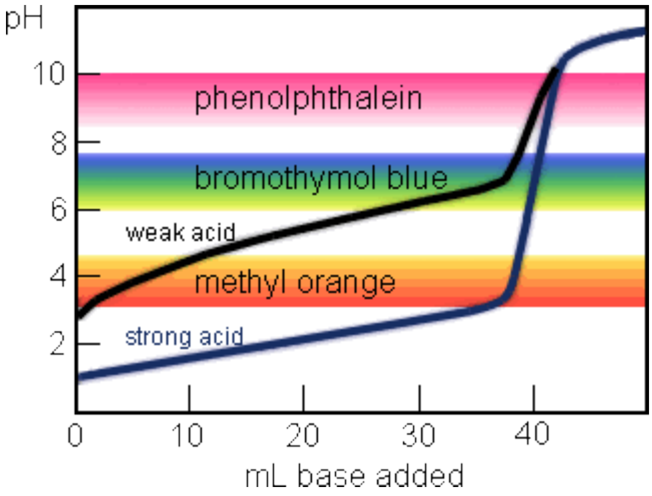
Use **methyl orange** with titrations with strong acids but not **weak acids**

Colour change: red acid to **yellow** alkali

(**Orange end point**)

Only use phenolphthalein in titrations with **strong bases** but not **weak bases**

Colour change: colourless acid to **pink** alkali



Buffers

A buffer solution can resist changes in pH when small amounts of acid or base are added. An acidic buffer maintains a pH below 7 and consists of **a weak acid and its salt**. A basic buffer maintains pH above 7 and consists of **a weak acid and its salt**.

For example, an acidic buffer could contain ethanoic acid and sodium ethanoate. This will produce the following reactions:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$

The equilibrium for the first reaction is far to the left and the equilibrium for the second reaction is shifted to the right. If an **acid is added** the H+ reacts with the excess CH3COO- and this become ethanoic acid, which doesn't change the equilibrium. If **a base is added** the

OH- reacts with hydrogen from reaction 1 to become water. However, this **disrupts the equilibrium and more H+ is produced to compensate. Some ethanoic acid molecules are changed to ethanoate ions but as there is a large concentration of the salt ion in the buffer the ratio [CH3CO2H]/ [CH3CO2-] stays almostconstant, so the pH stays fairly constant.**

Calculating pH of buffer solutions

Use expression $Ka= \frac{[H^+_{(aq)}][A^-_{(aq)}]}{[HA\ (aq)]}$ **then rearrange to** $[H^+_{(aq)}] = Ka \frac{[HA_{(aq)}]}{[A^-_{(aq)}]}$

Calculating pH of buffers on addition of small volumes of acid or alkali

If a small amount of alkali is added to a buffer then the moles of the buffer acid would reduce by the number of moles of alkali added and the moles of salt would increase by the same amount so a new calculation of pH can be done with the new values.

$$CH_3CO_2H_{\ (aq)} + OH^- \rightarrow CH_3CO_2^-{}_{(aq)} + H_2O_{\ (l)}$$

If a small amount of acid is added to a buffer then the moles of the buffer salt would reduce by the number of moles of acid added and the moles of buffer acid would increase by the same amount so a new calculation of pH can be done with the new values.

$$CH_3CO_2^-{}_{(aq)} + H^+ \rightarrow CH_3CO_2H_{\ (aq)}$$

Example:

0.005 mol of NaOH is added to 500cm3 of a buffer where the concentration of ethanoic

acid is 0.200 mol dm-3 and the concentration of sodium ethanoate is 0.250 mol dm-3.

(Ka = 1.7 x 10-5)

Calculate the pH of the buffer solution after the NaOH has been added.

Work out the moles of acid and salt in the initial buffer solution

Moles ethanoic acid= conc x vol = 0.200 x 0.500 = 0.100mol

Moles sodium ethanoate = conc x vol = 0.25 x 0.500 = 0.125mol

Work out the moles of acid and salt in buffer after the addition of 0.005mol NaOH

Moles ethanoic acid = 0.100 - 0.005 = 0.095 mol

Moles sodium ethanoate = 0.125 +0.005 = 0.130 mol

$$[H^+_{(aq)}] = Ka \frac{[CH_3COOH_{(aq)}]}{[CH_3COO^-_{(aq)}]} \longleftarrow$$

We can enter moles of acid and salt straight into the equation as they both have the same new final volume

$$[H^+_{(aq)}] = 1.7 \times 10^{-5} \times \frac{0.095}{0.130} \rightarrow [H^+_{(aq)}] = 1.24 \times 10^{-5}$$

$$\begin{aligned} pH &= -\log [H^+] \\ &= -\log 1.24 \times 10^{-5} \\ &= 4.91 \end{aligned}$$

Making buffers

Buffers can be made in several ways:

- **Adding a salt solution**

What would be the pH of a buffer made from 45cm3 of 0.1M ethanoic acid

and 50cm3 of 0.15 M sodium ethanoate (Ka = 1.7 x 10-5) ?

Work out the moles of both solutions

Moles ethanoic = conc x vol = 0.1 x 0.045 = 0.0045mol

Moles sodium ethanoate = conc x vol = 0.15 x 0.050 = 0.0075

$$[H^+_{(aq)}] = 1.7 \times 10^{-5} \times \frac{0.0045}{0.0075} \rightarrow [H^+_{(aq)}] = 1.02 \times 10^{-5}$$

$$\begin{aligned} pH &= -\log [H^+] \\ &= -\log 1.02 \times 10^{-5} \\ &= 4.99 \end{aligned}$$

- **Adding a solid salt**

A buffer solution is made by adding 1.1g of sodium ethanoate into 100 cm3 of 0.4M ethanoic acid. What is its pH? Ka =1.7 x10-5

Work out the moles of both solutions

Moles ethanoic = conc x vol = 0.4 x 0.1 = 0.04mol

Moles sodium ethanoate = mass/Mr= 1.1/82 = 0.0134

$$[H^+_{(aq)}] = 1.7 \times 10^{-5} \times \frac{0.04}{0.0134} \rightarrow [H^+_{(aq)}] = 5.07 \times 10^{-5}$$

$$\begin{aligned} pH &= -\log [H^+] \\ &= -\log 5.07 \times 10^{-5} \\ &= 4.29 \end{aligned}$$

To prepare a buffer solution of a given pH, it is necessary to have the acid and base concentrations in a suitable ratio.

Eg to prepare an NH3/NH4Cl buffer of pH = 10

$$\frac{[H3O+]}{Ka} = \frac{[acid]}{[base]} \quad \text{so} \quad \frac{[NH4+]}{[NH3]} = \frac{1 \text{ x } 10\text{-}10}{5.6 \text{ x } 10\text{-}10} = 1/5.6$$

So 5.6 moles of NH3 are required for every 1 mole of NH4Cl

Given equimolar solutions of both, 100 cm3 of this buffer could be made by taking 10 cm3 of NH4Cl, adding 56 cm3 of ammonia and the total volume made up to 100 cm3.

It is possible to express the pH directly in terms of the concentrations of the reactants:

$$[H3O+] = \frac{Ka[acid]}{[base]}$$

so log10[H3O+] = log10Ka + log10([acid]/[base])

so -log10[H3O+] = -log10Ka + log10([base]/[acid])

so pH = pKa + log10([base]/[acid])

pH = pKa + log10([base]/[acid])

$$\boxed{pH = pK_a + \log_{10}([base]/[acid])}$$

Natural buffers

There are many biological systems which rely on a fairly constant pH, and which rely on the use of buffer solutions to maintain this pH.

a) **Blood**

The pH of blood must be maintained at around 7.4. Hydrogen carbonate ions are used for this purpose:

$$HCO3\text{-}(aq) + H_3O+ (aq) \longrightarrow CO_2 (g) + 2H_2O(l)$$

$$HCO3\text{-}(aq) + OH\text{-}(aq) \longrightarrow CO_2 (aq) + H_2O (l)$$

b) **Tears**

The pH of tears must also be maintained at around 7.4, in this case by the use of amino acids:

$H_2NCH_2COOH(aq) + H_3O+(aq) \longrightarrow H_3N+CH_2COOH(aq) + H_2O(l)$

$H_2NCH_2COOH(aq) + OH-(aq) \longrightarrow H_2NCH_2COO-(aq) + H_2O(l)$

Enthalpy changes of neutralisation

The standard enthalpy change of neutralisation is the enthalpy change when solutions of an acid and an alkali react together under standard conditions to produce 1 mole of water. Enthalpy changes of neutralisation are always exothermic. For reactions involving strong acids and alkalis, the values are similar, with values between -56 and -58 kJ mol-1 because the same reaction is occurring $H+ + OH- \longrightarrow H2O$

Weak acids have a less exothermic enthalpy change of neutralisation because energy is absorbed to ionise the acid and break the bond to the hydrogen in the un-dissociated acid.

5.2 Energy

5.2.1 lattice enthalpy

Lattice energy Is the energy change when **one mole of an ionic solid** is formed from its **gaseous ions.**

Enthalpy change of atomisation, ΔatH

The enthalpy of atomisation of an element is the enthalpy change when 1 mole of gaseous atoms is formed from the element in its standard state

$Na(s) \longrightarrow Na(g)$ [ΔatH = +148 kJ mol-1]

$½ O2(g) \longrightarrow O(g)$ [ΔatH = +249 kJ mol-1]

Electron affinity

Electron affinity of an atom or molecule is defined as the amount of energy released or spent when an **electron** is added to a neutral atom or molecule in the gaseous state to form a negative ion.

$X_{(g)} + e^- \longrightarrow X^-_{(g)}$

First electron affinities have negative values. For example, the first electron affinity of chlorine is -349 kJ mol-1. By convention, the negative sign shows a release of energy.

Group 7 electron affinities

F	-328 kJ mol-1
Cl	-349 kJ mol-1
Br	-324 kJ mol-1
I	-295 kJ mol-1

The **first electron affinity** is **exothermic** for atoms that normally form negative ions because the ion is more stable than the atom and there is an attraction between the nucleus and the electron.
As you go down the group, first electron affinities become **less** (less energy is evolved when the negative ions are formed). Fluorine however breaks that pattern.

The electron affinity is a measure of the attraction between the incoming electron and the nucleus - the stronger the attraction, the more energy is released. The factors which affect this attraction are exactly the same as those relating to ionisation energies - nuclear charge, distance and screening.

Second electron affinity- this is the enthalpy change when one mole of gaseous 1- ions gains one electron per ion to produce gaseous 2- ions.

O –(g) + e-   O2- (g) [ΔHea = +798 kJ mol-1]

The second electron affinity for oxygen is **endothermic** because it take energy to overcome the repulsive force between the negative ion and the electron

Born haber cycles

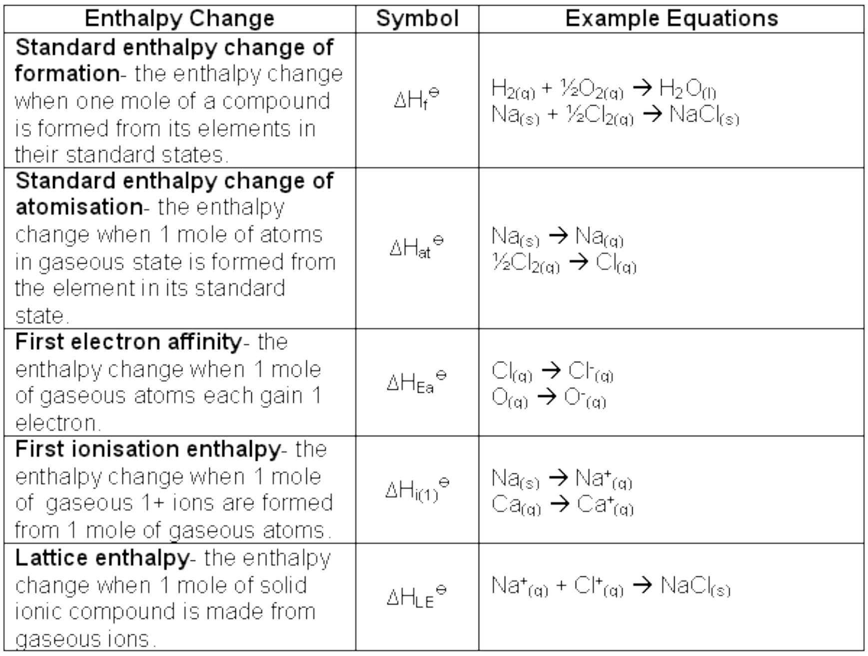
Lattice enthalpies for ionic compounds give a good indication as to the strength of the ionic bonding in the lattice.

Lattice enthalpies cannot be measured directly; they are calculated indirectly using a **Born-Haber cycle.**

This splits up the enthalpy of formation into individual enthalpy changes; one of which is the lattice enthalpy. For example, the above reaction can be split up into several steps:

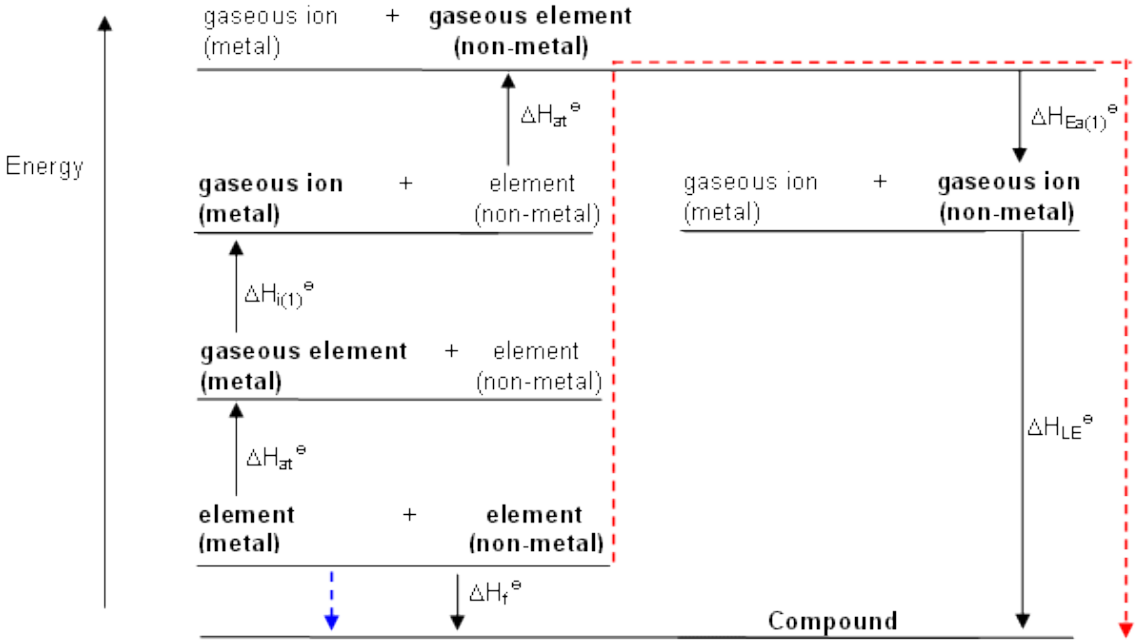
- The elements in their standard states are turned into gaseous atoms.
- The gaseous atoms become gaseous ions.
- The gaseous ions come together to form solid sodium chloride.
- By applying Hess's Law, the lattice enthalpy can then be calculated.

The following enthalpy changes are often used in Born-Haber cycles:



Enthalpy Change	Symbol	Example Equations
Standard enthalpy change of formation- the enthalpy change when one mole of a compound is formed from its elements in their standard states.	$\Delta H_f^\ominus$	$H_{2(g)} + ½O_{2(g)} \rightarrow H_2O_{(l)}$ $Na_{(s)} + ½Cl_{2(g)} \rightarrow NaCl_{(s)}$
Standard enthalpy change of atomisation- the enthalpy change when 1 mole of atoms in gaseous state is formed from the element in its standard state.	$\Delta H_{at}^\ominus$	$Na_{(s)} \rightarrow Na_{(g)}$ $½Cl_{2(g)} \rightarrow Cl_{(g)}$
First electron affinity- the enthalpy change when 1 mole of gaseous atoms each gain 1 electron.	$\Delta H_{Ea}^\ominus$	$Cl_{(g)} \rightarrow Cl^-_{(g)}$ $O_{(g)} \rightarrow O^-_{(g)}$
First ionisation enthalpy- the enthalpy change when 1 mole of gaseous 1+ ions are formed from 1 mole of gaseous atoms.	$\Delta H_{i(1)}^\ominus$	$Na_{(s)} \rightarrow Na^+_{(g)}$ $Ca_{(g)} \rightarrow Ca^+_{(g)}$
Lattice enthalpy- the enthalpy change when 1 mole of solid ionic compound is made from gaseous ions.	$\Delta H_{LE}^\ominus$	$Na^+_{(g)} + Cl^+_{(g)} \rightarrow NaCl_{(s)}$

At each stage of the Born-Haber scale, one change occurs.

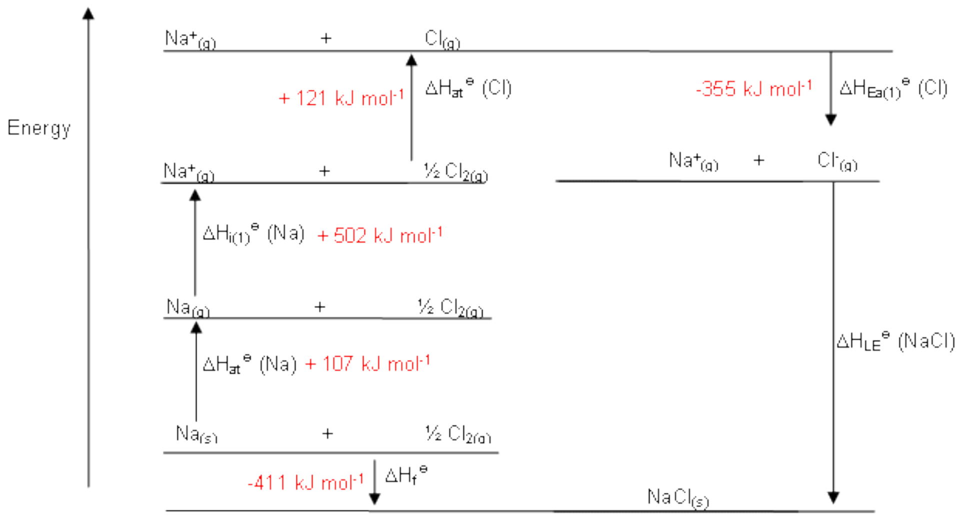


Applying Hess's law to this cycle, which states that the enthalpy change for a reaction is the same regardless of how many steps occur in that reaction, it is possible to calculate the lattice enthalpy.

The arrows pointing upwards represent endothermic changes, those pointing downwards show exothermic changes.

From the Born-Haber Cycle, the enthalpy change associated with the route depicted by the blue arrow is equal to the enthalpy change of the route shown by the red arrow.

The Born-Haber cycle for sodium chloride is shown below:



Therefore from the cycle:

$$\Delta H_f^{\ominus}\,(\text{NaCl}) = \Delta H_{at}^{\ominus}\,(\text{Na}) + \Delta H_{i(1)}^{\ominus}\,(\text{Na}) + \Delta H_{at}^{\ominus}\,(\text{Cl}) + \Delta H_{EA(1)}^{\ominus}\,(\text{Cl}) + \Delta H_{LE}^{\ominus}\,(\text{NaCl})$$

Rearranging gives:

$$\Delta H_{LE}^{\ominus}\,(\text{NaCl}) = \Delta H_f^{\ominus}\,(\text{NaCl}) - \Delta H_{at}^{\ominus}\,(\text{Na}) - \Delta H_{i(1)}^{\ominus}\,(\text{Na}) - \Delta H_{at}^{\ominus}\,(\text{Cl}) - \Delta H_{EA(1)}^{\ominus}\,(\text{Cl})$$

Substituting in the values:

$$\Delta H_{LE}^{\ominus}\,(\text{NaCl}) = (-411) - (107) - (502) - (121) - (-355)$$

$$= -786\ \text{kJ mol}^{-1}$$

Trends in lattice enthalpies

The strength of enthalpy of lattice formation depends on the following factors

1. The sizes of the ions:

The larger the ions, the less negative the enthalpies of lattice formation (i.e. a weaker lattice). As the ions are larger the charges become further apart and so have a weaker attractive force between them.

2. The charges on the ion:

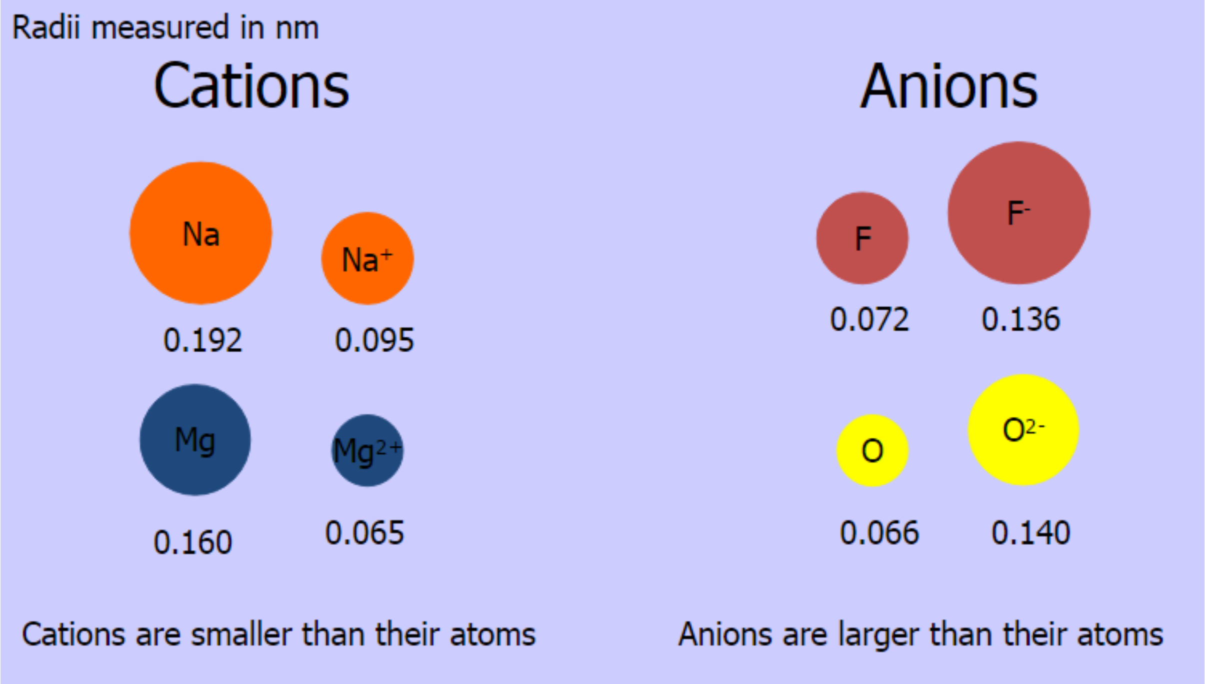
The bigger the charge of the ion, the greater the attraction between the ions so the stronger the lattice enthalpy (more negative values).

Theoretical lattice enthalpies and Born- Haber lattice enthalpies.

Theoretical lattice enthalpies assumes a perfect ionic model where the ions are 100% ionic and spherical and the attractions are purely electrostatic. The Born Haber lattice enthalpy is the real experimental value. When a compound shows covalent character, the theoretical and the born Haber lattice enthalpies differ. **The more the covalent character the bigger the difference between the values.**

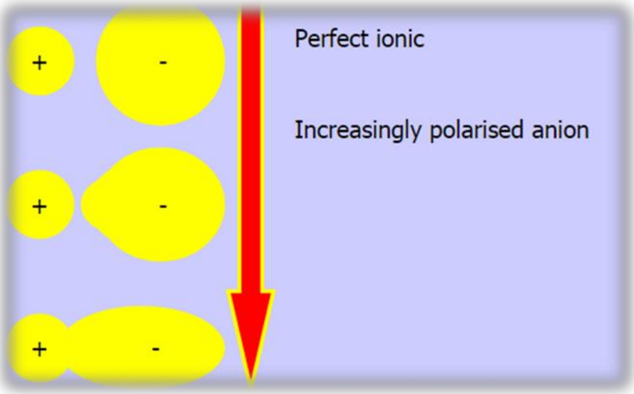
Polarisation

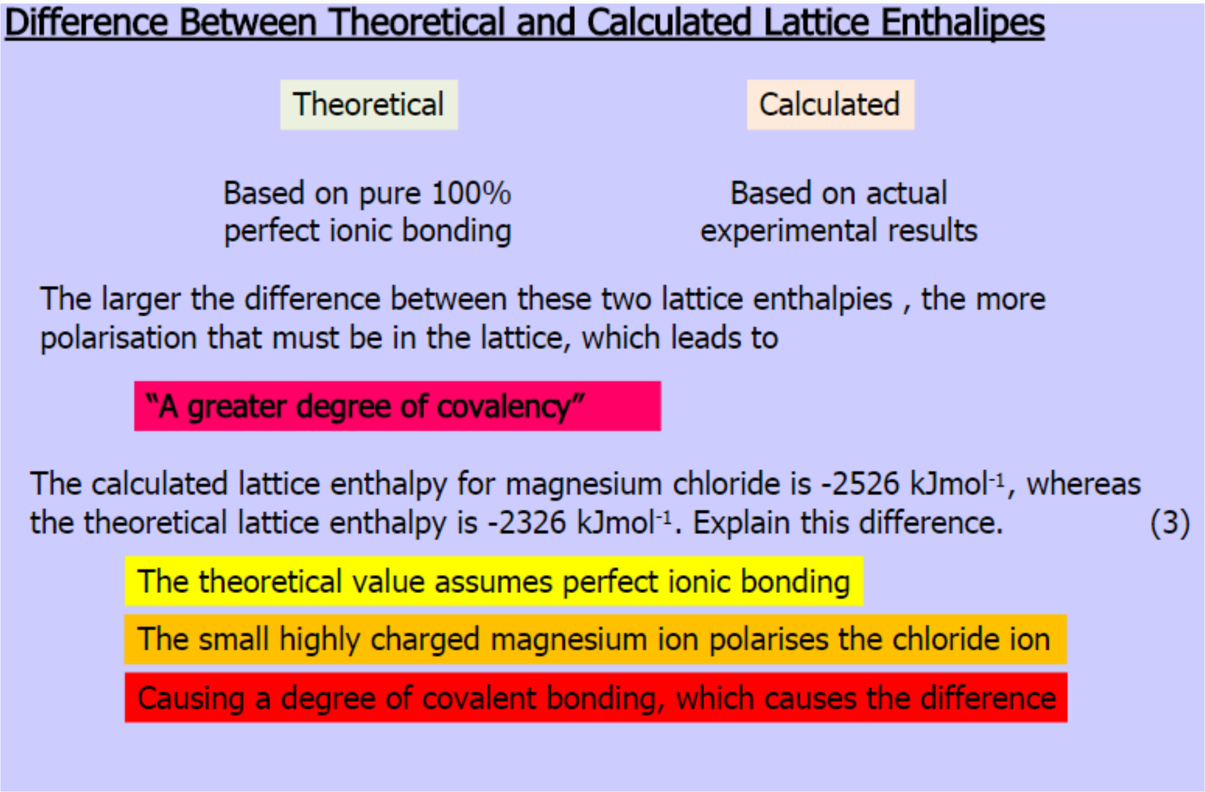
Ions



Ionic bonds can be polarised by the cations strongly attracting the outer shell electrons of the anion. This polarisation will depend on:

- Its charges density – dependent on ion size and charge
- Radius of ion- smaller ionic radii = greater charge so greater charge density
- For anions, larger radii = easier polarisation





Difference Between Theoretical and Calculated Lattice Enthalpies

Theoretical	Calculated
Based on pure 100% perfect ionic bonding	Based on actual experimental results

The larger the difference between these two lattice enthalpies , the more polarisation that must be in the lattice, which leads to

"A greater degree of covalency"

The calculated lattice enthalpy for magnesium chloride is -2526 kJmol^{-1}, whereas the theoretical lattice enthalpy is -2326 kJmol^{-1}. Explain this difference. (3)

The theoretical value assumes perfect ionic bonding

The small highly charged magnesium ion polarises the chloride ion

Causing a degree of covalent bonding, which causes the difference

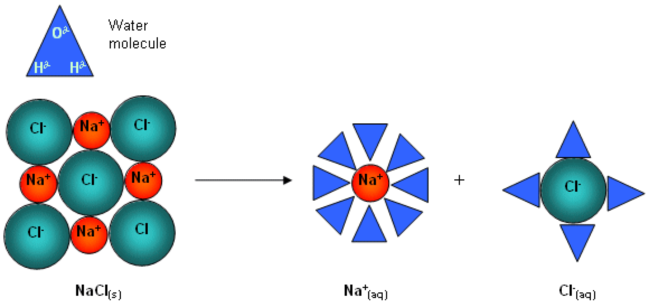
Enthalpy change of hydration ΔH_{hyd}

Even though energy is needed to break up the lattice, many ionic substances do dissolve.

Therefore, something else must happen to supply that energy.

Water molecules possess a dipole and are attracted to the ions on the surface of the lattice when an ionic compound is added to water.

The water molecules pull the ions from the surface of the compound; the ions in the solution become hydrated; they have water molecules bound to them:



The smaller the ion and the higher its charge, the more water molecules it attracts.

The strength of the attractions between the ions and the water molecules is measured by the enthalpy of hydration (**ΔH_{hyd}**).

The enthalpy change of hydration is defined as the enthalpy change for the production of a solution of ions from one mole of gaseous ions.

For example:

$$Na^+_{(g)} + aq \rightarrow Na^+_{(aq)} \qquad \Delta H_{le} = -406\ kJ\ mol^{-1}$$
$$Br^-_{(g)} + aq \rightarrow Br^-_{(aq)} \qquad \Delta H_{le} = -337\ kJ\ mol^{-1}$$

Enthalpies of hydration depend upon the concentration of the solution produced.

Values quoted refer to an infinitely dilute solution.

Enthalpies of hydration are always negative (exothermic).

Once again, the most exothermic values occur when the ionic radii decreases and the ionic charge increases.

Molecules of some other solvents, such as ethanol, are also polar and can bind to ions.

Enthalpy change of solution ΔH_{sol}

The difference between the enthalpies of hydration of ions and the lattice enthalpy gives the enthalpy change of solution (**ΔH_{sol}**).

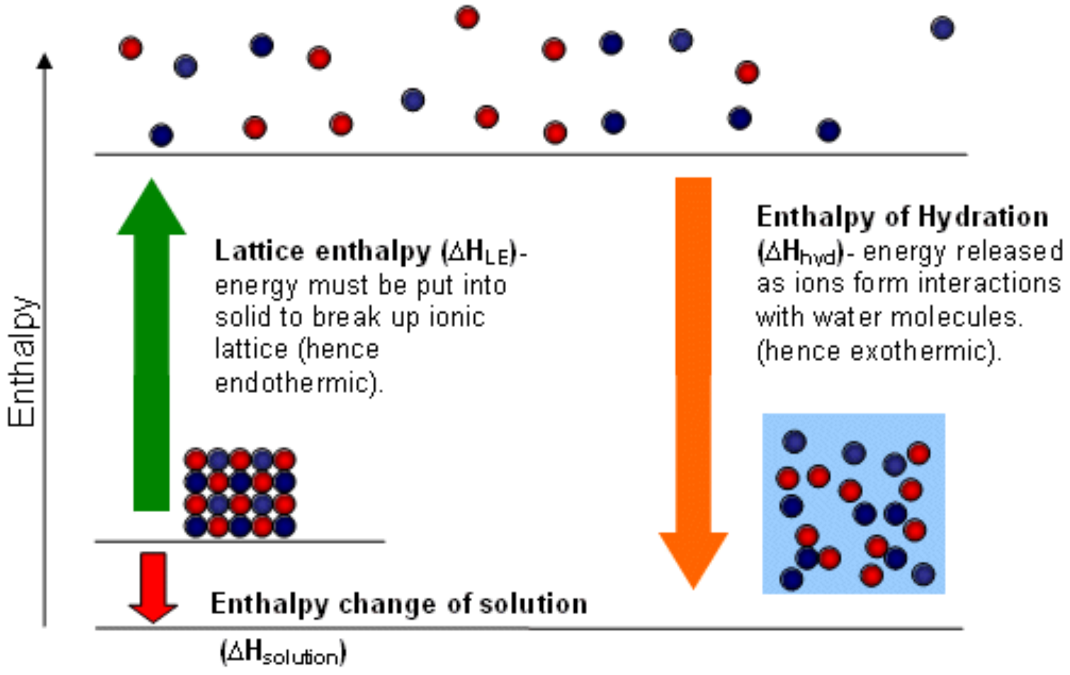
The enthalpy of solution, enthalpy of dissolution, or heat of solution is the enthalpy change associated with the dissolution of a substance in a solvent at constant pressure resulting in infinite dilution. The enthalpy of solution is most often expressed in kJ/mol at constant temperature. Enthalpies of solution may be either positive or negative - in other words, some ionic substances dissolved endothermically (for example, NaCl); others dissolve exothermically (for example NaOH)

Hess' law is used to calculate enthalpy changes of solution

The hydration of ions favours dissolving and helps to supply the energy needed to separate the ions from a lattice.

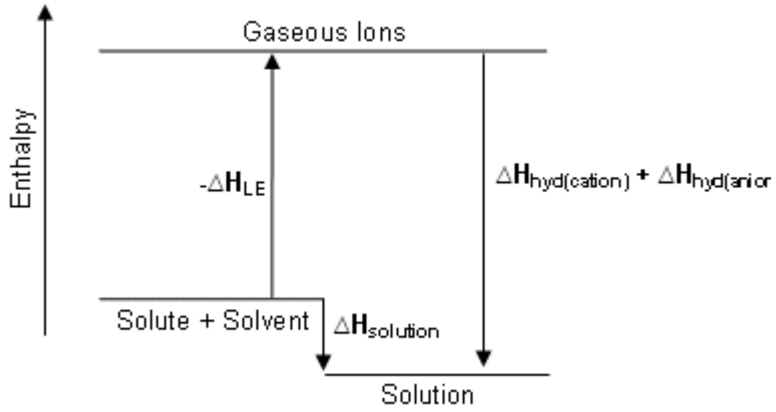
The process of dissolving can be broken down into two steps:

- The solid ionic compound is split up into a gas of ions (requires the energy equal to the lattice energy to be supplied).
- The ions dissolve in solution and become hydrated; the energy equal to the hydration energies of the two ions is given out.

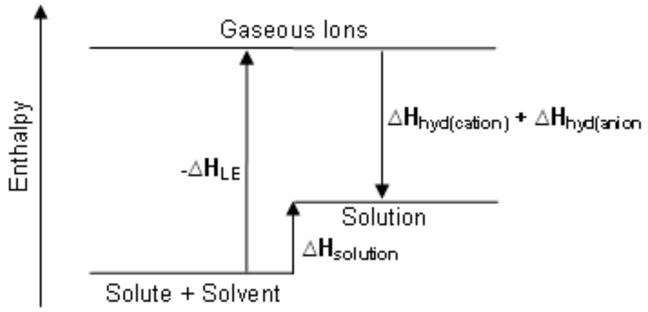


Examples of enthalpy changes of solutions

- **When ΔH_{sol} is slightly negative**



- **When ΔH_{sol} is slightly positive**



The value of $\Delta H_{solution}$ depends upon the difference between the enthalpy of hydration of the individual ions and the lattice enthalpy of the compound.

Even if the value of $\Delta H_{solution}$ is positive, the substance may still dissolve; this is related to the change in entropy of the system that occurs.

ΔH_{LE} and ΔH_{Hyd} values are often very large and are dependent on the size and charge of the ions involved.

As a result, the values of $\Delta H_{solution}$ are often small by comparison, and can be either positive or negative.

5.2.2 Enthalpy and entropy

Since some endothermic reactions can occur at room temperature, enthalpy changes alone do not control whether reactions occur. Consideration of entropy is vital.

Entropy is a **measure of the disorder of a system** and the **natural direction of change is increasing total entropy (positive entropy change)**

The entropy of a system increases when a solute dissolves, as it becomes more disordered as the ions spread out through the solution.

Substances with more ways of arranging their atoms and energy (more disordered) have a higher entropy.

An increase in entropy favours dissolving- even if a small amount of energy is needed.

So substances with a small positive enthalpy change of solution are still able to dissolve, provided there is a sufficient increase in entropy.

This can be used to explain why salt (NaCl) dissolves, but calcium carbonate (chalk) does not.

When salt dissolves there is a large increase in entropy, which counteracts the small positive enthalpy change of solution value that it has.

Calcium carbonate, on the other hand, has a small negative enthalpy change of solution; however a decrease in entropy results from it dissolving and so it is insoluble in water.

The decrease in entropy occurs because the solvent, water, is becoming more ordered as the water molecules cluster around the doubly charged ions.

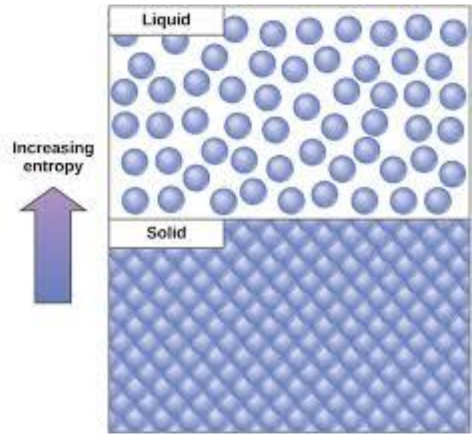
When considering entropy it is useful to split the system (the chemicals) from the surroundings.

