CHEMISTRY AS – UNIT 1
The Language of Chemistry, Structure of Matter and Simple Reactions

1.1 – Formulae and Equations

Formulae of Compounds and Ions

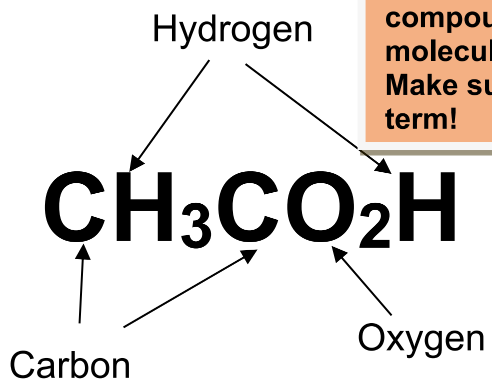
A **formula tells you the number and type of elements present in one molecule of a compound** (ionic or covalent). In an equation, a number in front of the formula tells you how many molecules there are in a reaction.

TIP! Examiners expect you to know the difference between atoms, compounds, ions and molecules in your answers. Make sure you use the right term!

Ethanoic acid is a covalent compound.

One molecule contains 2 carbon atoms, 4 hydrogen atoms and 2 oxygen atoms (8 in total).

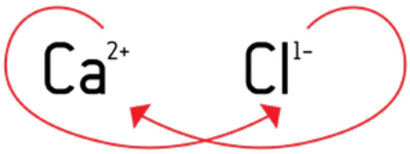
2 molecules of ethanoic acid will contain 16 atoms.



Many compounds contain **ions** (atoms or groups of atoms that have lost or gained one or more electrons). Ionic molecules have no charge, which means that **the number of positive charges cancel out the number of negative charges** in the formula of the compound.

Follow these steps to write the formula for an ionic compound: -

1. Write the symbols of the ions next to each other, including the charges.
2. Check to see if the charges cancel out. If they do, **that's your formula!!!**
3. If they don't, use the 'cross-over' method to make them balance. This uses the charge on one ion as the subscript for the other one – here's two examples: -



The 1 from the charge on the chloride is moved as a subscript for calcium (NOT SHOWN AS PART OF THE FINAL FORMULA). The 2 from the calcium is moved as a subscript for the chloride. Formula is $CaCl_2$

The 3 from the charge on the aluminium is moved as a subscript for the sulphate. The 2 from the charge on the sulphate is moved as a subscript FOR the Aluminium. Formula is $Al_2(SO_4)_3$

Oxidation Numbers

Oxidation numbers can be used to show how many of each type of atom combine in compounds. It is **the number of electrons that need to be added (or taken away from) an element to make it neutral.** (You don't need to learn this definition.)

Eg, a calcium ion, Ca^{2+} needs two electrons added to it in order to make a neutral calcium atom. Its oxidation number is therefore +2 (add 2 electrons). A sulphide ion, S^{2-}, needs to lose two electrons in order to make a neutral sulfur atom. Its oxidation number is therefore -2 (take 2 electrons away).

Oxidation numbers can also be used with covalent compounds. Atoms don't lose or gain electrons here, so certain rules have to be followed so that oxidation numbers can be given to elements in a covalent compound.

You need to learn the following rules and know how to apply them so that you can work out the oxidation numbers of individual atoms in compounds or ions. Once you're able to do that, you can work out what has been oxidised and what has been reduced in a redox reaction. We will look at this later on.

Rule	**Example**
An uncombined element has an oxidation number of zero	Oxygen gas, O_2, oxidation number = 0 Magnesium metal, Mg, oxidation number = 0
The sum of oxidation numbers in a compound is zero. In a complex ion, the sum of the oxidation numbers = charge on the ion	In MgO, the sum of the oxidation numbers is zero – Mg = +2, O = -2. In SO_4^{2-}, the sum of the oxidation numbers of sulfur and oxygen is -2.
Group 1 metals have an oxidation number of +1 and Group 2 metals have an oxidation number of +2 in compounds.	In $CaCl_2$, calcium has an oxidation number of +2 (leaving each chlorine with an oxidation number of -1)
Oxygen **always** has an oxidation number of -2 in compounds (**except** with fluorine and in peroxides and superoxides)	In CO_2, the oxidation number of each oxygen is -2 (making carbon +4) In H_2O_2, the oxidation number of oxygen is -1 (making hydrogen +1)
The oxidation number of hydrogen is **always** +1 in compounds, except in metal hydrides.	In H_2O. the oxidation number of hydrogen is +1 (making oxygen -2, as it should be) In LiH, the oxidation number of hydrogen is -1, because Group 1 metals are always +1.
When you have ions or compounds with atoms of more than one element, the most electronegative element is given the negative oxidation number.	In CCl_4, chlorine is the more electronegative element, so it has the negative oxidation number (-1), whilst carbon has the positive oxidation number of +4.

Chemical and ionic equations

Chemical equations summarise what is happening in a chemical reaction. It is possible to explain a fairly complex reaction using symbols and formulae, whilst telling us the ratio in which the atoms or molecules react.

For example, sodium (a solid), reacts with water (a liquid with no solid dissolved in it) to form sodium hydroxide solution (solid sodium hydroxide dissolved in water) and hydrogen gas. This is quite a long-winded way of writing it out, it is much simpler to write an equation that tells us exactly the same thing: -

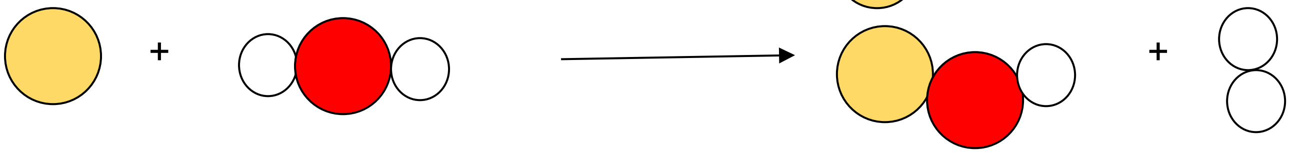
State symbols (in brackets):-
(s) = solid
(l) = pure liquid
(g) = gas
(aq = aqueous solution

$$\text{Na (s)} + \text{H}_2\text{O (l)} \longrightarrow \text{NaOH (aq)} + \text{H}_2\text{ (g)}$$

(**This equation is NOT balanced yet**!)

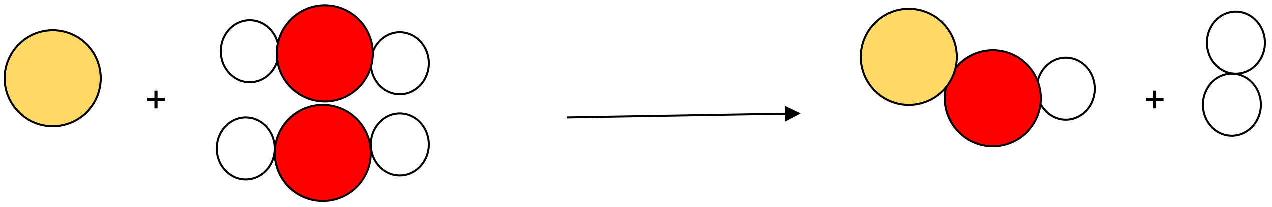
How do we work out how many of each atom or molecule is needed on each side?
As atoms can't be created or destroyed in a chemical reaction, then the number of atoms of each element on the reactants side **must equal** the number of atoms of each element on the products side.
This *balancing* process is best shown using diagrams representing the atoms: -

Key:- ○ hydrogen atom 🔴 oxygen atom 🟡 sodium atom



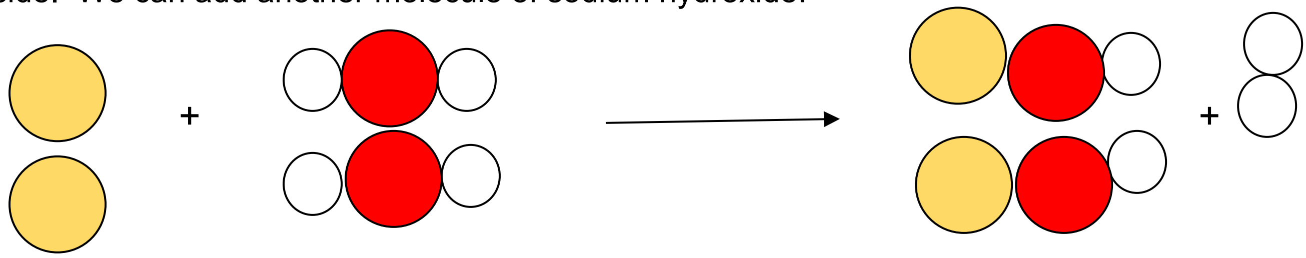
LHS = 1 x Na, 1 x O, 2 x H RHS = 1 x Na, 1 x O, 3 x H

There are more hydrogen atoms on the right hand side. We have to add more to the left hand side. The only way we can do that is to add an extra water molecule: -



LHS = 1 x Na, 2 x O, 4 x H RHS = 1 x Na, 1 X O, 3 x H

Now the hydrogens and oxygens do not balance. We need one more of each on the right hand side. We can add another molecule of sodium hydroxide:



LHS = 2 x Na, 2 x O, 4 x H RHS = 2 x Na, 2 X O, 4 xO

You will notice an extra sodium atom was sneaked into the diagram in order to save space! That would have been the next step. We can now write the fully balanced equation: -

$$2\text{Na(s)} + 2\text{H}_2\text{O(l)} \rightarrow 2\text{NaOH(aq)} + \text{H}_2\text{(g)}$$

Ionic Equations

You will find that several reactions involve ions in solution. In these reactions, not all of the ions actually take part in the reaction, they just seem to float around doing nothing and are known as ‘spectator ions’. If you take these ions out of the equation, you end up with an **ionic equation**, which concentrates only on those ions that react with each other. . . .

If we take the **neutralisation reaction** between hydrochloric acid and sodium hydroxide as one example. We need to write out the equation, then write it down in the form of ions. Then we look and see which ions **haven’t changed**. These are the spectator ions and they can be removed.

$HCl\,(aq) + NaOH\,(aq) \rightarrow NaCl\,(aq) + H_2O\,(l)$

As ions: $H^+(aq) + Cl^-\,(aq) + Na^+\,(aq) + OH^-\,(aq) \rightarrow Na^+\,(aq) + Cl^-\,(aq) + H_2O\,(l)$

The spectator ions have been highlighted – you can see that they haven’t changed. The ionic equation for this neutralisation reaction is therefore: -

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

Displacement reactions can also be written as ionic equations. Think about the reaction between magnesium and copper chloride. Magnesium displaces the copper and a red-brown solid will appear on the magnesium: -

$Mg\,(s) + CuCl_2\,(aq) \rightarrow MgCl_2\,(aq) + Cu\,(s)$

As ions: $Mg(s) + Cu^{2+}\,(aq) + 2Cl^-\,(aq) \rightarrow Mg^{2+}\,(aq) + 2Cl^-\,(aq) + Cu(s)$

The chloride ions are the spectator ions, so we can write the ionic equation for the reaction as-

$Mg\,(s) + Cu^{2+}\,(aq) \rightarrow Mg^{2+}\,(aq) + Cu\,(s)$

Precipitation reactions can also be represented by ionic equations. Here, the product is a solid (precipitate).