A system will consist of reactants and then products. It does not change temperature or pressure, and mass cannot be transferred to the surroundings. Energy can be transferred to the surroundings.

$$\Delta S = \Delta S_{system} + \Delta S_{surroundings}$$
$$\Delta S = Overall\ Change\ in\ Entropy$$
$$\Delta S_{system} = Change\ in\ Entropy\ of\ the\ System$$
$$\Delta S_{surroundings} = Change\ in\ Entropy\ of\ the\ Surroundings$$

$$\Delta S > 0, + entropy\ change, reaction\ is\ spontaneous$$
$$\Delta S < 0, - entropy\ change, reaction\ is\ nonspontaneous$$

Equation for the Total Change in Entropy



Solids have lower entropies than liquids which are lower than gases.

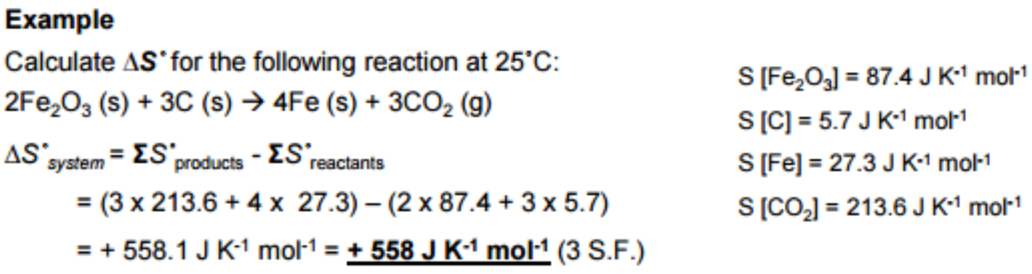
When a solid increases in Temperature its entropy increases as the particles vibrate more.

There is a bigger jump in entropy with boiling than that with melting.

Gases have large entropies as they are much more disordered

Elements in their standard states do not have zero entropy. Only perfect crystals at absolute zero (T = 0 K) will have zero entropy:

$$\Delta S^{\circ}system = \Sigma\ S^{\circ}products - \Sigma S^{\circ}reactants$$



Example

Calculate ΔS° for the following reaction at 25°C:

$2Fe_2O_3\ (s) + 3C\ (s) \rightarrow 4Fe\ (s) + 3CO_2\ (g)$

$\Delta S^{\circ}_{system} = \Sigma S^{\circ}_{products} - \Sigma S^{\circ}_{reactants}$

$= (3 \times 213.6 + 4 \times 27.3) - (2 \times 87.4 + 3 \times 5.7)$

$= +\ 558.1\ J\ K^{-1}\ mol^{-1} = \underline{+\ 558\ J\ K^{-1}\ mol^{-1}}$ (3 S.F.)

S [Fe_2O_3] = 87.4 J K^{-1} mol^{-1}

S [C] = 5.7 J K^{-1} mol^{-1}

S [Fe] = 27.3 J K^{-1} mol^{-1}

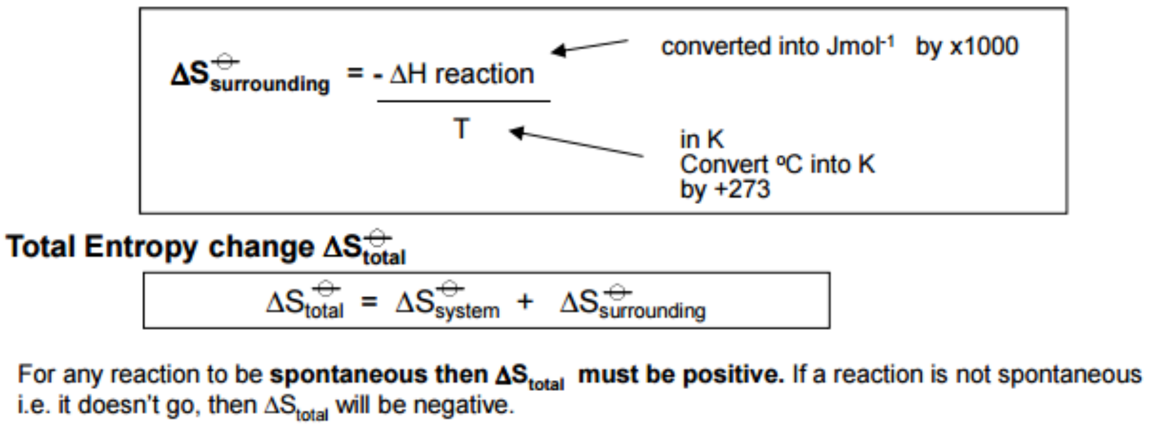
S [CO_2] = 213.6 J K^{-1} mol^{-1}

Entropy of surroundings $\Delta S^{\ominus}_{surrounding}$

Exothermic versus endothermic reactions

In an exothermic reaction energy is given out into the surroundings. The number of	In an endothermic reaction energy is transferred from the surroundings. The

ways of arranging the energy therefore increases and so ΔSsurrounding increases and is positive.	number of ways of arranging the energy in the surroundings therefore decreases and so ΔSsurrounding decreases and is negative.



$$\Delta S^{\ominus}_{surrounding} = \frac{-\Delta H\ reaction}{T}$$

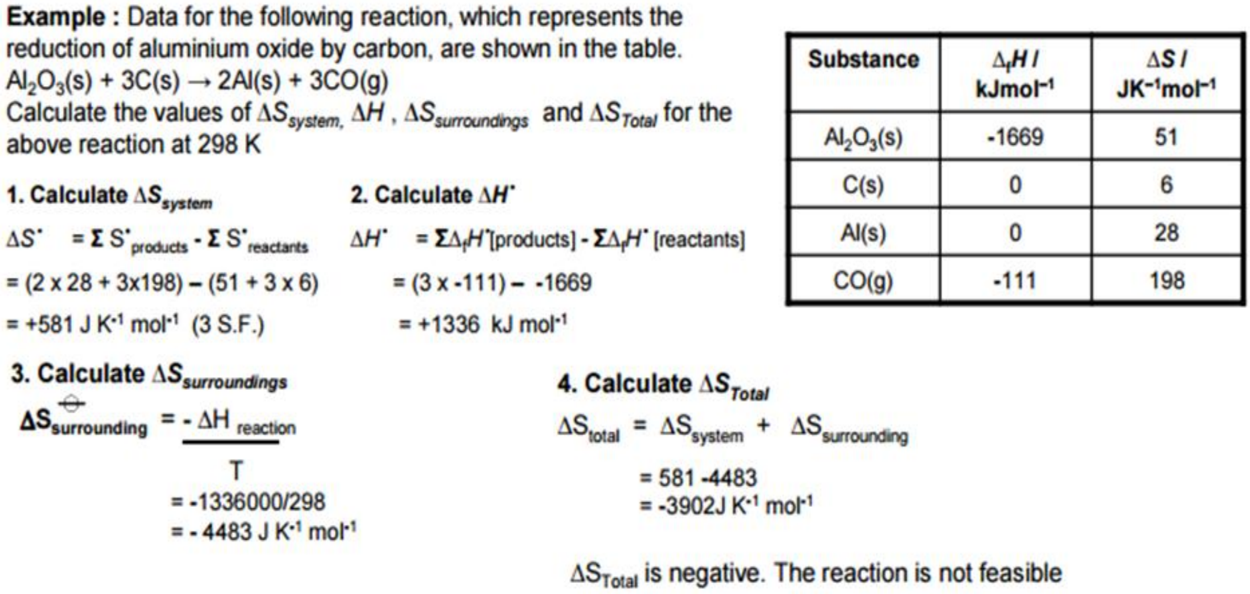
converted into $Jmol^{-1}$ by x1000

in K
Convert °C into K
by +273

Total Entropy change $\Delta S^{\ominus}_{total}$

$$\Delta S^{\ominus}_{total} = \Delta S^{\ominus}_{system} + \Delta S^{\ominus}_{surrounding}$$

For any reaction to be **spontaneous then ΔS_{total} must be positive.** If a reaction is not spontaneous i.e. it doesn't go, then ΔS_{total} will be negative.



Example : Data for the following reaction, which represents the reduction of aluminium oxide by carbon, are shown in the table.
$Al_2O_3(s) + 3C(s) \rightarrow 2Al(s) + 3CO(g)$
Calculate the values of ΔS_{system}, ΔH, $\Delta S_{surroundings}$ and ΔS_{Total} for the above reaction at 298 K

Substance	$\Delta_f H$ / $kJmol^{-1}$	ΔS / $JK^{-1}mol^{-1}$
$Al_2O_3(s)$	-1669	51
C(s)	0	6
Al(s)	0	28
CO(g)	-111	198

1. Calculate ΔS_{system}

$\Delta S^{\circ} = \Sigma S^{\circ}_{products} - \Sigma S^{\circ}_{reactants}$

$= (2 \times 28 + 3 \times 198) - (51 + 3 \times 6)$

$= +581\ J\ K^{-1}\ mol^{-1}$ (3 S.F.)

2. Calculate ΔH°

$\Delta H^{\circ} = \Sigma \Delta_f H^{\circ}[products] - \Sigma \Delta_f H^{\circ}[reactants]$

$= (3 \times -111) - -1669$

$= +1336\ kJ\ mol^{-1}$

3. Calculate $\Delta S_{surroundings}$

$$\Delta S^{\ominus}_{surrounding} = \frac{-\Delta H_{reaction}}{T}$$

$= -1336000/298$

$= -4483\ J\ K^{-1}\ mol^{-1}$

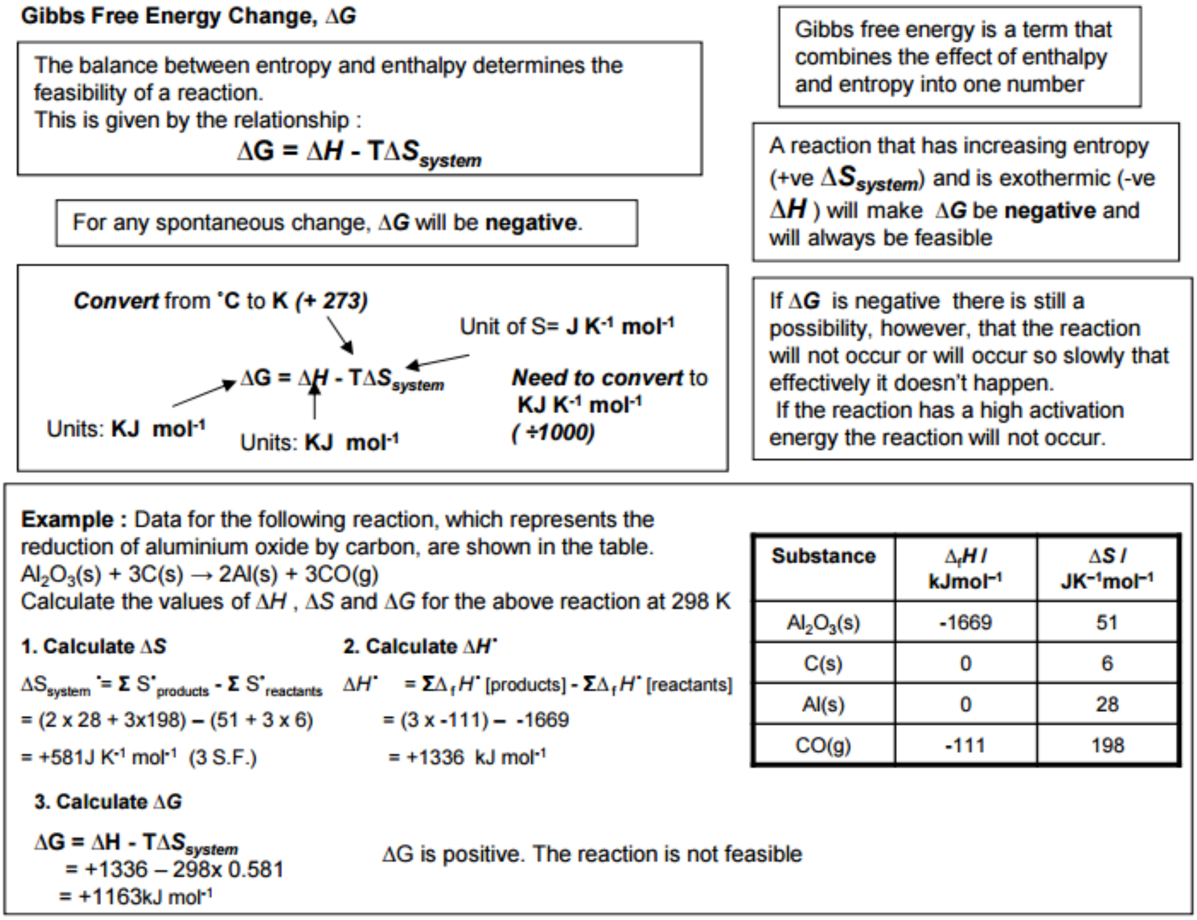
4. Calculate ΔS_{Total}

$\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding}$

$= 581 - 4483$

$= -3902 J\ K^{-1}\ mol^{-1}$

ΔS_{Total} is negative. The reaction is not feasible



Gibbs Free Energy Change, ΔG

The balance between entropy and enthalpy determines the feasibility of a reaction.
This is given by the relationship :

$$\Delta G = \Delta H - T\Delta S_{system}$$

For any spontaneous change, Δ*G* will be **negative**.

Convert from **°C** to **K** ***(+ 273)***

Unit of S= **J K⁻¹ mol⁻¹**

$$\Delta G = \Delta H - T\Delta S_{system}$$

Need to convert to **KJ K⁻¹ mol⁻¹** ***(÷1000)***

Units: **KJ mol⁻¹**

Units: **KJ mol⁻¹**

Gibbs free energy is a term that combines the effect of enthalpy and entropy into one number

A reaction that has increasing entropy (+ve ΔS_{system}) and is exothermic (-ve Δ*H*) will make Δ*G* be **negative** and will always be feasible

If Δ*G* is negative there is still a possibility, however, that the reaction will not occur or will occur so slowly that effectively it doesn't happen.
If the reaction has a high activation energy the reaction will not occur.

Example : Data for the following reaction, which represents the reduction of aluminium oxide by carbon, are shown in the table.
$Al_2O_3(s) + 3C(s) \rightarrow 2Al(s) + 3CO(g)$
Calculate the values of Δ*H* , Δ*S* and Δ*G* for the above reaction at 298 K

Substance	$\Delta_f H$ / kJmol⁻¹	Δ*S* / JK⁻¹mol⁻¹
$Al_2O_3(s)$	-1669	51
C(s)	0	6
Al(s)	0	28
CO(g)	-111	198

1. Calculate Δ*S*

$\Delta S_{system}{}^{\circ} = \Sigma S^{\circ}_{products} - \Sigma S^{\circ}_{reactants}$

$= (2 \times 28 + 3 \times 198) - (51 + 3 \times 6)$

$= +581 J K^{-1} mol^{-1}$ (3 S.F.)

2. Calculate Δ*H*°

$\Delta H^{\circ} = \Sigma\Delta_f H^{\circ}$ [products] $- \Sigma\Delta_f H^{\circ}$ [reactants]

$= (3 \times -111) - -1669$

$= +1336$ kJ mol⁻¹

3. Calculate ΔG

$$\Delta G = \Delta H - T\Delta S_{system}$$
$= +1336 - 298 \times 0.581$
$= +1163 kJ mol^{-1}$

ΔG is positive. The reaction is not feasible

Predicting feasibility

- It follows from this formula that feasibility is dependent on temperature
- An exothermic reaction with a positive entropy change will be feasible at all temperatures
- An endothermic reaction with a negative entropy change will be infeasible at all temperatures
- An exothermic reaction with a reduction in entropy will become feasible at low temperatures (when ΔH outweighs TΔS**) – see example below**
- An endothermic reaction with an increase in entropy will become feasible at high temperatures (when TΔS outweighs ΔH**)**
- In the last two cases, the temperature at which the reaction becomes feasible is when **ΔG =0** (i.e. ΔH = TΔS, or T = ΔH/ΔS)

  <u>**Example**</u>

  $$TiO_2(s) + C(s) + 2Cl_2(g) \rightarrow TiCl_4(l) + CO_2(g)$$

  For this reaction, ΔH = -258 kJ mol⁻¹ and ΔS = -35.6 J K⁻¹ mol⁻¹

  Calculate the temperature at which this reaction ceases to be feasible

T = $\Delta H/\Delta S$

= (-258 x 1000)/-35.6 (common mistake is to leave out x 1000)

= 7247K (infeasible above this temperature)

- For changes of state, such as melting and boiling, $\Delta G = 0$ and the two states are in equilibrium

If the reaction involves an increase in entropy (ΔS is +ve) then increasing Temperature will make it more likely that ΔG is negative and more likely that the reaction occurs

If the reaction involves an decrease in entropy (ΔS is -ve) then increasing Temperature will make it more less likely that ΔG is negative and less likely for the reaction to occur .

If the reaction has a ΔS close to zero then temperature will not have a large effect on the feasibility of the reaction as - TΔS will be small and ΔG won't change much

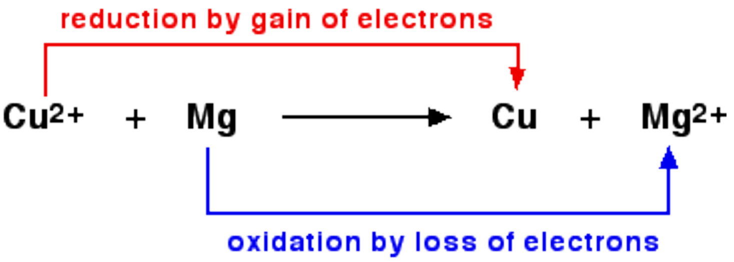
Equilibrium constants values may also be used to predict feasibility of reactions. Large equilibrium constants lead to more negative values for Gibbs free energy and thus high feasibility.

5.2.3 Redox and electrode potentials

OIL RIG

oxidation is loss reduction is gain

Oxidation can be defined as loss of electrons and reduction as gain of electrons. For example:



The oxidation gives a compound its name, for example Iron (IV) oxide means the oxidation state of iron is 4 so therefore there must be two oxygen atoms bonded to it. S-block metals loose their electrons in a reaction, so are good reductants (they are oxidized easily). There are also p-block elements which can have different oxidation states; and those in group VII, gain electrons in reactions so are good oxidants (they gain electrons easily).

Electrode potentials- Standard hydrogen electrode

This is the 'potential' of a redox system to lose or gain electrons when compared to the standard hydrogen electrode - assigned a value of 0 volts.

In any reduction-oxidation half equation the electrons are gained by the species on the left hand side:

$Cu^{2+} + 2e \rightleftharpoons Cu$

The electrode potential measures the tendency of electrons to flow away from or towards a redox equilibrium. They are always measured with respect to the standard hydrogen electrode (which is assigned a value of zero volts).

Components of a standard hydrogen electrode.

To make the electrode a standard reference electrode

some conditions apply:

1. Hydrogen gas at pressure of 100 kPa

2. Solution containing the hydrogen ion at 1.00 mol dm-3

(solution is usually 1M HCl)

3. Temperature at 298K

Standard conditions are needed because the position of the redox equilibrium will change with conditions.

Equilibrium redox systems with the reduced side (usually a metal) more reactive than hydrogen have a negative electrode potential, i.e. they can lose electrons more easily than hydrogen.

Equilibrium redox systems with the reduced side less reactive than hydrogen have a positive electrode potential, i.e. they can lose electrons less easily than hydrogen.

Example: Zinc has a standard electrode potential of - 0.76 volts

Consequently the equilibrium...

$Zn \rightleftharpoons Zn^{2+} + 2e$

has more of a tendency to move to the right hand side than the equilibrium...

$H_2 \rightleftharpoons 2H^+ + 2e$

Hence if the two equilibria are brought into electrical contact using an external wire and a salt bridge, the electrons will be pushed from the zinc equilibrium to the hydrogen equilbrium with a force of - 0.76V (the negative sign simply indicates the direction of flow - from zinc to hydrogen ions)

The two equations then may be summed together to give the reaction occuring in the whole cell.

$Zn \longrightarrow Zn^{2+} + 2e$

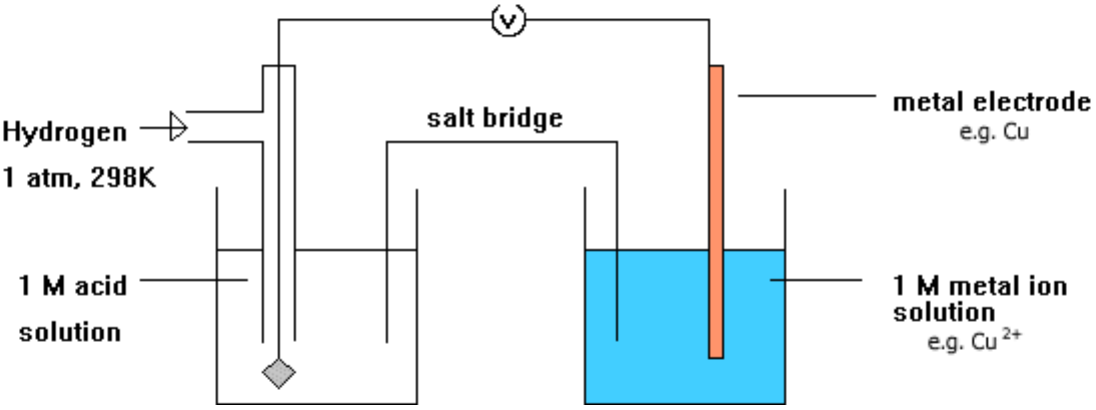
$2H^+ + 2e \longrightarrow H_2$

overall cell reaction

$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$

Using the SHE to measure electrode potential

In the actual experimental setup the two half cells are connected together via an external circuit wire and a salt bridge to make the whole cell.



In the above apparatus setup the copper | copper sulphate (aq) half cell is connected to the SHE via an external circuit containing a high resistance voltmeter (high resistance to prevent passage of current)

There is a salt bridge to complete the circuit - this allows the ions to flow from one side to another to equalise the movement of charge.

Once the apparatus is setup the reading on the high resistance voltmeter records the electrode potential of the $Cu|Cu^{2+}{}_{(aq)}$ system

In this particular case the voltmeter will read +0.34 V indicating that copper is less reactive than hydrogen and that there is a force pushing electrons around the external circuit from the hydrogen half cell to the copper half cell.

Representing the cell

The whole cell can be represented by showing the half cells in order of phase (solid, | solution, |salt bridge | solution | solid)

The above cell diagram can be represented as:

$H_{2(g)}$,Pt | $H^+_{(aq)}$ || $Cu^{2+}_{(aq)}$ | Cu $_{(s)}$

Electrochemical cells

- A cell has two half–cells.
- The two half cells have to be connected with a salt bridge.
- Simple half cells will consist of a metal (acts an electrode) and a solution of a compound containing that metal (eg Cu and $CuSO_4$).
- These two half cells will produce a small voltage if connected into a circuit. (i.e. become a Battery or cell).

Why use a High resistance

voltmeter? The voltmeter needs to be of very high resistance to stop the current

from flowing in the circuit. In this state it is possible to measure the

maximum possible potential difference (E).

The reactions will not be occurring because the very high resistance voltmeter stops the current from flowing.

Salt Bridge

The salt bridge is used to connect up the circuit. The free moving ions conduct the charge. A salt bridge is usually made from a piece of filter paper (or material) soaked in a salt solution, usually Potassium Nitrate. The salt should be unreactive with the electrodes and electrode solutions. E.g. potassium chloride would not be suitable for copper systems as Chloride ions can form complexes with copper ions. A wire is not used because the metal wire would set up its own electrode system with the solutions

What happens if current is allowed to flow? If the voltmeter is removed and replaced with a bulb or if the circuit is short circuited, a current flows. The reactions will then occur separately at each electrode. The voltage will fall to zero as the reactants are used up. The most positive electrode will always undergo reduction.

Cu^{2+} (aq) + 2e- ◊ Cu(s) (positive as electrons are used up)

The most negative electrode will always undergo oxidation.

Zn(s) ◊ Zn^{2+} (aq) + 2e- (negative as electrons are given off)

Systems that do not include metals to act as electrodes use platinum which provides a conducting surface and allows for electron transfer.

Calculating the EMF of a cell

In order to calculate the Ecell, we must use ‘standard electrode potentials’ for the half cells.

Use the equation

Ecell= Erhs – Elhs

Using electrode potentials

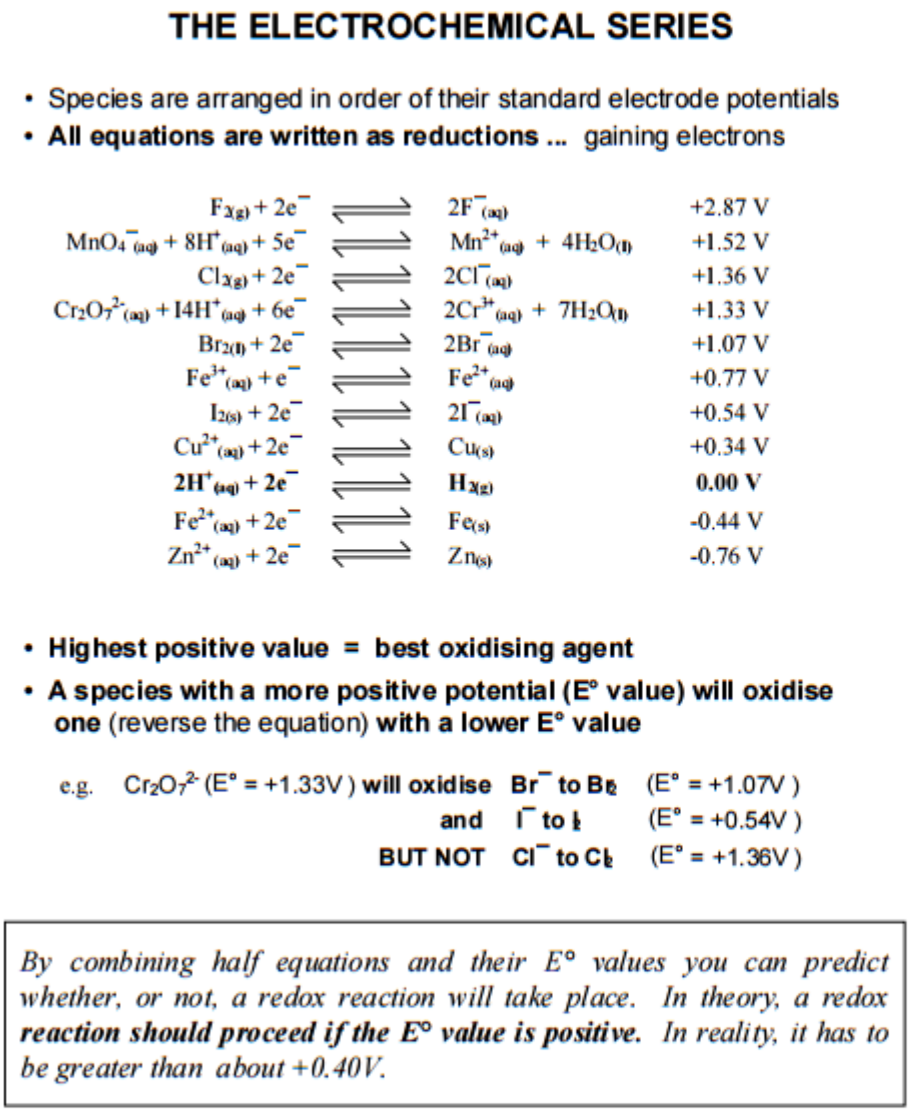
If we want to work out the Ecell that corresponds to this spontaneous change then use Ecell = Ered – Eox A spontaneous change will always have a positive Ecell

The more negative half cell will always oxidise (go backwards)

Mg2+ (aq) + 2e- → Mg(s) E= -2.37V

Cu2+ (aq) + 2e- → Cu (s) E = +0.34V

The more positive half cell will always reduce (go forwards)



THE ELECTROCHEMICAL SERIES

- Species are arranged in order of their standard electrode potentials
- **All equations are written as reductions ...** gaining electrons

$F_{2(g)} + 2e^-$	$\rightleftharpoons$	$2F^-_{(aq)}$	+2.87 V
$MnO_4{}^-_{(aq)} + 8H^+_{(aq)} + 5e^-$	$\rightleftharpoons$	$Mn^{2+}_{(aq)} + 4H_2O_{(l)}$	+1.52 V
$Cl_{2(g)} + 2e^-$	$\rightleftharpoons$	$2Cl^-_{(aq)}$	+1.36 V
$Cr_2O_7{}^{2-}_{(aq)} + 14H^+_{(aq)} + 6e^-$	$\rightleftharpoons$	$2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$	+1.33 V
$Br_{2(l)} + 2e^-$	$\rightleftharpoons$	$2Br^-_{(aq)}$	+1.07 V
$Fe^{3+}_{(aq)} + e^-$	$\rightleftharpoons$	$Fe^{2+}_{(aq)}$	+0.77 V
$I_{2(s)} + 2e^-$	$\rightleftharpoons$	$2I^-_{(aq)}$	+0.54 V
$Cu^{2+}_{(aq)} + 2e^-$	$\rightleftharpoons$	$Cu_{(s)}$	+0.34 V
$\mathbf{2H^+_{(aq)} + 2e^-}$	$\rightleftharpoons$	$\mathbf{H_{2(g)}}$	**0.00 V**
$Fe^{2+}_{(aq)} + 2e^-$	$\rightleftharpoons$	$Fe_{(s)}$	-0.44 V
$Zn^{2+}_{(aq)} + 2e^-$	$\rightleftharpoons$	$Zn_{(s)}$	-0.76 V

- **Highest positive value = best oxidising agent**
- **A species with a more positive potential (E° value) will oxidise one** (reverse the equation) **with a lower E° value**

e.g. $Cr_2O_7{}^{2-}$ (E° = +1.33V) **will oxidise** **Br^- to Br_2** (E° = +1.07V)
and **I^- to I_2** (E° = +0.54V)
BUT NOT **Cl^- to Cl_2** (E° = +1.36V)

By combining half equations and their E° values you can predict whether, or not, a redox reaction will take place. In theory, a redox ***reaction should proceed if the E° value is positive.*** *In reality, it has to be greater than about +0.40V.*

Summary of standard electrode potentials

Standard electrode potentials (redox potentials) are one way of measuring how easily a substance loses electrons. In particular, they give a measure of relative positions of equilibrium in reactions such as:

$$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)} \qquad E^\circ = -0.76\ v$$

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)} \qquad E^\circ = +0.34\ v$$

The more negative the E° value, the further the position of equilibrium lies to the left. **Remember that this is always relative to the hydrogen equilibrium - and not in absolute terms.**

The negative sign of the zinc E° value shows that it releases electrons more readily than hydrogen does. The positive sign of the copper E° value shows that it releases electrons less readily than hydrogen.

Whenever you link two of these equilibria together (either via a bit of wire, or by allowing one of the substances to give electrons directly to another one in a test tube) electrons flow from one equilibrium to the other. That upsets the equilibria, and Le Chatelier's Principle applies. The positions of equilibrium move - and keep on moving if the electrons continue to be transferred.

The two equilibria essentially turn into two one-way reactions:

- The equilibrium with the more negative (or less positive) E° value will move to the left.
- The equilibrium with the more positive (or less negative) E° value will move to the right.

Predicting reactivity trends of metals using electrode potentials

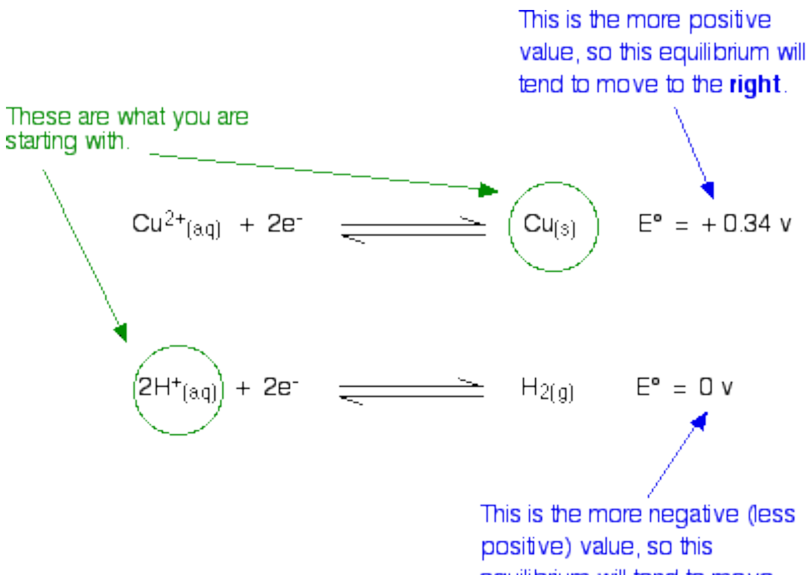
As an example;

Copper is well known not to react with dilute sulphuric acid

Using E®values,

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)} \qquad E^\circ = +0.34\ v$$

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \qquad E^\circ = 0\ v$$



If we start from copper metal, the copper equilibrium is already completely to the right. If it were to react at all, the equilibrium will have to move to the left - directly opposite to what the E° values are saying.

$E^{\ominus}_{cell}$ is directly proportional to the total entropy change and to ln *K* for a reaction.

Limitations of using standard electrode potentials to predict reactions

At times, E° values suggest that a reaction ought to happen, but it doesn't. Occasionally, a reaction happens although the E° values seem to be the wrong way around

All the E° values show is that a reaction **is *possible***. They don't tell you that it will actually happen. There may be very large activation barriers to the reaction which prevent it from taking place. Always treat what E° values tell you with some caution. All they tell you is whether a reaction **is *feasible*** - they tell you nothing about how fast the reaction will happen.

SPONTANEOUS REACTIONS

If two half-cells are connected electrically and a current allowed to flow, the more positive electrode will undergo reduction and the more negative electrode will undergo oxidation. The oxidising agent at the more positive electrode is reduced, and thus oxidises the reducing agent at the more negative electrode.

Eg If the zinc electrode and the copper electrode are connected, the following reaction takes place:
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

It can be assumed that if a reaction occurs electrochemically, it will also occur chemically. Thus if zinc metal is added to a solution of copper (II) sulphate, the above reaction will occur.
If copper metal is added to a solution of zinc (II) sulphate, however, no reaction will occur. If any reaction did occur, it would have to be
$Cu(s) + Zn^{2+}(aq) \rightarrow Cu^{2+}(aq) + Zn(s)$

This reaction is not the one which takes place if the two half-cells are connected, and therefore cannot be expected to take place in other circumstances.

1. Oxidising agents and reducing agents

Since the more positive electrodes are at the bottom of the electrochemical series, the oxidising agents in these systems will oxidise any reducing agent which lies above it in the electrochemical series.

Eg $H^+(aq)$ will oxidise $Pb(s)$ to $Pb^{2+}(aq)$, and any other metal above it, but will not oxidise $Cu(s)$ to $Cu^{2+}(aq)$ or any metal below it.

$Pb(s) + 2H^+(aq) \rightarrow Pb^{2+}(aq) + H_2(g)$

Acids such as nitric acid, however, which contains the more powerful oxidising agent $NO_3^-(aq)$, will oxidise any reducing agent with a standard electrode potential more negative than +0.81V, eg Cu(s)
$Cu(s) + 4H^+(aq) + 2NO_3^-(aq) \rightarrow Cu^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$

Reducing agents will reduce any oxidising agent which lies below it in the electrochemical series.

Eg $Fe^{2+}(aq)$ will reduce $VO_2^+(aq)$ to $VO^{2+}(aq)$, but not $VO^{2+}(aq)$ to $V^{3+}(aq)$ or $V^{3+}(aq)$ to $V^{2+}(aq)$
$VO_2^+(aq) + 2H^+(aq) + Fe^{2+}(aq) \rightarrow VO^{2+}(aq) + H_2O(l) + Fe^{3+}(aq)$

2. Cell potential

A more systematic method of predicting whether or not a reaction will occur is to construct two half-equations, one reduction and one oxidation, for the reaction trying to take place. Since reduction occurs at the more positive electrode, consider the reduction process to be the right-hand electrode and the oxidation process to be the left-hand electrode.
The cell potential for the reaction is given by $E_{RHS} - E_{LHS}$, or $E_{Reduction} - E_{Oxidation}$.
If the cell potential is positive, the reaction will occur.
If the cell potential is negative, the reaction will not occur.
This method can be used to predict whether or not any given redox reaction will take place.

a) Displacement reactions

Eg. Predict whether or not zinc metal will displace iron from a solution of $FeSO_4(aq)$.
The reaction under consideration is $Zn(s) + Fe^{2+}(aq) == Zn^{2+}(aq) + Fe(s)$
Reduction: $Fe^{2+}(aq) + 2e == Fe(s)$ ($E^o = -0.44V$)
Oxidation: $Zn(s) == Zn^{2+}(aq) + 2e$ ($E^o = -0.76V$)
$E_{CELL} = -0.44 -(-0.76) = +0.32V$
So the reaction will occur.

Eg Predict whether or not zinc metal will desplace manganese from a solution of $MnSO_4(aq)$
The reaction under consideration is $Zn(s) + Mn^{2+}(aq) \rightarrow Zn^{2+}(aq) + Mn(s)$
Reduction: $Mn^{2+}(aq) + 2e == Mn(s)$ ($E^o = -1.19V$)
Oxidation: $Zn(s) == Zn^{2+}(aq) + 2e$ ($E^o = -0.76V$)
$E_{CELL} = -1.19 -(0.76) = -0.43V$
So the reaction will not occur.

Eg Predict whether or not bromine will displace iodine from a solution of KI(aq)
The reaction under consideration is $Br_2(aq) + 2I^-(aq) == 2Br^-(aq) + I_2(aq)$
Reduction: $Br_2(aq) + 2e == 2Br^-(aq)$ ($E^o = +1.09V$)
Oxidation: $2I^-(aq) == I_2(aq) + 2e$ ($E^o = +0.54V$)
$E_{CELL} = 1.09 - 0.54 = +0.55V$
So the reaction will occur.

Eg Predict whether or not bromine will displace chlorine from a solution of NaCl(aq)
The reaction under consideration is $Br_2(aq) + 2Cl^-(aq) == 2Br^-(aq) + Cl_2(aq)$
Reduction: $Br_2(aq) + 2e == 2Br^-(aq)$ ($E^o = +1.09V$)
Oxidation: $2Cl^-(aq) == Cl_2(aq) + 2e$ ($E^o = +1.36V$)
$E_{CELL} = 1.09 - 1.36 = -0.27V$
So the reaction will not occur.

b) Disproportionation

Standard electrode potentials can be used to predict whether or not a species will disproportionate.

Eg Predict whether or not Ag^+ ions will disproportionate in aqueous solution.
Ag^+ might be expected to disproportionate according to the following half-reactions:
$Ag^+(aq) + e == Ag(s)$ reduction, $E^o = + 0.80V$
$Ag^+(aq) == Ag^{2+}(aq) + e$ oxidation, $E^o = + 1.98V$
$E_{CELL} = 0.80 - 1.98 = -1.18V$
Therefore Ag^+ will not disproportionate

Eg Predict whether or not H_2O_2 will disproportionate in aqueous solution.
H_2O_2 might be expected to disproportionate according to the following half-reactions:
$H_2O_2(aq) + 2H^+(aq) + 2e == 2H_2O(l)$ reduction, $E^o = +1.77V$
$H_2O_2(aq) == 2H^+(aq) + O_2(g) + 2e$ oxidation, $E^o = +0.68V$
$E_{CELL} = 1.77 - 0.68 = +1.09V$
Therefore $H_2O_2(aq)$ will disproportionate:
$2H_2O_2(aq) + 2H^+(aq) \rightarrow 2H^+(aq) + O_2(g) + 2H_2O(l)$
$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

3. Non-standard conditions

Though cell potential is often a correct prediction of whether or not a given reaction will take place, it does strictly apply only to standard conditions. If the solutions used are either very concentrated or very dilute, then the electrode potentials will not be the standard electrode potentials and the sign of the cell potential may be different from that predicted under standard conditions. Thus many reactions which are not expected to occur do in fact take place if the solutions are hot or concentrated, and many reactions which are expected to occur do not take place if the solutions are too dilute.

Eg The reaction between manganese dioxide and hydrochloric acid.
$MnO_2(s) + 4H^+(aq) + 2Cl^-(aq) \rightarrow Mn^{2+}(aq) + Cl_2(g) + 2H_2O(l)$
Reduction: $MnO_2(s) + 4H^{2+}(aq) + 2e == Mn^{2+}(aq) + 2H_2O(l)$ $E^o = +1.23V$
Oxidation: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e$ $E^o = +1.36V$
$E_{CELL} = E_r - E_o = -0.13V$

This reaction does not occur under standard conditions. However if hot concentrated HCl is used, the high Cl^- concentration favours oxidation, the electrode potential becomes less positive and E_{CELL} thus becomes positive and the reaction occurs.

Eg The reaction between potassium dichromate (VI) and hydrochloric acid.

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Cl^-(aq) \rightarrow 2Cr^{3+}(aq) + 3Cl_2(g) + 7H_2O(l)$

Reduction: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e == 2Cr^{3+}(aq) + 7H_2O(l)$ $E^o = +1.33V$

Oxidation: $2Cl^-(aq) == Cl_2(g) + 2e$ $E^o = +1.36V$

$E_{CELL} = E_r - E_o = -0.03V$

This reaction does not occur under standard conditions. However if solid potassium dichromate is dissolved in hydrochloric acid, the high $Cr_2O_7^{2-}$ concentration favours reduction and makes the electrode potential more positive. Thus E_{CELL} becomes positive and the reaction occurs.

4. Kinetic stability

Cell potentials can be used effectively to predict whether or not a given reaction will take place, but they give no indication as to how **fast** a reaction will proceed. In many cases E_{CELL} is positive but no apparent reaction occurs. This is because the reactants are kinetically stable; the reaction has a high activation energy so is very slow at room temperature. There are many examples of this in inorganic chemistry:

Eg $Mg(s) + 2H_2O(l) \rightarrow Mg^{2+}(aq) + 2OH^-(aq) + H_2(g)$

$E = -0.42V$, $E = -2.38V$ so $E_{CELL} = E_r - E_o = +1.96V$

So a reaction is expected but no reaction takes place.

This is because the activation energy is too high (magnesium will react with steam and slowly with hot water).

Thus if a reaction is expected to take place but is found not to, there are two possible reasons:

- **the solutions are too dilute (ie conditions are non-standard)**
- **the reaction is very slow (ie reactants are kinetically stable)**

If a reaction is not expected to take place but does take place, then it is because the conditions are non-standard (ie the solutions are concentrated).

Rechargeable and non-rechargeable cells

Electrochemical cells are the basis for all batteries. Batteries contain two separate half-cells. The solutions are connected by a salt bridge or semi-permeable membrane which allows ions to flow through without allowing complete mixing of the solutions. The electrodes are connected to the terminals of the battery, and when the battery is connected to an electrical device a current can flow.

If the reactions taking place in the half-cells are reversible, the battery is rechargeable. By connecting the battery to another power supply with a larger emf, electrons and ions are forced around the circuit in the opposite direction. This reverses the spontaneous chemical reaction and hence recharges the battery.

If the reactions taking place in the half-cells are irreversible the battery is non-rechargeable.

Fuel Cells

A fuel cell is a cell in which a chemical reaction between a fuel and oxygen is used to create a voltage. The fuel and oxygen flow into the cell continuously and the products flow out of the cell. Therefore the cell does not need to be recharged.

The most widely used fuel cell is the **hydrogen-oxygen fuel cell**:

A fuel cell, like a regular electrochemical cell, consists of two half-cells connected by a semi-permeable membrane. An aqueous solution of sodium hydroxide is used as the electrolyte.

Oxygen is pumped into one of the half-cells:
$O_2(g) + H_2O(l) + 4e^- = 4OH^-(aq)$ $E^0 = +0.40$ V

Hydrogen is pumped into the other half-cell:
$H_2O(l) + 2e^- == H_2(g) + 2OH^-(aq)$ $E^0 = -0.83$ V

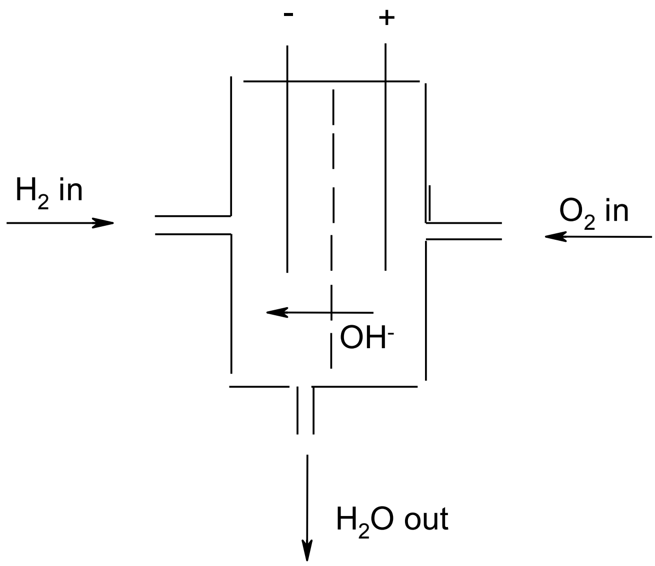
The oxygen half-cell is more positive and therefore undergoes reduction. The hydrogen half-cell is more negative and undergoes oxidation:

$O_2(g) + H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ reduction
$H_2(g) + 2OH^-(aq) \rightarrow H_2O(l) + 2e^-$ oxidation

$O_2(g) + 2H_2(g) \rightarrow 2H_2O(l)$ overall cell reaction, emf = 1.23 V

Hydroxide ions are generated in the oxygen half-cell and travel through the membrane into the hydrogen half-cell, where they are used up.

Water is the product of the reaction and it is allowed to run off.



There are a number of advantages of fuel cells as a way of producing energy:

- The hydrogen-oxygen fuel cell produces water as the only product. It therefore does not produce any of the greenhouse or polluting gases associated with combustion engines. The process of generating hydrogen for use in fuel cells does produce a small quantity of carbon dioxide, but much less than would be generated by a combustion engine.

- Fuel cells are more efficient than combustion engines. Typically fuel cells are approximately 50% efficient but combustion engines are approximately 20% efficient.

However there are also a number of limitations of fuel cells as a way of producing energy:

- Hydrogen is a flammable gas with a low boiling point. It is therefore both difficult and dangerous to store and transport. It can be stored as a liquid under pressure or as a solid adsorbed to the surface of a solid, but both of these techniques are expensive.
- As a result, obtaining hydrogen as a fuel is difficult and this means that people will not buy hydrogen-powered vehicles.
- Fuel cells use toxic chemicals in their manufacture
- Fuel cells have a limited lifetime

Redox Titrations

Oxidising agents in aqueous solution can be determined by titrating against standard solutions of reducing agents. Reducing agents in aqueous solution can be determined by titrating against standard solutions of oxidising agents.

Potassium manganate (VII), $KMnO_4$ is a powerful oxidizing agent:

$$MnO_4^-(aq) + 8H^+(aq) + 5e \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

It can be used to determine the amount of a reducing agent present by titration.

It can therefore be used to determine reducing agents. Common examples of reducing agents which are determined using $KMnO_4$ are $Fe^{2+}(aq)$ and $C_2O_4^{2-}(aq)$

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e$

$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$

$C_2O_4^{2-}(aq) \rightarrow 2CO_2(g) + 2e$

$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$

The most important principles involved in titrations involving $KMnO_4$ are:

i) **The colour change associated with the above reduction is:**

MnO_4^- (intense purple) → Mn^{2+} (colourless)

The colour change is so intense that no indicator is required for the reaction.

ii) **Since the MnO_4^- ion is only an effective oxidising agent in acidic medium, it is necessary to add excess acid to the conical flask before carrying out the titration.**

Sulphuric acid is generally used for this purpose. Hydrochloric acid should not be used since Cl^- is a reducing agent and will react with the MnO_4^- before the MnO_4^- can react with the reducing agent under investigation. Nitric acid should not be used as NO_3^- is an oxidizing agent and will react with the reducing agent before the MnO_4^- can. Ethanoic acid should not be used as it is week acid and does not release enough H^+ ions.

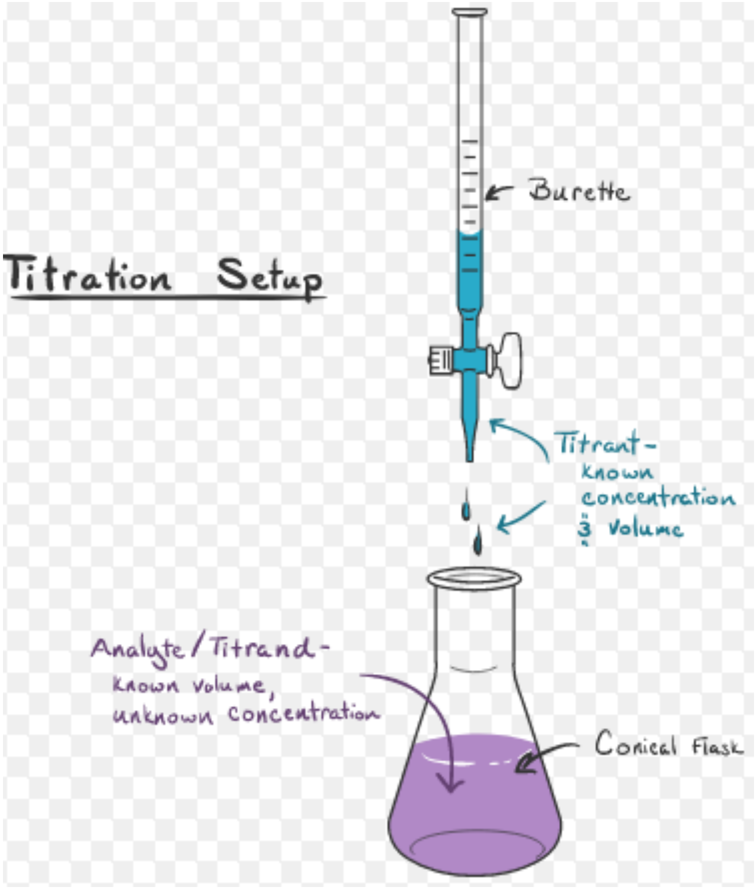
iii) The $KMnO_4$ solution is generally placed in the burette. This causes two problems:

- the intense colour of $KMnO_4$ means that it is very difficult to see the graduation marks on the burette, and so it is difficult to read accurately.
- The $KMnO_4$ reacts slightly with the glass, causing a slight stain if the burette is used too often.

The reason the $KMnO_4$ is placed in the burette is as follows:

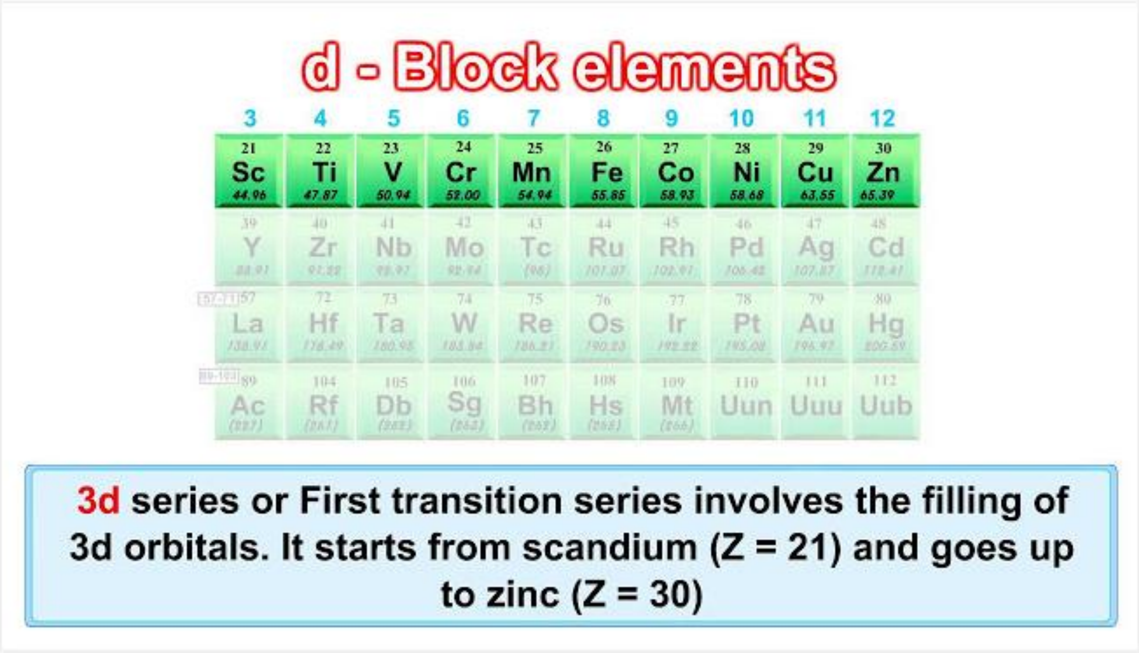
As the $KMnO_4$ is added to the solution under investigation, it is immediately decolorised by the reducing agent. The end-point is detected by the failure of the purple colour to disappear - a pink colour persists in the conical flask, indicating that the MnO_4^- ions are no longer being reduced. This permanent pink colour is easily detected.

If the $KMnO_4$ were in the conical flask, it would slowly decolorise until the solution became completely colourless. The gradual disappearance of the pink colour is much harder to detect than the sudden appearance of the pink colour, and for this reason the $KMnO_4$ is always placed in the burette, despite the difficulties it presents in reading the burette.



5.3 Transition elements

Periodic table D block:



d - Block elements

	3	4	5	6	7	8	9	10	11	12
	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.68	29 Cu 63.55	30 Zn 65.39
	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
57-71	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg
89-103	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub

3d series or First transition series involves the filling of 3d orbitals. It starts from scandium (Z = 21) and goes up to zinc (Z = 30)

Determining the electron configurations of the first row d block elements.

Starting with the atomic numbers of these d block elements, you ought to be able to correctly build up the electron configurations of these elements.

Up to Argon Z=18, all the metals have the same electron configuration. Things only get tricky beyond that number. For example, iron Z= 26 so as the 4s fills before the 3d that leaves 6 electrons in the 3d and an electron configuration of :

Fe: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$

But look at Chromium Z=24 how do the six electrons fill the 3d and 4s?

Half filled subshells confer an added degree of energetic stability to the atom so chromium has $3d^5\ 4s^1$

Cr: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

By a similar consideration the electron configuration of copper Cu Z= 29 the extra 11 electrons fill the 3d and 4s, one in the 4s and the rest (10) in the 3d to confer the greatest energetic stability.

Cu: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

Recall that the 4s fills before the 3d and that the electrons above the 18 fill the subshells to confer the greatest energetic stability by half filling or filling subshells.

Electron configurations of the first row d block elements.

		3*d*	4*s*
Ca	[Ar]$4s^2$	[ ][ ][ ][ ][ ]	[↑↓]
Sc	[Ar]$3d^1 4s^2$	[↑][ ][ ][ ][ ]	[↑↓]
Ti	[Ar]$3d^2 4s^2$	[↑][↑][ ][ ][ ]	[↑↓]
V	[Ar]$3d^3 4s^2$	[↑][↑][↑][ ][ ]	[↑↓]
Cr*	[Ar]$3d^5 4s^1$	[↑][↑][↑][↑][↑]	[↑]
Mn	[Ar]$3d^5 4s^2$	[↑][↑][↑][↑][↑]	[↑↓]
Fe	[Ar]$3d^6 4s^2$	[↑↓][↑][↑][↑][↑]	[↑↓]
Co	[Ar]$3d^7 4s^2$	[↑↓][↑↓][↑][↑][↑]	[↑↓]
Ni	[Ar]$3d^8 4s^2$	[↑↓][↑↓][↑↓][↑][↑]	[↑↓]
Cu*	[Ar]$3d^{10} 4s^1$	[↑↓][↑↓][↑↓][↑↓][↑↓]	[↑]
Zn	[Ar]$3d^{10} 4s^2$	[↑↓][↑↓][↑↓][↑↓][↑↓]	[↑↓]

Transition elements are mostly those elements or their ions with incomplete outer d subshell.

Transition metals and variable oxidation states.

What is oxidation state?

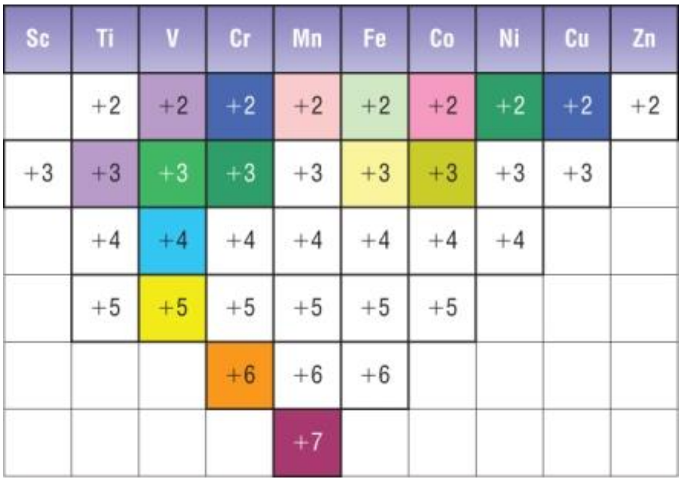
Oxidation state is the oxidation number a particular species carries.

So the sodium ion Na^+ has oxidation number +1 and sodium is in oxidation state +1.

Or the chloride ion $Cl^—$ has oxidation number —1 and chlorine is in oxidation state —1.

Transition metals show variable oxidation states unlike group 1 or Group 17 elements.

The illustration below shows these oxidation states some of which of more stable (shown in colour) at room temperature than others

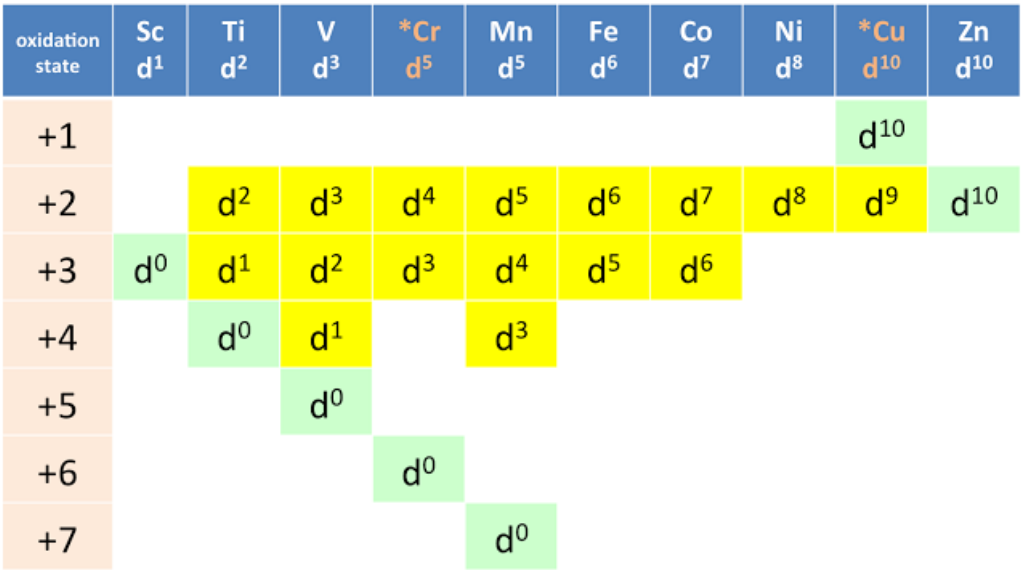


Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+4	+4	+4	+4	+4	+4	+4		
	+5	+5	+5	+5	+5	+5			
			+6	+6	+6				
				+7					

Variable Oxidation States

These metals exhibit variable oxidation states due to the fact that the 4s energy level and the 3d energy level are very close in value so that the metals can bond to other elements using electrons from both the 4s and the 3d levels.

Below are the 3d and 4s electron arrangements for the stable oxidation states of these metals



oxidation state	Sc d^{1}	Ti d^{2}	V d^{3}	*Cr d^{5}	Mn d^{5}	Fe d^{6}	Co d^{7}	Ni d^{8}	*Cu d^{10}	Zn d^{10}
+1									d^{10}	
+2		d^{2}	d^{3}	d^{4}	d^{5}	d^{6}	d^{7}	d^{8}	d^{9}	d^{10}
+3	d^{0}	d^{1}	d^{2}	d^{3}	d^{4}	d^{5}	d^{6}			
+4		d^{0}	d^{1}		d^{3}					
+5			d^{0}							
+6				d^{0}						
+7					d^{0}					

Higher oxidation states of the transition metals are stabilised as oxo anions i.e the metal ion is combined with oxide ions. For example:

Orange Dichromate (VI)	$Cr_2O_7^{2-}$
Yellow Chromate (VI)	CrO_4^{2-}
Black Manganese (IV)oxide	MnO_2
Yellow Metavanadate (V)	VO_3^{-}
Purple Manganate(VII)	MnO_4^{-}
Green Manganate(VI)	MnO_4^{2-}

COMPLEX IONS

A complex ion is an ion comprising one or more ligands attached to a central metal cation by means of a dative covalent bond.

A ligand is a species which can use its lone pair of electrons to form a dative covalent bond with a transition metal. Examples of ligands are H_2O, NH_3, Cl^-, OH^-, CN^-, Cations which form complex ions must have two features:

- they must have a high charge density, and thus be able to attract electrons from ligands.
- they must have empty orbitals of low energy, so that they can accept the lone pair of electrons from the ligands.

Cations of d-block metals are small, have a high charge and have available empty 3d and 4s orbitals of low energy. They thus form complex ions readily.

The number of lone pairs of electrons which a cation can accept is known as the coordination number of the cation. It depends on the size and electronic configuration of that cation, and also on the size and charge of the ligand. 6 is the most common coordination number, although 4 and 2 are also known.

Examples of complex ions are $[Fe(H_2O)_6]^{2+}$, $[CoCl_4]^{2-}$, $[Cu(NH_3)_4(H_2O)_2]^{2+}$. Note that the formula of the ion is always written inside square brackets with the overall charge written outside the brackets.

Some ligands are capable of forming more than one dative covalent bond per ligand. These are known as **multidentate** ligands. Examples are ethanedioate ($C_2O_4^{2-}$) and 1,2-diaminoethane ($H_2NCH_2CH_2NH_2$), both of which donate 2 lone pairs per ligand and are said to be **bidentate**. One unusual ligand, known as edta^{4-}, can form 6 dative covalent bonds per ligand. It is thus said to be **hexadentate.** Ligands such as H_2O, Cl^- and CN^- form only one dative covalent bond per ligand and are said to be **monodentate.**

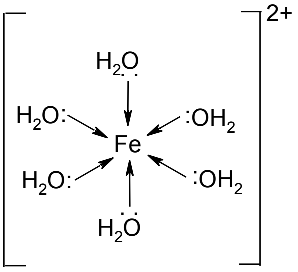
With polydentate ligands it often appears that the coordination number of the complex is 1 or 3, when in fact the coordination number is 6 as normal - it is just that each ligand is bonded twice. Some examples of complex ions are:

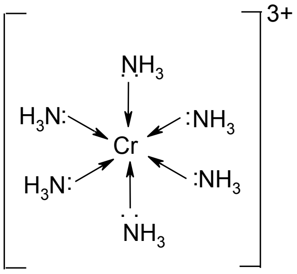
$[Fe(C_2O_4)_3]^{3-}$ **$[Cr(H_2NCH_2CH_2NH_2)_3]^{3+}$** **$[Cu(edta)]^{2-}$**

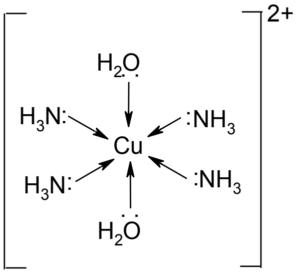
Shapes

6-coordinate complexes are all octahedral, and are formed with **small ligands such as H_2O and NH_3**. They can thus be drawn as follows:

$[Fe(H_2O)_6]^{2+}$ $[Cr(NH_3)_6]^{3+}$ $[Cu(NH_3)_4(H_2O)_2]^{2+}$

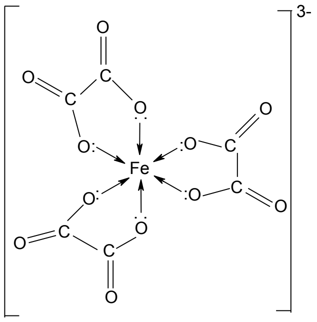


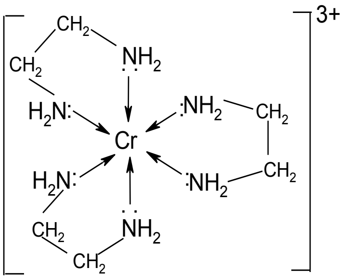


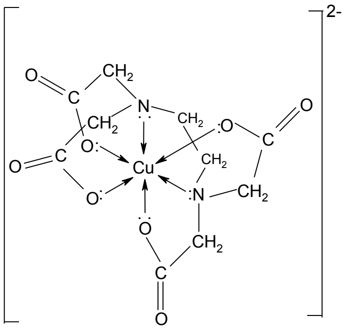


Most complexes involving multidentate ligands are octahedral:

$[Fe(C_2O_4)_3]^{3-}$ **$[Cr(H_2NCH_2CH_2NH_2)_3]^{3+}$** **$[Cu(edta)]^{2-}$**

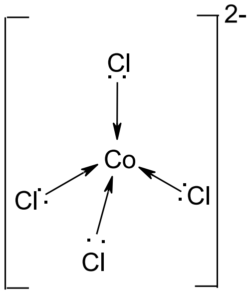






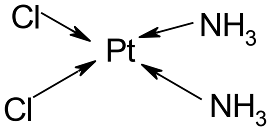
4-coordinate complexes are generally tetrahedral, and are formed with **larger ligands such as Cl^-**. Larger ligands cannot fit around the transition metal so easily and hence form smaller complexes. They can be drawn as follows:

$[CoCl_4]^{2-}$



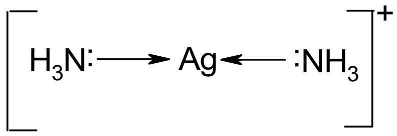
Some 4-coordinated complexes however, especially if they involve Pt, are square planar:

$Pt(NH_3)_2Cl_2$



2-coordinate complexes are in general linear, and are formed with **Ag^+ ions**. They can be drawn as follows:

$[Ag(NH_3)_2]^+$



The rules covering the likely coordination number of transition metal complexes are:

a) Silver ions form linear complexes with a coordination number of 2;

b) Platinum ions form square planar complexes with a coordination number of 4

c) Chloride ions and other large ions form tetrahedral complexes with a coordination number of 4;

d) Most other transition metal complexes are octahedral with a coordination number of 6.

Representation

When metal ions are in solution, they are usually represented as the simple ion, such as Fe^{2+}(aq), Co^{2+}(aq), Cr^{3+}(aq) or Fe^{2+}(aq).

This is, however, a simplified representation as all d-block cations and many other cations with high polarising power exist as the hexaaqua complex, eg $[Fe(H_2O)_6]^{2+}$.

Eg $FeSO_4$(aq) consists of $[Fe(H_2O)_6]^{2+}$ and SO_4^{2-} ions

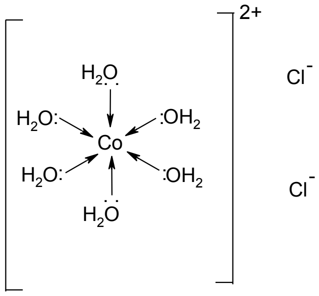
Eg $Fe_2(SO_4)_3$(aq) consists of $[Fe(H_2O)_6]^{3+}$ and SO_4^{2-} ions

Eg $CuCl_2$(aq) consists of $[Cu(H_2O)_6]^{2+}$ and Cl^- ions

Many complex ions exist in the solid state. In these cases the ligands are often written after the rest of the compound, separated by a dot:

Eg $[Co(H_2O)_6]Cl_2$(s) is often represented as $CoCl_2.6H_2O$

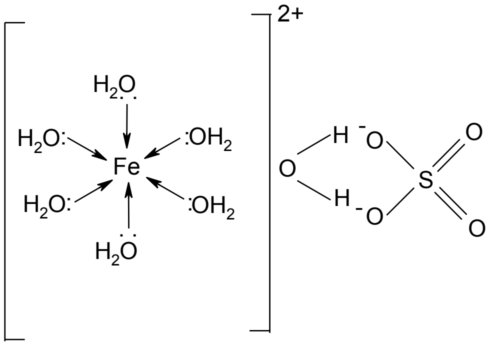
The six water molecules are behaving as ligands:



The dot does not always, however, mean that there are ligands present; some salts contain water of crystallisation, where the water is not a ligand but a link between the ions.

Eg in $Na_2CO_3.10H_2O$, the water molecules are not behaving as ligands, but as water molecules of crystallisation.

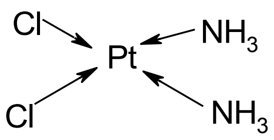
Eg in $FeSO_4.7H_2O$, six of the water molecules are behaving as ligands, and the seventh is a water of crystallisation. It helps link the cation to the anion:

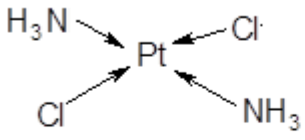


Isomerism

a) Square planar complexes

Square planar complexes in which the ligands are not all identical can display a form of E-Z isomerism (isomers different due to restricted rotation) known as cis-trans isomerism. The most common example of this is in complexes which contain two each of two different types of ligand – for example $Pt(NH_3)_2Cl_2$. The identical ligands can either be adjacent to each other or opposite each other:



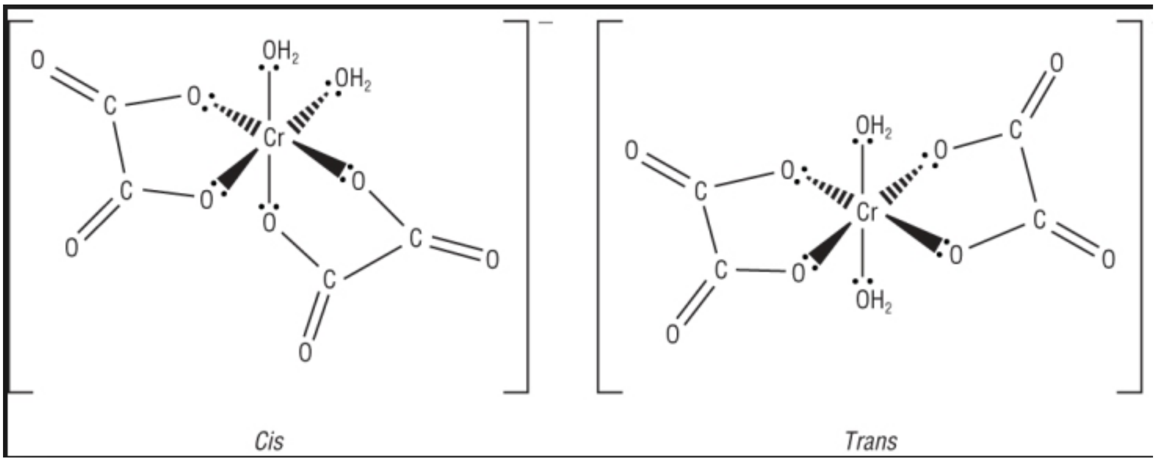


Identical ligands adjacent to each other	Identical ligands opposite each other
Z or cis isomer	E or trans isomer
This molecule is known as cisplatin	This molecule is known as transplatin
It is an anti-cancer drug	It is not an anti-cancer drug

b) Octahedral complexes

i) Cis-trans isomerism

Octahedral complexes also show cis-trans isomerism when they contain four ligands (or two bidentate ligands) of one type and two ligands of another type – for example $[Cr(Cl_2)(H_2O)_4]^+$ or $[Cr(C_2O_4)(H_2O)_2]^+$. The two minority ligands can either be adjacent to each other or opposite each other:

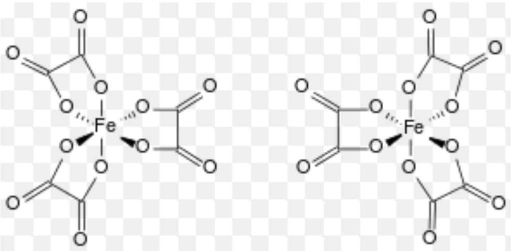


Cis Trans

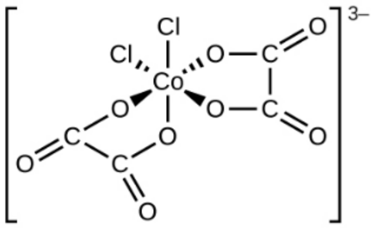
Optical isomerism

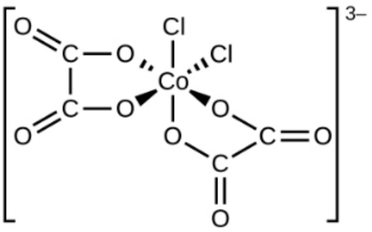
Octahedral complexes can display optical isomerism (non-superimposable mirror images) when they contain one of the following combinations:

- Three bidentate ligands, eg $[Fe(C_2O_4)_3]^{3-}$
- Two bidentate ligands and two monodentate ligands (cis isomer only), eg $[Co(C_2O_4)_2Cl_2]^{3-}$
- One hexadentate ligand, eg $[Co(edta)]^{2-}$



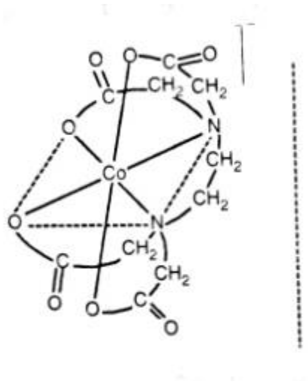
Isomer 1 Isomer 2 $[Fe(C_2O_4)_3]^{3-}$

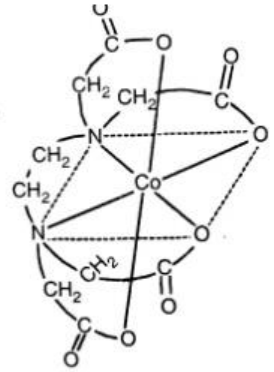




[Co(C$_2$O$_4$)$_2$Cl$_2$]$^{3-}$

Isomer 1 Isomer 2





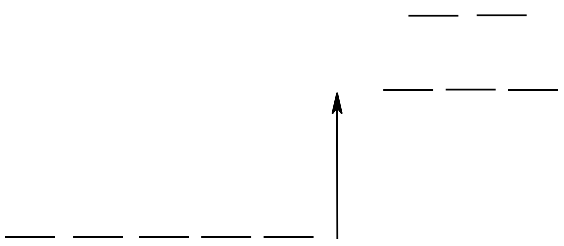
[Co(edta)]$^{2-}$

Isomer 1 Isomer 2

Colour

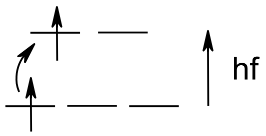
a) Explanation

When a cation forms a complex ion, the incoming ligands repel the electrons in the atom, and thus they are raised in energy. Some of the d-orbitals, however, are repelled more than others and the result is that the d-orbitals are split into 2 groups of orbitals, with three orbitals being slightly lower in energy than the other two:



The difference in energy between these groups of orbitals is similar to the energy of visible light. The energy of the light is related to the frequency of the light by the equation E = hf.