Eg, $2KI\,(aq) + Pb(NO_3)_2\,(aq) \rightarrow 2KNO_3\,(aq) + PbI_2\,(s)$

The potassium (K^+) and nitrate (NO_3^-) ions are the spectator ions, so the ionic equation for this reaction is: -

$Pb^{2+}\,(aq) + 2I^-\,(aq) \rightarrow PbI_2\,(s)$

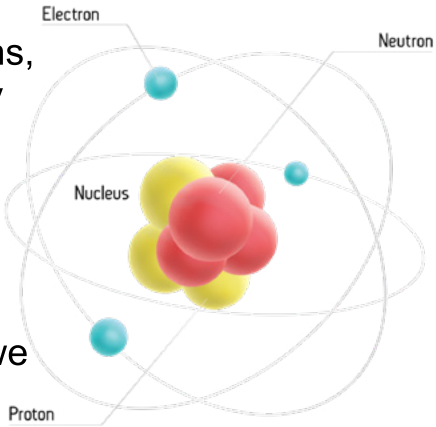
It’s important to notice that state symbols **have** to be used in ionic equations. If you look carefully at the state symbols for all of the ionic equations above, you will see that: -

- The products are never aqueous – above you have a liquid and two solids.
- Spectator ions are the ones that remain in aqueous solution.

1.2 - Basic ideas about atoms

Atomic Structure

This is re-visiting what you learnt at GCSE.
All atoms have a nucleus containing protons and neutrons, with electrons surrounding the nucleus in orbits or energy levels.



Almost all of the mass of the atom is in the nucleus and we can see the reason for this in the table below.

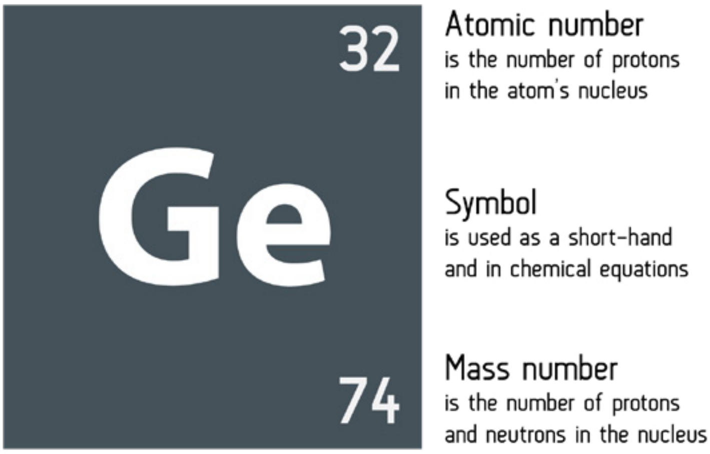
Particle	Relative Mass	Relative Charge
Proton	1	+1
Neutron	1	0
electron	1/1840	-1

You'll see 'relative' mass and charge in the table. This is because the mass and charge of each particle is so very small. Both are given as relative to each other in order to give them a value.

An atom is electrically neutral because the number of positive protons and negative electrons in an atom is always the same.

Mass number and atomic number

When you see an element represented on a Periodic Table, you will see that each one has two different numbers associated with it.



We can use the atomic number and mass number to work out the number of particles in the atom:-

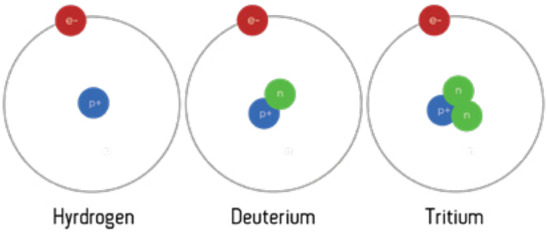
TIP!! It is incorrect to state that the atomic number is the number of protons and electrons, which you may have learnt at GCSE

Number of protons = atomic number
Number of electrons = number of protons
Number of neutrons = mass number – atomic number

Isotopes

Atoms of an element are not always identical. They all have to have the same number of protons in order to be the same element, but they can have different numbers of neutrons. These atoms are called **isotopes.**

Hydrogen isotopes



Definition:- Isotopes are atoms that have the same number of protons, but different numbers of neutrons.

Most elements occur naturally as two or more different isotopes.

Ions

Ions are particles where the number of electrons is not equal to the number of protons.

Positive ions (cations) are formed when an atom loses one or more electrons. eg: -

$$Mg \rightarrow Mg^{2+} + 2e^-$$

A magnesium ion has 10 electrons, having lost 2 of its original 12.

Negative ions (anions) are formed when an atom gains one or more electrons, eg: -

$$S + 2e^- \rightarrow S^{2-}$$

A sulphide ion has 18 electrons, having gained 2 electrons to add to its original 16.

Radioactivity

Types of radioactive emission and how they behave

Type	What it is	Symbol	Effect of electric field	Effect of magnetic field	Penetrating power
Alpha - α	2 protons and 2 neutrons. Often called a helium nucleus	${}^{4}_{2}He^{2+}$ or ${}^{4}_{2}\alpha$	Attracted to the negative plate.	Deflected in one direction	Least penetrating - stopped by a sheet of paper
Beta - β	An electron	${}^{0}_{-1}e$ or β^{-}	Attracted to the positive plate	Deflected in the opposite direction to α	Stopped by a thin layer of metal, eg Al
Gamma - γ	High energy electromagnetic radiation	${}^{0}_{0}\gamma$	No effect	No effect	Most penetrating – it may need more than 2cm of lead to stop it.

Changes in mass number and atomic number

Gamma radiation has no effect on the mass and atomic number of the atom that emits it. This is because it is a form of energy and is not an atomic particle.

Alpha particles, when emitted, cause the **mass number to decrease by 4** and the **atomic number to decrease by 2**.

mass number decreases by 4

$$ {}^{238}_{92}U \longrightarrow {}^{234}_{90}Th + \alpha $$

atomic number decreases by 4

or

$$ {}^{238}_{92}U \longrightarrow {}^{234}_{90}Th + {}^{4}_{2}He $$

Thorium is two places to the left of uranium in the Periodic Table as it has a lower atomic number.

TIP!! When you're writing a nuclear equation like this one, one way to check if you're correct is to add the atomic and mass numbers of the product and the alpha particle on the right hand side of the equation and make sure they are equal to the atomic and mass number on the left hand side.

When an atom emits a particle of **beta radiation**, then its **mass number is unchanged** and the **atomic number increases by 1**.

$$^{131}_{53}I \rightarrow ^{131}_{54}Xe + ^{0}_{-1}e$$

Xenon is one place to the right of iodine as it has a higher atomic number.

Electron capture is when one of the electrons is captured by a proton, turning it into a neutron. An **electron neutrino** is emitted (v_e). Atomic number **goes down** by one here due to the changing of the proton into a neutron.

$$^{40}_{19}K + ^{0}_{-1}e^{-} \rightarrow ^{40}_{18}Ar + v_e$$

Another type of β-decay is called **positron emission (β^+ decay).** Here, a proton is converted to a neutron, whilst releasing a positron and an electron neutrino. The positron is a type of beta particle (β^+). Atomic number **goes down** by one here as a proton is again changed into something else.

$$^{15}_{8}O \rightarrow ^{15}_{7}N + ^{0}_{+1}\beta$$

Half Life

Radioactive atoms breaking down by emitting radiation are *decaying* and forming new atoms. The nuclei of different radioactive elements (also known as radioisotopes) decay at different rates. This is measured using the **half-life** of a radioisotope.

Half-life is the time it takes for half of the atoms in a radioisotope to decay. (You can also say it's the time taken for the radioactivity of the sample to fall to half its original value.)

TIP!! These are the types of calculations you may be given in an exam: -

- working out the time it takes for the radioactivity of a sample to fall to a specified fraction of its original value.
- the mass of a radioisotope remaining after a specific time, when you know the starting mass.
- the half-life of a radioisotope if you know how long it takes for sample to fall to a specific fraction of its original value.

Worked example

An isotope of iodine, ^{131}I, has a half-life of 8 days.
i) Calculate how long it would take for 3.2g of ^{131}I to be reduced to 0.2g of ^{131}I.
ii) If you started with 8.0g of ^{131}I, calculate the mass remaining after 48 days.

Answer:

i) 3.2g → 1.6g → 0.8g → 0.4g → 0.2g

There are 4 arrows, therefore 4 x half-lives. So the time is 4 x 8 = 32 days.

ii) 48 days = 6 half-lives

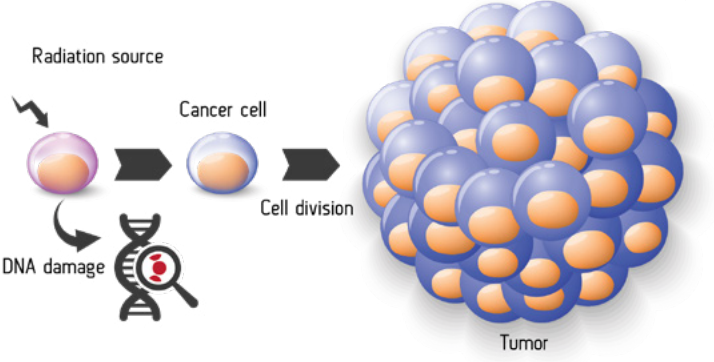
8.0g → 4.0g → 2.0g → 1.0g → 0.5 → 0.25 → 0.125

After 6 half-lives, there is 0.125g remaining.

Effect on living cells

We are constantly exposed to some radiation from background radiation. This is not considered to be harmful. Workers in industries exposed to radiation have to be monitored to ensure that they don't receive more than the allowable amount of radiation.

This diagram simplifies what can happen to cells when they are exposed to radiation.

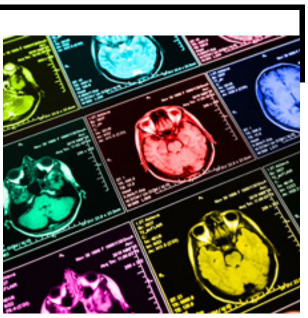


DNA can become damaged, which can cause mutations and cancerous cells at lower doses. At higher doses the cell can be killed.

γ-rays are the most dangerous source of ionising radiation **outside** the body because of its penetrating power. However, if an α-source is swallowed, then they are far more dangerous that the other two types of radiation as they are already **inside** the body and are very large particles. These will cause a great deal of damage to cell DNA.