If these d-orbitals are partially filled, some of the electrons in the lower energy orbitals are excited into the higher energy orbitals, and in doing so absorb the light that corresponds to that frequency. The resultant light is deficient in the light of that frequency and thus appears coloured.



Transition metal ions are coloured because d-electrons can absorb light and get excited into higher energy d-orbitals. The resultant light is thus missing certain frequencies and is hence coloured.

Note that two criteria must be satisfied if the ion is to be coloured:

- there must be a splitting of the d-orbitals. This only happens in the presence of ligands and thus only complex ions are coloured. Anhydrous ions do not have split d-orbitals and so cannot aborb light in the visible spectrum and are thus white.

Eg anydrous $CuSO_4$ (d^9) is white but hydrated $CuSO_4.5H_2O$ is blue.

- the d-orbitals must be partially filled. If the d-orbitals are empty (Eg Sc^{3+}, Al^{3+}) then there are no electrons which can be excited into the higher energy d-orbitals and the ions will be colourless. If the d-orbitals are full (Eg Cu^+, Zn^{2+}) then there are no empty orbitals into which the electrons can be excited and the ions will be colourless.

b) Application

The colour of a complex ion depends on:

- the ligand
- the coordination number
- the oxidation state of the metal
- the identity of the metal

As transition metal ions can show a huge variety of colours, it is often possible to identify a complex ion simply by its colour.

It is also possible to determine the concentration of a solution containing a coloured ion using a technique called **ultraviolet and visible spectrophotometry.** As the absorbance of a solution is proportional to its concentration, the concentration of any solution can be determined by comparing its absorbance to the absorbance of a solution of known concentration.

The technique can be summarised as follows:

i) A solution containing a known concentration of the ion is prepared, and a suitable ligand is added in excess in order to intensify the colour (thiocyanate ions, SCN^-, are often used for this purpose).

ii) A sample of the solution is placed into a cuvette in a colorimeter and the filter which gives the maximum absorbance is selected.

iii) The absorbance of the solution is recorded.

iv) This process is repeated using a range of other known concentrations, and a graph is plotted of absorbance against concentration.

v) The solution of unknown concentration is mixed with an excess of the same ligand to intensify the colour.

vi) The absorbance of the solution of unknown concentration is then recorded using the same filter.

vii) The concentration of this solution can then be determined from the concentration-absorbance graph.

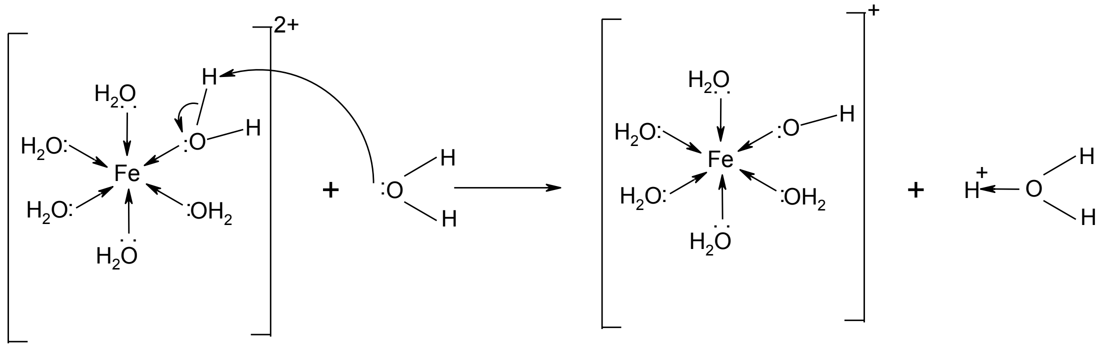
Chemical Reactions

Most metal cations exist as the hexaaqua complex in solution. Main group metals form colourless ions but most transition metal ions are coloured.

$[Fe(H_2O)_6]^{2+}$	$[Co(H_2O)_6]^{2+}$	$[Cu(H_2O)_6]^{2+}$	$[Al(H_2O)_6]^{3+}$	$[Fe(H_2O)_6]^{3+}$
pale green	**pink**	**pale blue**	**colourless**	**yellow**

a) Acid-base reactions

If the charge density of the cation is particularly high, the electron density in the aqua ligand moves even closer to the cation and the bonds in the water are weakened. In such cases the hydrogen in the water ligand can be lost as a proton.



Eg $[Fe(H_2O)_6]^{2+}$ == $[Fe(H_2O)_5OH]^+ + H^+$

This process is known as **deprotonation**.

Deprotonation is the loss of a proton by a water ligand to form a hydroxo ligand.

Deprotonation is caused by the high charge density on the central cation, which weakens the O-H bonds in the water ligands, and enables the H^+ (the proton) to leave.

The proton which is lost is given to a base. This can be water, hydroxide ions or ammonia. The extent to which deprotonation takes place depends on the strength of the base.

i) Deprotonation by water

Water is a weak base. The hexaaqua complex will therefore behave as a weak acid and will partially dissociate:

Eg $[Fe(H_2O)_6]^{2+}(aq) + H_2O(l)$ == $[Fe(H_2O)_5(OH)]^+(aq) + H_3O^+(aq)$

Eg $[Fe(H_2O)_6]^{3+}(aq) + H_2O(l)$ == $[Fe(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$

Eg $[Al(H_2O)_6]^{3+}(aq) + H_2O(l)$ == $[Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$

Eg $[Cu(H_2O)_6]^{2+}(aq) + H_2O(l)$ == $[Cu(H_2O)_5(OH)]^+(aq) + H_3O^+(aq)$

Aqueous solutions of transition metal ions are thus acidic.

The greater the charge density on the central cation, the greater the extent of deprotonation and the more acidic the solution. For example, solutions of iron (III) salts are more acidic than solutions of iron (II) salts.

ii) Deprotonation by hydroxide ions

The hydroxide ion is a strong base. It will pull protons away from water ligands more than water molecules, and more than one deprotonation will take place.

In all cases, the hydrated hydroxide will be formed:

Eg $[Fe(H_2O)_6]^{2+}(aq) + 2OH^-(aq) == [Fe(H_2O)_4(OH)_2](s) + 2H_2O(l)$

Iron (II) hydroxide

Eg $[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) == [Cu(H_2O)_4(OH)_2](s) + 2H_2O(l)$

Copper (II) hydroxide

Eg $[Al(H_2O)_6]^{3+}(aq) + 3OH^-(aq) == [Al(H_2O)_3(OH)_3](s) + 3H_2O(l)$

aluminium (III) hydroxide

Eg $[Fe(H_2O)_6]^{3+}(aq) + 3OH^-(aq) == [Fe(H_2O)_3(OH)_3](s) + 3H_2O(l)$

Iron (III) hydroxide

The hydroxides are all insoluble. Thus a precipitate is formed when sodium or potassium hydroxide solution is added to any solution containing transition metal cations.

$Fe(OH)_2$	$Cu(OH)_2$	$Al(OH)_3$	$Fe(OH)_3$
Green	**pale blue**	**white**	**brown**

In some cases (eg Al^{3+}), the hydroxide ions can remove even more protons, and hydroxoanions are formed:

Eg $[Al(H_2O)_3(OH)_3](s) + 3OH^-(aq) == [Al(OH)_6]^{3-}(aq) + 3H_2O(l)$

White precipitate colourless solution

$Al(OH)_6^{3-}$
Colourless

The precipitate is found to dissolve in excess alkali to give a solution.

Reaction of hydroxides with acid

The precipitates can all be converted back to the hexaaqua complex by the addition of acid:

Eg $[Fe(H_2O)_4(OH)_2](s) + 2H_3O^+(aq) == [Fe(H_2O)_6]^{2+}(aq) + 2H_2O(l)$

Eg $[Al(H_2O)_3(OH)_3](s) + 3H_3O^+(aq) == [Al(H_2O)_6]^{3+}(aq) + 3H_2O(l)$

Metal hydroxides such as $Fe(OH)_2(H_2O)_4$, $Fe(OH)_3(H_2O)_3$ and $Cu(OH)_2(H_2O)_4$, which dissolve in acid but not in excess alkali, are said to be **basic**.

Metal hydroxides such as $Al(OH)_3(H_2O)_3$, which dissolve in acid but and in excess alkali, are said to be **amphoteric**.

Deprotonation by ammonia

Ammonia is also a stronger base than water, so can also cause deprotonation of the hexaaqua complex and form the hydroxide precipitate:

Eg $[Fe(H_2O)_6]^{2+}(aq) + 2NH_3(aq) == [Fe(H_2O)_4(OH)_2](s) + 2NH_4^+(aq)$

Iron (II) hydroxide

Eg $[Cu(H_2O)_6]^{2+}(aq) + 2NH_3(aq) == [Cu(H_2O)_4(OH)_2](s) + 2NH_4^+(aq)$

Copper (II) hydroxide

Eg $[Cr(H_2O)_6]^{3+}(aq) + 3NH_3(aq) == [Al(H_2O)_3(OH)_3](s) + 3NH_4^+(aq)$

Aluminium (III) hydroxide

Eg $[Fe(H_2O)_6]^{3+}(aq) + 3NH_3(aq) == [Fe(H_2O)_3(OH)_3](s) + 3NH_4^+(aq)$

Iron (III) hydroxide

The ammonia is not a sufficiently strong base to cause further deprotonation, so the hydroxoanions are not formed with excess ammonia.

Deprotonation by carbonate ions

Carbonate ions are bases and can deprotonate the +3 ions to form the hydroxide precipate. The carbonate ions are converted into carbon dioxide gas.

$2[Fe(H_2O)_6]^{3+}(aq) + 3CO_3^{2-}(aq) \rightarrow 2[Fe(H_2O)_3(OH)_3](s) + 3CO_2(g) + 3H_2O(l)$

$2[Al(H_2O)_6]^{3+}(aq) + 3CO_3^{2-}(aq) \rightarrow 2[Al(H_2O)_3(OH)_3](s) + 3CO_2(g) + 3H_2O(l)$

The +2 ions, however do not deprotonate so readily and do not behave as acids in the presence of carbonate ions. Instead they form a precipitate directly with the carbonate ion. No carbon dioxide is evolved.

$[Fe(H_2O)_6]^{2+}(aq) + CO_3^{2-}(aq) \rightarrow FeCO_3(s) + 6H_2O(l)$

$[Co(H_2O)_6]^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CoCO_3(s) + 6H_2O(l)$

$[Cu(H_2O)_6]^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CuCO_3(s) + 6H_2O(l)$

$FeCO_3$	$CuCO_3$
green	**green-blue**

b) Ligand exchange reactions

Ligand exchange is the replacement of one ligand by another in a complex.

Many ligands are capable of replacing water in transition metal complexes, but only two will be considered:

i) ligand exchange by ammonia

With hexaaqua complexes, ammonia acts as a base and facilitates deprotonation. Excess ammonia, however, will undergo ligand exchange with some hydroxides, replacing aqua and hydroxo ligands with ammine ligands.

With $Co(H_2O)_4(OH)_2$ the substitution is complete:

$[Co(H_2O)_6]^{2+}(aq) + 2NH_3(aq) == [Co(OH)_2(H_2O)_4](s) + 2NH_4^+(aq)$

Pink solution → blue precipitate

$[Co(H_2O)_4(OH)_2](s) + 6NH_3(aq) == [Co(NH_3)_6]^{2+}(aq) + 4H_2O(l) + 2OH^-(aq)$

blue precipate → straw-coloured solution

With $Cu(H_2O)_4(OH)_2$ the substitution is incomplete:

$[Cu(H_2O)_6]^{2+}(aq) + 2NH_3(aq) == [Cu(H_2O)_4(OH)_2](s) + 2NH_4^+(aq)$

pale blue solution → pale blue precipitate

$[Cu(H_2O)_4(OH)_2](s) + 4NH_3(aq) == [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 2H_2O(l) + 2OH^-(aq)$

pale blue precipitate → dark blue solution

The hydroxides of iron (II), iron (III) and aluminium do not dissolve in aqueous ammonia.

On slow addition of ammonia to a solution containing aqua complexes of Co^{2+} and Cu^{2+}, a precipitate is formed of the hydroxide, which redissolves in excess ammonia to give a solution again.

$Co(NH_3)_6{}^{2+}$	$Cu(NH_3)_4(H_2O)_2{}^{2+}$
Straw	Dark blue

Note than when ammonia replaces water as ligands, the coordination number does not change. This is because water and ammonia are small ligands with no charge, so they don't get in each other's way or repel each other too much. Therefore both form octahedral complexes.

ii) ligand exchange by chloride ions

In the presence of concentrated hydrochloric acid, the chloride ions can replace the water ligands in some complex ions and form an anionic complex:

$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) == [CuCl_4]^{2-}(aq) + 6H_2O(l)$

pale blue solution → yellow solution

$[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) == [CoCl_4]^{2-}(aq) + 6H_2O(l)$

pink solution → blue solution

$[Fe(H_2O)_6]^{3+}(aq) + 4Cl^-(aq) == [FeCl_4]^-(aq) + 6H_2O(l)$

orange solution → yellow solution

Note than when chloride ions replace water ligands, the coordination number decreases from 6 to 4. This is because chloride ions are large and negatively charged, so they repel each other more are cannot pack so closely together.

These reactions are favoured because they cause an increase in entropy. There are 5 species on the left hand side of the equation and 7 species on the right. The entropy of the system thus increases.

This is counterbalanced, however, by the fact that more coordinate bonds (6) are broken than are formed (4), and that chloride ligands do not form very strong coordinate bonds. The reaction is thus endothermic.

These reactions are generally readily reversible, and addition of water to the solution will cause the chloride ligands to be replaced by aqua ligands. This reaction is used in the test for water; blue cobalt chloride paper turns pink in the presence of water.

$[CoCl_4]^{2-}(aq) + 6H_2O(l) == [Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq)$

blue pink

$CoCl_4^{2-}$	$CuCl_4^{2-}$	$FeCl_4^-$
Blue	**yellow**	**yellow**

Ligand exchange by multidentate ligands

multidentate ligands such as $H_2NCH_2CH_2NH_2$, $C_2O_4^{2-}$ and edta^{4-} readily replace water ligands in complex ions. The resulting complex ions always remain six coordinate:

$[Fe(H_2O)_6]^{3+}(aq) + 3NH_2CH_2CH_2NH_2(aq) == [Fe(H_2NCH_2CH_2NH_2)_3]^{3+}(aq) + 6H_2O(l)$

$[Cr(H_2O)_6]^{3+}(aq) + 3C_2O_4^{2-}(aq) == [Cr(C_2O_4^{2-})_3]^{3-}(aq) + 6H_2O(l)$

$[Cu(H_2O)_6]^{2+}(aq) + edta^{4-}(aq) == [Cu(edta)]^{2-}(aq) + 6H_2O(l)$

These reactions are favoured because they cause an increase in entropy. There are always less species on the left hand side of the equation than on the right. The entropy of the system thus increases, and multidentate complexes are therefore more stable than complexes involving monodentate ligands. This is known as **the chelate effect.**

The entropy increase is not counterbalanced by a decrease in coordination number as the coordination number is still 6.

Ligand exchange in heamoglobin

Another important complex ion involving multidentate ligands is **haemoglobin**.

Haem is a complex ion consisting Fe^{2+} and a complex tetradentate ligand called porphyrin. The complex is generally found with a protein called globin, which provides the fifth coordinate bond, and a molecule of oxygen which forms the sixth bond. The complete six coordinate complex is called haemoglobin. This structure is responsible for carrying oxygen in the blood throughout the human body.

Fe^{2+} + porphyrin → haem

haem + globin + O_2 → haemoglobin

Carbon monoxide is a similar size and shape to oxygen and forms a much stronger bond with the iron. It thus diplaces the oxygen from the complex and reduces the blood's ability to carry oxygen. It is thus a very poisonous gas.

Summary of chemical reactions of complex ions

Many of these reactions are characterised by clear colour changes. A summary of the colour changes occurring is in the table below:

Ion	With NH_3 or NaOH, not in excess	With excess NaOH	With excess NH_3	With conc. HCl	With Na_2CO_3
$[Fe(H_2O)_6]^{2+}$ pale green soln	dark green ppt	insoluble	insoluble	-	green ppt (carbonate)
$[Al(H_2O)_6]^{3+}$ colourless soln	white ppt	colourless solution	insoluble	-	white ppt (hydroxide)
$[Fe(H_2O)_6]^{3+}$ orange soln	brown ppt	insoluble	insoluble	yellow solution	brown ppt (hydroxide)
$[Co(H_2O)_6]^{2+}$ pink soln	-	-	straw solution	blue soln	-
$[Cu(H_2O)_6]^{2+}$ blue soln	pale blue ppt	insoluble	deep blue solution	yellow soln	green/blue ppt (carbonate)

These colour changes for the basis of simple tests for transition metal ions.

REDOX CHEMISTRY OF TRANSITION METALS

Since transition metals show a variety of transition states in their compounds, much of their chemistry is dominated by movement between these transition states.

When the oxidation state changes, the colour changes as the electron distribution in the d-orbitals is different. The colour is also affected by the ligands involved, as the type of ligand affects the amount of splitting in the d-orbitals.

1. Redox Reactions of Individual Elements

a) Iron

Iron exists in two common oxidation states, +2 (Fe^{2+}) and +3 (Fe^{3+}).

In aqueous solution, the Fe is readily oxidised from Fe^{2+} to Fe^{3+}:

$$\mathbf{Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e}$$

The Fe^{2+} ion is thus a reducing agent and the Fe^{3+} ion is an oxidising agent. Concentrations of Fe^{2+} in solution can be determined by titration with oxidising agents.

b) Manganese

Manganese can exist in a number of oxidation states, but is most stable in an oxidation state of +2, +4 or +7

In the +7 oxidation state it exists as the intense purple ion MnO_4^-. This can be reduced to the pale pink Mn^{2+} in acidic solution:

$$\mathbf{MnO_4^-(aq) + 8H^-(aq) + 5e \rightarrow Mn^{2+}(aq) + 4H_2O(l)}$$

c) Vanadium

Vanadium forms stable compounds in 4 different oxidation states, +2, +3, +4 and +5.

In aqueous solution, the ions formed are:

Oxidation state	+5	+4	+3	+2
Colour	**Yellow**	**Blue**	**green**	**Violet**
Ion	**VO_2^+**	**VO^{2+}**	**V^{3+}**	**V^{2+}**

All vanadium (V) compounds can be reduced to the +4, +3 and then +2 oxidation state by strong reducing agents such as zinc in acid solution:

$VO_2^+(aq) + 4H^+(aq) + 3e \rightarrow V^{2+}(aq) + 2H_2O(l)$

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e$

Overall: $2VO_2^+(aq) + 8H^+(aq) + 3Zn(s) \rightarrow 2V^{2+}(aq) + 3Zn^{2+}(aq) + 4H_2O(l)$

Yellow violet

The reaction proceeds via the +4 and +3 oxidation states, so the colour change observed is **yellow(VO_2^+) → green (VO_2^+ and VO^{2+}) → blue (VO^{2+}) → green (V^{3+}) → violet (V^{2+}).**

d) Silver

Diamine silver (I) has the formula $[Ag(NH_3)_2]^+$ and is the active ion in **Tollen's reagent**.

It is reduced to silver by reducing sugars and aldehydes (but not ketones). It produces a characteristic silver mirror on the side of the test-tube and this is used as the basis of the test for aldehydes. The silver (I) ion is reduced to silver and the aldehyde is oxidized to a carboxylic acid:

$[Ag(NH_3)_2]^+ + e^- \rightarrow Ag + 2NH_3$ (x2)

$R\text{-}CHO + H_2O \rightarrow RCOOH + 2H^+ + 2e^-$

$2[Ag(NH_3)_2]^+ + R\text{-}CHO + H_2O \rightarrow Ag + 2NH_3 + R\text{-}COOH + 2H^+$

Factors affecting the ease of oxidation and reduction of transition metals

i) pH

The relative tendency of a transiton metal ion to undergo oxidation and reduction often depends dramatically on the pH of the solution. In general, oxidation is favoured by alkaline conditions and reduction is favoured by acidic conditions:

$Fe^{3+} + e^- == Fe^{2+}$ +0.77 V (more +ve, reduction favoured)

$Fe(OH)_3 + e == Fe(OH)_2 + OH^-$ -0.56 V (more -ve, oxidation favoured)

The dichromate(VI) ion, $Cr_2O_7^{2-}$,
i **can be reduced to Cr3+ and Cr2+ ions using zinc in acidic conditions**
$Cr_2O_7^{2-} + 14H^+ + 6e^- == 2Cr^{3+} + 7H_2O$ +1.33 V (more +ve, reduction favoured)

ii can be produced by the oxidation of Cr3+ ions using hydrogen peroxide in alkaline conditions (followed by acidification)

$CrO_4^{2-} + 4H_2O + 3e^- == Cr(OH)_3 + 5OH^-$ -0.13 V (more -ve, oxidation favoured)

iii can be converted into chromate(VI) ions as a result of the equilibrium

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

ii) choice of ligand

The relative tendency of a transition metal ion to undergo oxidation and reduction also depends on the ligand surrounding the metal ion:

$Co(H_2O)_6^{3+} + e^- == Co(H_2O)_6^{2+}$ +1.81 V (more +ve, reduction favoured)

$Co(NH_3)_6^{3+}(aq) + e == Co(NH_3)_6^{2+}$ +0.10 V (more -ve, oxidation favoured)

$Fe(H_2O)_6^{3+} + e^- == Fe(H_2O)_6^{2+}$ +0.77 V (more +ve, reduction favoured)

$Fe(CN)_6^{4-}(aq) + e == Fe(CN)_6^{3-}$ +0.36 V (more -ve, oxidation favoured)

Transition metals as catalysts

The ability of transition metals to form more than one stable oxidation state means that they can accept and lose electrons easily. This enables them to catalyse certain redox reactions. They can be readily oxidised and reduced again, or reduced and then oxidised again, as a consequence of having a number of different oxidation states of similar stability.

They can behave either as homogeneous catalysts or as heterogeneous catalysts.

a) Homogeneous catalysis

A homogeneous catalyst is a catalyst in the same phase as the reactants.

Homogeneous catalysis involves aqueous transition metal ions catalysing reactions, often between two anions. The cation reacts with each anion in turn, thus avoiding the need for a direct collision between two anions (this is difficult since they repel each other).

Eg 1 $S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$

This can be catalysed by Fe^{2+} or Fe^{3+} ions:

With Fe^{2+}: $S_2O_8^{2-}(aq) + 2Fe^{2+}(aq) \rightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$

$2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

With Fe^{3+}: $2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

$2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$

Eg 2 $2MnO_4^{-}(aq) + 5C_2O_4^{2-}(aq) + 16H^{+}(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$

This is a good example of **auto-catalysis**.

One of the products in this reaction, $Mn^{2+}(aq)$, behaves as a catalyst **and thus the reaction is slow at first but is much faster after a little of the products are formed**.

b) Heterogeneous catalysis

A heterogeneous catalyst is a catalyst in a different phase from the reactants. In most cases, the catalyst is a solid and the reactants are liquids or gases.

The reaction occurs at active sites on the catalyst surface. The catalyst therefore needs to have a large surface area to be effective, which in turn means it needs to be very thinly spread out in order to reduce its cost, and might need a special support. Catalytic converters in cars, for example, use rhodium (Rh) on a special ceramic support

Heterogeneous catalysts can be poisoned by impurities, which are often present in the raw materials used. These impurities bond very strongly to the catalyst surface and block the active sites. This reduces the efficiency of the catalyst, making the process less economic and requiring the catalyst to be regularly replaced, which can be expensive.

Examples of heterogenous catalysts are; Fe in the production of ammonia, V_2O_5 in the contact process or Pt and Rh in a catalytic converter.

i) $N_2(g) + 3H_2(g) == 2NH_3(g)$ **Fe catalyst**

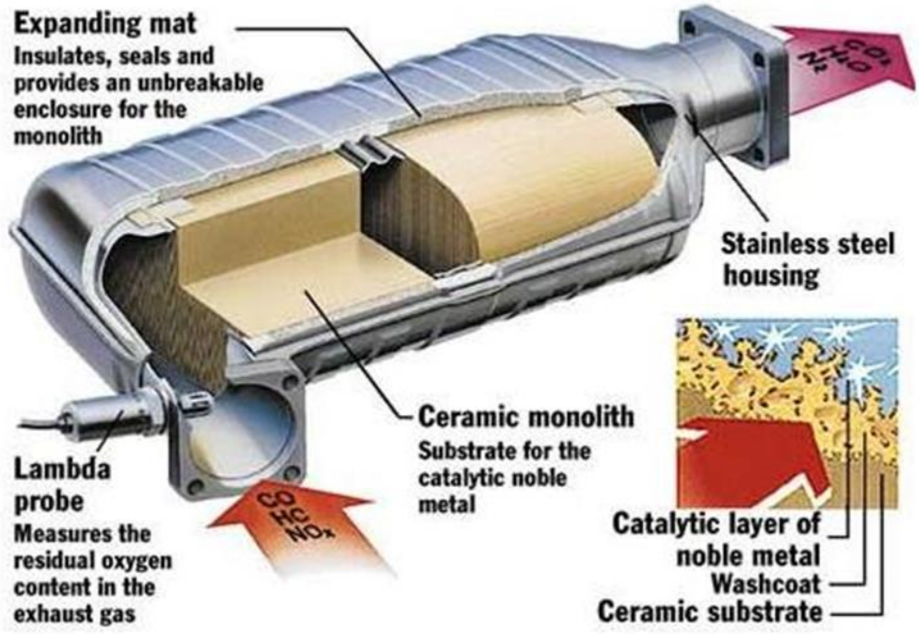
ii) $2SO_2(g) + O_2(g) == 2SO_3(g)$ **V_2O_5 catalyst**

V_2O_5 oxidises SO_2 to SO_3, itself getting reduced: $SO_2 + V_2O_5 \rightarrow SO_3 + V_2O_4$

V_2O_4 then uses the O_2 to get oxidised back to V_2O_5: $V_2O_4 + 1/2O_2 \rightarrow V_2O_5$

iii) $2CO(g) + 2NO(g) == N_2(g) + 2CO_2(g)$ Rh catalyst

The catalytic converter converts toxic carbon monoxide and nitrogen monoxide to non-toxic carbon dioxide and nitrogen.



Module 6: Organic chemistry and analysis

6.1 Aromatic compounds, carbonyls and acids

OPTICAL ISOMERISM

Isomers are compounds with the same molecular formula but different structures.

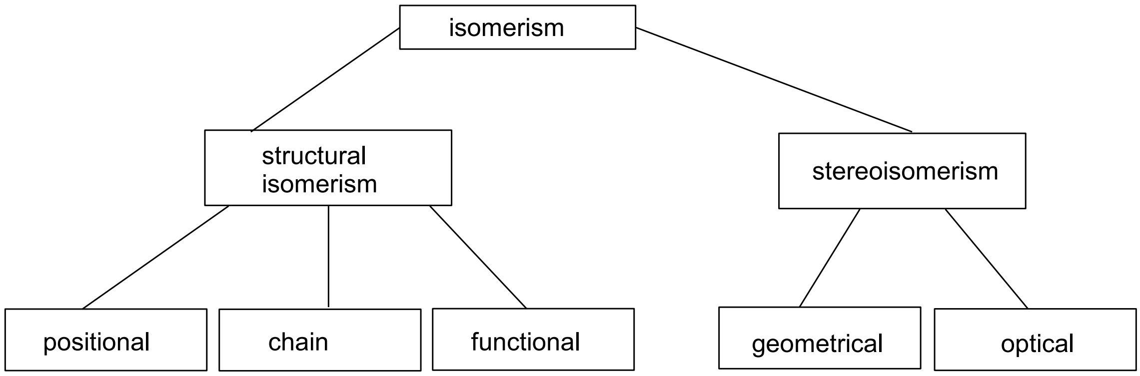
Isomerism can be divided into two types; **structural isomerism** and **stereoisomerism**.

These in turn can be further subdivided:

There are three types of structural isomerism; **positional isomerism**, **chain isomerism** and **functional isomerism**.

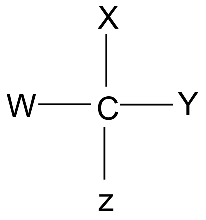
There are two types of stereoisomerism: **geometrical isomerism** and **optical isomerism**.

The different types of isomerism are summarised in the following diagram:

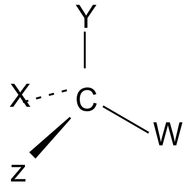


i) Introduction to Optical Isomerism

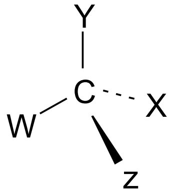
Consider the following molecule:



It is tetrahedral and is thus more accurately represented in the following way:



Since the carbon atom is attached to four different groups, it is asymmetric and so cannot be superimposed on its mirror image:



These two mirror images cannot be interconverted without breaking covalent bonds.

Molecules which contain a carbon atom which is attached to four different groups are said to be **chiral**. Chiral molecules cannot be superimposed on their mirror image.

The two non-superimposable mirror images are **optical isomers** or **enantiomers**.

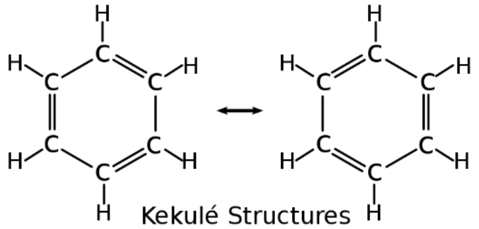
Any molecule which contains at least one carbon atom attached to four different groups will thus exhibit optical isomerism.

6.1.1 Aromatic compounds - Benzene

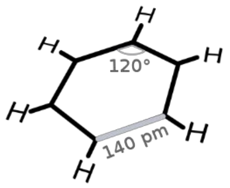
Bonding in Benzene is represented using the Kekulé and the delocalised model, the latter in terms of overlap of p-orbitals to form π-bonds

C_6H_6

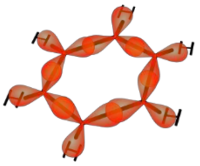
Benzene
Molecular formula



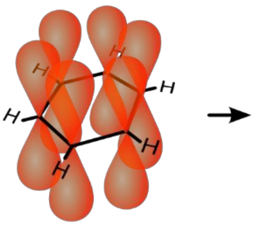
Kekulé Structures
(Isomers)



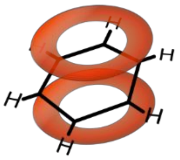
Planar Hexagon
Bond Length 140 pm



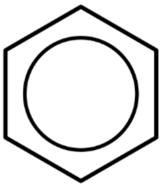
Sigma Bonds
sp^2 Hybridized orbitals



6 p_z orbitals



delocalized pi
system

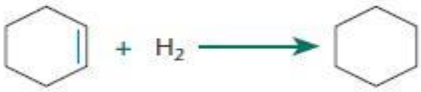


Benzene ring
Simplified depiction

Evidence for the delocalised model of the bonding in benzene is provided by data from enthalpy changes of hydrogenation and carbon-carbon bond lengths

Hydrogenation of cyclohexene

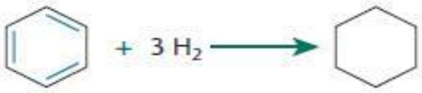
Each molecule of cyclohexene has one C=C double bond. The enthalpy change for the reaction of cyclohexene with hydrogen is shown below.



$\Delta H^\ominus = -120\ \text{kJ mol}^{-1}$

Hydrogenation of benzene

The Kekulé structure of benzene as cyclohexa-1,3,5-triene has three double C=C bonds. It would be expected that the enthalpy change for the hydrogenation of this structure would be three times the enthalpy change for the one C=C bond in cyclohexene.



predicted enthalpy change:
$\Delta H^\ominus = 3 \times -120 = -360\ \text{kJ mol}^{-1}$

- When benzene is reacted with hydrogen, the enthalpy change obtained is far less exothermic, $\Delta H^\ominus = -208\ \text{kJ mol}^{-1}$.

KEY POINT

- The difference between the thermochemical data for cyclohexa-1,3,5-triene and benzene suggests that benzene has **more stable bonding** than the Kekulé structure.
- The delocalisation stability of benzene of $-152\ \text{kJ mol}^{-1}$ is the difference between the two enthalpy changes above. This is extra energy that must be provided to break the delocalised benzene ring.

Resistance of benzene to bromination compared to alkenes

Alkenes tend to surcome to bromination easily, unlike benzene, this can be seen in cyclohexene

As the pi-bond contains localised electrons, it produces an area of high electron density, allowing it to repel the electrons in the Bromine bond, this induces a dipole making one bromine atom partially positive and therefore attracting it to the negative double bond in the cyclohexene. This then leaves a slightly positive intermediate molecule, which the negative bromine molecule is attracted to, hence forming 1,2-dibromocyclohexane, by addition.

In Benzene, there are no areas of **high electron density**, preventing it from being able to polarise the bromine molecule, this means that a halogen carrier must be present in order for it to even undergo a substitution reaction.

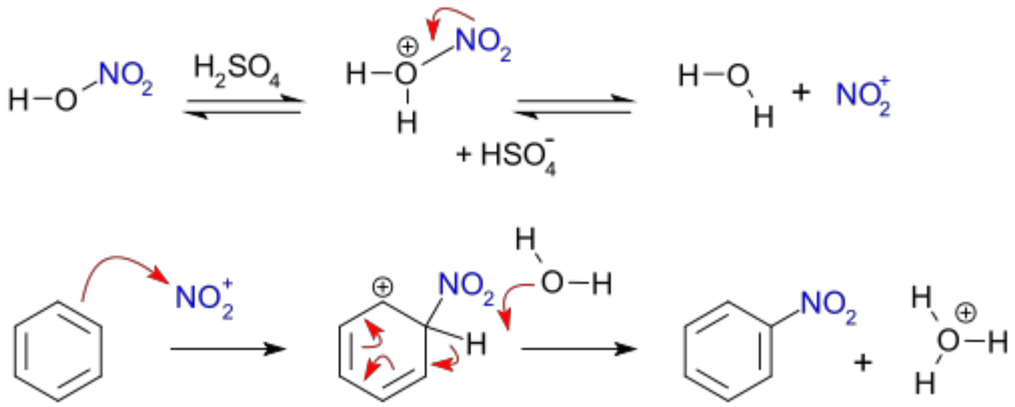
Reactions of benzene

(1) Nitration :

This is a relatively easy process to accomplish with a mixture of concentrated sulphuric and concentrated nitric acids. This mixture reacts together to produce an unstable nitronium ion, NO2+ :

HNO3 + 2H2SO4 → NO2+ + 2HSO4- + H3O+

This ion is attracted to the electron rich benzene ring - causing an electrophilic substitution reaction to occur :



The products of the reaction are nitrobenzene and hydrogen/oxonium ions.

(2) Halogenation :

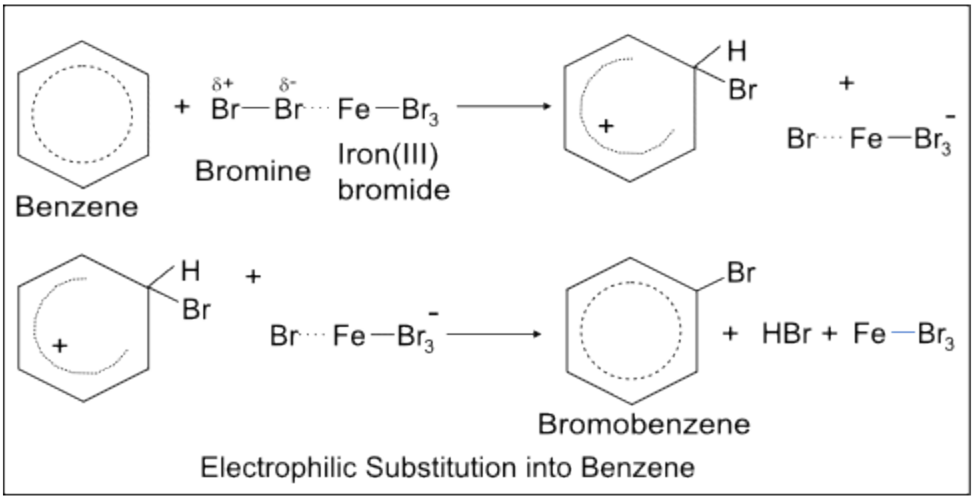
All normal unsaturated compounds, i.e. alkenes, will react with halogens, in the absence of light, to give the dihalogenated addition product.

The nature of the benzene ring and its delocalised electrons prevents this sort of reaction from occurring.

Aromatic compounds will react with halogens (i.e. Cl2 and Br2), however, they require a catalyst - a metal halide (e.g. iron(III) bromide or aluminium chloride) or iron filings.

These catalysts act to polarise the halogen bond forming a d+ charge on a halogen atom (Cl or Br)

This species is then able to react with the benzene ring in exactly the same manner as the nitronium ion does in the nitration reaction

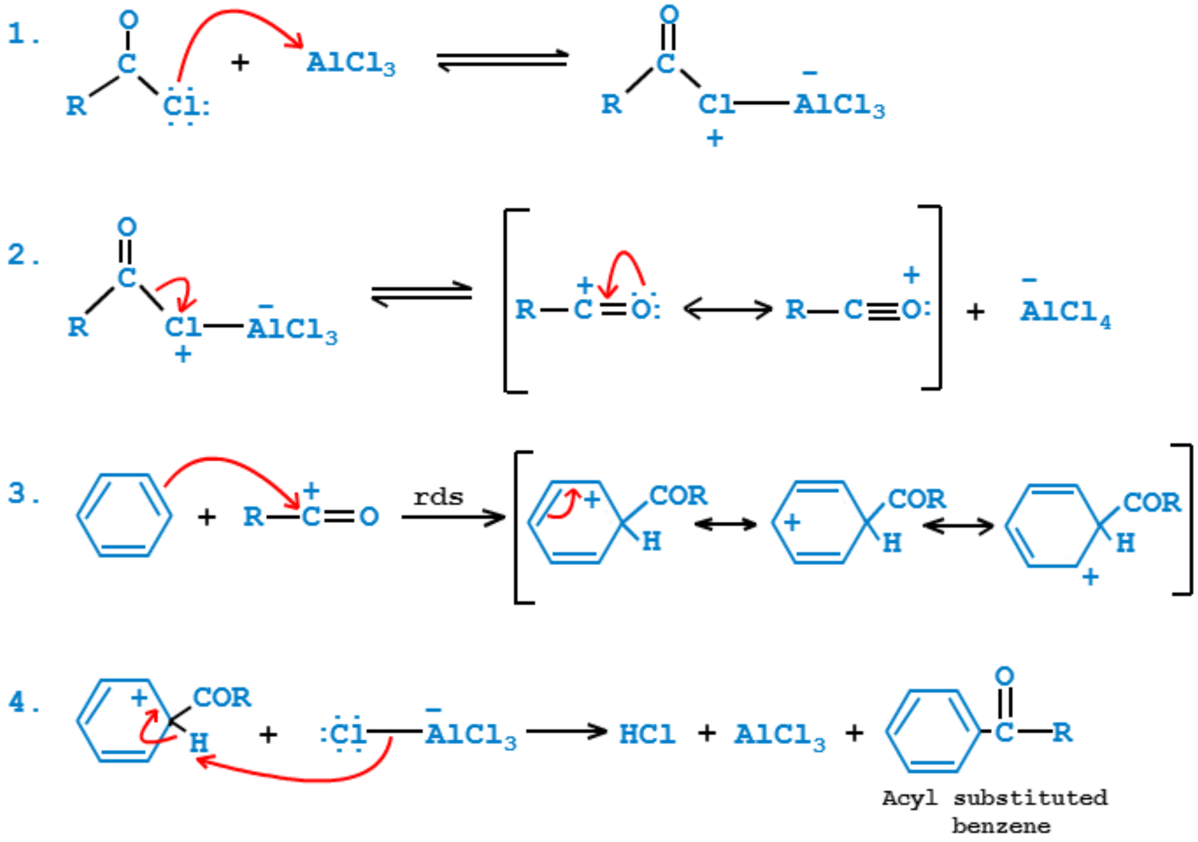


The products will be the monohalogenated benzene compound (i.e. chlorobenzene or bromobenzene) and the hydrogen halide (i.e. HCl or HBr).

The above example shows only iron(III) bromide and bromine as an example of one set of reactants. Aluminium chloride and chlorine works in exactly the same manner.

(3) Friedel-Crafts reaction :

This type of reaction involves using a haloalkane to add an alkyl group to a benzene ring. As with the halogenation above a metal halide catalyst is needed to generate the necessary alkyl electrophile. This complex then reacts with the benzene ring in a similar manner to the other electrophiles looked at so far, to form an alkyl benzene compound.



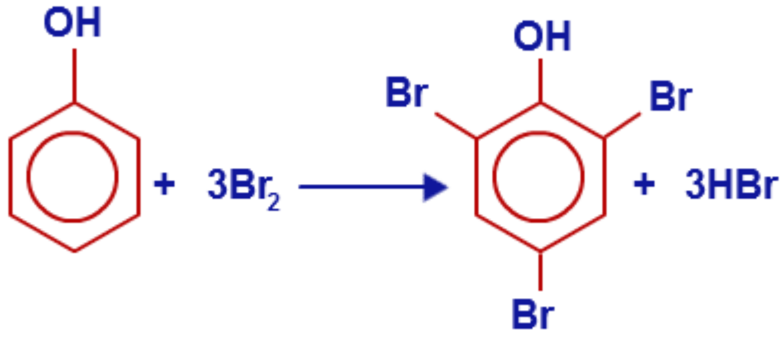
(4) Benzene with oxygen in air

Benzene completely burns in high supply of oxygen to give carbon dioxide and water.

$2C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O$ However, complete combustion rarely occurs and the hydrocarbon burns with extremely smoky flames.

Reaction of phenol with bromine water

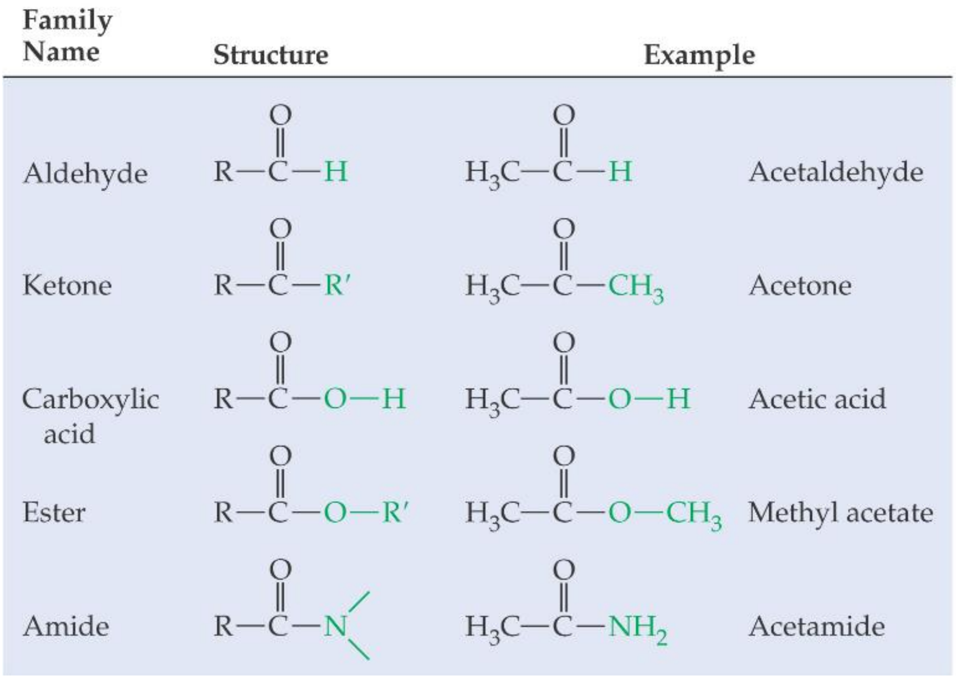
Unlike other arenes, the benzene ring in phenol is about 100 times more reactive than in benzene itself, because of the hydroxyl group attached to it. Therefore phenol does decolourise bromine water, though it still undergoes a substitution reaction (rather than the addition of a normal alkene) :



2, 4, 6-tribromophenol

6.1.2 Carbonyl compounds

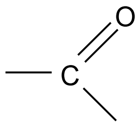
Some common Carbonyl compounds



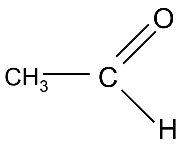
Family Name	Structure	Example	
Aldehyde	$R-\overset{O}{\overset{\|}{C}}-H$	$H_3C-\overset{O}{\overset{\|}{C}}-H$	Acetaldehyde
Ketone	$R-\overset{O}{\overset{\|}{C}}-R'$	$H_3C-\overset{O}{\overset{\|}{C}}-CH_3$	Acetone
Carboxylic acid	$R-\overset{O}{\overset{\|}{C}}-O-H$	$H_3C-\overset{O}{\overset{\|}{C}}-O-H$	Acetic acid
Ester	$R-\overset{O}{\overset{\|}{C}}-O-R'$	$H_3C-\overset{O}{\overset{\|}{C}}-O-CH_3$	Methyl acetate
Amide	$R-\overset{O}{\overset{\|}{C}}-N\langle$	$H_3C-\overset{O}{\overset{\|}{C}}-NH_2$	Acetamide

Aldehydes and ketones

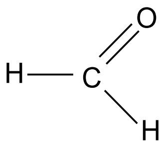
Aldehydes and ketones are collectively known as carbonyls and represented by the general formula $C_nH_{2n}O$. They have the following functional group:



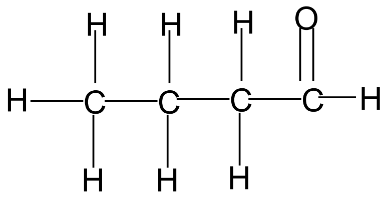
In aldehydes one of the groups attached to the carbon is a hydrogen atom and the other is a hydrogen atom or an alkyl groups. In ketones both of the groups attached to the carbon are alkyl groups:



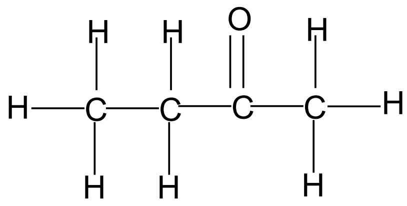
ethanal



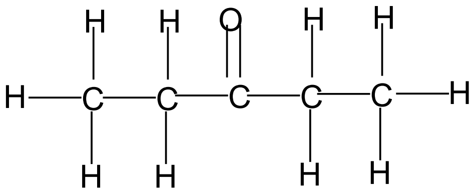
methanal



butanal



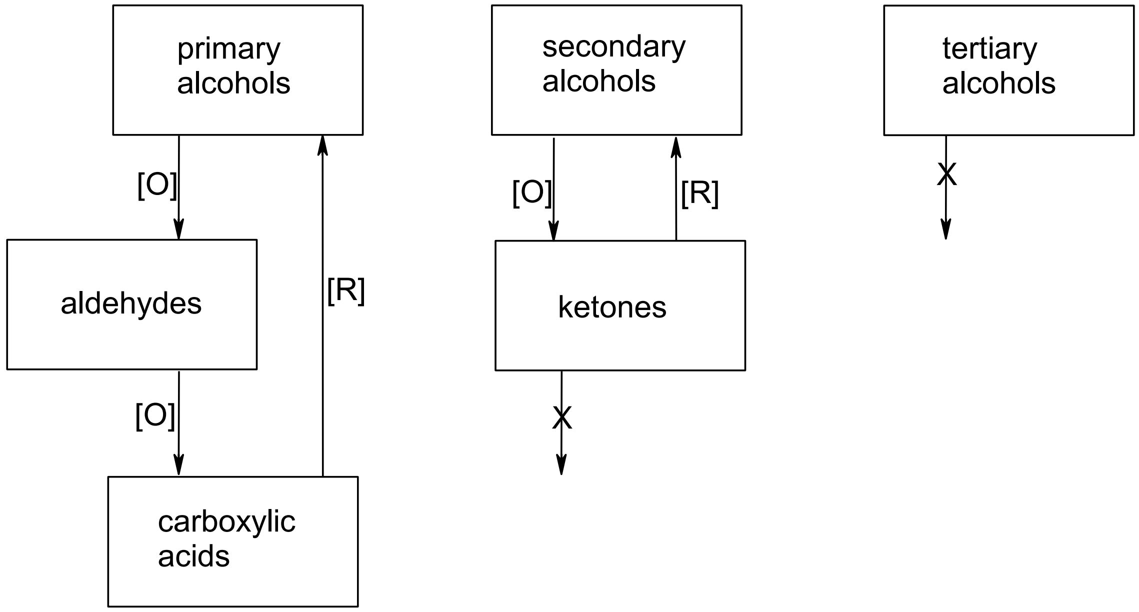
butanone



pentan-2-one

2. Redox reactions

The redox reactions involving carbonyls have been discussed at AS level and are summarized by the following diagram:



a) oxidation reactions

Carbonyls are formed by the oxidation of alcohols.

Partial oxidation of a primary alcohol results in the formation of an **aldehyde**.

Oxidation of a secondary alcohol results in the formation of a **ketone**.

Primary alcohols, secondary alcohols and aldehydes are oxidized using potassium dichromate ($K_2Cr_2O_7$) in sulphuric acid (H_2SO_4). Gentle warming is necessary to start the reaction.

When making an aldehyde, care must be taken to prevent further oxidation to the carboxylic acid. This is achieved by using distillation apparatus so that the aldehyde can be distilled off as soon as it is formed.

The orange $Cr_2O_7^{2-}$ is reduced to the green Cr^{3+}.

Simplified equations for these oxidation reactions can be written using the symbol [O] as the oxidant:

Primary alcohol → aldehyde

$R\text{-}CH_2OH + [O] \rightarrow R\text{-}CHO + H_2O$

Secondary alcohol → ketone

$R_1\text{-}CH(OH)\text{-}R_2 + [O] \rightarrow R_1\text{-}CO\text{-}R_2 + H_2O$

Aldehyde → carboxylic acid

$R\text{-}CHO + [O] \rightarrow R\text{-}COOH$

The most important difference in the reactions of aldehydes and ketones is the fact that **aldehydes can be readily oxidised to carboxylic acids but ketones are not readily oxidised**. This is used as the basis for two important distinguishing tests between aldehydes and ketones.

Ammoniacal silver nitrate, $[Ag(NH_3)_2]^+$, is known as **Tollen's reagent**. It is a mild oxidising agent:

$[Ag(NH_3)_2]^+(aq) + e \rightarrow Ag(s) + 2NH_3(aq)$

It can be reduced by aldehydes, oxidising them to carboxylic acids:

$R\text{-}CHO + H_2O \rightarrow RCOOH + 2H^+(aq) + 2e$

The overall equation for the reaction is:

$\mathbf{R\text{-}CHO + 2[Ag(NH_3)_2]^+ + H_2O \rightarrow RCOOH + 2Ag + 4NH_3 + 2H^+}$

Thus aldehydes give a grey precipitate or "silver mirror" if boiled with ammoniacal silver nitrate. This is a standard test for an aldehyde, since ketones cannot be oxidised in this way.

Fehling's solution is an alkaline solution containing Cu^{2+} ions. It is a mild oxidizing agent:

$2Cu^{2+} + 2e + 2OH^- \rightarrow Cu_2O + H_2O$

It is also reduced by aldehydes, and the overall equation for the reaction is:

$\mathbf{R\text{-}CHO + 4OH^- + 2Cu^{2+} \rightarrow R\text{-}COOH + Cu_2O + 2H_2O}$

The blue Cu^{2+} is reduced to the brick-red precipitate Cu_2O on gentle warming. This is another standard test for an aldehyde.

b) reduction reactions

Aldehydes and ketones can be reduced to primary and secondary alcohols respectively using the reducing agent sodium tetrahydroborate (III), $NaBH_4$.

Simplified equations for these reduction reactions can be written using the symbol [H] as the reductant:

Aldehyde → primary alcohol

$R\text{-}CHO + 2[H] \rightarrow R\text{-}CH_2OH$

Ketone → Secondary alcohol

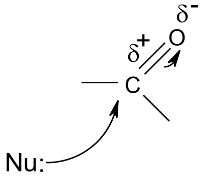
$R_1\text{-}CO\text{-}R_2 + 2[H] \rightarrow R_1\text{-}CH(OH)\text{-}R_2$

Carboxylic acids cannot be reduced using $NaBH_4$ but can be reduced to primary alcohols using the stronger reducing agent $LiAlH_4$.

3. Nucleophilic addition

Carbonyls are unsaturated and can thus undergo addition reactions.

The C=O bond is polar so the carbon is a positive centre. Thus carbonyls can react with nucleophiles:



Carbonyls therefore tend to undergo nucleophilic addition.

Mechanism of nucleophilic addition:

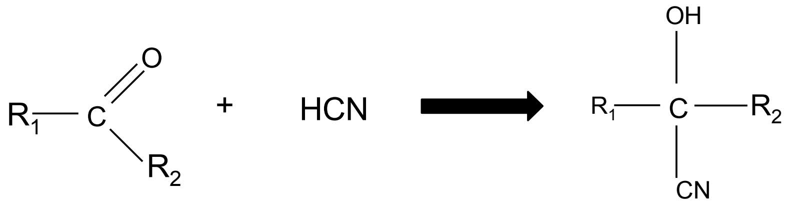
Example 1: addition of HCN to make hydroxynitriles

NB

- **HCN is a very poisonous gas. It is not safe to carry out this reaction in the laboratory. HCN is not stored, but made in situ by mixing KCN and HCl.**
- **KCN is also very poisonous but it is safer to store as it is a solid.**

Hydrogen cyanide, HCN, is a nucleophile. It reacts with carbonyls as follows:

$R_1\text{-CO-}R_2 + HCN \rightarrow R_1\text{-C(CN)(OH)-}R_2$



HCN is a very toxic gas, so is generated in situ:

$KCN(s) + HCl(aq) \rightarrow HCN(g) + KCl(aq)$

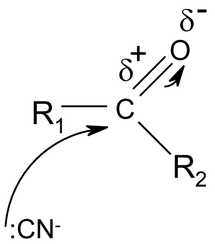
The mechanism consists of three steps:

Step 1: the HCN is a weak acid and dissociates:

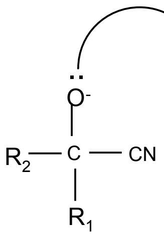
$HCN \rightarrow H^+ + CN^-$

The CN^- behaves as a nucleophile.

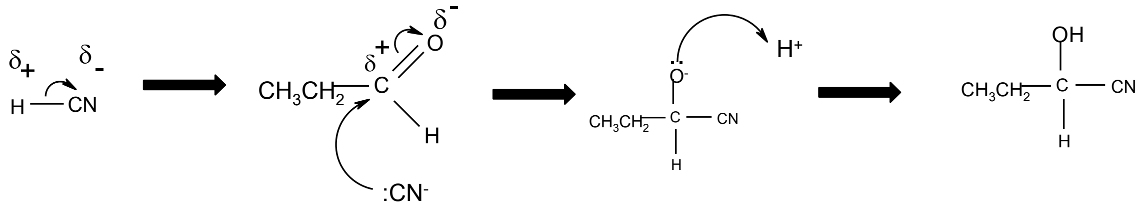
Step 2: The nucleophile attacks the carbonyl:



Step 3: The O atom picks up the H^+ ion:



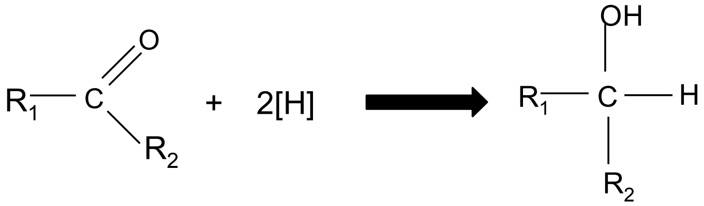
Eg propanal + HCN → 2-hydoxybutanenitrile



Example 2: reduction by $NaBH_4$ to make alcohols

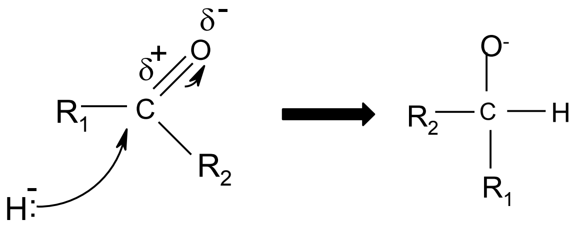
The reduction of aldehydes and ketones as described above is another example of a nucleophilic addition reaction.

R_1-CO-R_2 + 2[H] → R_1-CH(OH)-R_2

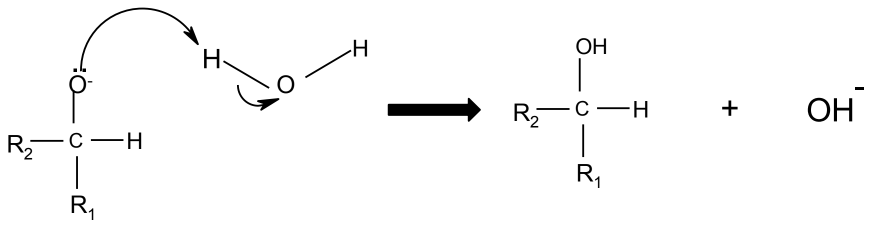


$NaBH_4$ contains hydrogen in a negative oxidation state, which can therefore behave as a nucleophile.

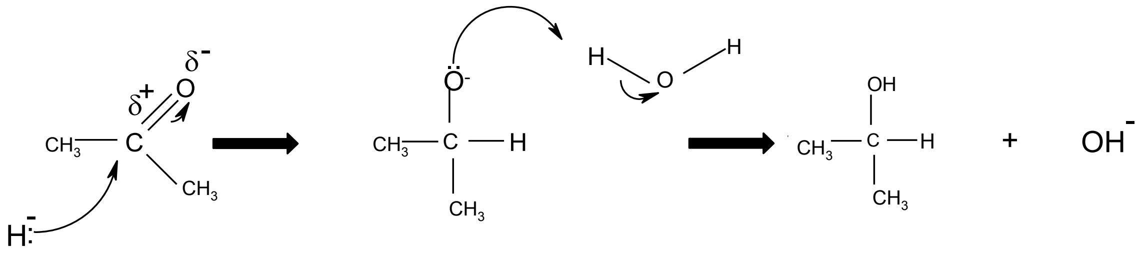
Step 1: the H^- ion attacks the δ^+ carbon atom:



Step 2: the O^- pulls a H atom off a water molecule



eg propanone + 2[H] → propan-2-ol

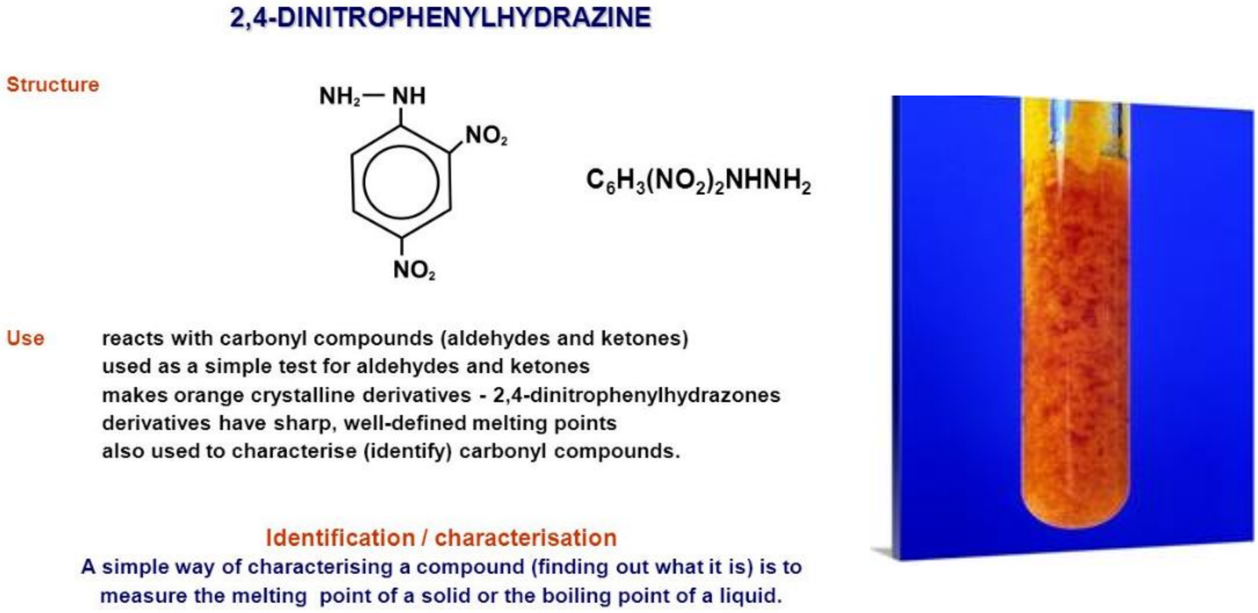


Qualitative test for Carbonyl presence

2,4-dinitrophenylhydrazine (2,4-DNPH) is used as a qualitative test for the

presence of a carbonyl group . 2,4-Dinitrophenylhydrazine (DNPH, Brady's reagent,) is the chemical compound $C_6H_3(NO_2)_2NHNH_2$. Dinitrophenylhydrazine is a red to orange solid. It is a substituted hydrazine, and is often used to qualitatively test for carbonyl groups associated with aldehydes and ketones.

Identifying carbonyl compound from melting points of derivatives.



2,4-DINITROPHENYLHYDRAZINE

Structure

$C_6H_3(NO_2)_2NHNH_2$

Use

reacts with carbonyl compounds (aldehydes and ketones)
used as a simple test for aldehydes and ketones
makes orange crystalline derivatives - 2,4-dinitrophenylhydrazones
derivatives have sharp, well-defined melting points
also used to characterise (identify) carbonyl compounds.

Identification / characterisation

A simple way of characterising a compound (finding out what it is) is to measure the melting point of a solid or the boiling point of a liquid.

4. Summary of reactions of aldehydes and ketones

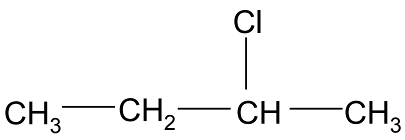
Type of reaction	**Mechanism**
1. **oxidation** (aldehydes only): aldehyde → carboxylic acid reagents: potassium dichromate ($K_2Cr_2O_7$) in sulphuric acid (H_2SO_4) conditions: warm under reflux equation: R-CHO + [O] → R-COOH observation: orange to green to distinguish between aldehydes and ketones: either: add Fehling's solution and heat observation: blue solution to brick red precipitate equation: $R\text{-}CHO + 4OH^- + 2Cu^{2+} \rightarrow R\text{-}COOH + Cu_2O + 2H_2O$ or: add Tollen's reagent and heat observation: colourless solution to silver mirror equation: $R\text{-}CHO + 2[Ag(NH_3)_2]^+ + H_2O \rightarrow RCOOH + 2Ag + 4NH_3 + 2H^+$	n/a
2. **reduction**: carbonyl → alcohol reagents: $NaBH_4(aq)$ conditions: room temperature equation: $R_1\text{-}CO\text{-}R_2 + 2[H] \rightarrow R_1\text{-}CH(OH)\text{-}R_2$	Nucleophilic addition (required)
3. **addition of HCN**: carbonyl → hydroxynitrile reagents: KCN and HCl(aq) conditions: room temperature equation: $R_1\text{-}CO\text{-}R_2 + HCN \rightarrow R_1\text{-}C(CN)(OH)\text{-}R_2$	Nucleophilic addition (required)

Isomerism

Consider the four structural isomers of C_4H_9Cl:

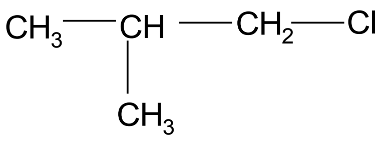
$CH_3-CH_2-CH_2-CH_2-Cl$

1-chlorobutane



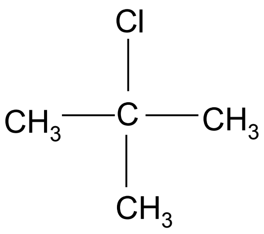
$CH_3-CH_2-CH(Cl)-CH_3$

2-chlorobutane



$CH_3-CH(CH_3)-CH_2-Cl$

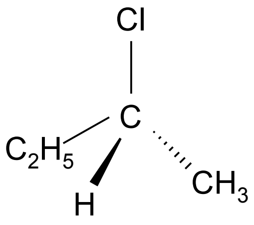
1-chloro, 2-methylpropane

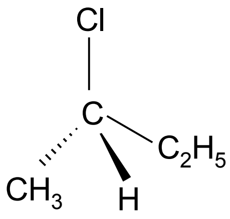


$CH_3-C(Cl)(CH_3)-CH_3$

2-chloro, 2-methylpropane

Of these molecules only 2-chlorobutane shows optical isomerism:



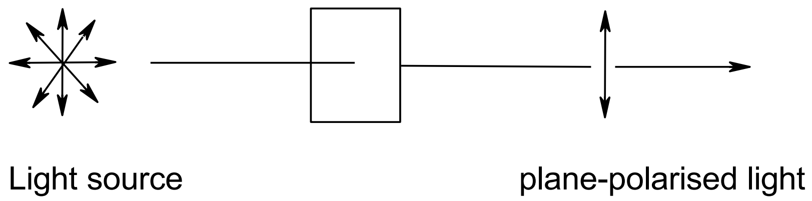


ii) Distinguishing between the different enantiomers

Optical isomers show identical physical and chemical properties in most respects.

In fact there is only one physical method by which they can be distinguished.

Plane-polarised light is light which has been filtered into a two-dimensional plane:



If plane-polarised light is passed through a liquid containing a chiral molecule, the plane of the light will be rotated. This can be detected using a polarimeter.

Molecules which are not chiral will not rotate the plane of plane-polarised light.

Chiral molecules will rotate plane-polarised light. Two optical isomers will rotate plane polarised light equally, but in opposite directions.

It is this difference in physical properties which enables them to be distinguished.

It is not possible to predict the direction in which a particular optical isomer will rotate plane polarised light, but two optical isomers will always rotate plane polarised light in opposite directions.

A substance which can rotate plane polarised light is said to be **optically active**.

The isomer which rotates plane polarised light clockwise is given the prefix (+) or D-. The isomer which rotates plane polarised light anticlockwise is given the prefix (-) or L-.

iii) **Importance of optical isomers in biochemistry**

Optical isomers show identical chemical properties in most reactions. However, certain biochemical processes require the molecule to have a specific orientation of groups. Many drugs and enzymes are chiral and so only one of the optical isomers will be able to interact effectively with the target molecule in the body. Different optical isomers may therefore have very different biochemical effects.

iv) racemates

Optical isomers are often found together in a mixture in equal quantities. The opposite effect they have on the rotation of plane polarised light will thus result in no overall rotation. An equimolar mixture of two optical isomers will thus have no effect on plane polarised light and is thus not optically active.

Such mixtures are said to be **racemic mixtures** or **racemates**.

A racemic mixture is an equimolar mixture of two optical isomers. Racemic mixtures are not optically active.

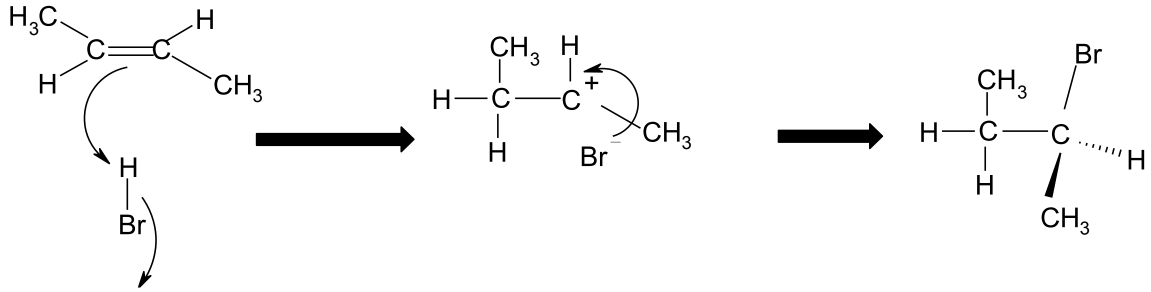
Thus chiral molecules will only show optical activity if one isomer is present in greater quantities than the other.

It is possible to predict whether a single enantiomer or a racemate will be produced,

If the chiral substance is produced by an addition reaction, then the product will always be a racemate as the attacking nucleophile or electrophile can attack the planar molecule from above or below with equal probability:

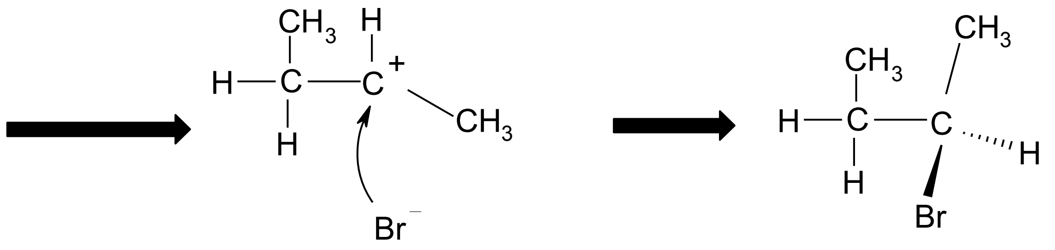
Eg formation of 2-bromobutane from but-2-ene (electrophilic addition)

The bromide ion can attack the carbocation from above or below, producing an equimolar mixture of the two enantiomers – ie a racemate:



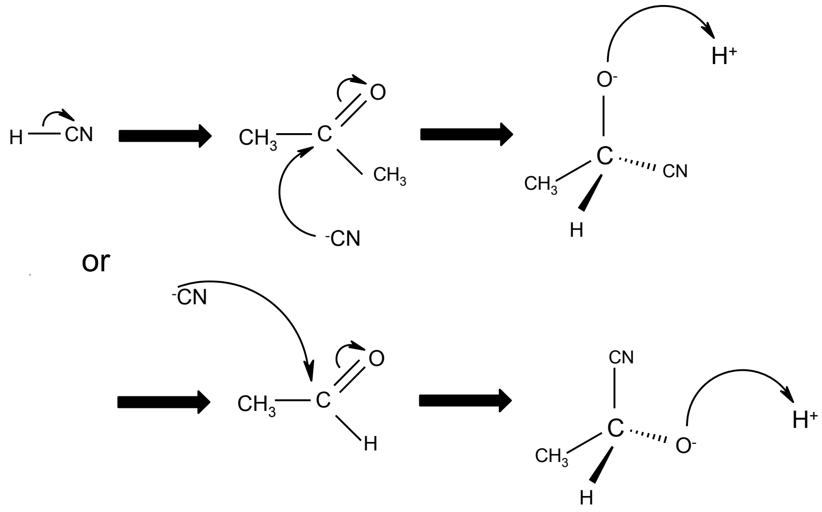
bromide attacks planar species from above

or



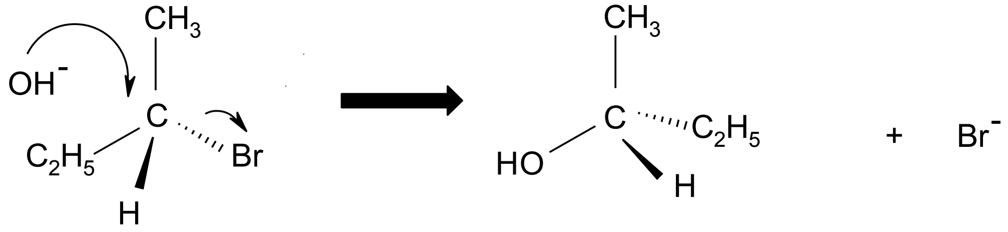
bromide attacks planar species from below

Nucleophilic addition reactions also produce racemates for the same reason. In the preparation of the chiral molecule 2-hydroxypropanenitrile from ethanal for example, the cyanide ion can attack the planar carbonyl group from above or below, producing a racemate.



If the chiral molecule is produced by a substitution reaction and the starting molecule is a single enantiomer, then the attacking species can only attack from one side and a single enantiomer will be produced.