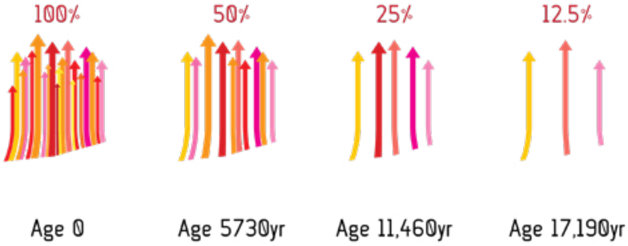
Uses of radioactive isotopes

You need to be able to give an example and a brief outline of a beneficial use of radioactivity in each of the following contexts: -

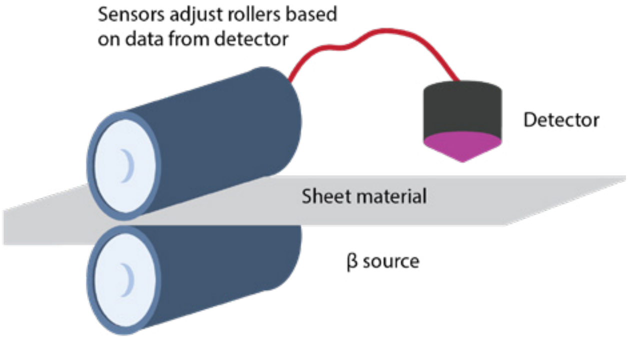


Health and Medicine
We have just stated that radiation is harmful to health. However, it can be used successfully in a controlled way in order to treat and trace disease. **Cobalt-60** is used as a treatment for cancer in radiotherapy. The high energy rays are used to kill cancer cells and prevent a tumour from developing. **Technetium-99m** is the most commonly used medical radioisotope. It's used as a tracer by labelling a molecule which is taken preferentially up by the tissue to be studied.

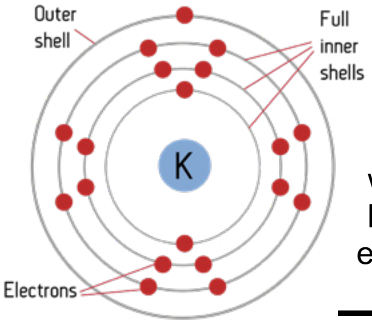
Radio-dating
Carbon-14 has a half-life of 5570 years and is used to calculate the age of the remains of plants and animals. All living organisms must contain a small percentage of carbon-14 through absorption. This absorption stops when the animal dies, so the carbon-14 that is present will start to decay. The rate of decay decreases over the years and the activity that remains can be used to calculate the age of organisms.
Potassium-40 has a very long half-life of 1300 million years. It is used to estimate the age of rocks. It can change into argon-40 by the nucleus gaining an inner electron. Measuring the ratio of potassium-40 to argon-40 in a rock gives an estimate of its age.



Analysis and Industry
Dilution analysis. Substances containing radioisotopes can be used to find the mass of substance in a mixture. This is useful when the substance can be extracted in its pure state from the mixture, but it can't be extracted in such a way that its concentration cannot be determined.
Thickness monitoring of metal strips or foil. The metal is rolled between two rollers in order to obtain the right thickness. A β-source is placed on one side of the metal with a detector on the other. If the metal comes out too thick, then the detector with sense a reduced amount of radiation, so the rollers will move closer together.

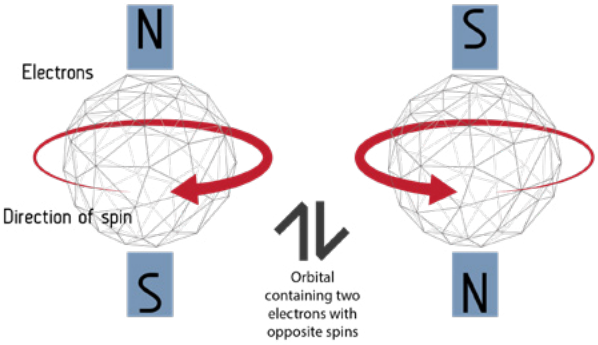


Electronic Structure

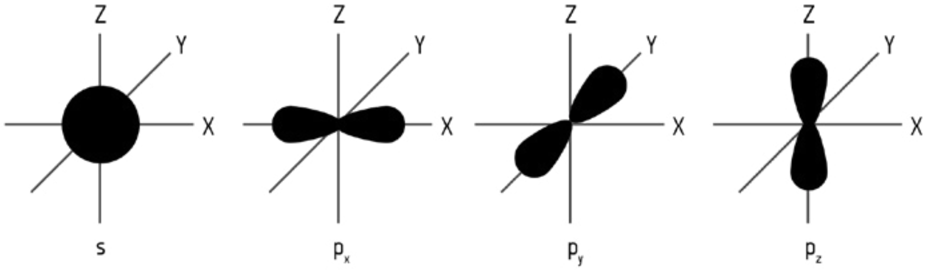


Chemical reactions involve electrons, so the way that they are arranged is key to understanding Chemistry. We know from GCSE that electrons occupy shells (or orbits) or energy levels. These are numbered 1,2,3,4 etc (principal quantum numbers), with the lowest number being the closest to the nucleus and also the lowest energy level. The diagram to the left shows how we drew electronic structure at GCSE – electrons appeared on the shells.

We now have to look at what happens within each shell. Shells are actually split into regions of space around the nucleus where there is a high probability of finding an electron of a particular energy. These regions are called **orbitals**. Shells are split into subshells, which contain orbitals of the same type. Each orbital can contain a maximum of two electrons. These electrons both have a negative charge and, in order to stop them repulsing each other totally, they have opposing spins, which means they can move away from each other. The diagram shows how it is believed the electrons move and how they are represented in diagrams of electronic structure. The arrows indicate the opposite spins and the box represents the orbital.



There are four different types of orbital, named *s, p, d* and *f*. You need to know the shapes of the *s* orbital and *p* orbital. These are shown below. Note that the *p* orbital is made up of three different lobes at right angles to each other.



An *s* orbital can hold **2** electrons.
As there are **3** *p* orbitals, each one holding **2** electrons, a *p* subshell can hold **6** electrons.
There are **5** different *d* orbitals, so each *d* subshell holds **10** electrons.
f orbitals are not studied at this level, but there are 7 different orbitals, so each subshell holds 14 electrons.

Shell/Energy level = area around a nucleus which is occupied by electrons. Those closest to the nucleus have lowest energy.
Orbital = region of a shell where there is a high probability of finding an electron of a particular energy. **Each orbital can hold up to two electons.**
Subshell = part of a shell that contains orbitals of the same type. The table on the next page shows the subshells that are found in each shell and the number of electrons in each.

Shells, subshells and electrons

Shell	Subshell	Number of orbitals in subshell	Number of electrons per subshell	Number of electrons per main shell
1	s	1	2	2
2	s p	1 3	2 6	8
3	s p d	1 3 5	2 6 10	18
4	s p d f	1 3 5 7	2 6 10 14	32

Filling up shells with electrons

In GCSE, we knew that the way that electrons are arranged is called their **electronic structure** or **configuration**. These are slightly more complex as GCE level and we can work them out by following three basic rules: -

1 Electrons fill the lowest available subshell first.

2 Each orbital can hold a maximum of two electrons, each with opposite spin.

3 Each orbital in a sub-shell will fill with **one electron first** before pairing starts, eg in *p* orbitals, each orbital will fill with one electron and then pairing will start. This is to minimise repulsion: -

Half-filled p orbitals. Each electron has the same spin. The next electron will pair up with one of those already there.

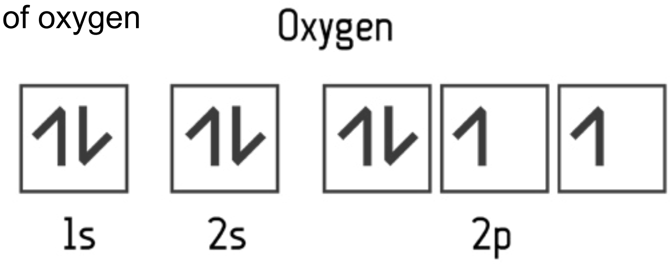
If we look at the table above, we see that there is 1 x *s* orbital in the first shell, 1 x *s* and 3 x *p* orbitals in the second shell and so on.

Taking Oxygen (8 electrons as an example), we can see that it has:
2 electrons in the 1s orbital (1 = shell number 1)
2 electrons in the 2*s* orbital and 4 electrons in the 2*p* orbitals (2 = shell number 2)

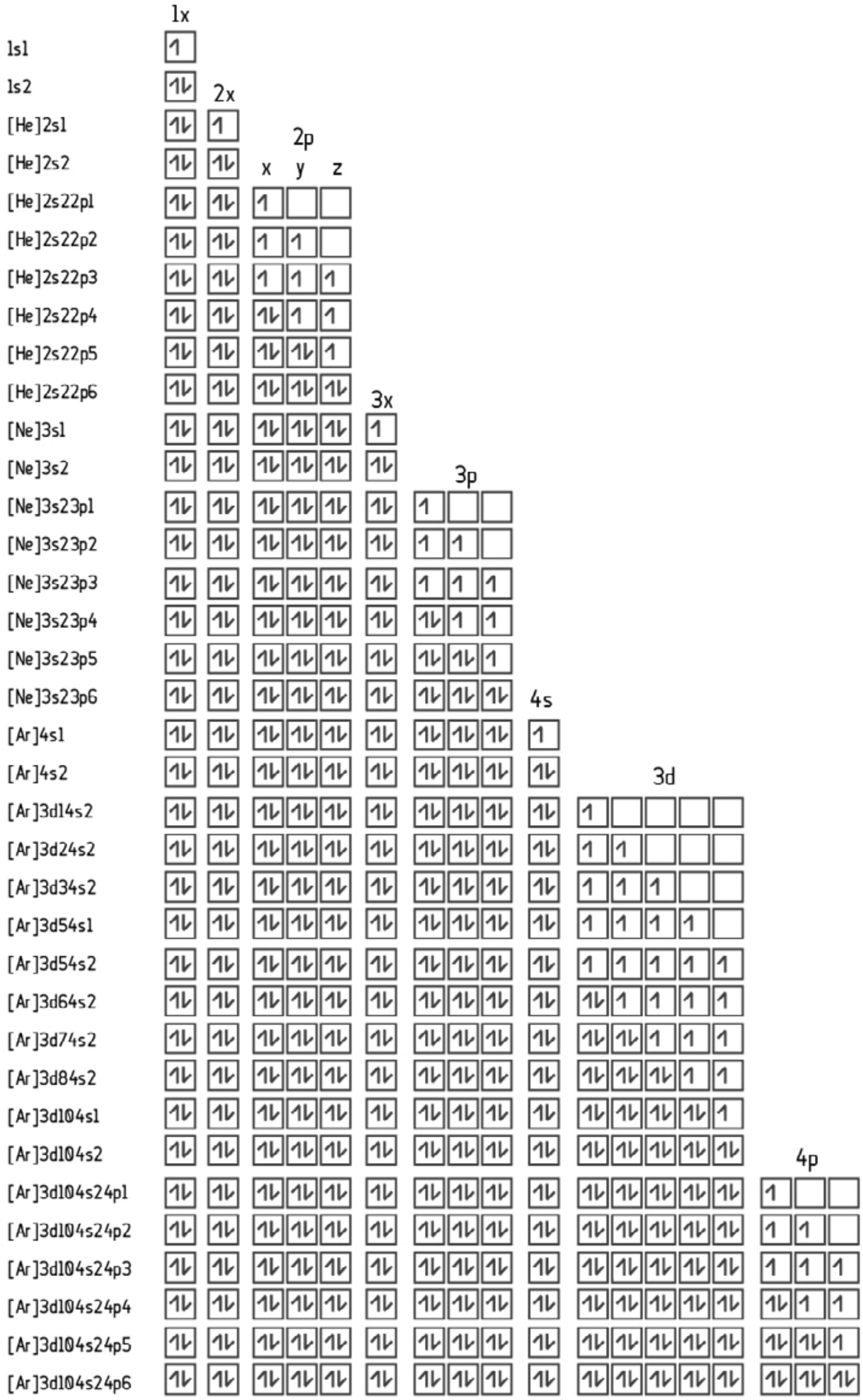
We can write this down as:

$1s^2\ 2s^2\ 2p^4$ - this is the electronic configuration of oxygen

It can also be shown as ‘arrows in boxes’. The direction of the arrow indicates the direction in which the electron is spinning.



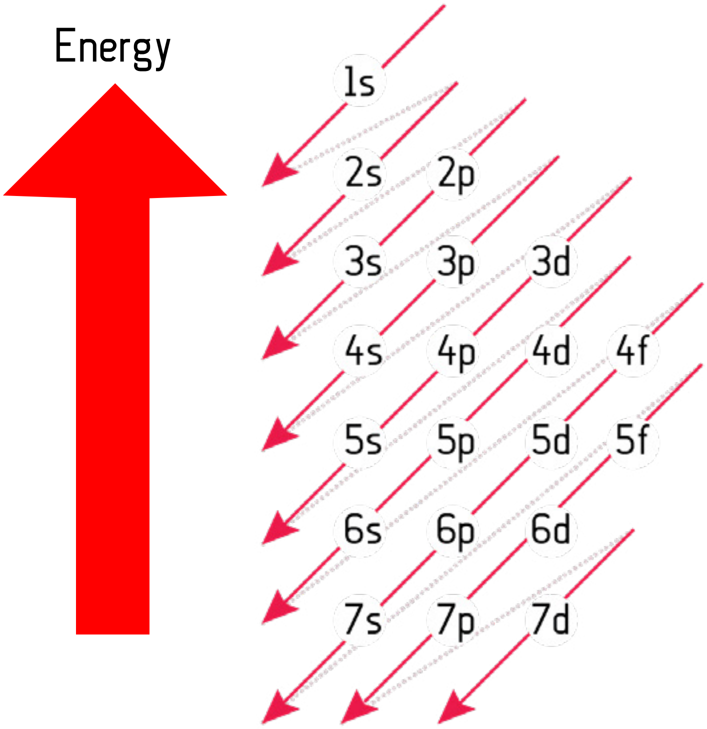
You need to know the electronic configuration for the first 36 electrons. These are shown using notation and arrows in boxes in the chart below:-



You will notice that after neon, the notation on the electronic configurations changes slightly. [Ne] is used instead of: $1s^2 2s^2 2p^6$. (On the chart, the 2*p* subshell is shown as orbitals (p_x, p_y and p_z).

This use of 'Noble gas cores' can make it more convenient to write the configurations of the larger atoms. Each time a noble gas configuration is reached, its configuration is used for the next period of elements.

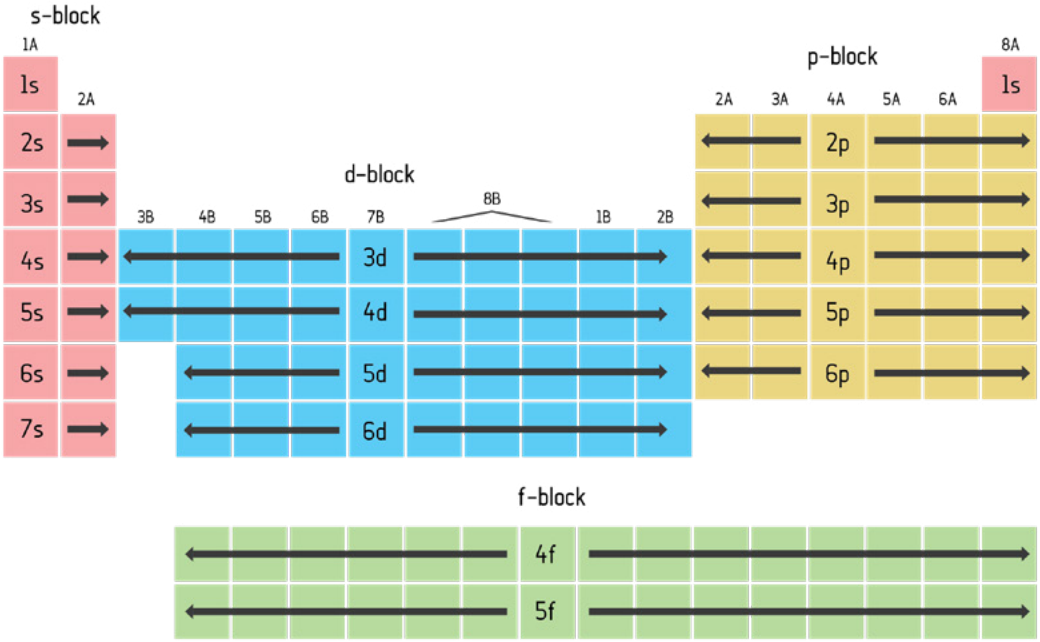
You will also see that the 4*s* orbital fills before the 3*d* orbital. This is because the *s* orbitals have slightly lower energy than the *d* orbitals of the shells that are below them. The diagram on the next page gives you a useful tool for remembering how the subshells fill up.



The order of electron filling – start at 1*s* and go up diagonally through the rows and columns.

So the order of filling is 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p and so on….

It is also useful to know why the Periodic Table is split up into different **blocks**. You will have seen the s-block, p-block and d-block labelled on most Periodic Tables. The following diagram shows this.



s-block elements are so-called because their outer electrons appear in *s*-orbitals. The same can be said for *p- and* d-block elements as well. Their outer electrons appear in these subshells.

The electronic configuration of **ions** is shown in the same way as atoms. Remember that **negative ions have more electrons than their parent atoms** and **positive ions have less electrons than their parent atoms.**

Ionisation Energy

You can think of ionisation as the removal of one or more electrons from an atom to form a positive ion. The energy needed for this to happen is called the **first**, **second, third** (and so on) **ionisation energy**.

Definition: The molar first ionisation energy (IE) of an element is the energy required to completely remove one mole of electrons from one mole of its *gaseous* atoms.

The following equation summarises the first ionisation energy for an element: -

$$X(g) \rightarrow X^+(g) + e^-$$

TIP!! It is essential that you include the (g) state symbol in any exam answer, or you'll lose a mark.

If an outer electron is held in place strongly by the nucleus, then it takes a lot of energy to remove it, so the IE will be high. If it is not held as strongly, the IE will be lower. This attraction between nucleus and electron depends on three factors: -

Nuclear charge – the greater the nuclear charge, the greater the attraction for the outer electron.
Electron shielding – filled inner shells or subshells of electrons act as shields. The outer electron is **shielded** from the nuclear charge by these shells or subshells.
Distance of outer shell from nucleus – the attraction decreases the further away the outer electron is from the nucleus.

Trends in Ionisation Energy

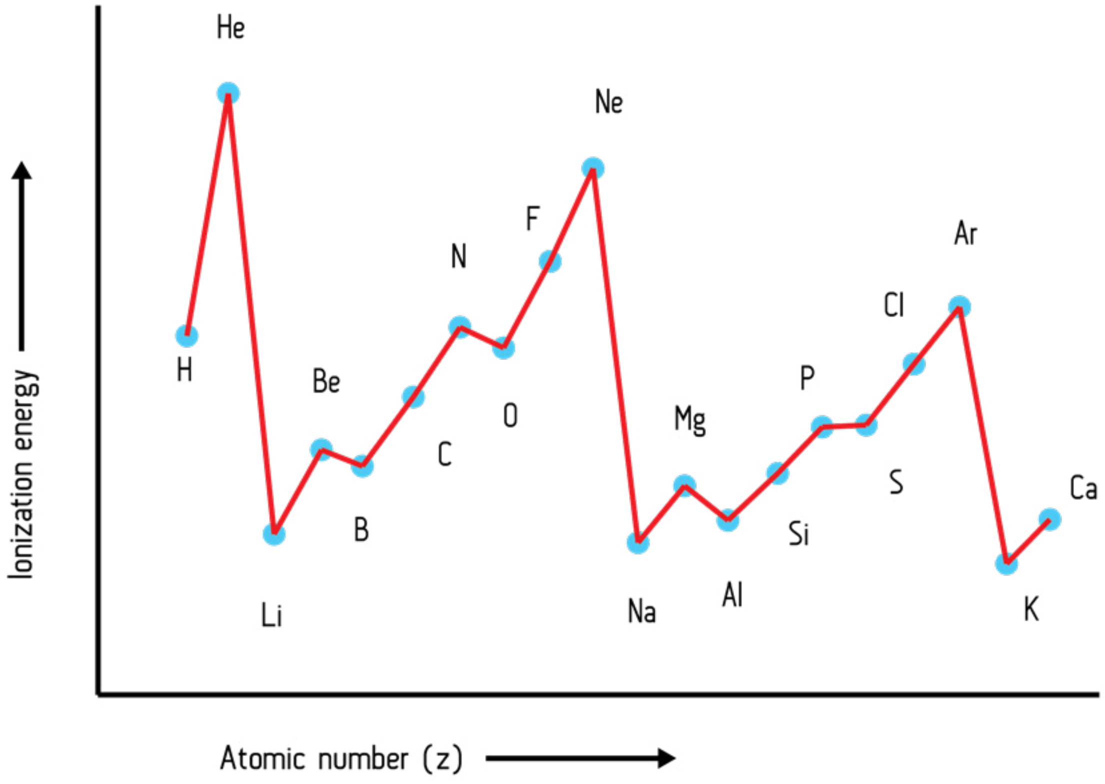
From one element to another

Down groups – atoms increase in size down groups due to the increasing number of electron shells.