Eg preparation of butan-2-ol from 2-bromobutane

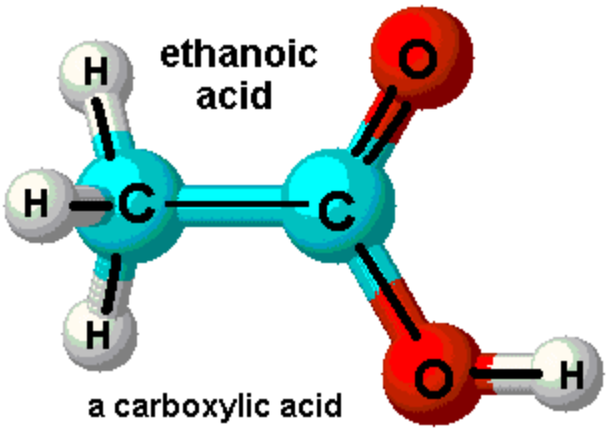


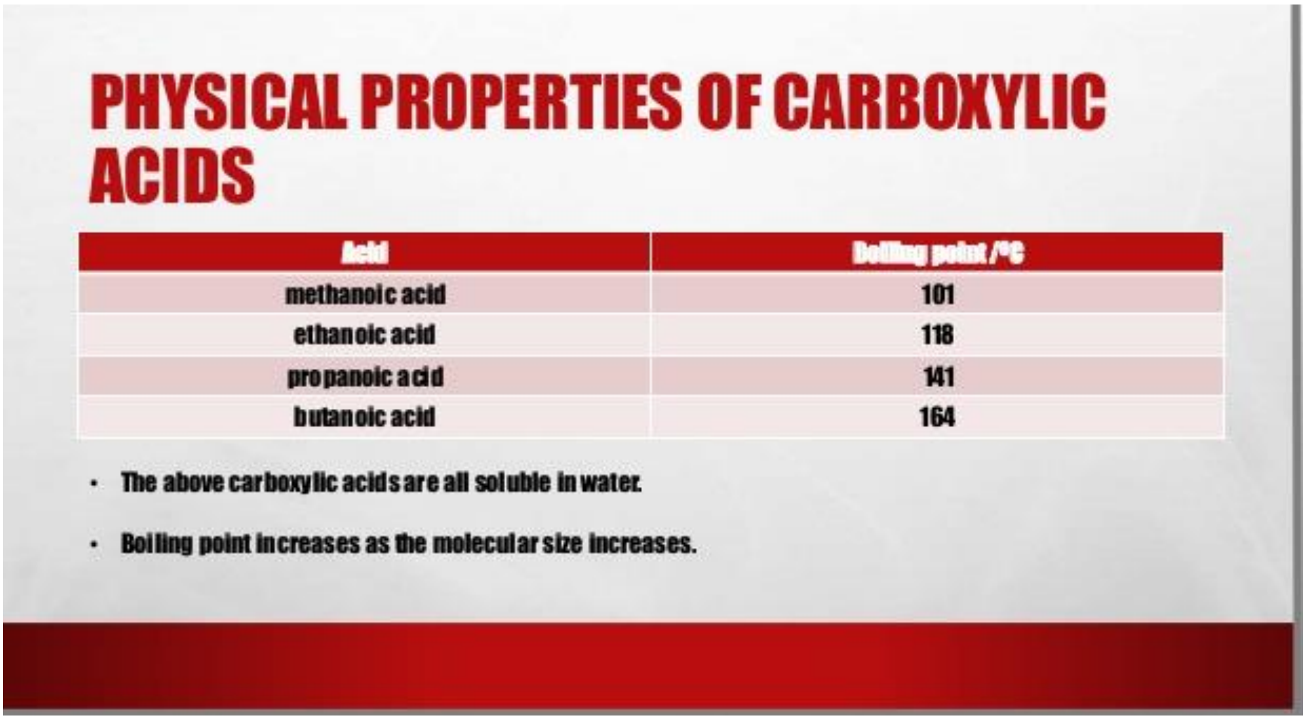
The hydroxide ion always attacks from behind, always producing the same enantiomer.

So nucleophilic substitution reactions produce single enantiomers provided that the substrate was also a single enantiomer. Nucleophilic and electrophilic addition reactions always produce racemates.

6.1.3 Carboxylic acids and esters

All carboxylic acids have the functional group COOH





PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS

Acid	Boiling point /°C
methanoic acid	101
ethanoic acid	118
propanoic acid	141
butanoic acid	164

- The above carboxylic acids are all soluble in water.
- Boiling point increases as the molecular size increases.

Carboxylic acids can be prepared by the oxidation of alcohols or aldehydes, and the hydrolysis of nitriles

1. **Oxidation of alcohols or aldehydes**
   Normally primary alcohols form carboxylic acids when **fully oxidised**. Initial oxidation produces **aldehydes and these can be further oxidised to carboxylic acids**

An excess of the oxidising agent must be used, and the aldehyde formed as the half-way product should remain in the mixture. The alcohol is heated under reflux with an excess of the oxidizing agent. When the reaction is complete, the carboxylic acid is distilled off.

The full equation for the oxidation of ethanol to ethanoic acid is as follows:

$$3CH_3CH_2OH + 2Cr_2O_7^{2-} + 16H+ \rightarrow 3CH_3COOH + 4Cr^{3+} + 11H_2O$$

The more typical simplified version looks like this:

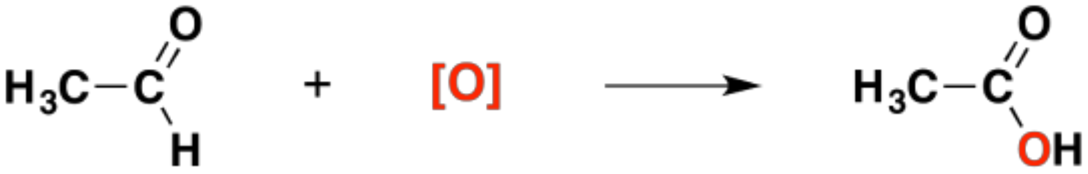
$$CH_3CH_2OH + 2[O] \rightarrow CH_3COOH + H_2O$$

Alternatively, you could write separate equations for the two stages of the reaction - the formation of ethanal and then its subsequent oxidation.

$$CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$$

$$CH_3CHO + [O] \rightarrow CH_3COOH$$

This is what is happening in the second stage:



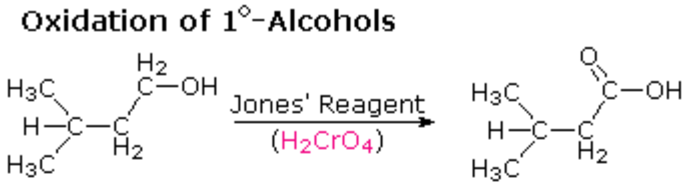
2. Hydrolysis of nitriles

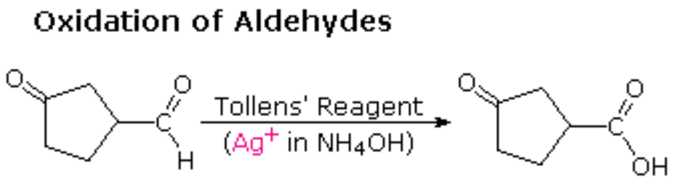
The nitrile is heated under reflux with dilute hydrochloric acid. Instead of getting an ammonium salt as you would do if the reaction only involved water, you produce the free carboxylic acid.

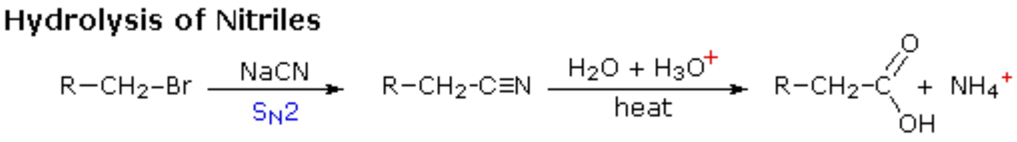
For example, with ethanenitrile and hydrochloric acid you would get ethanoic acid and ammonium chloride.

$$CH_3CN + 2H_2O + HCl \longrightarrow CH_3COOH + NH_4Cl$$

Summary on preparation of carboxylic acids



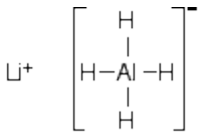




Reactions of carboxylic acids

i lithium tetrahydridoaluminate (lithium aluminium hydride) in dry ether

Lithium tetrahydridoaluminate is a reducing agent and has the structure:



lithium tetrahydridoaluminate

The reaction happens in two stages - first to form an aldehyde and then a primary alcohol. Because lithium tetrahydridoaluminate reacts rapidly with aldehydes, the reaction gors to completion. The full equation is :

$$RCOOH + 4[H] \longrightarrow RCH_2OH + H_2O$$

[H] is the reducing agent.

"R" is hydrogen or a hydrocarbon group. For example, ethanoic acid will reduce to the primary alcohol, ethanol.

$$CH_3COOH + 4[H] \longrightarrow CH_3CH_2OH + H_2O$$

Dry ether is used as the reducing agent lithium tetrahydridoaluminate is highly reactive in water.

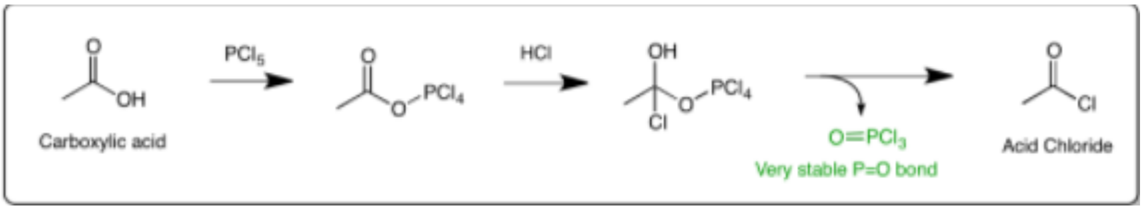
ii bases to produce salts

Because of their enhanced acidity, carboxylic acids react with bases to form ionic salts

$$\begin{aligned}
&RCO_2H + NaHCO_3 \longrightarrow RCO_2^{(-)}\,Na^{(+)} + CO_2 + H_2O\\
&RCO_2H + (CH_3)_3N{:} \longrightarrow RCO_2^{(-)}\,(CH_3)_3NH^{(+)}\\
&RCO_2H + AgOH \longrightarrow RCO_2^{\delta(-)}\,Ag^{\delta(+)} + H_2O
\end{aligned}$$

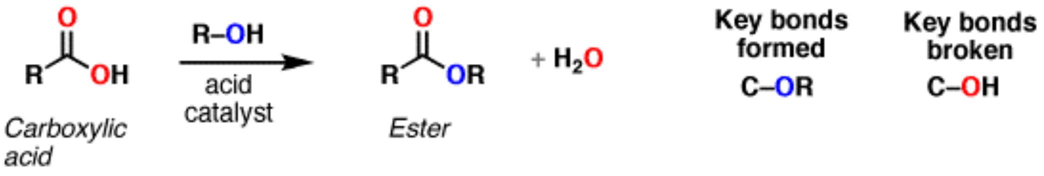
iii phosphorus(V) chloride (phosphorus pentachloride)

The reaction of a carboxylic acid with phosphorus pentachloride produces an acid chloride. The reaction goes firstly by starting with the removal of HCl. Then via a nucleophilic addition of chloride where the carbonyl is simultaneously protonated. The final step is formation of the acid chloride, HCl and phosphorus oxychloride. Formation of the strong P=O bond drives the reaction.



iv alcohols in the presence of an acid catalyst

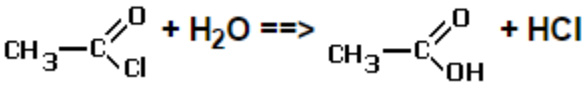
When a **carboxylic acid** is treated with an **alcohol** and an **acid catalyst**, an **ester** is formed (along with water). This **reaction** is called the Fischer esterification



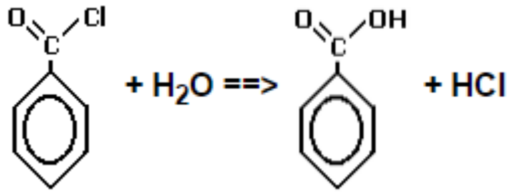
Reactions of acyl chlorides with:

i water

Examples of nucleophilic addition of water to acid/acyl chlorides, subsequent elimination on hydrolysis to give the carboxylic acid and hydrogen chloride/hydrochloric acid. The reaction is a nucleophilic substitution Cl by OH via H_2O



ethanoyl chloride + water ==> ethanoic acid + hydrogen chloride/hydrochloric acid



(ii)

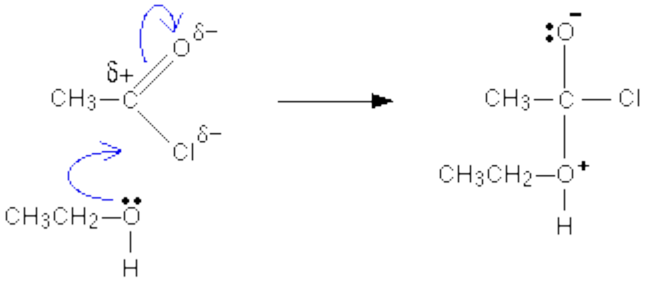
benzoyl chloride + water ==> benzoic acid + hydrogen chloride/hydrochloric acid

ii alcohols

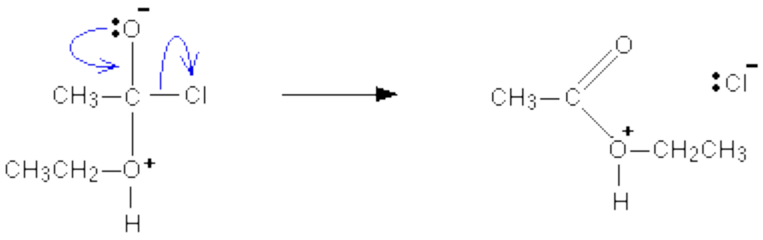
Inthis reaction an ester and hydrogen chloride gas are formed. The example below is in the context of ethyl chloride but all acyl chlorides behave the same way.

Mechanism:

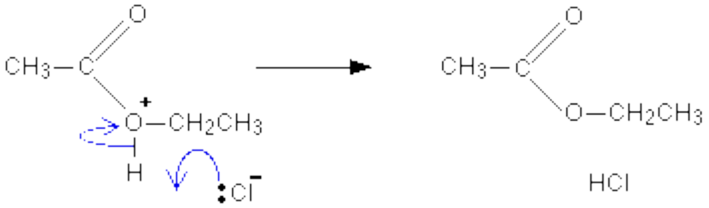
First there is a nucleophilic attack on the very positive carbon atom by an lone pair from the oxygen of the alcohol.



Then there is elimination of the chloride



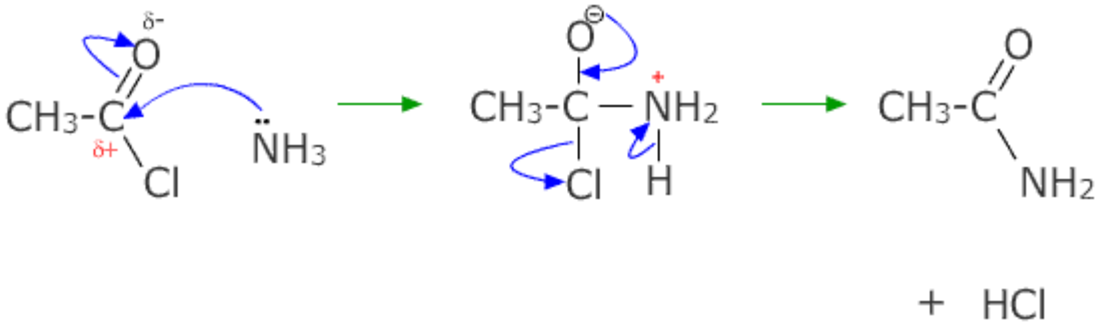
Followed by removal of hydrogen



iii concentrated ammonia

Acyl Chlorides react at room temperature with ammonia to form amides.

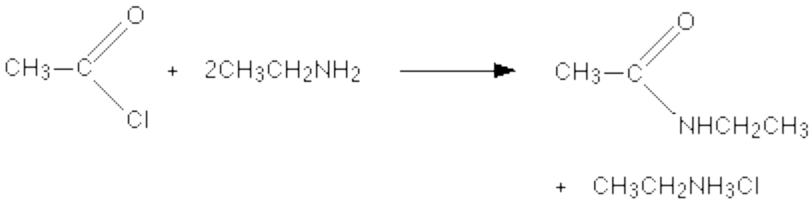
Ethanoyl chloride reacts violently with a cold concentrated solution of ammonia. A white solid product is formed which is a mixture of ethanamide (an amide) and ammonium chloride.



iv amines

This is a nucleophilic addition/elimination reaction.

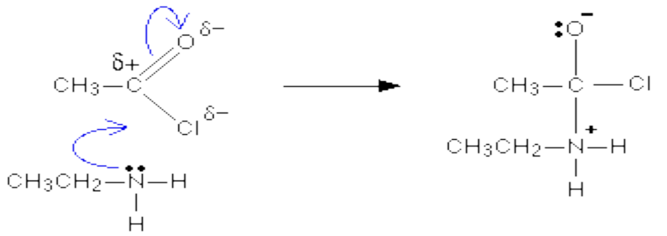
Produces amides and ammonium chlorides.



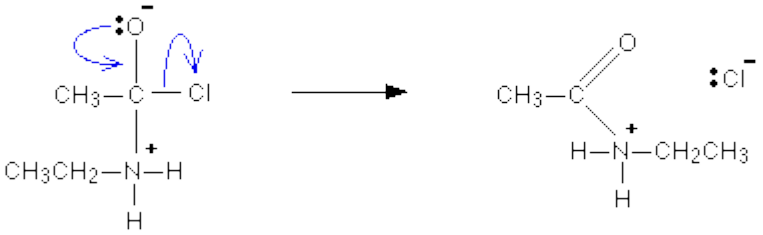
Mechanism- 2 stages:

In the addition stage, an amine molecule becomes attached to the carbon in the acyl chloride.

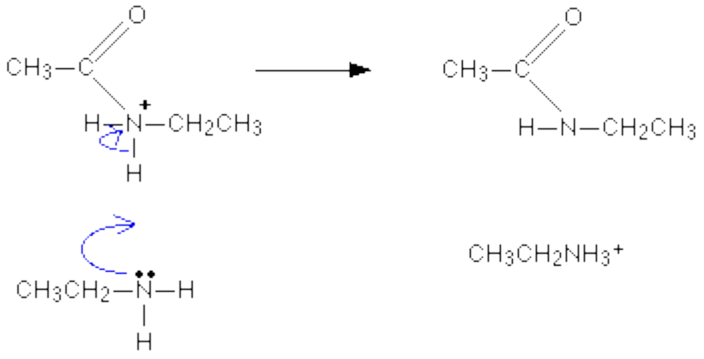
As the lone pair on the nitrogen approaches the fairly positive carbon in the acyl chloride, it moves to form a bond with it. In the process, the two electrons in one of the carbon-oxygen bonds are repelled entirely onto the oxygen, leaving it negatively charged.



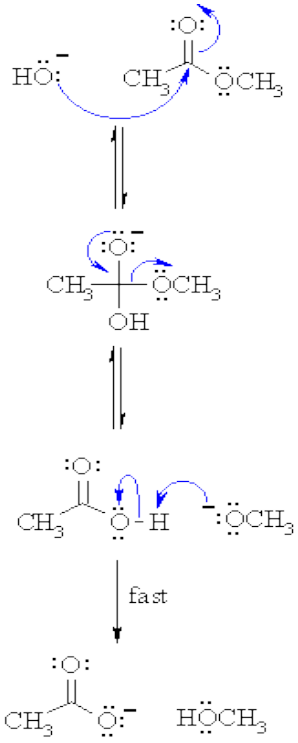
The **elimination** stage of the reaction happens in two steps. In the first, the carbon-oxygen double bond reforms. As the electron pair moves back to form a bond with the carbon, the pair of electrons in the carbon-chlorine bond are forced entirely onto the chlorine to give a chloride ion.



The amine molecule will more likely remove the hydrogen ion and make acylammonium chloride



Hydrolysis of esters



In alkaline conditions- This reaction is known as "saponification" because it is the basis of making soap from glycerol triesters in fats.

Step 1:

The hydroxide nucleophiles attacks at the electrophilic C ofthe ester C=O, breaking the π bond and creating the tetrahedral intermediate.

Step 2:

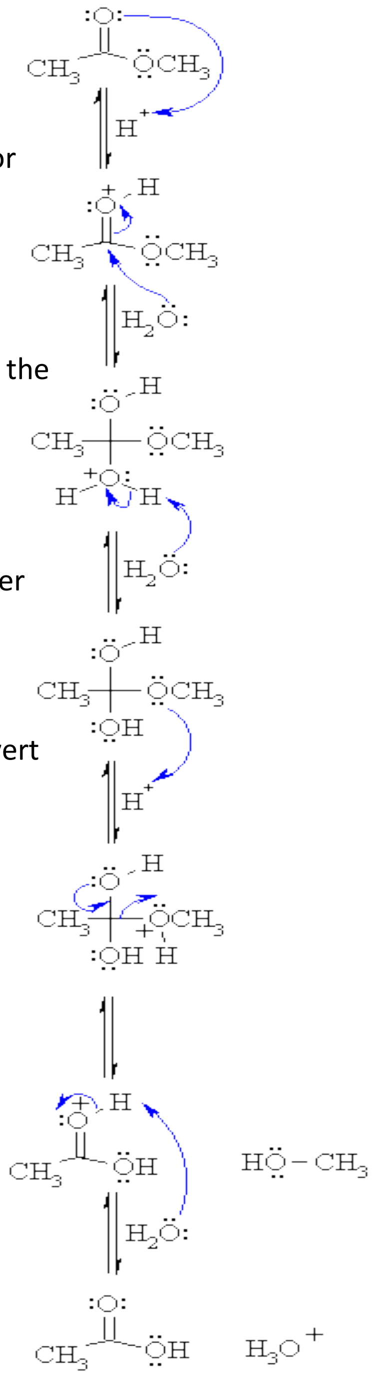
The intermediate collapses, reforming the C=O

results in the loss of the leaving group the alkoxide, RO-, leading to the carboxylic acid.

Step 3:

An acid / base reaction. A very rapid equilibrium where the alkoxide,RO- functions as a base deprotonating the carboxylic acid, RCO_2H

In acidic conditions



Step 1:

An acid/base reaction. Since we only have a weak nucleophile and a poor electrophile we need to activate the ester. Protonation of the ester carbonyl makes it more electrophilic.

Step 2:

The water O functions as the nucleophile attacking the electrophilic C in the C=O, with the electrons moving towards the oxonium ion, creating the tetrahedral intermediate.

Step 3:

An acid/base reaction. Deprotonate the oxygen that came from the water molecule to neutralise the charge.

Step 4:

An acid/base reaction. Need to make the -OCH3 leave, but need to convert it into a good leaving group first by protonation.

Step 5:

Use the electrons of an adjacent oxygen to help "push out" the leaving group, a neutral methanol molecule.

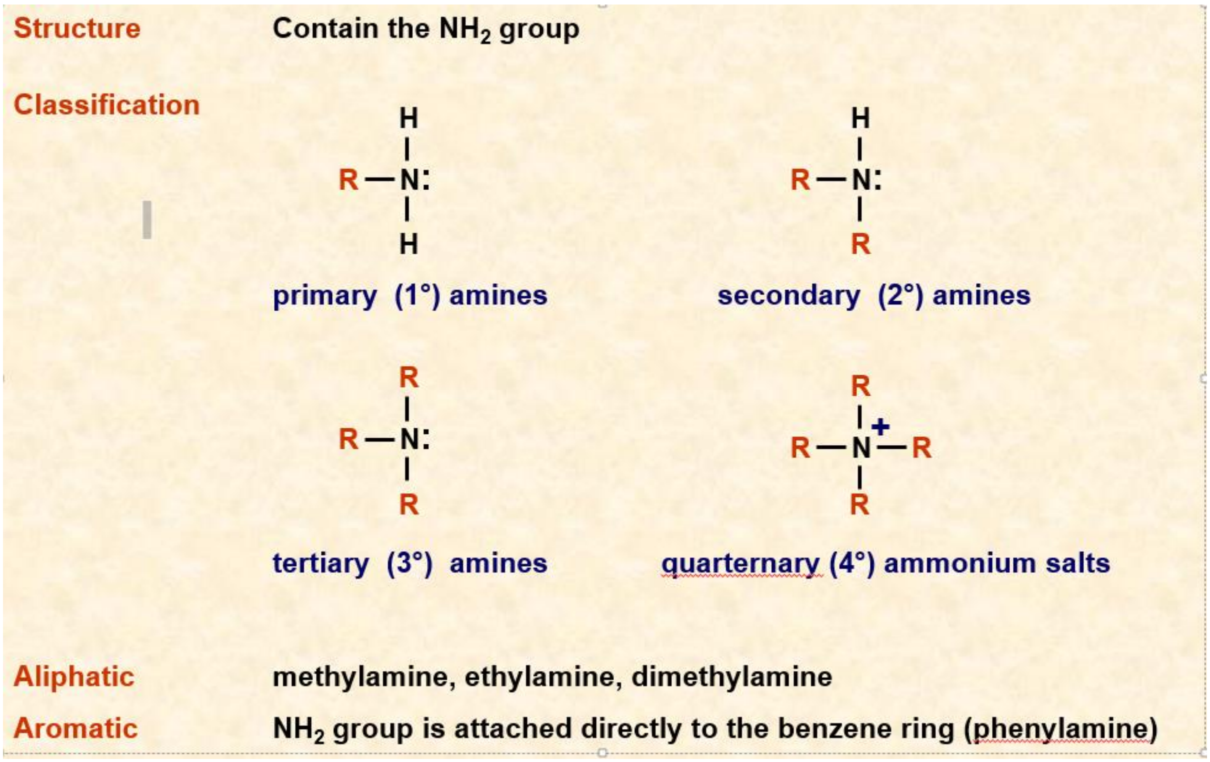
Step 6:

An acid/base reaction. Deprotonation of the oxonium ion reveals the carbonyl C=O in the carboxylic acid product and regenerates the acid catalyst.

6.2 Nitrogen compounds polymers and synthesis

Amines

Amines are derivatives of ammonia whereby one or more hydrogen atoms have been replaced by alkyl groups. Amines can be primary, secondary or tertiary depending on how many hydrogen atoms have been replaced.



Structure Contain the NH_2 group

Classification

primary (1°) amines

secondary (2°) amines

tertiary (3°) amines

quarternary (4°) ammonium salts

Aliphatic methylamine, ethylamine, dimethylamine

Aromatic NH_2 group is attached directly to the benzene ring (phenylamine)

Primary amines: One alkyl group is attached to the nitrogen atom.

Secondary amines: Two alkyl groups are attached to the nitrogen atom.

Tertiary amines: All three hydrogen atoms are replaced by alkyl groups.

Naming amines

The naming of amines is based around the length of the longest alkyl chain connected to the nitrogen atom. Below are some examples of amines:

Primary amine

$$CH_3CH_2CH_2CH_2NH_2$$

This is butylamine, a primary amine. The -butyl part comes from the four carbon alkyl group while the -amine part is due to the secondary amine group, NH2

Secondary amines

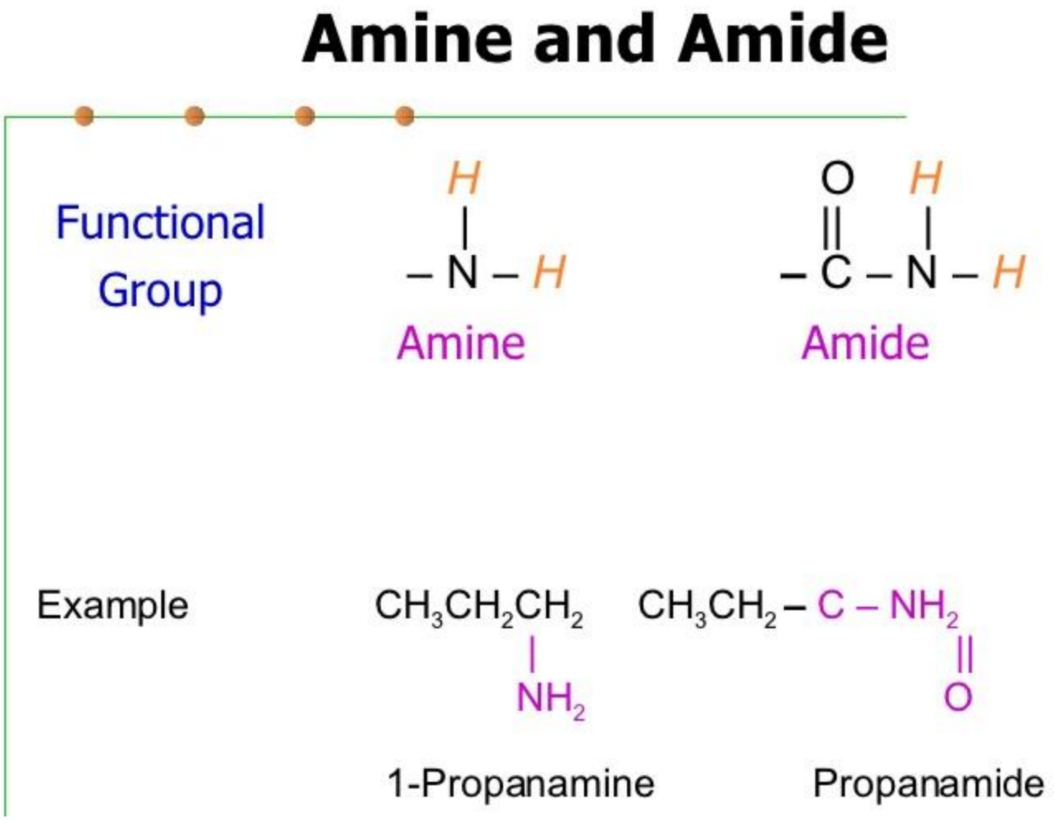
$$CH_3(CH_3CH_2CH_2)NH$$

This is N-methylpropylamine. The -propyl part comes from the longer three carbon chain while the -methyl part is from the other CH3 group. The preceding N indicates that the methyl group is attached to the nitrogen atom.

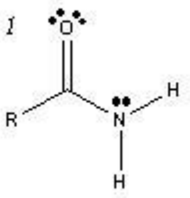
Tertiary amines

$$(CH_3CH_2)_2CH_3CH_2CH_2N$$

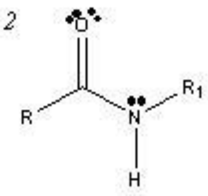
This is N,N-diethylpropylamine. The -propyl part comes from the longer three carbon chain while the diethyl is from the two ethyl groups connected to the nitrogen atom.



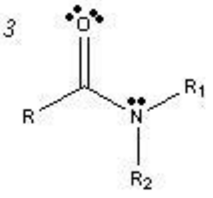
Types of amides

Fig. 1


Primary Amide

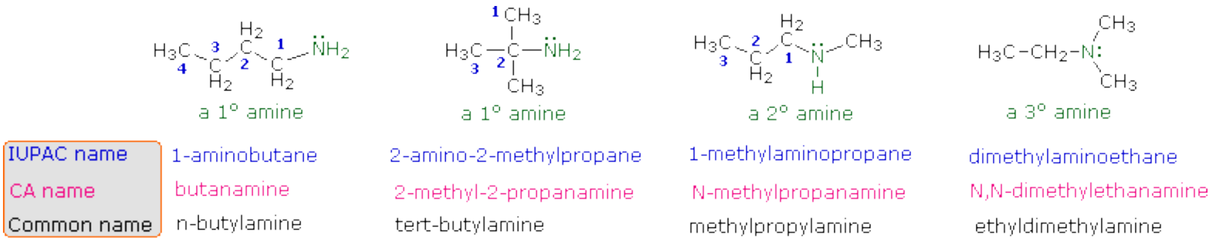
Fig. 2


Secondary Amide

Fig. 3


Tertiary Amide

Naming amines



	a 1° amine	a 1° amine	a 2° amine	a 3° amine
IUPAC name	1-aminobutane	2-amino-2-methylpropane	1-methylaminopropane	dimethylaminoethane
CA name	butanamine	2-methyl-2-propanamine	N-methylpropanamine	N,N-dimethylethanamine
Common name	n-butylamine	tert-butylamine	methylpropylamine	ethyldimethylamine

Reactions of primary aliphatic amines, using butylamine as an example, with:

i water to form an alkaline solution

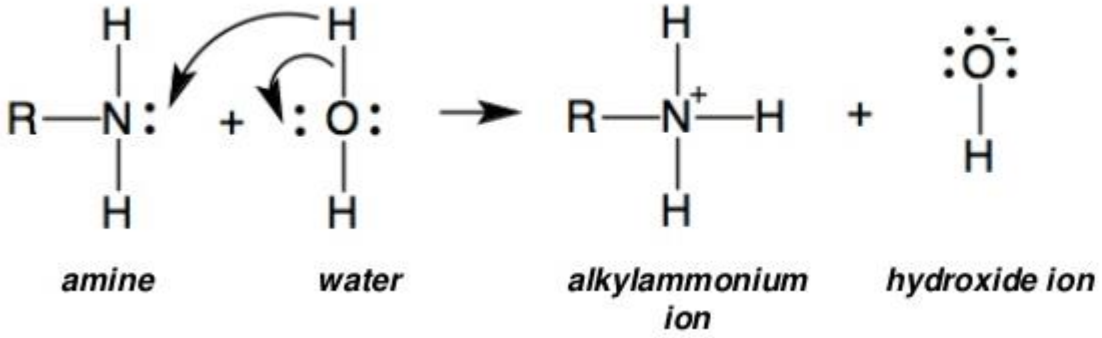
Amines react with water and act as weak bases in solution.

Butylamine does dissolve in water due to the NH2 group forming Hydrogen bonds with water. Butylamine solution is alkaline because the NH2 group accepts Hydrogen ions.

Equation:

$$C_4H_9NH_2 + H_20 \longrightarrow C_4H_9NH_3^+ + OH^-$$

Mechanism:



ii acids to form salts

Amines can react with acids to produce alkylammonium salts. For example, ethylamine can react with hydrochloric acid to form ethylammonium chloride.

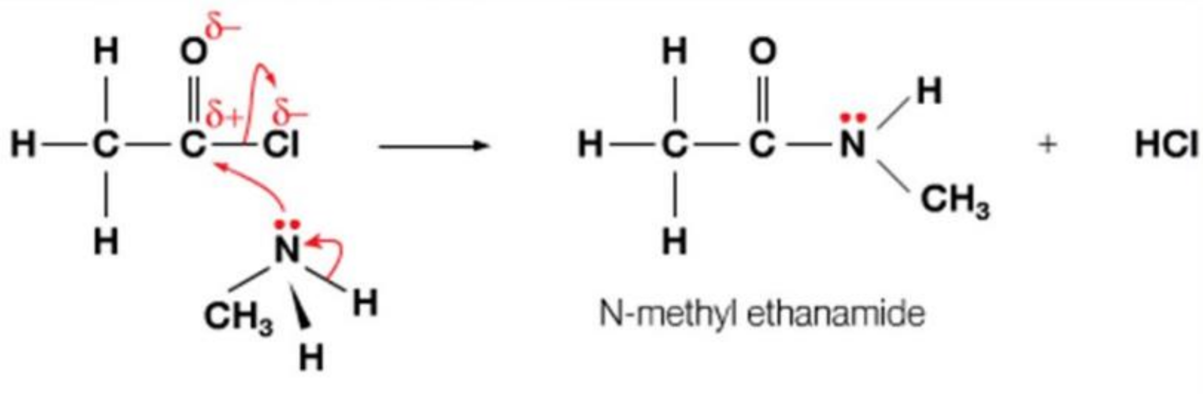
$$CH_3CH_2NH_{2(aq)} + HCl_{(aq)} \rightarrow CH_3CH_2NH_3^+Cl^-_{(aq)}$$

iii ethanoyl chloride

Ammonia and amines can act as nucleophiles in attacking the positive centres in molecules such as ethanoyl chloride, CH3COCl. This produces N-substituted amides

> When ethanoyl chloride is added an amide is formed and the gas HCl is vigourously given off. When ethanoyl chloride is added an amide is formed and the gas HCl is vigourously given off.

$$C_4H_9NH_2 + CH_3COCl \longrightarrow C_4H_9NHCOCH_3 + HCl$$



iv halogenoalkanes

Amines are also nucleophiles (lone pair on N) and can attack halogenoalkanes to produce a 2° amine. This too is a nucleophile and can react further producing a 3° amine and, eventually an ionic quarternary ammonium salt.

$C_2H_5NH_2 + C_2H_5Br \longrightarrow HBr + (C_2H_5)_2NH$ **diethylamine, 2° amine**

$(C_2H_5)_2NH + C_2H_5Br \longrightarrow HBr + (C_2H_5)_3N$ **triethylamine, 3° amine**

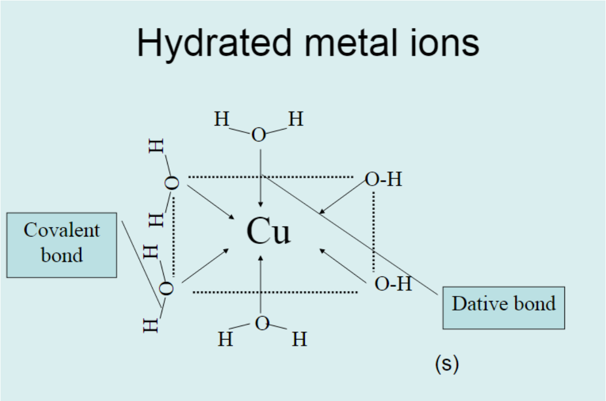
$(C_2H_5)_3N + C_2H_5Br \longrightarrow (C_2H_5)_4N^+ Br^-$ **tetraethylammonium bromide**

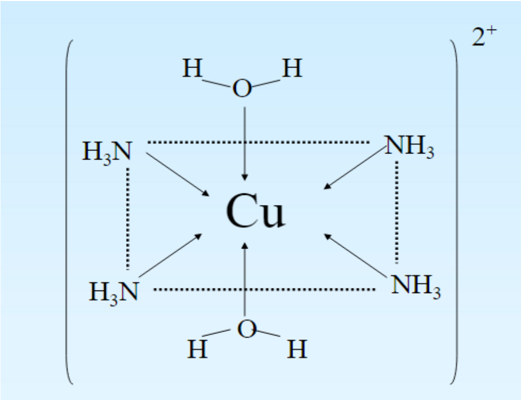
a quaternary (4°) salt

Uses **Quarternary ammonium salts with long chain alkyl groups are used as cationic surfactants in fabric softening e.g. [CH3(CH2)17]2N+(CH3)2 Cl⁻**

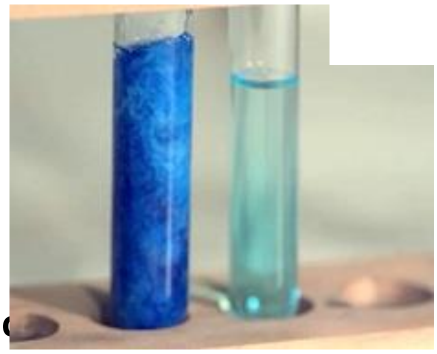
v copper(II) ions to form complex ions

A deep blue complex is formed when copper is added, $[Cu(C_4H_9NH_2)_4(H_20)_2]^{2+}$.