Increased shells = increased shielding = lower IE.

Ionisation energy decreases down a group

Across a period – the diagram shows the ionisation energies of the first twenty elements



The green numbers highlight the evidence for shells and subshells in the first ten elements: -

1 From H to He, IE increases as helium has a greater nuclear charge in the same subshell, so there is no extra shielding.

2 From He to Li, a decrease in IE due to the outer electron being in a new shell in lithium, so there is increased shielding and the outer electron is further away from the nucleus.

3 Fall in IE from Be to B as boron's outer electron is in a new subshell of slightly higher energy. This subshell is shielded from the nucleus by the 2s electrons.

4 Slight decrease in IE between N and O. This is because in oxygen, electrons in the p-orbital have to start pairing, which causes repulsion, thereby making the electron easier to remove. Nitrogen has no paired electrons in its p-orbital.

Finally, there is a fall in IE between He and Ne as neon has more shells and there is increased shielding by its inner electrons and the outer shell electrons are further from the nucleus.

Ionisation energy increases generally across a period, with sub-shells and electron pairing causing slight discrepancies in this rule.

Successive Ionisation Energies within an atom

All of the electrons can be removed from an atom, each one with its own ionisation energy. An atom has the same number of ionisation energies as it does electrons, eg calcium has 20 electrons and therefore 20 ionisation energies. These are called the 1st, 2nd, 3rd ……… ionisation energies (it goes up to 20 – these are the *successive ionisation energies* of calcium).

The ionisation energy equation has to be adapted to show which electron it is referring to. For example, the equation below represents the fourth ionisation energy of calcium. It is a measure of how easily a 3^+ ion loses an electron to become a 4^+ ion.

$$Ca^{3+}(g) \quad \tau \quad Ca^{4+}(g) + e^-$$

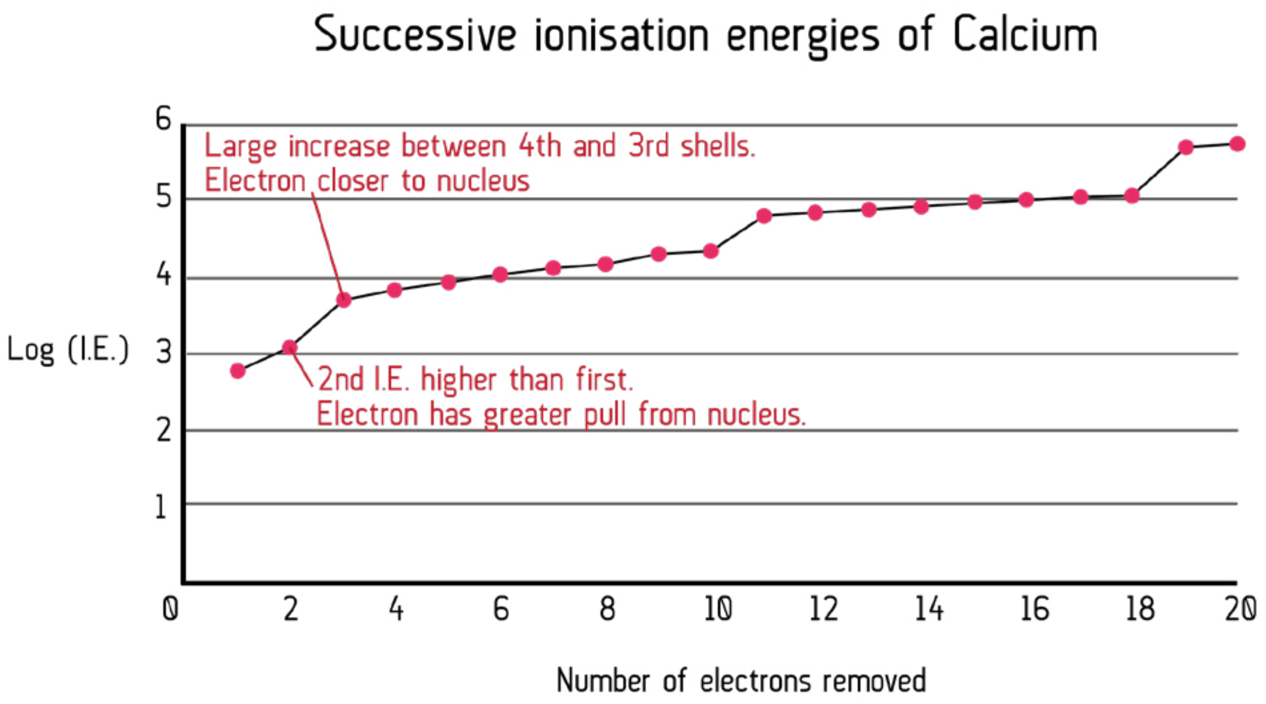
Successive ionisation energies **always increase**. This is because:-

the number of protons stays the same, but they are effectively holding fewer and fewer electrons (**greater effective nuclear charge**)

each shell is drawn slightly closer into the nucleus as each electron is removed (**less electron-electron repulsion**)

as the distance between the nucleus and the electrons decreases, nuclear attraction increases.

Successive ionisation energies provide evidence for the existence of shells. This can be shown on a graph as shown here for calcium: -

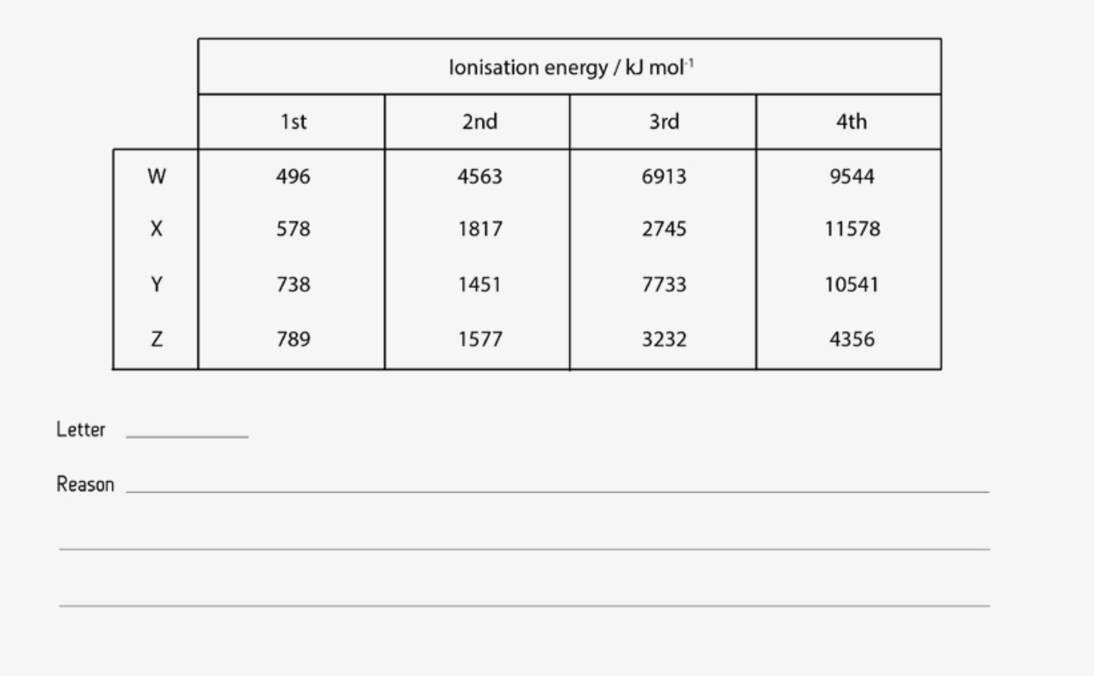


You can also see large increases between electrons 10 and 11 (3rd to 2nd shell) and 18 and 19 (2nd to 1st shell). **You may be examined on your understanding of this type of graph.**

Worked examples

You can also be examined on successive ionisation energies shown in a table, here is an example:-

State, giving a reason for your choice, which **one** of the following gives the first four ionisation energies for silicon, Si.



	Ionisation energy / kJ mol^{-1}			
	1st	2nd	3rd	4th
W	496	4563	6913	9544
X	578	1817	2745	11578
Y	738	1451	7733	10541
Z	789	1577	3232	4356

Letter ____________

Reason ____________

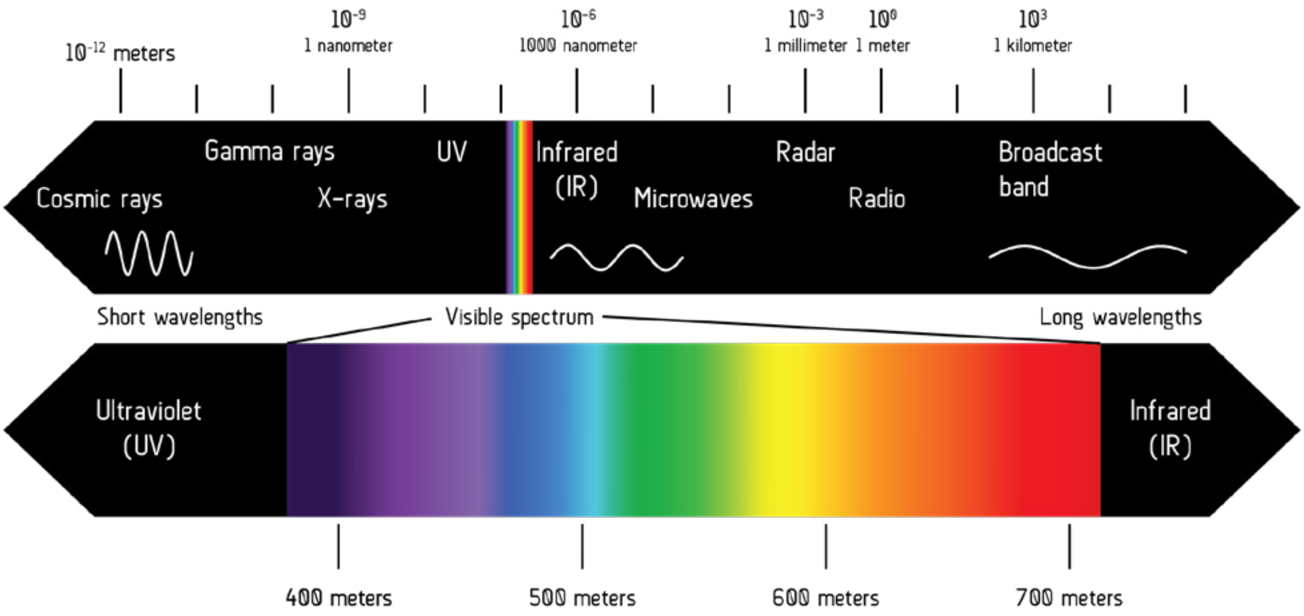
In order to answer this question successfully, you need to look at the **differences** between each successive ionisation energy. Silicon is in **Group IV**, so you're going to be looking for a large leap **after the removal of the fourth electron**.