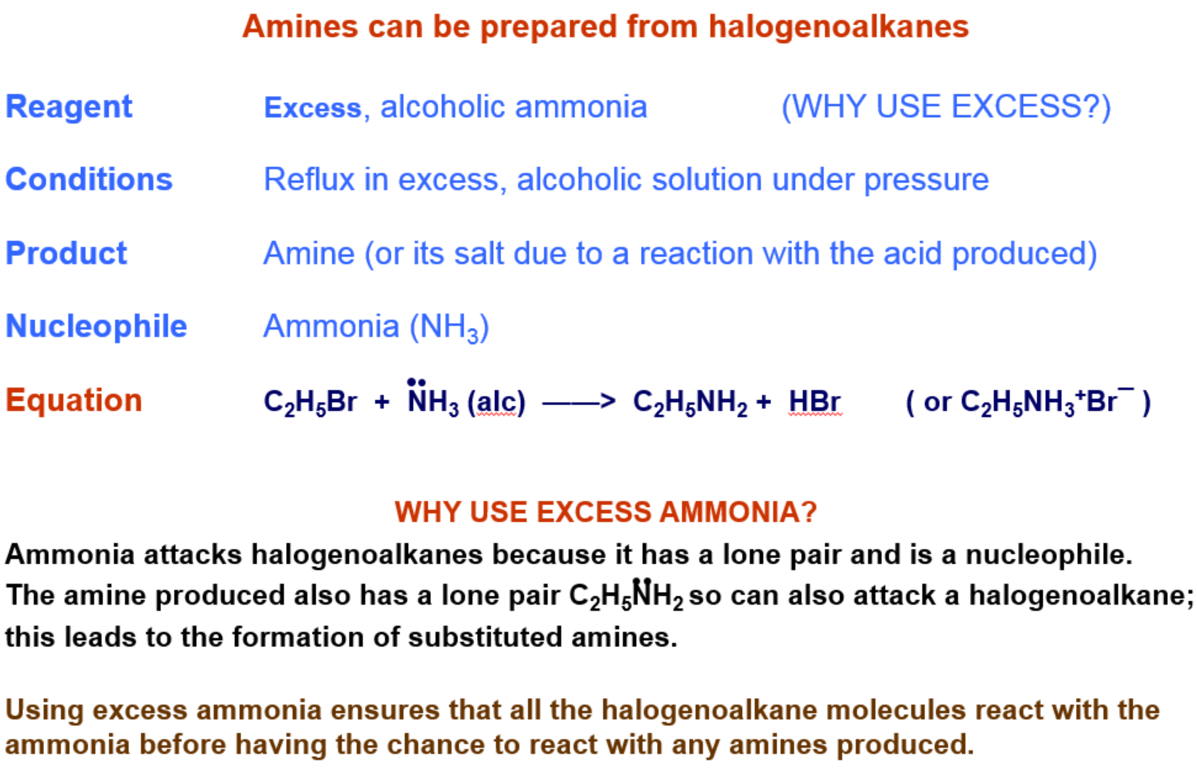




Amine complex ion



Preparation



Amines can be prepared from halogenoalkanes

Reagent	**Excess**, alcoholic ammonia (WHY USE EXCESS?)
Conditions	Reflux in excess, alcoholic solution under pressure
Product	Amine (or its salt due to a reaction with the acid produced)
Nucleophile	Ammonia (NH_3)
Equation	C_2H_5Br + $\ddot{N}H_3$ (alc) ——> $C_2H_5NH_2$ + HBr (or $C_2H_5NH_3^+Br^-$)

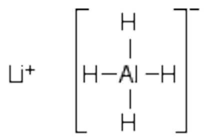
WHY USE EXCESS AMMONIA?

Ammonia attacks halogenoalkanes because it has a lone pair and is a nucleophile. The amine produced also has a lone pair $C_2H_5\ddot{N}H_2$ so can also attack a halogenoalkane; this leads to the formation of substituted amines.

Using excess ammonia ensures that all the halogenoalkane molecules react with the ammonia before having the chance to react with any amines produced.

Primary amines can be prepared by

- **Reduction of lithium tetrahydridoaluminate(III) (lithium aluminium hydride) or hydrogen and a metal catalyst.**



lithium tetrahydridoaluminate

The nitrile reacts with the lithium tetrahydridoaluminate in solution in ethoxyethane followed by treatment of the product of that reaction with a dilute acid.

$$CH_3CN + 4[H] \longrightarrow CH_3CH_2NH_2$$

- **The reduction of nitriles using hydrogen and a metal catalyst**

The carbon-nitrogen triple bond in a nitrile can also be reduced by reaction with hydrogen gas in the presence of a variety of metal catalysts such as palladium, platinum or nickel.

The reaction will take place at a raised temperature and pressure. For example, ethanenitrile can be reduced to ethylamine by reaction with hydrogen in the presence of a palladium catalyst. $CH_3CN + 2H_2 \xrightarrow{Pd} CH_3CH_2NH_2$

- **Aromatic nitro-compounds can be reduced, using tin and concentrated hydrochloric acid, to form amines**

e.g Nitrobenzene to phenylamine

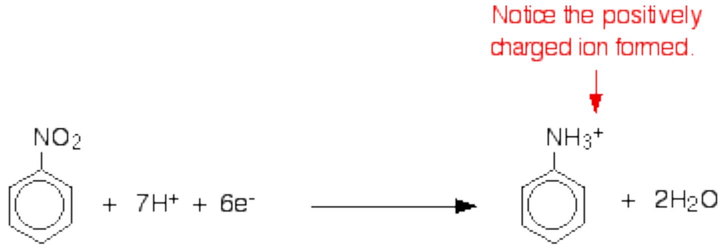
The conversion is done in two main stages:

Stage 1: conversion of nitrobenzene into phenylammonium ions

Nitrobenzene is reduced to phenylammonium ions using a mixture of tin and concentrated hydrochloric acid. The mixture is heated under reflux in a water bath.

Under the acidic conditions, phenylammonium ions are formed. The lone pair on the nitrogen in the phenylamine picks up a hydrogen ion from the acid.

The electron-half-equation for this reaction is:


Notice the positively charged ion formed.

The nitrobenzene has been reduced by gaining electrons in the presence of the acid.

The electrons come from the tin, which forms both tin(II) and tin(IV) ions.

$$Sn \longrightarrow Sn^{2+} + 2e^-$$

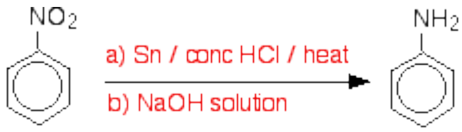
$$Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$$

Stage 2: conversion of the phenylammonium ions into phenylamine

All you need to do is to remove the hydrogen ion from the -NH3+ group.

Sodium hydroxide solution is added to the product of the first stage of the reaction.

Summary

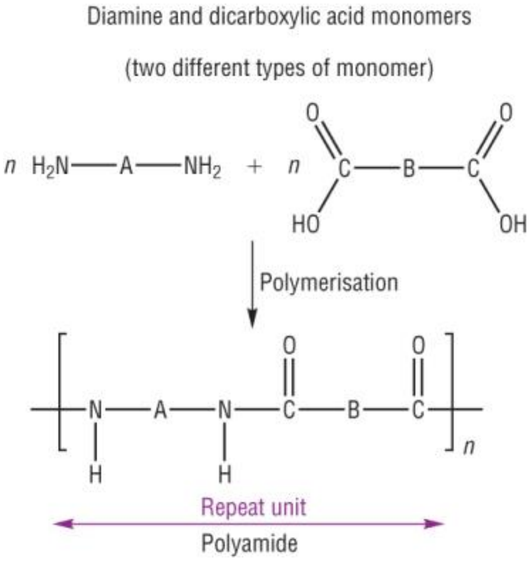


Polyamides

All polyamides are made by the formation of an amide function to link two molecules of monomer together. The monomers can be amides themselves

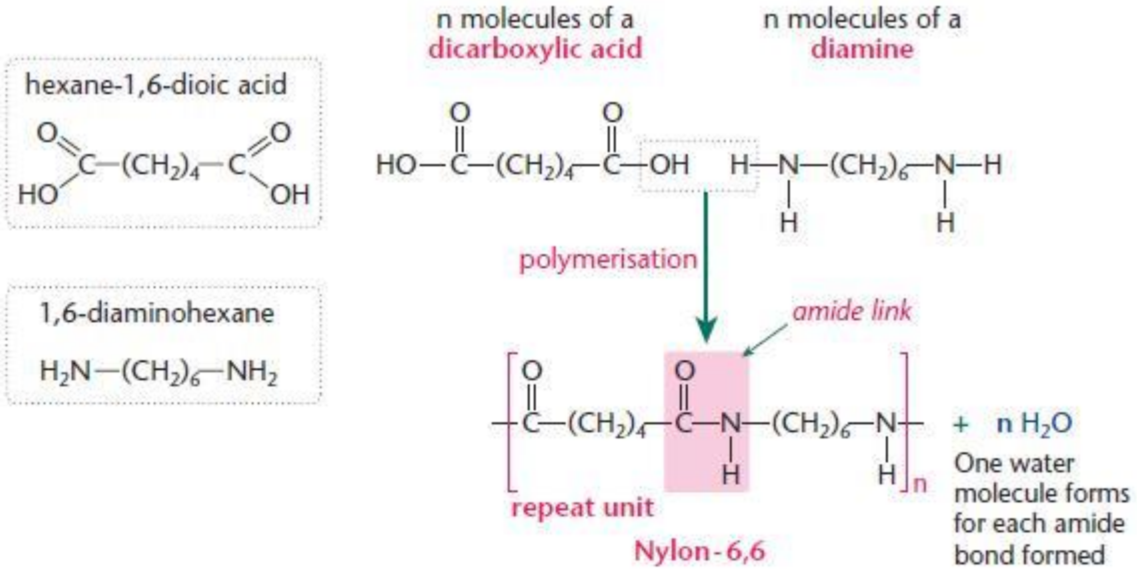
Polyamides such as nylon are also condensation polymers. The formation of a polyamide follows the same procedure as in the synthesis of a simple amide.

- **Dicarboxylic acids and diamines**



These are condensation polymerisation polymers

The diagrams below show how *nylon-6,6* is formed from its monomers.

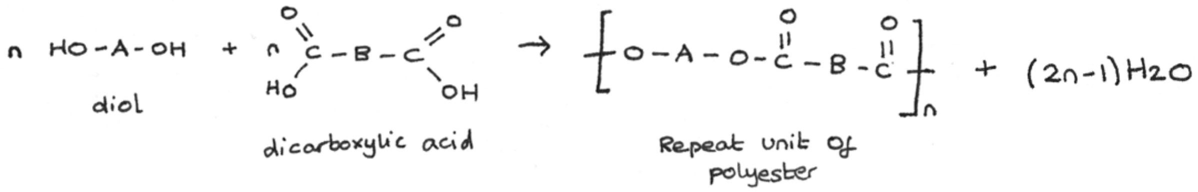


Polyamides can also be made using a diacyl chloride instead of a dicarboxylic acid.

- The greater reactivity of an acyl chloride results in easier polymerisation.
- Hydrogen chloride is lost instead of water.

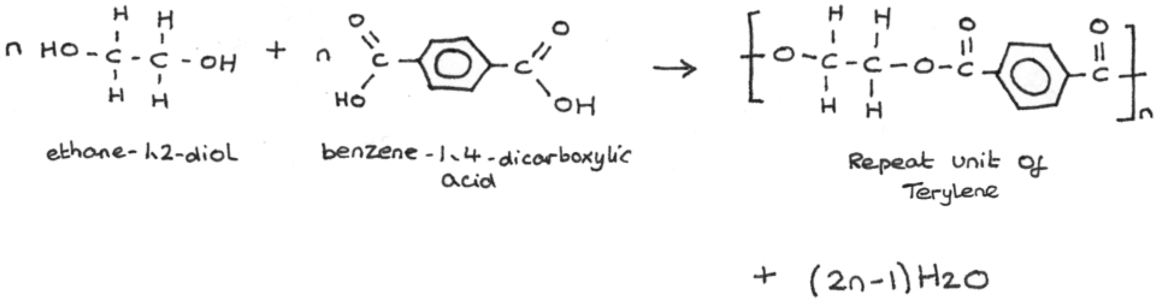
(ii) Dicarboxylic acids and diols

With this method, one monomer is a dicarboxylic acid with two −COOH groups while the other is a diol with two −OH groups. The general formation is shown below:



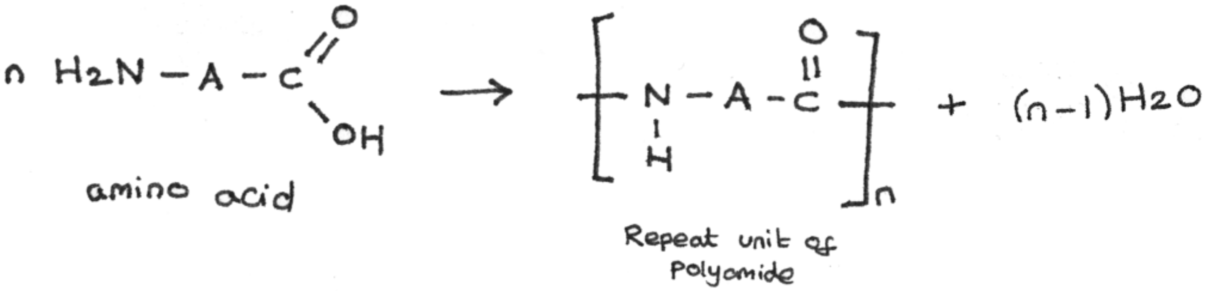
General formation of polyester from different monomer units.

An example of this condensation reaction is the formation of Terylene which is made from the monomers ethane-1,2-diol and benzene-1,4-dicarboxylic acid.



(iii) Amino acids

Polyamides can also be formed from amino acids, which contain both the amine group (−NH2) and a carboxyl group (−COOH). Polypeptides and proteins are polyamides formed from one type of monomer unit. The general formation is shown below:

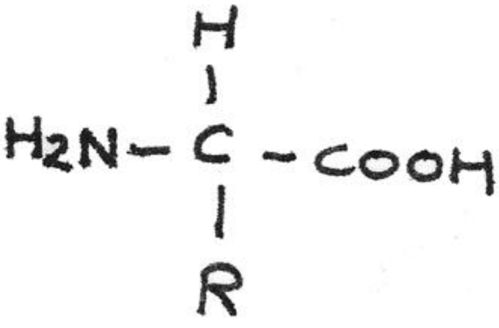


Amino acids

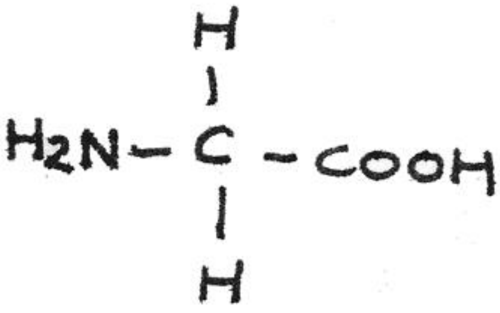
Amino acids are compounds which contain both an amine group (−NH2) and a carboxylic acid group (−COOH). They are important in the human body as they are building blocks for proteins and peptides. They also act as enzymes and antibodies.

α-amino acids

α-amino acids have a basic amine group and an acidic carboxyl group bonded to the same carbon atom. The general formula is RCH(HN2)COOH. The body has 20 amino acids that can be arranged to form proteins. The simplest α-amino acid is glycine which has a hydrogen atom as the −R group.



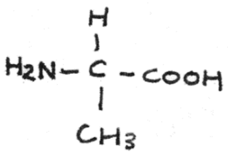
α-amino acid



glycine

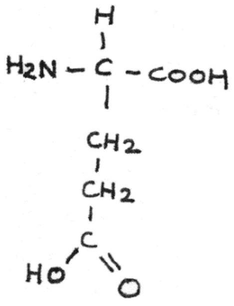
Other examples of α-amino acids include alanine (2-aminopropanoic acid) and glutamic acid (2-aminopentanedioic acid).

2-aminopropanoic acid



Alanine

2-aminopentanedioic acid

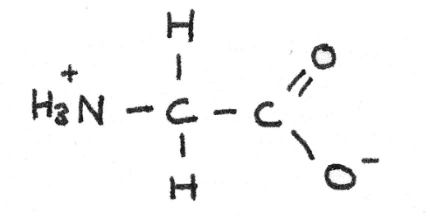


Glutamic acid

Zwitterions

The acidic carboxyl group and the basic amine group in an amino acid can interact with each other to form an internal salt known as a zwitterion. In this process:

- A proton is transferred from the acid carboxyl group to the basic amine group.
- The zwitterion has no overall net charge as the positive and negative charges cancel each other out.



zwitterion of glycine

Isoelectric point

The isoelectric point is the pH at which there is no net electrical charge. At this pH, a zwitterion is formed. Different amino acids have different isoelectric points. A higher isoelectric point indicates the $-R$ group may contain $-NH2$ while a lower isoelectric point could show the presence of a $-COOH$ group.

Acid and base properties

Amino acids are amphoteric, meaning they can react as an acid or a base.

- At a pH more acidic than the isoelectric point, the amino acid behaves as a base and accepts a proton from the acid. This results in a positively charged ion.

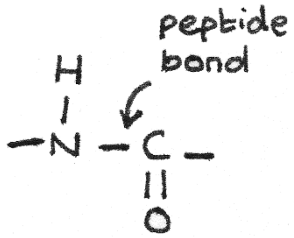
$$H_3^+NCH_2COO^- \rightarrow H_3^+NCH_2COOH$$

- At a pH less acidic than the isoelectric point, the amino acid behaves as an acid and donates a proton to the base. This results in a negatively charged ion.

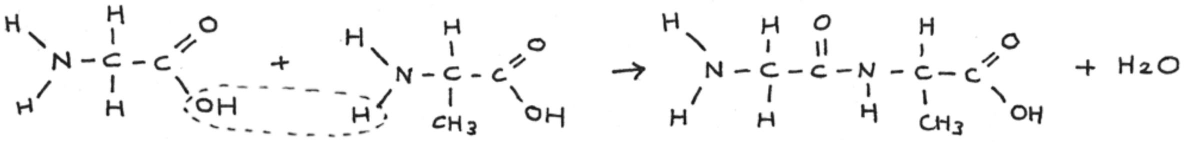
$$H_3^+NCH_2COO^- \rightarrow H_2NCH_2COO^-$$

Peptides

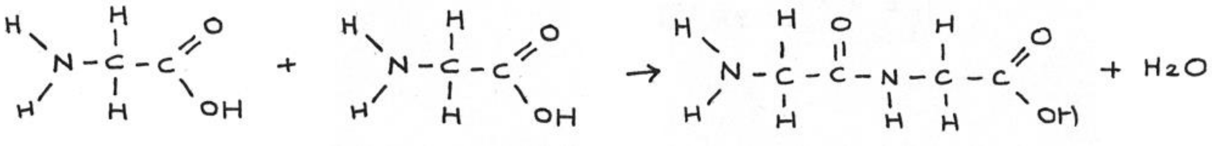
A peptide is a compound containing two or more amino acids joined by a peptide bond.



When two amino acids join together, a dipeptide is formed through the elimination of water in a condensation reaction.



It is also possible to form a dipeptide by reacting two of the same amino acids together. The amine group on one of the molecules reacts with the carboxyl group on the other.

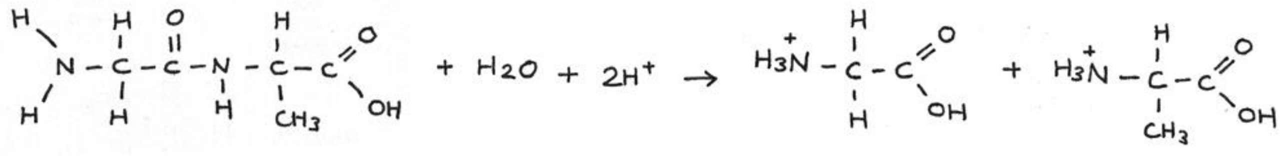


Polypeptides

A polypeptide is a long chain of amino acids joined together with peptide bonds. A polypeptide can be formed through a series of condensation reactions of amino acids. A dipeptide is a molecule formed from two amino acids joined by a single peptide bond.

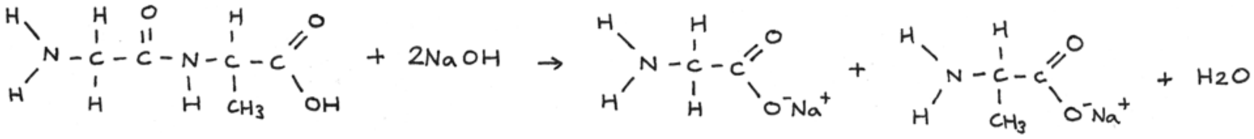
Acid hydrolysis

Polypeptides can be hydrolysed using aqueous acid. In this reaction the peptide bond is broken forming two positively charged amino acids. This reaction is traditionally carried out by heating under reflux with 6 *mol dm*−3hydrochloric acid for 24 hours.

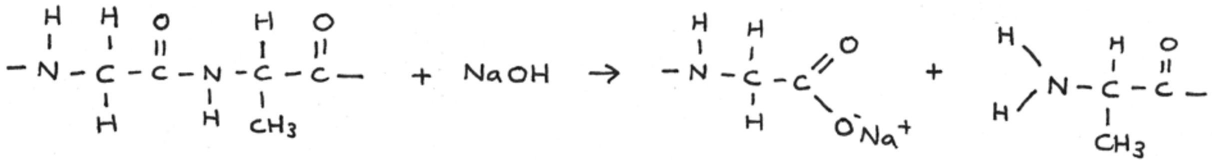


Alkaline hydrolysis

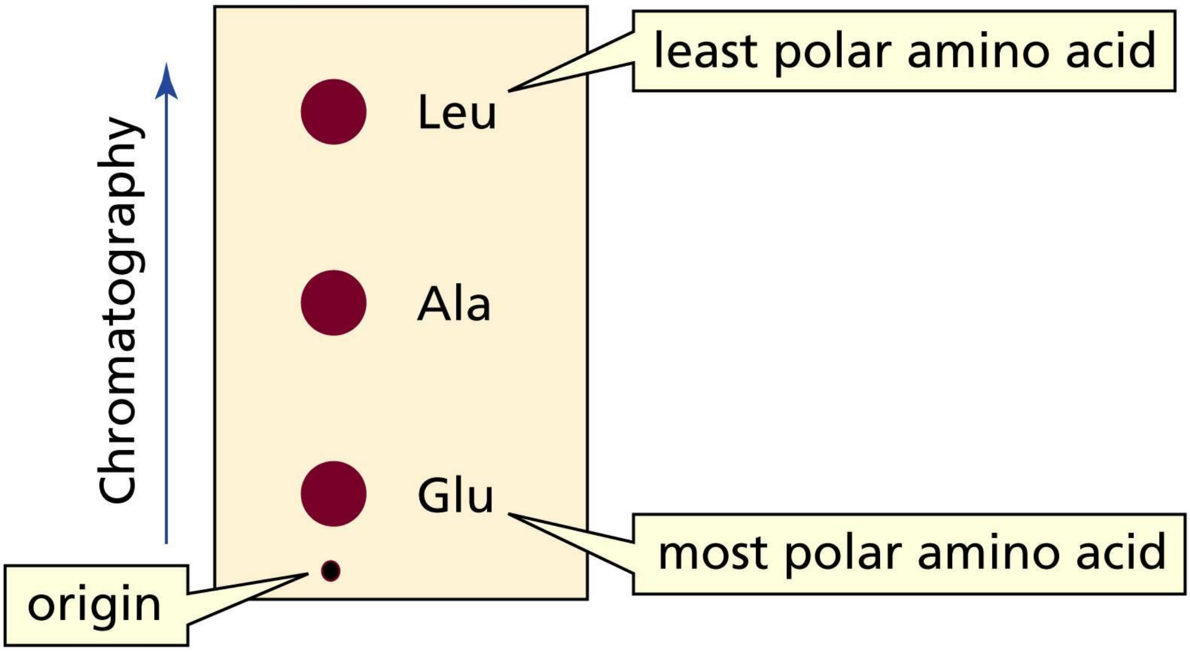
Polypeptides can be broken down through alkaline hydrolysis. A solution of sodium hydroxide can be used just above 100° C. In this reaction the polypeptide is broken down into salts.



In the reaction below a long amino acid chain is broken through alkaline hydrolysis.



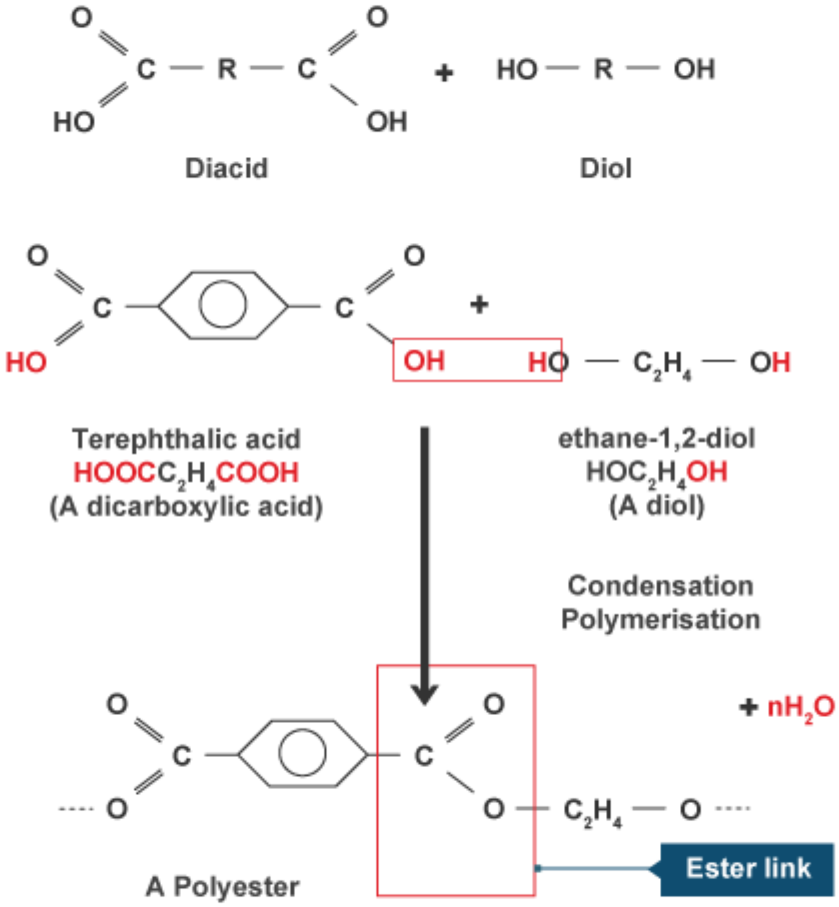
Polypeptides can be hydrolysed to form the constituent amino acids, which can be separated by chromatography



6.2.3 Polyester and polyamide formation by condensation polymerisation

A polyester is a polymer (a chain of repeating units) where the individual units are held together by ester linkages. A polyester is made by a reaction involving an acid with two -

COOH groups, and an alcohol with two -OH groups. Unlike addition polymerisation which involves monomers joining up with no by product condensation polymerisation produces small molecules such as water. Common polyesters are PET, Nylon and Terylene.



6.2.5 Organic Synthesis

Deducing empirical formulae, molecular formulae and structural formulae from data drawn from combustion analysis, elemental percentage composition, characteristic reactions of functional groups, infrared spectra, mass spectra and nuclear magnetic resonance

Combustion Analysis

You will be given the mass of the sample initially, mass of CO2 produced and mass of H2O produced:

1 – Calculate the mass of C and H produced.

2 – Subtract the mass of C & H from initial mass to find the mass of Oxygen produced.

3 – Calculate moles of C, H & O produced.

4 – Find the empirical formula by putting moles in a ratio.

Percentage Composition

Given the % of each element in the compound:

1 – Divide each percentage by the RAM of the element.

2 – Put the results into a ratio.

3 – Divide through by the smallest answer to give a simple whole number ratio.

% → % ÷ RAM → X:Y:Z

IR spectroscopy

- The wavenumber of different peaks correspond to different bonds absorbing energy in the molecule which can be looked up in a data book.

Mass spectroscopy

- Parent peak ion gives RMM of compound.

- Particularly abundant peaks show where a group of the compound has broken off.

NMR

- No. of peaks = No. of H environments.

- Splitting number shows 1 more than the number of adjacent H environments.

- Area beneath graph represents number of H's in that environment.

Functional Group	Test	Positive Result
C=C	-Bromine -$KMnO_4$ acidified	-Orange → Colourless -Purple → Colourless
-OH	-PCl_5 -Na	-Steamy Fumes -Fizzing
C=O (Aldehyde/Ketone)	Brady's Reagent	Yellow/Orange Precipitate
C=O (Aldehyde)	-Benedict's or Fehling's & heat -Tollens Reagent	-Blue → Brick Red Precipitate -Silver precipitate
-COOH	-Sodium Carbonate -Indicator	-Fizzing -Colour change
Carbonyl (*or alcohol*) adjacent to methyl	Iodoform reaction: Add Iodine and NaOH then warm	Pale yellow precipitate and faint medical smell
Amino Acid	Ninhydrin	Goes Purple
High C:H ratio	Combustion	Smokey flame
-Cl -Br -I	Nitric acid & silver nitrate solution	- White precipitate - Cream precipitate - Yellow precipitate
Ester	Smell	Fruity
Hydrogen	Lit Splint	Squeaky pop
Ammonia	HCl	White smoke
NO_2	Appearance	Brown gas
CO_2	Limewater	Goes Cloudy
Cl_2	Litmus paper	Bleached white
Oxygen	Glowing splint	Relights

Identifying appropriate control measures to reduce risk during a synthesis based upon data of hazards

Hazard is the potential of a substance to cause harm.

Risk is the likelihood of it actually harming you.

For example $K_2Cr_2O_7$ is highly toxic and carcinogenic so it is very hazardous. But it was used in breathalysers in a sealed tube so the risk to the subject was very low.

Some precautions that can be taken are to:

- Use a fume cupboard to vent harmful gases.

- Reduce the scale of working so if something goes wrong, adverse effects are minimised.

- Look for an alternative route of synthesis.

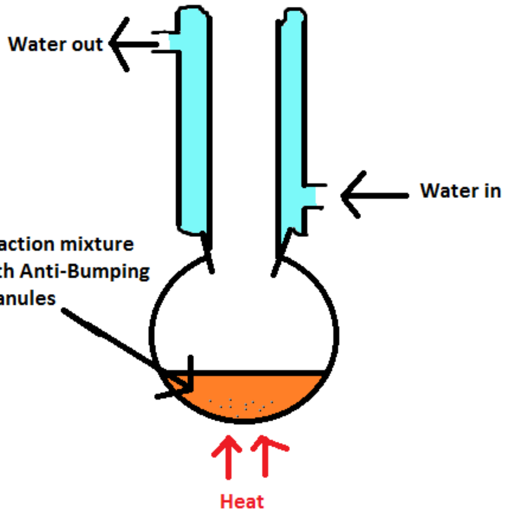
- Replace a reactant for a safer one with similar chemical properties.

Common hazards:

- Corrosive
- Flammable
- Toxic
- Caustic
- Carcinogenic
- Explosive

– Refluxing

Use a condenser while heating to minimise the loss of product while allowing the reaction to go to completion.



2 - Purification by washing, eg with water and sodium carbonate solution

This is a method of purification that can for example clean a non-polar product with a polar solvent.

Na_2CO_3 can absorb any excess acid and water can dissolve any water soluble impurities (like sodium salts).

3 - Solvent extraction

Separating funnels can be used to separate immiscible liquids. Different solvents are added to dissolve the product in them and then separated out at the bottom of the funnel.

4 - Recrystallization

- Dissolve impure crystals in the minimum amount of hot solvent possible (this creates a saturated solution so the crystals are more likely to re-precipitate out).
- Cool and put through Buchner funnel.
- Rinse with ice cold water (this rinses off any insoluble purities stuck to the surface).
- Dry the product.

5 - Drying

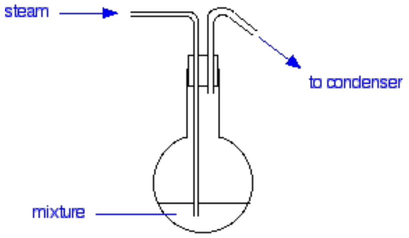
Can be done in an oven or padded using filter paper to remove liquid from crystals etc. Alternatively use anhydrous $CaCl_2$ to absorb any water.

6 - Distillation

Used to separate mixtures with different boiling points; requires thermometer and Liebig condenser.

7 - Steam distillation

It is used to separate organic products which might otherwise decompose from sustained heating.

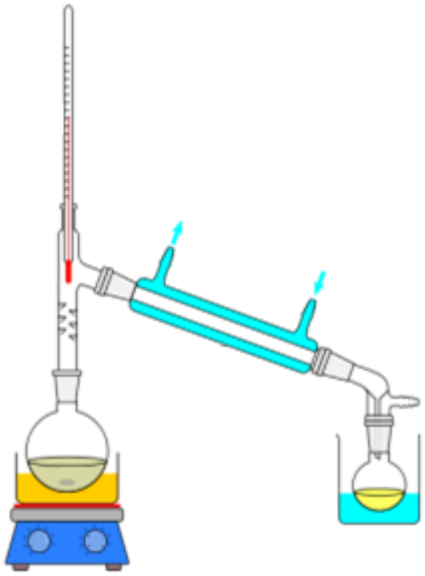


8 - Melting temperature determination

Put crystal sample into capillary tube and place into melting point apparatus to find it out.

9 - Boiling temperature determination.

Use distillation apparatus to determine the BP.



10 (Extra) - Shaking

Shaking mixtures can expose them to the air and so in some cases this is enough to cause oxidation from Oxygen in the air.

Reactions in organic synthesis

Creating C-C bonds:

- Nucleophilic Addition to an aldehyde with HCN and a KCN catalyst: Changes =O to –OH and adds on a C≡N.

- Friedel-Crafts reaction: Benzene reacts with a halogenoalkane for alkylation or acyl chloride for acylation. Both use an $AlCl_3$ catalyst.

Reduction:

- $LiAlH_4$ dissolved in dry ether reduces carbonyls and carboxylic acids to alcohols.

- Sn & conc. HCl reduces $–NO_2$ to $–NH_2$

Oxidation:

-$Na_2Cr_2O_7$ and sulphuric acid oxidise to carbonyls or carboxylic acids. Colour change from orange to green.

Making –OH Groups:

- Adding $KMnO_4$ to alkenes will create 2 –OH groups around where the double bond was.

You also observe a colour change from purple to colourless.

Adding on Halogens:

- A diatomic halogen molecule or a hydrogen halide will react with alkenes to add on 2 or 1 halogen respectively. (Remember Markovnikov's rule with HX)

- Alcohol/Carboxylic acids and PCl_5 adds –Cl in place of –OH & gives off steamy fumes of HCl.

- Halogens with an $FeBr_3$ catalyst will substitute halogens onto a benzene ring.

Adding on a Nitrogen Group:

- Conc. HNO_3 & conc. H_2SO_4 refluxed with benzene will substitute an NO_2 group on.

- Acyl Chloride and ammonia or carboxylic acid and ammonium carbonate will make an amide group.

- Reducing a nitrile with $LiAlH_4$ and then adding a weak acid produces amines.

- NH_3 and halogenoalkanes → NH_2 replaces the halogens.

Esterification:

- Add an alcohol to a carboxylic acid or acyl chloride (with an acid catalyst like H_2SO_4) to get a condensation reaction resulting in an ester.

Hydrogenation:

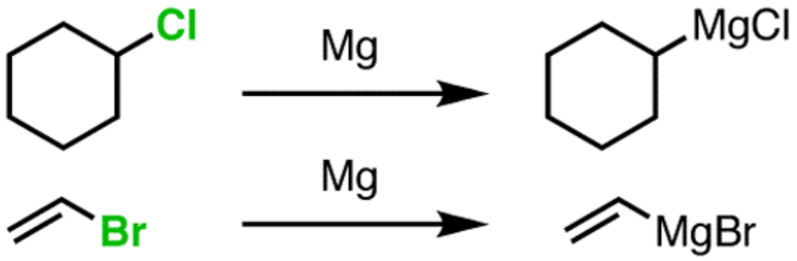
- Benzene and alkenes both have an addition reaction when Hydrogen is added in the presence of a Nickel catalyst.

Grignard reagents

Grignard reagents are formed by the reaction of magnesium metal with alkyl or alkenyl halides. They're extremely good nucleophiles, reacting with electrophiles such as carbonyl compounds (aldehydes, ketones, esters, carbon dioxide, etc) and epoxides. They’re also very strong bases and will react with acidic hydrogens (such as alcohols, water, and carboxylic acids).