W has a large leap after the 1st IE, so is in Group 1.
X's largest leap is after the 3rd IE, so is in Group 3.
Y's largest leap is after the 2nd IE, so is in Group 2.
Z does not appear to have a large leap during the first four IEs, so we can assume that this is silicon.

Emission and Absorption Spectra

In order to fully understand what is happening here, you need to recall the basics of the **Electromagnetic Spectrum** from GCSE Physics and also remember that **electrons in different energy levels have different amounts of energy** (the nearer the nucleus, the less energy the electron has).

The Electromagnetic Spectrum
This shows the different types of electromagnetic radiation arranged in order of frequency and wavelength. The spectrum learned at GCSE contains seven different types, ranging from radio waves (at the lowest frequency and longest wavelength) to gamma rays (at the highest frequency and shortest wavelength). This diagram summarises the spectrum, highlighting the area between UV and IR: -



The **frequency (f) and energy (E)** of electromagnetic radiation are related by the following equation: -

$$E = hf$$ (h is Planck's *constant* and is unchanged)

If h remains unchanged, then $E \ \alpha \ f$, so **if the frequency increases, the energy increases**. *From this we see that UV rays have the highest energy and IR rays have the lowest. Purple light has higher energy than red light.*

The **frequency (f) and wavelength (λ)** of light are related by the following equation:-

$$c = f\lambda$$ (c is the speed of light and is unchanged)

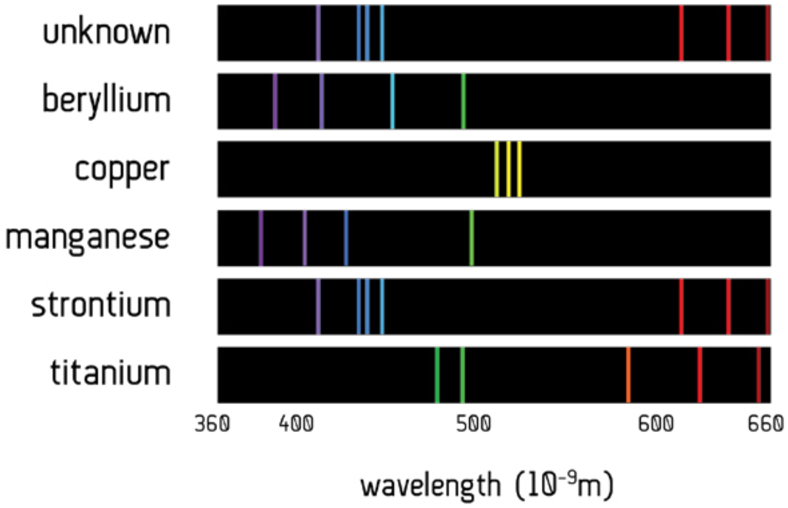
This means that, as c is unchanged, $f \ \alpha \ \frac{1}{\lambda}$ so **if frequency increases, wavelength decreases.**
From this we see that what is seen from the first equation is confirmed by the second. UV rays have the shortest wavelength/highest frequency and IR rays have the longest wavelength/lowest frequency. Is it the same for purple and red light?

Absorption Spectra

When you see light from all visible wavelengths, it is called white light. Every atom and molecule absorb light of certain wavelengths. So, if white light is passed through the vapour of a particular element, some wavelengths will be absorbed by the atoms of the element and removed from the white light. If you look at this happening through a spectrometer, black lines appear in the spectrum of visible light, indicating that light of those particular wavelengths have been absorbed. The wavelengths of the lines correspond to the amount of energy taken in by the atoms to **promote electrons from low energy levels to high energy levels.**

Emission Spectra

Promotion of electrons from low energy levels to high energy levels required energy via heating or the application of an electric field. **When this source of energy is taken away, the electrons fall back to a lower energy level.** The energy lost is released as a quantum (or packet) of energy. It will be the same as electromagnetic radiation of a specific frequency. When it is viewed through a spectroscope, the spectrum is seen as coloured lines on a black background, the direct opposite of an absorption spectrum. The following diagram shows the emission spectra of several elements and an unknown element. What is the unknown element?



Worked Example

(b) The visible emission spectrum of sodium shows a strong yellow-orange line at a wavelength of 589 nm and a weaker green line at 569 nm.

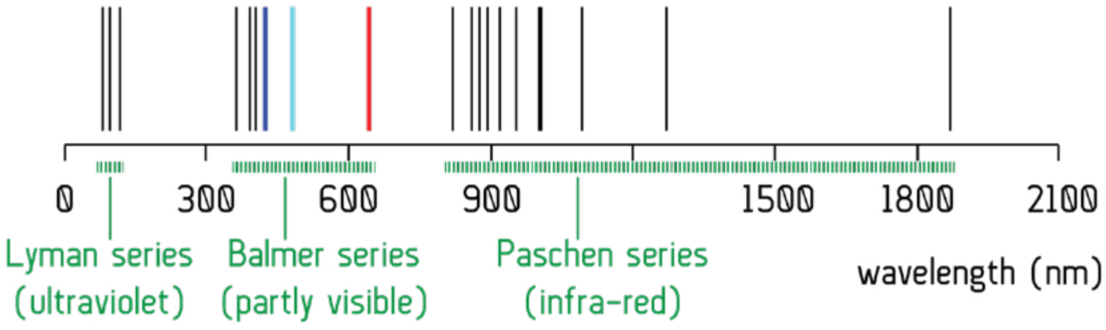
Complete the sentences below by using the words **higher** or **lower** as appropriate. . . . . . .

The frequency of the green line at 569 nm is ....than the frequency of the yellow-orange line at 589 nm. Another line is seen at 424 nm. This is caused by an electronic transition of . . . . .energy than the line at 569 nm.

Orange-yellow has a longer wavelength than green. As $f\ \alpha\ \frac{1}{\lambda}$*, green must have a higher frequency than range-yellow. 424nm is shorter than 569nm, so frequency is higher. As* $E\ \alpha\ f$*, the energy of the line must*

The Hydrogen Spectrum

Hydrogen has the simplest emission spectrum as it only has the one electron. It has its lines mainly in the UV, visible and IR regions of the electromagnetic spectrum: -



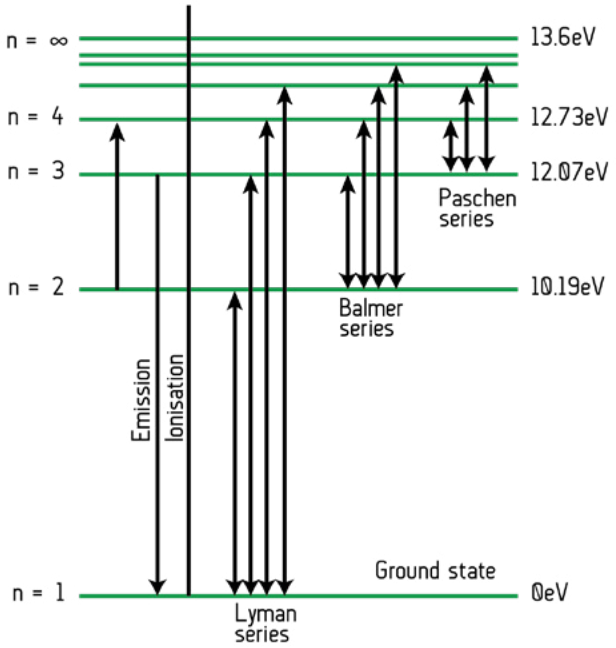
Because it is an emission spectrum, the lines represent energy released as the promoted electron falls back down to lower energy levels or shells. **Each line is equal to the difference in energy, ΔE, between two particular energy levels, which means it is a fixed quantity of energy or a quantum.**

As there are different shells, movement between them will result in emission of radiation of different frequencies (because of ΔE = *hf*), so the lines will be produced at different wavelengths.

The distance between the shells becomes less the further away from the nucleus you go. This means that ΔE is less and the lines on the spectrum therefore get closer.

Lyman, Balmer and Paschen series

The diagram above shows these series. The lines in the Lyman series are in the area with highest frequency/energy. This is because they are due to electrons falling down to the n=1 shell (closest to the nucleus). The Balmer series is in the visible part of the spectrum, which has lower energy. Lines here are due to electrons falling down to the n=2 shell. Lines in the Paschen series are due to electrons falling down to the n=3 shell, so are seen in the area with the lowest frequency.



Ionisation of the hydrogen atom

Turning the hydrogen atom into an ion by removing its electron can be measured using the **convergent frequency** of the Lyman series.

It was mentioned that the spectral lines get closer and closer together as the frequency of the radiation increases until eventually they converge together. This is known as the **convergence limit**. When the electron reaches this, its energy is no longer quantised and the nucleus has lost all influence over the electron, so the atom has become ionised.

Calculating the ionisation energy of one mole of hydrogen atoms

The first step is to record the convergent frequency (difference from n=1 to n= ∞) from the Lyman series.
Use $\Delta E = hf$ to calculate the ionisation energy of one atom.
Multiply ΔE by Avogadro's constant (L) in order to calculate the first ionisation energy for one mole of atoms.

This is fairly straightforward if you know the convergent frequency**, but you may be set a question which only gives you a value for wavelength.**

If you are, then you will need to combine several equations:-

Ionisation Energy = ΔE x L

But, $\Delta E = hf$ and $f = \frac{c}{\lambda}$

So, Ionisation Energy = $\frac{Lhc}{\lambda}$

Where:
L = Avogadro's constant
h = Planck's constant
c = speed of light
λ = wavelength

Worked example

You will have a diagram of the Lyman series for hydrogen, with one line labelled A (omitted in order to save space). The following is the question relating to the diagram:-

Line A represents the convergence limit of this series and is found at a wavelength of 91.2 x10$^{-9\text{m.}}$
Use the equation below to calculate the frequency, f, of line A and hence its energy, E, in Joules (J). Show your working.

$$c = f \times \lambda$$

c = 2.99 x108m^{s}–1

^{h} = 6.63 x10–3^{4Js}

$$f = \frac{c}{\lambda} \quad \frac{2.99\text{x}10^{8}}{91.2 \text{ x } 10^{-9}} = 3.28 \text{ x}10^{15}$$

$$E = hf = 6.63 \text{ x}10^{-34} \text{ x } 3.28 \text{ x}10^{15} = \underline{2.17 \text{ x } 10^{-18} \text{ J}}$$

1.3 Chemical Calculations

Relative Mass Terms

Masses of Atoms

The mass of an atom is expressed relative to a standard atomic mass. This is because the actual masses of atoms are too small to be used in calculations. The standard atomic mass used is the carbon-12 isotope.

As most elements exist naturally as two or more isotopes, the mass of an element depends on the relative abundance of all of the isotopes present in the sample. Chemists therefore use an average mass of all the atoms, the **relative atomic mass (A_r).** It has no units as masses are measured relative to another mass.