Grignard reagents are made through the addition of magnesium metal to alkyl or alkenyl halides. The halide can be Cl, Br, or I (not F). It’s slightly easier to make Grignards from the iodides and bromides

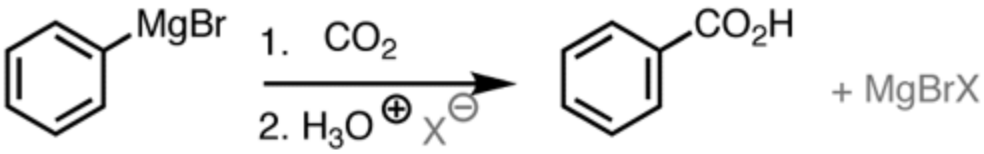
Example 1: Formation of Grignard reagents



Grignards can be formed from alkyl or alkenyl chlorides, bromides or iodides (never fluorides)

Reactions of Grignard reagents

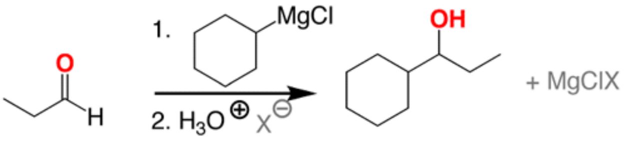
- With Carbon dioxide to make carboxylic acids



Grignard reagents also add to carbon dioxide (CO2) to form carboxylates, in a reaction similar to their reactions with ketones and aldehydes. The carboxylates are converted to carboxylic acids after addition of acid.

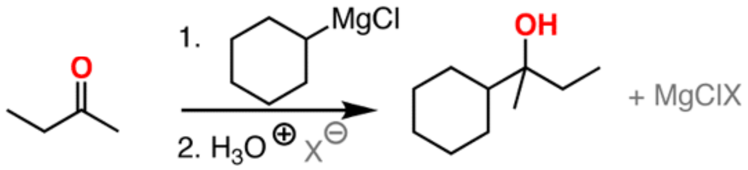
- Reaction with Carbonyl compounds such as ketones, aldehydes and esters

Reaction with aldehydes to form secondary alcohols

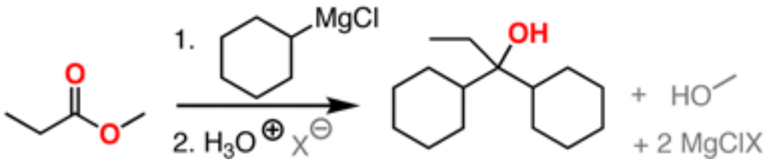


Acid is added in the second step to protonate the negatively charged oxygen

Example 3: Reaction with ketones to form tertiary alcohols



Example 4: Reaction with esters to give tertiary alcohols



Grignard reagents add twice to esters, acid halides, and anhydrides

Reaction with acid halides to give tertiary alcohols

Grignard reagents add twice to esters, acid halides, and anhydrides

6.3.1 Chromatography

Chromatography is a technique by which different compounds in a mixture can be separated and then analysed.

1) Principles of separation

Chromatography always involves moving a solvent (called the mobile phase) along or through a solid or viscous liquid (called the stationery phase). Different components of the mixture have different tendencies to adsorb onto (or dissolve in) the stationery phase, and hence move through the apparatus at different speeds relative to the mobile phase. This is how the components are separated.

There are three main types of chromatography:

- **thin-layer chromatography**
  In thin-layer chromatography a liquid solvent is allowed to flow up a piece of TLC plate coated with a solid. The mixture is placed in a small area on the plate and allowed to flow up the plate with the solvent. The distance travelled by a component compared to the solvent is called the **retention factor** and can be used to identify the component.

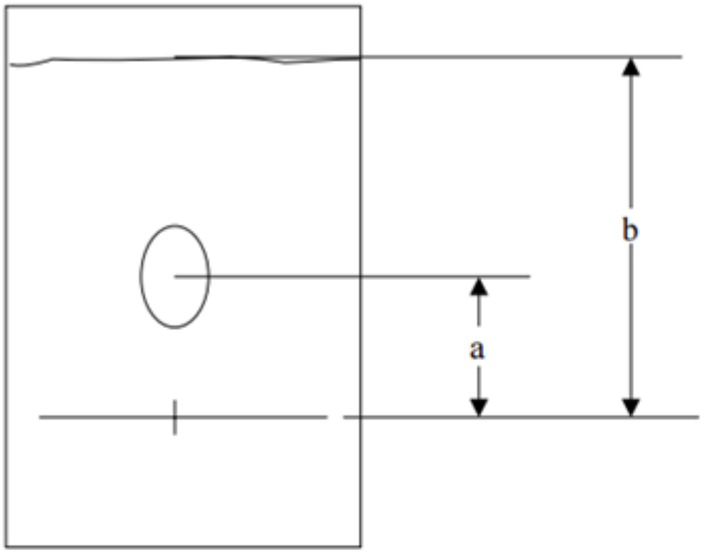
- **column chromatography**
  In column chromatography a column is packed with a solid and a solvent moves down the column. The component is added to the solvent at the top of the column. The time it takes for a component to exit the base of the column is called the **retention time** and can be used to identify the component

- **gas chromatography**
  In gas chromatography a gaseous mixture is allowed to flow, under pressure and at high temperature, through a column lined with a solid or a solid coated with a liquid. Volatile liquids can also be vaporised and then allowed to flow through the column. The time it takes for a component to exit the column is called the **retention time** and can be used to identify the component.

The separation of the components depends on the balance between its solubility in the mobile phase and its retention by the stationary phase. A component which is highly soluble in the mobile phase and not well retained by the stationery phase will have a high **retention factor** and a small **retention time**. A component which is not very soluble in the mobile phase and well retained by the stationery phase will have a low **retention factor** and a high **retention time**.

The retention factor can be calculated from the chromatogram produced on the TLC plate after the experiment. It is defined as:

$$\frac{\text{distance moved by component}}{\text{distance moved by solvent front}}$$



Measure the distance from the starting point to the center of the spot on the TLC plate (distance a).

Measure the distance from the starting point to the solvent front (distance b).

Calculate the Retention Factor as:

$$R_f = \frac{a}{b}$$

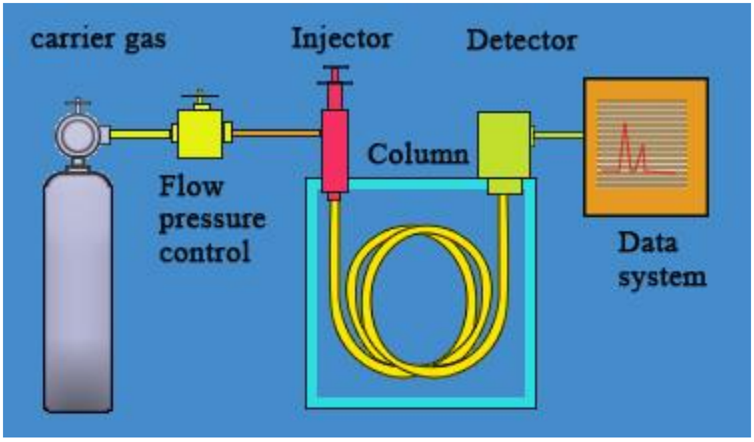
High Performance Liquid Chromatography, HPLC, and Gas Chromatography, GC

GC

All forms of chromatography involve a stationary phase and a mobile phase. In all the other forms of chromatography you will meet at this level, the mobile phase is a liquid. In gas-liquid chromatography, the mobile phase is a gas such as helium and the stationary phase is a high boiling point liquid adsorbed onto a solid.

How fast a particular compound travels through the machine will depend on how much of its time is spent moving with the gas as opposed to being attached to the liquid in some way.

Diagram



Stages in gas chromatography

Very small quantities of the sample that you are trying to analyse are injected into the machine using a small syringe. The syringe needle passes through a thick rubber disc (known as a septum) which reseals itself again when the syringe is pulled out.

The injector is contained in an oven whose temperature can be controlled. It is hot enough so that all the sample boils and is carried into the column as a gas by the helium (or other carrier gas).

The column is packed with finely ground diatomaceous earth, which is a very porous rock. This is coated with a high boiling liquid - typically a waxy polymer.

The temperature of the column can be varied from about 50°C to 250°C. It is cooler than the injector oven, so that some components of the mixture may condense at the beginning of the column.

How separation works on the column

One of three things might happen to a particular molecule in the mixture injected into the column:

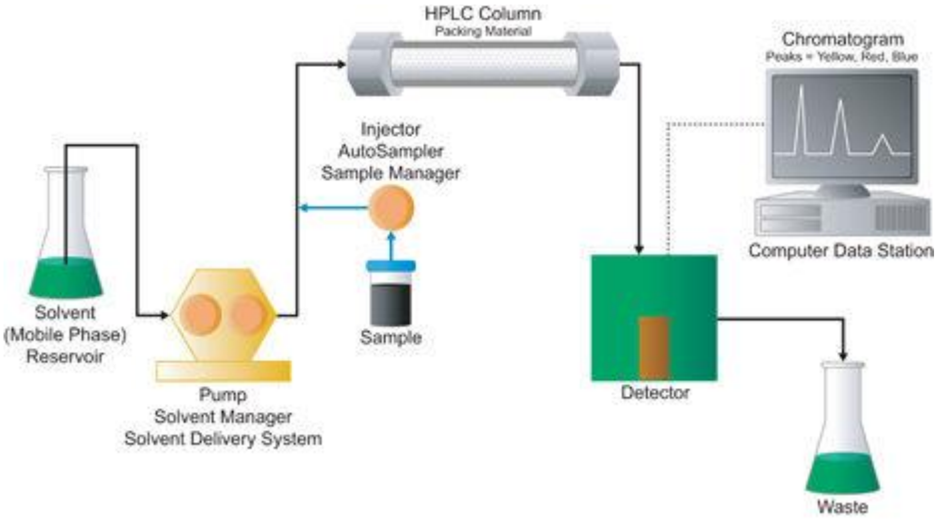
- It may condense on the stationary phase.
- It may dissolve in the liquid on the surface of the stationary phase.
- It may remain in the gas phase.

The time taken for a particular compound to travel through the column to the detector is known as its ***retention time***. This time is measured from the time at which the sample is injected to the point at which the display shows a maximum peak height for that compound.

Different compounds have different retention times. For a particular compound, the retention time will vary depending on:

- the boiling point of the compound. A compound which boils at a temperature higher than the column temperature is going to spend nearly all of its time condensed as a liquid at the beginning of the column. So high boiling point means a long retention time.
- the solubility in the liquid phase. The more soluble a compound is in the liquid phase, the less time it will spend being carried along by the gas. High solubility in the liquid phase means a high retention time.
- the temperature of the column. A higher temperature will tend to excite molecules into the gas phase - either because they evaporate more readily, or because they are so energetic that the attractions of the liquid no longer hold them. A high column temperature shortens retention times for everything in the column.

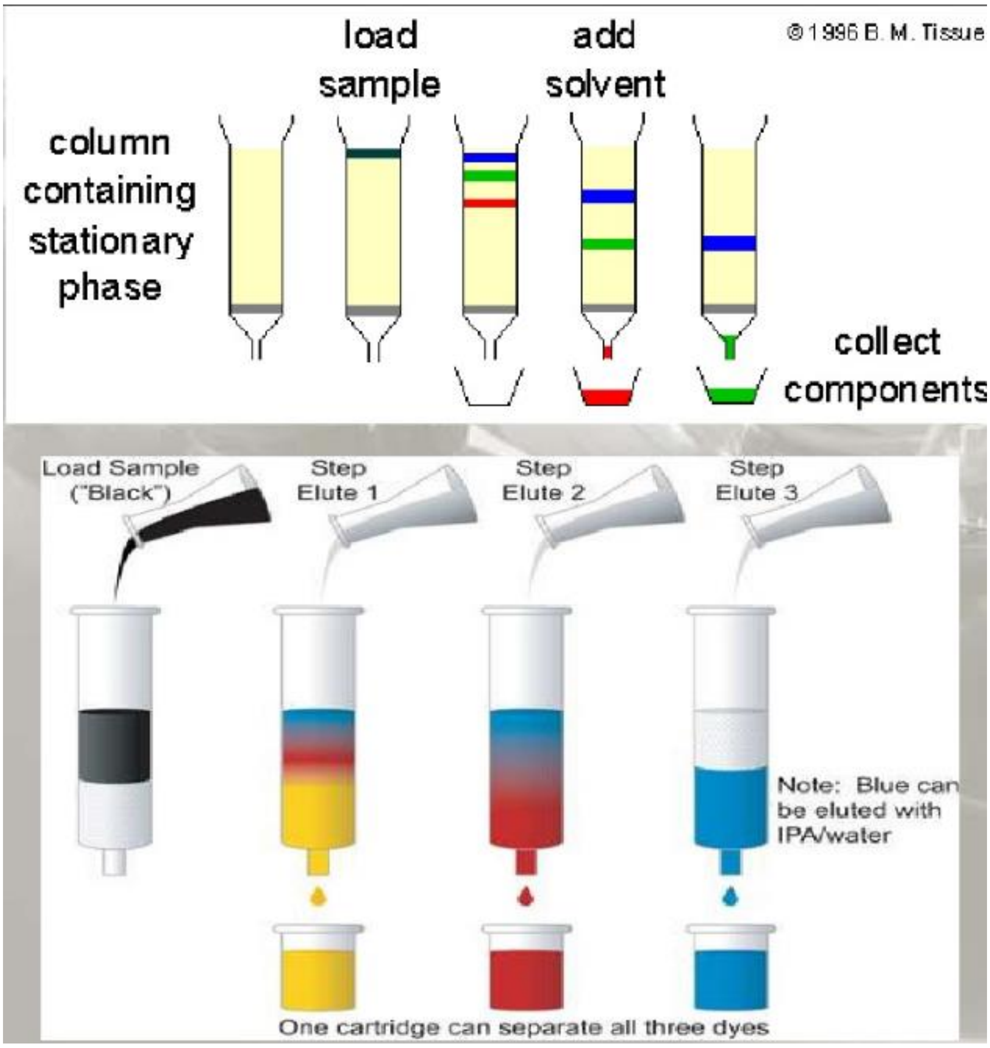
HPLC



HPLC is a type of liquid chromatography used to separate a mixture of compounds. The sample is forced through a column packed with a stationary phase composed of irregularly shaped particles and a porous membrane at high pressure.

When a mixture of compounds is introduced to the column, the molecules interact with the column packing according to their affinities and they then travel to the stationary phase. A compound with less affinity towards the stationary phase travels faster.

The compounds are therefore separated.



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Note: Blue can be eluted with IPA/water

One cartridge can separate all three dyes

HPLC is faster, more efficient, highly sensitive and easier than standard liquid chromatography.

HPLC and GC may be used in conjunction with mass spectrometry, in applications such as forensics or drugs testing in sport

6.3.2 Spectroscopy

Mass Spectrometry

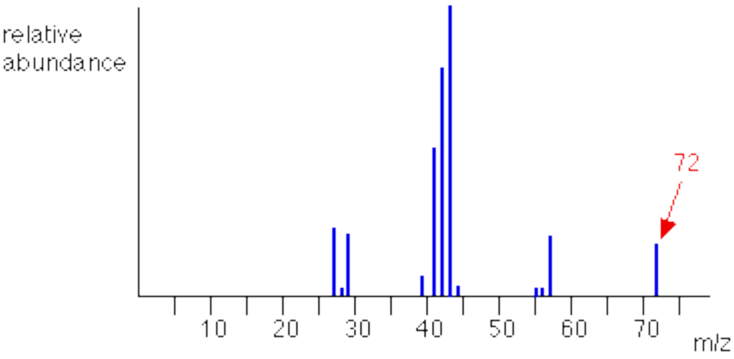
Working out relative molecular mass of compounds

Vaporised organic samples are passed through the ionisation chambers of the mass spectrometer and this allows electrons to knock an electron off the organic molecule. The organic molecule forms a positive ion called the **molecular ion**

Molecular ions can then be used to find relative formula mass

In the mass spectrum, the heaviest ion (the one with the greatest m/z value) is likely to be the molecular ion.

simplified mass spectrum of pentane - $CH_3CH_2CH_2CH_2CH_3$



In the spectra peaks above, he largest value is **72** so an assumption is made that this is the molecular ion and therefor the **relative formula mass** of the sample.

Getting more accurate results:

High resolution mass spectrometers can be used to get more accurate relative isotoic masses to 4 decimal points. For example:

^{1}H	1
^{12}C	12
^{14}N	14
^{16}O	16

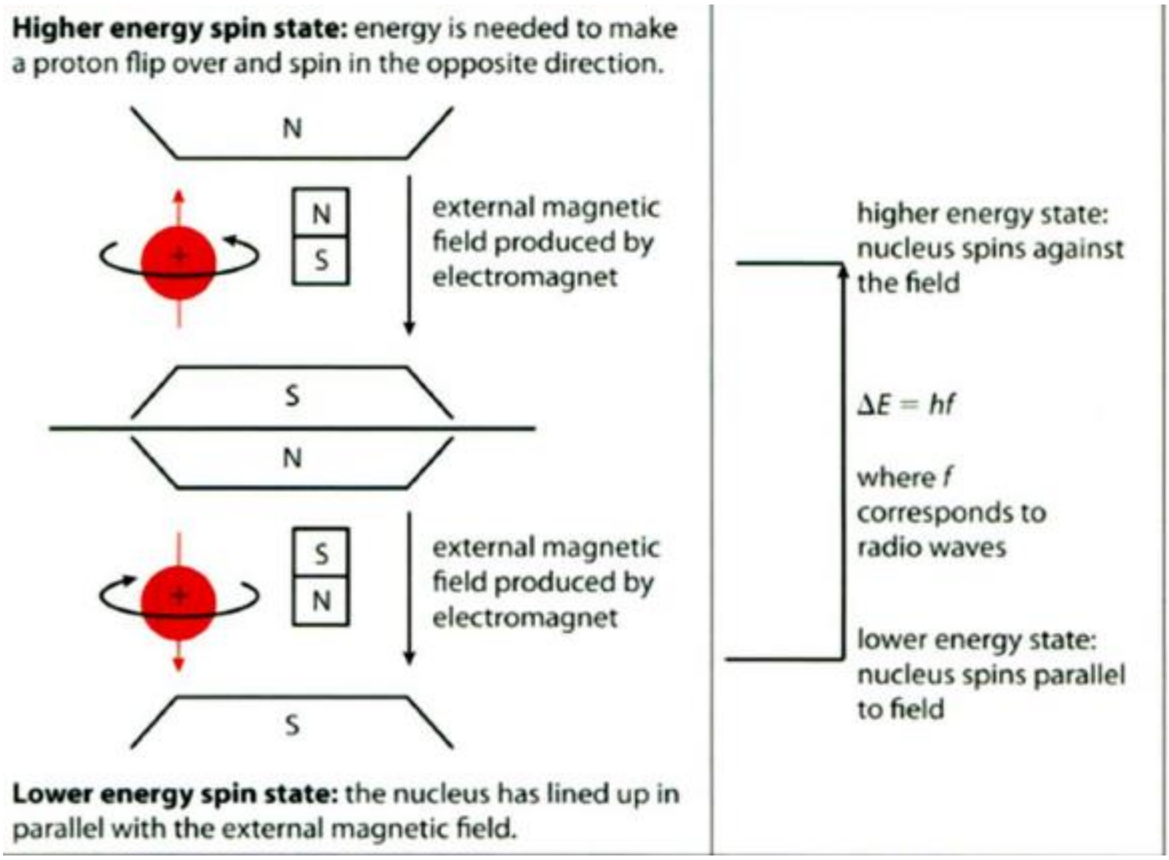
→

^{1}H	1.0078
^{12}C	12.0000
^{14}N	14.0031
^{16}O	15.9949

Using accurate isotopic masses will aid differentiation between rounded up relative formula masses of compounds.

Nuclear magnetic resonance (NMR)

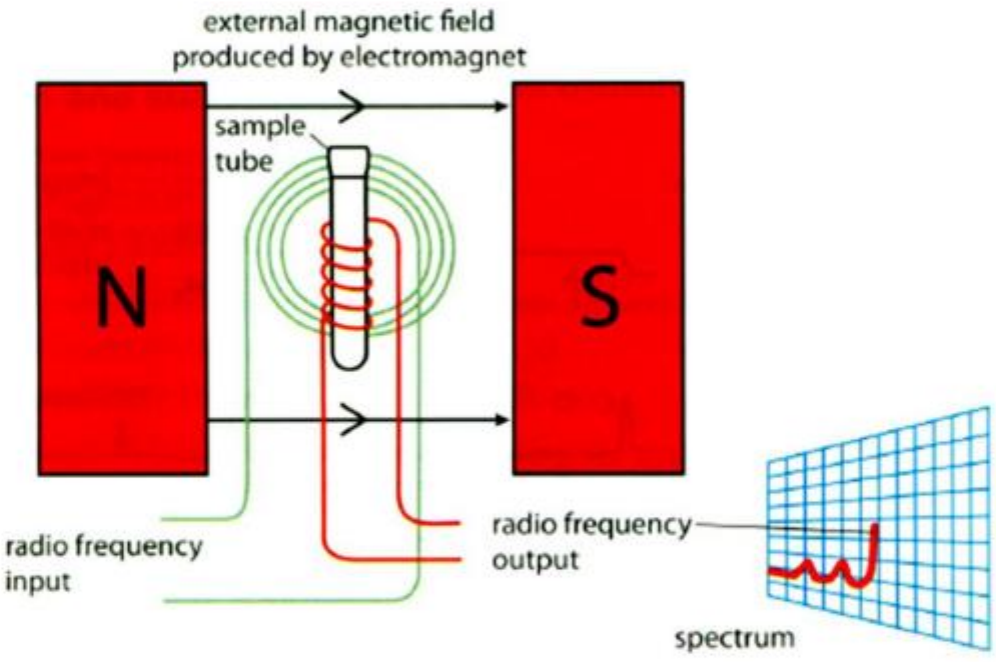
Nuclear magnetic resonance spectroscopy, a powerful technique for finding the structure and shape of molecules, depends on a combination of nuclear physics and chemistry. The nuclei of atoms with an odd number of protons such as 1H, 13C, 19F, and 31P, spin and behave like tiny bar magnets. If placed in an external magnetic field, some of these nuclei will line up with an applied field and, if they have sufficient energy, some will line up against it. This arrangement leads to two nuclear energy levels; the energy needed for the nuclei to reverse their spin and change their orientation in a magnetic field can be provided by radio waves.



Higher energy spin state: energy is needed to make a proton flip over and spin in the opposite direction.

Lower energy spin state: the nucleus has lined up in parallel with the external magnetic field.

In practice, a sample is placed in an electromagnet. The field strength is varied until the radio waves have the exact frequency needed to make the nuclei flip over and spin in the opposite direction. This is called **resonance** and can be detected electronically and recorded in the form of a spectrum.



C-13 NMR

Naturally-occurring carbon is composed of 98.9% 12C and 1.1% 13C (along with extremely small, and variable, amount of 14C). Although the 12C : 13C ratio is very small for compounds like methane which contain just one carbon atom, the ratio increases in proportion to the number of carbon atoms, as the chances of a molecule containing at least one 13C atom increase

13C NMR spectroscopy provides information about the positions of 13C atoms in a molecule

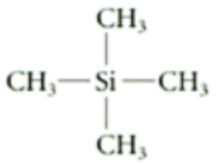
Data from 13C NMR spectroscopy can be used to:

i predict the different environments for carbon atoms present in a molecule, given values of chemical shift, δ

The chemical shift

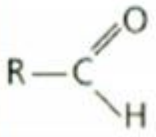
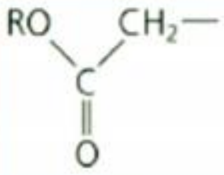
As electrons shield the nucleus from the full effects of external magnetic field, differences in electron distribution produce different energy separations between the two spin energy levels. The technique is a very useful analytical tool, as nuclei in different chemical environments produce different signals in the spectrum.

Proton or 1H NMR is particularly useful. The hydrogen nuclei, present in all organic molecules, effectively act as spies and give information about their position in a molecule. The signals are measured against the standard signal produced by the 12 hydrogen nuclei in tetramethylsilane (TMS), the structure of which is shown below:



$$\begin{array}{ccc} & CH_3 & \\ & | & \\ CH_3- & Si & -CH_3 \\ & | & \\ & CH_3 & \end{array}$$

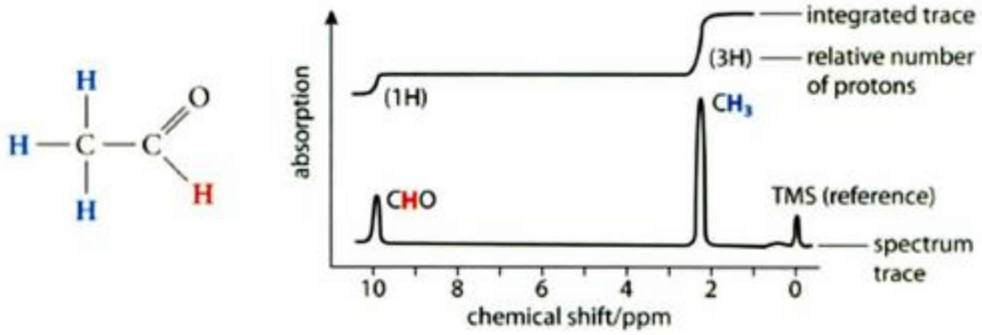
The position of the NMR signal relative to this standard is called the chemical shift of the proton. Hydrogen nuclei in particular environments have characteristic chemical shifts. Some examples are given in the table below.

Type of proton	Chemical shift/ppm
TMS	0
R—CH_3	0.9–1.0
	9.4–10.0
	2.2–2.7
R—OH	4.0–12.0*
R—CH_2—O	3.5–3.7
R—CH_2—R	1.3–1.4

ii justify the number of peaks present in a 13C NMR spectrum because of carbon atoms in different environments

Interpreting 1NMR spectra

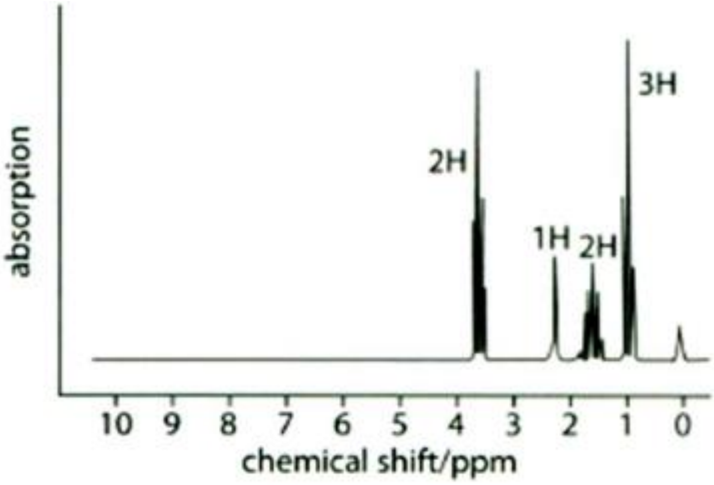
The 1H NMR spectrum of ethanal is shown below.



The spectrum trace has a peak at 9.7, which corresponds to the CHO proton and a peak at 2.1 which corresponds to the three protons in the CH3 group. The area under the CH3 peak is three times larger than that under the CHO peak as it indicates the relative number of protons in the different environment. The integrated trace gives this information more directly, as it goes up in steps which are proportional to the number of protons

Worked example

The NMR spectrum of a compound which has the molecular formula C_3H_8O is shown below.



(a) Draw the full structural formulas and give the names of the three possible isomers of C_3H_8O.

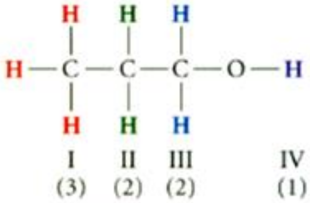
(b) Identify the substance responsible for the peak at 0 ppm and state its purpose.

(c) Identify the unknown compound from the number of peaks in the spectrum.

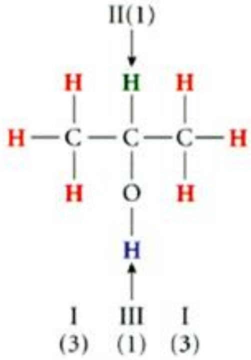
(d) Identify the group responsible for the signal at 0.9 ppm.

Solution

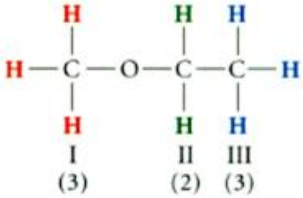
(a) The structures and names are:



propan-1-ol



propan-2-ol



methoxyethane

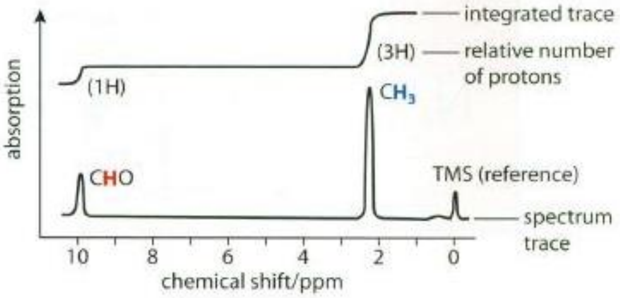
(b) Tetramethylsilane is used as a reference standard.

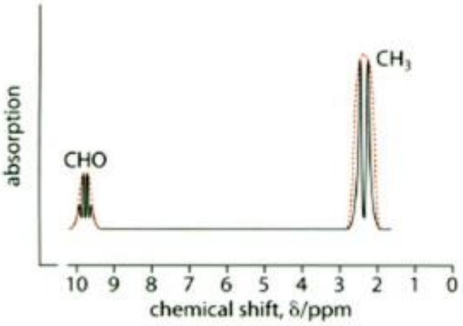
(c) For each structure, I-IV identifies the different environments of the H atoms in the molecule. 1-3 represents the number of atoms in each environment. There are four peaks in the spectrum. Propan-1-ol has four peaks with the correct areas.

(d) Peaks at 0.9 ppm correspond to the CH_3 group.

Splitting of peaks in NMR

High-resolution NMR machine reveals a hidden structure with the single peaks split or resolved into a group of smaller parts. For example, compare the low-resolution spectrum of ethanal (below, left) with the high resolution figure below on the right. The figure on the right was obtained under more carefully controlled operating conditions.





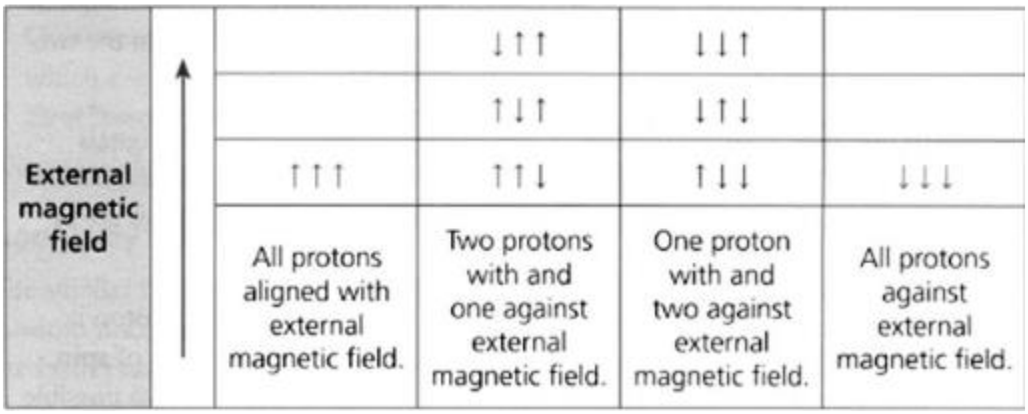
The splitting of the peaks occurs as the effective magnetic field, experienced by particular nuclei, is modified by the magnetic field produced by neighboring protons. This effect is known as **spin-spin coupling.**

The magnetic field experienced by the protons in the methyl group, for example, depends on the spin of the proton attached to the carbon atom of the carbonyl group (CHO). The local magnetic field is increased when the magnetic field of the CHO proton is aligned with the external field and decreased when aligned against it.

As the energy separation between the two spin states of a proton depends on the local magnetic field, this results in two possible values for the energy difference between the two nuclear energy levels for the CH3 protons. Instead of one signal corresponding to one energy difference, ΔE, two signals corresponding to ΔEa and ΔEn are produced.

Each line corresponds to a different spin of the neighbouring proton. As they are both equally likely, the lines are of equal intensity. In a similar way, the low-resolution peak corresponding to the CHO proton is split due to the different magnetic fields produced by the combinations of spin for the three protons of the neighbouring methyl group.

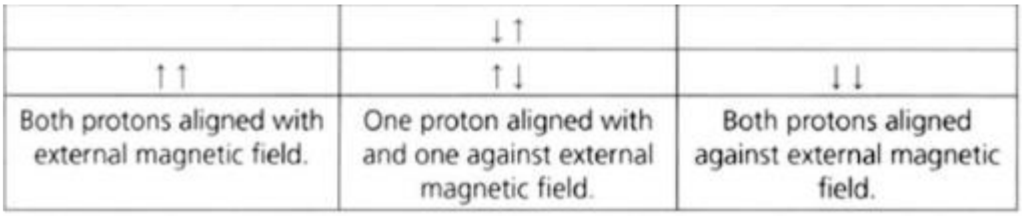
As there are two possible orientations for each proton, a total of 23 combinations are possible, resulting in four different local magnetic fields. This produces four signals with relative intensities 1, 3, 3, 1 – as shown in the table below



External magnetic field	↑				
			↓↑↑	↓↓↑	
			↑↓↑	↓↑↓	
		↑↑↑	↑↑↓	↑↓↓	↓↓↓
		All protons aligned with external magnetic field.	Two protons with and one against external magnetic field.	One proton with and two against external magnetic field.	All protons against external magnetic field.

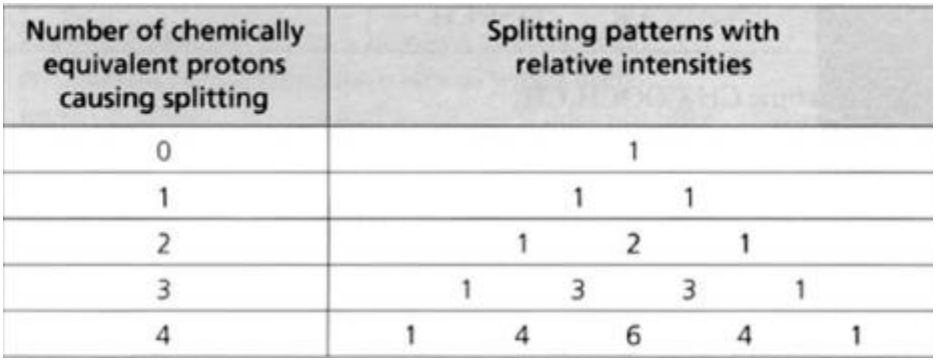
Worked example: Predict the splitting pattern produced by a neighboring CH2 group.

Solution: There are 2^2 different combinations.



	↓↑	
↑↑	↑↓	↓↓
Both protons aligned with external magnetic field.	One proton aligned with and one against external magnetic field.	Both protons aligned against external magnetic field.

Three lines are produced with relative intensities of 1, 2, 1. The splitting patterns produced from different numbers of neighboring protons can be deduced from Pascal's triangle and are summarized in the table below.



Number of chemically equivalent protons causing splitting	Splitting patterns with relative intensities
0	1
1	1 1
2	1 2 1
3	1 3 3 1
4	1 4 6 4 1

When analysing high-resolution NMR spectra, the following additional points should be noted:

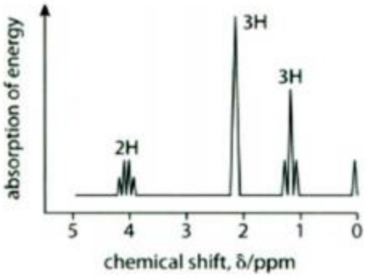
- protons bonded to the same atom do not interact with one another as they are equivalent and behave as a group
- protons on non-adjacent carbon atoms do not generally interact with one another
- the O−H single peak in ethanol does not split unless the sample is pure. Rapid exchange of the protons between ethanol molecules averages out the different possible spins.

Worked example:

The ^1H NMR spectrum of a compound with the empirical formula C_2H_4O is shown on the right.

(a) Deduce the molecular formula of the compound.

(b) Draw possible structures of molecules with this molecular formula.

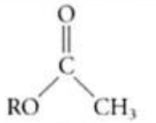
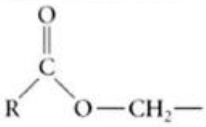


Solution

(a) The ^1H NMR spectrum shows the presence of 8 hydrogens. Molecular formula: $C_4H_8O_2$

(b) Possible structures $CH_3CH_2CH_2COOH$, $CH_3CH(CH_3)COOH$, $CH_3CH_2COOCH_3$, $CH_3COOCH_2CH_3$, $HCOOCH_2CH_2CH_3$, and $HCOOCH(CH_3)_2$

(c)

Chemical shift/ppm	Integration	Type of proton	Splitting pattern	Structural information
1.0–1.50	3H	$-CH_3$	triplet	CH_3 next to CH_2
2.0–2.5	3H		singlet	CH_3 next to CO
3.8–4.1	2H		quartet	OCH_2 next to CH_3