Relative isotopic mass is the mass of a particular isotope.

Masses of compounds

The mass of a compound is the sum total of the relative atomic masses of the atoms within a molecule of the compound. The mass is called the **relative formula mass (M_r).**

Eg, the relative formula mass of sulfuric acid, H_2SO_4 is: -

$(2 \times 1.01) + (1 \times 32) + (4 \times 16) = 98.02$

Definitions

You may be asked to define any of the above terms. This is what you should learn: -

Relative atomic mass is the average mass of one atom of the element *relative to one-twelfth the mass of one atom of carbon-12*.

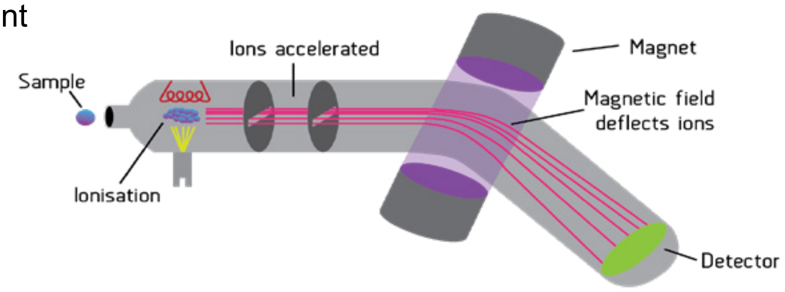
Relative isotopic mass is the mass of an atom of an isotope *relative to one-twelfth the mass of an atom of carbon-12*.

Relative formula mass is the average mass of a molecule *relative to one-twelfth the mass of an atom of carbon-12*.

The Mass Spectrometer

The average mass of an atom can be calculated using the mass of the isotopes of an element along with their relative abundances. This information can be found using a **mass spectrometer.**

This diagram shows the processes that occur in the mass spectrometer.



Summary of Processes

Vaporisation – the sample is heated and turned into a gas before it enters the spectrometer.
Ionisation – the gaseous sample is bombarded with high energy electrons, which forms positive ions.
Acceleration – the positive ions are accelerated through an electric field.
Deflection – the ions are deflected by a magnetic field. The amount of deflection depends on the mass and charge of the ion. (Lighter ions are deflected more than the heavier ones. Think about a table tennis ball and a tennis ball being blown by a gust of wind. The lighter one will move more)
Detection – some ions pass through a slit and are detected by the detector. Only those ions of the correct mass/charge ratio will be able to pass through the slit.

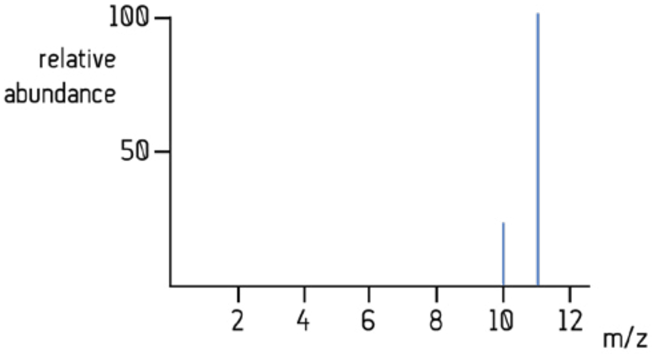
The inside of the spectrometer is under vacuum conditions so that air molecules do not interfere with the movement of the ions.

Using data from the mass spectrometer

Relative atomic mass determination

The chart below shows the mass spectrum for boron.

The relative abundance scale here has a maximum of 100, with the most abundant isotope being given a value of 100. You will often see the scale shown as relative *percentage* abundance, which means the abundance of all of the isotopes added together is 100.
Either method is acceptable, as long as you ensure your calculation is made using the **total** abundance of all the isotopes.



As there are two peaks, you can assume that there are two isotopes. One isotope has a relative isotopic mass of 10 and the other one has a relative isotopic mass of 11 on the carbon-12 scale.

The relative abundance of each isotope can be found using the graph: -

boron 10 = 23
boron 11 = 100

The relative abundances are often printed above each peak on the graph!

This means that if you have 123 atoms of boron, 100 will have a relative isotopic mass of 11 and 23 will have a relative isotopic mass of 10. You can now use this information to calculate the RAM of boron: -

$$\frac{(100 \times 11) + (23 \times 10)}{123} \quad \begin{array}{l}\text{(total mass of 123 atoms)} \\ \text{(number of atoms in the sample}\end{array}$$

$$= \frac{1330}{123}$$

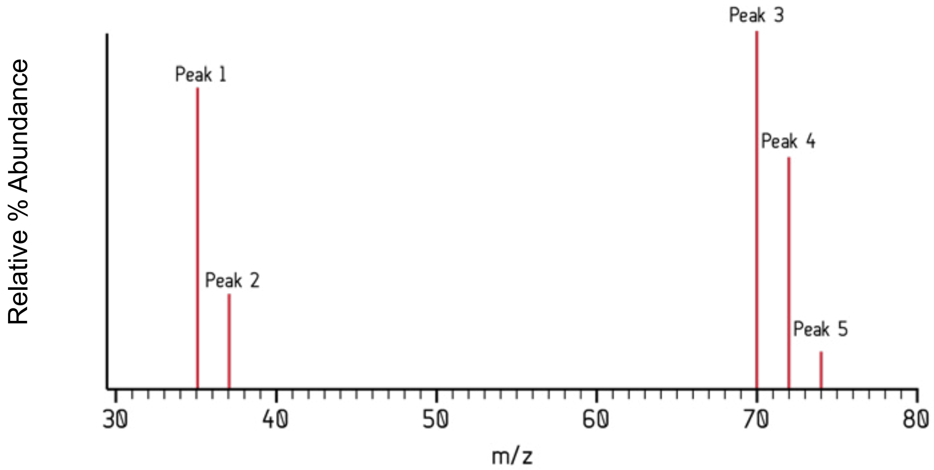
= 10.8 (to 3 significant figures)

The mass spectrum of chlorine, Cl_2

Chlorine is an example of a diatomic molecule – it exists as two atoms of chlorine covalently bonded together. The mass spectrum of chlorine therefore includes peaks for chlorine atoms (which exists as two isotopes) and chlorine molecules (which can exist in any combination of the two isotopes).

Peaks in ratio 3:1 for Cl^+ ions

Peaks in ratio 9:6:1 for Cl_2^+ ions



When Cl_2 molecules enter the ionisation chamber of the mass spectrometer, one of two things can happen to them – they can have one electron knocked off the molecule to give a molecular ion, Cl_2^+, or the unstable molecular ion will fall apart to give a chlorine atom and a chlorine ion, Cl^+. (Fragmentation) The atom formed here is also ionised.

Using this information, we can now analyse the mass spectrum of chlorine.

Peak 1 is caused by ^{35}Cl and Peak 2 by ^{37}Cl.

These are in the ratio of 3:1, which means that the ^{35}Cl isotope is three times more likely to exist than the ^{37}Cl isotope.

In order to explain the 9:6:1 ratio for the molecular ions, we have to think about all the possible combinations of Cl_2 molecules that can be made from the two isotopes: -

$(^{35}Cl - ^{35}Cl)^+$ - this is responsible for Peak 3 at m/z = 70

$(^{35}Cl - ^{37}Cl)^+$ and $(^{37}Cl - ^{35}Cl)^+$ - these are responsible for Peak 4 at m/z = 72

$(^{37}Cl - ^{37}Cl)^+$ - this is responsible for Peak 5 at m/z = 74

Now we can use simple probability to calculate why the ratios are 9:6:1. The probability of an atom being ^{35}Cl is $\frac{3}{4}$ and ^{37}Cl is $\frac{1}{4}$, so we can work out:-

molecule	$^{35}Cl - ^{35}Cl$	$^{35}Cl - ^{37}Cl$	or	$^{37}Cl - ^{35}Cl$	$^{37}Cl - ^{37}Cl$
probability	$\frac{3}{4} \times \frac{3}{4}$	$\frac{3}{4} \times \frac{1}{4}$		$\frac{1}{4} \times \frac{3}{4}$	$\frac{1}{4} \times \frac{1}{4}$
	$\frac{9}{16}$		$\frac{6}{16}$		$\frac{1}{16}$

So, the ratio of peaks is 9:6:1

Moles, molar mass and the Avogadro constant

This section is all to do with the ‘amounts of substances’. In a chemical reaction, a fixed sum of reactants makes a fixed sum of products, so reacting masses need to be carefully worked out. Because they are so small, it is impossible to do this by measuring the masses of individual atoms, so the mass of a fixed number of atoms is used.

The mass of this fixed number of atoms of carbon-12 is 12g. (This, again, is chosen as the standard with which we compare other atoms.) The number of atoms of carbon-12 that weighs 12g is 6.02×10^{23} (a huge number!) and this number is called the **Avogadro constant (L)**.

A **mole** of any substance (atom, ion or molecule) is the amount of that substance that contains the same number of particles as there are atoms in exactly 12g of carbon-12. (This is the definition you need to learn.)

You can also think of one mole of a substance as the amount of that substance that contains Avogadro’s constant in particles. **You must state the type of particle that you’re referring to**, a mole of hydrogen **atoms** is different to a mole of hydrogen **molecules**.

The **molar mass** is the mass of one mole of a substance. It is the same number as the relative atomic or molecular mass (A_r or M_r), but as we’re talking about proper masses, it has a unit. The unit is g mol^{-1}.

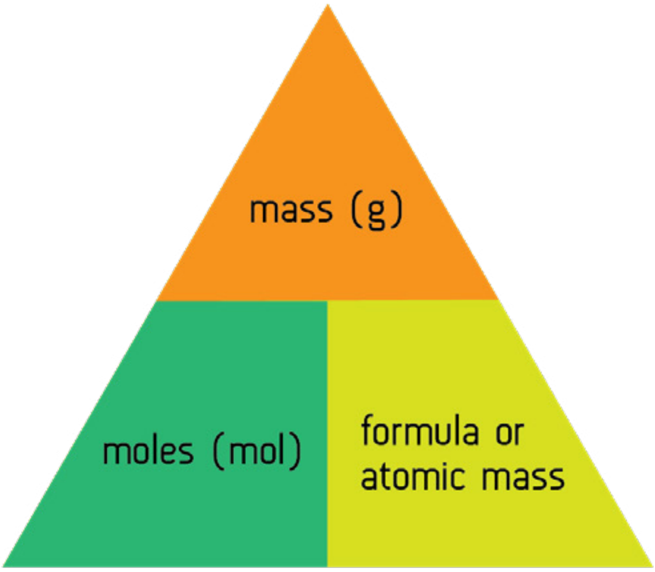
This is one of the most important equations you need to know in Chemistry when it comes to calculations: -

$$\text{number of moles (n)} = \frac{\text{mass of substance (m)}}{\text{molar mass (M)}}$$

You should also be able to re-arrange the equation in order to find out the mass of substance and molar mass. This is easily done using a formula triangle – you’ve probably used these before.

Cover up the part you want to find out and your calculation will be between the other two.

LEARN IT!



Empirical and molecular formulae

A formula tells us the number and type of atom present.

An **empirical formula** tells us the *simplest formula*, giving us the proportions of elements present in a compound as the simplest ratio, but not the actual number of atoms of each element.

A **molecular formula** gives us the actual number of atoms of each element that are present in the molecule. The empirical formula is multiplied by a whole number in order to give the molecular formula. The relative formula mass is required in order to determine the molecular formula when the empirical formula is known.

Worked example 1

A compound is found to contain 50.05 % sulfur and 49.95 % oxygen by mass.
(a) What is the empirical formula for this compound? (b) The relative formula mass for this compound is 64.0 g mol^{-1}. What is its molecular formula?

(a)	S	O
Molar ratio of atoms	50.05	49.95
Divide by A_r	32	16
	= 1.56	= 3.12
Divide by smallest number	1	2

Empirical formula is SO_2

(b) Mass of empirical formula = 32 + (2 x 16) = 64

Number of SO_2 units in a molecule = $\frac{64.0}{64} = 1$

Molecular formula is SO_2

Worked example 2

Caffeine has the following percent composition: carbon 49.48%, hydrogen 5.19%, oxygen 16.48% and nitrogen 28.85%. Its relative formula mass is 194.19 g/mol. (a) What is its empirical formula? (b) What is the molecular formula?

(a)	C	H	O	N
Molar ratio of atoms	49.48	5.19	16.48	28.85
Divide by A_r	12	1.01	16	14
	= 4.12	= 5.14	= 1.03	= 2.06
Divide by smallest	4	4.99	1	2

Empirical formula is $C_4H_5ON_2$

Mass of empirical formula = (4 x 12) + (5 x 1.01) + 16 + (14 x 2) = 97.05

Number of $C_4H_5ON_2$ units in a molecule = $\frac{194.19}{97.05} = 2$

Molecular formula is $C_8H_{10}O_2N_4$

Calculating reacting masses (of solid substances)

A chemical equation tells us what the reactants and products are and also, which is very important when calculating reacting masses, how many moles of each substance react and are formed. The ratios between these moles of reactants and products are called **stoichiometric** (or **mole**) ratios. Simply, the number of moles of each substance in a reaction is the number preceding each symbol or formula in an equation.

Worked example

Sodium burns in oxygen to produce sodium oxide. Here is the equation for this reaction: -

$$4Na + O_2 \rightarrow 2Na_2O$$

It tells us that 4 moles of sodium react with 1 mole of oxygen to produce 2 moles of sodium oxide.

What mass of sodium is burned in excess oxygen in order to produce 1.24g of sodium oxide?

You know most about sodium oxide as you know its mass and can work out M_r easily.

Step 1: Calculate the number of moles of sodium oxide formed in the reaction.

Step 2: Use the balanced equation to find out the mole ratio of sodium and sodium oxide. From this, work out the number of moles of sodium needed.

Step 3: Calculate the mass of sodium needed from the number of moles discovered in **Step 2**.

1 $\text{moles} = \frac{\text{mass}}{A_r} = \frac{1.24}{62} = 0.020 \text{ mol}$

2 Ratio from the equation is $4Na : 2Na_2O$, so the simplest ratio is 2:1

For every one mole of sodium oxide formed, two moles of sodium are required. If there are 0.020 moles of sodium oxide formed, **0.040 moles of sodium must be required**.

3 Use the equation, $\text{mass} = \text{moles} \times A_r$ to calculate the mass of sodium that needs to be burned.

$$\text{mass} = 0.040 \times 23 = 0.92\text{g of sodium}$$

Calculating volumes of gases in chemical reactions

Rather than trying to measure the mass of gases, it is more usual to calculate the volume of gases in chemical reactions. This is a lot more convenient than trying to work out the relative molecular mass of gases because all gases (in an ideal situation) follow a particular set of rules.

One mole of any gas at standard temperature and pressure (stp), 0°C and 1atm, will occupy a volume of 22.4dm^3. When the temperature rises to room temperature and pressure (rtp), 25°C and 1atm, one mole of gas occupies 24dm^3. These values are called the **molar volume (V_m) of a gas.**

(NB, you do not need to learn these values, they will be provided as part of the question.)

The steps involved when working out the volumes of gases are very similar to those used when working out reacting masses – work out the number of moles reacting, then convert into volume rather than mass.

Worked example

Carbon dioxide gas is produced in the reaction between calcium carbonate and hydrochloric acid. What volume of carbon dioxide is produced at rtp when 25g of calcium carbonate reacts with excess hydrochloric acid? [1 mole of carbon dioxide occupies 24dm^3 at rtp]

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

Step 1: Calculate the number of moles of calcium carbonate used in the reaction.

Step 2: Use the balanced equation to find out the mole ratio of calcium carbonate and carbon dioxide. From this, work out the number of moles of carbon dioxide produced.

Step 3: Calculate the volume of calcium carbonate produced from the number of moles discovered in **Step 2**.

1: $\text{moles} = \frac{\text{mass}}{M_r} = \frac{25}{100} = 0.25 \text{ moles}$

2. ratio from the equation is $1CaCO_3 : 1CO_2$, therefore there are 0.25 mol of CO_2.

3. volume of CO_2 = number of moles x molar volume (at rtp)
= 0.25 x 24
= 6dm^3

Calculations involving changes of conditions

It was stated earlier that molar volumes depend on particular conditions of temperature and pressure. What happens when temperature or pressure are changed? We can use the equation of state for an ideal gas to work out volumes when this happens: -

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

1 represents the conditions at the beginning of the experiment and 2 represents the conditions after a change.
P = pressure, V = volume (units not important as long as they are the same for both 1 and 2.
T = temperature, always has to be in Kelvin, K. (K = °C + 273)

The ideal gas equation

This equation links pressure, volume, temperature and the number of moles of a gas. It was derived from gas laws and Avogadro's principle.

$$PV = nRT$$

P = pressure (**must be in Pascals or Nm^{-2}**)
V = volume (**must be in m^3**)
n = number of moles
R = the gas constant (always given to you in the question)
T = temperature (**always in Kelvin**)

These questions are fairly straightforward once you have converted the values into the correct units, have worked out what the question is asking for and then rearranged the equation.

Solution concentrations

A solution is made up of a dissolved substance (the solute) in a certain volume of liquid (the solvent). The concentration of a solution gives a measure of how much solute is dissolved in a given volume of solvent.

The volume of solution used in concentration measurement is 1 dm^3 of solution (this is the equivalent of 1 litre or 1000 cm^3). The amount of solute present in this 1 dm^3 of solution is given in moles. This means that the unit for concentration is: -

$$\text{concentration} = \text{mol dm}^{-3} \text{ (or mol/dm}^3\text{)}$$

This unit is very useful when it comes to calculations involving solutions because it is easily remembered and can be used to work out concentration of a solution, as well as the number of moles or a required volume.

If we write out the equation with explanation: -

$$\text{concentration} = \frac{\text{moles (of solute)}}{\text{dm}^3 \text{ (volume of solution in dm}^3\text{)}}$$

In simple calculations involving concentration, amount of solute is usually given in grams and the volumes are in cm^3. You must therefore convert mass to moles and cm^3 to dm^3 before you can answer them successfully.

You may also see questions that give you the *solubility* of a solute, usually expressed in grams that can dissolve in 100 cm^3 of water. All you do with this is use the values given in the solubility and use them as in the worked example below.

Worked example

0.037g of calcium hydroxide ($Ca(OH)_2$) is dissolved in 200cm^3 of water. Calculate the concentration of the solution formed in mol dm^{-3}.

1. **Convert mass of calcium hydroxide to moles.** Use moles = mass/M_r

   M_r $Ca(OH)_2$ = (40 +16 + 16 + 1.01 +1.01) = 74.02

   number of moles = 0.037/74.02 = 0.0005 moles

2. **Convert the volume of water from cm^3 to dm^3 by dividing by 1000**

   200/1000 = 0.2 dm^3

3. **Fill in the equation:**

   concentration = 0.0005/0.2 = 0.0025 (or 2.5×10^{-3} in standard form) mol dm^{-3}

Calculations involving acid-base titrations

Acid-base titration is a means by which the concentration of an acidic or basic solution can be discovered. The concentration of one solution is known and it is reacted precisely with the other solution until the exact moment of neutralisation occurs (measured by an indicator). The known volumes of both reactants and the concentration of one can be used to find out the concentration of the second. You also need to have a balanced equation for the reaction. (This procedure will be covered in more depth in the last chapter of Unit 1.)

Here are the steps that need to be followed. **Let's imagine that we don't know the concentration of the base**: -

1 Work out the number of moles of acid used in the reaction – you know the volume and concentration, so you will use: - moles = concentration x volume (in dm^{-3})

2 Using the balanced chemical equation, work out the stoichiometric ratio of acid:base and from this the number of moles of base that the acid reacted with.

3 Now you know the number of moles of base, use the volume of it that reacted with the acid to work out its concentration. Use the equation: - concentration = moles/volume in dm^3.

Worked example

25.0 cm^3 of sulfuric acid were exactly neutralised by 28.5 cm^3 of sodium hydroxide that had a concentration of 0.750 mol $dm^{-3.}$ Calculate the concentration of the sulfuric acid.

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + H_2O$$

In this question, we know the concentration of the NaOH, so we find the number of moles of this first and then use the information gained to calculate the concentration of the sulfuric acid.

1 Number of moles of NaOH = concentration x volume
= 0.750 x 28.5/1000
= 0.0214 mol (to 3 sig.figs)

2 Ratio of H_2SO_4: NaOH from equation = 1:2
So, if we have 0.0214 moles NaOH, we'll have 0.0107 moles of H_2SO_4.

3 Concentration of sulfuric acid = 0.0107/0.0285 = $\underline{0.375 \text{ mol dm}^{-3}}$

Back titration

In a back titration, there is always an excess reagent used, eg acid reacting with eggshells in order to find the calcium carbonate in them. Some of the acid you started with will react with the eggshell, but there will be some left over. You react this left over acid with a base to find out how many moles of acid you are left with and, from this, you can find out how much was used in the reaction. From this you can find out how much calcium carbonate was in the eggshell.

Worked example

A sample of crushed eggshell weighing 0.135g was reacted with 40.00cm^3 of 1.00 mol dm^{-3} hydrochloric acid (an excess). After the reaction was complete the solution was transferred to a 250cm^3 volumetric flask and made up to the mark with distilled water. 25.00cm portions of this solution were then titrated against 0.15mol dm^{-3} sodium hydroxide. An average of 25.00cm^3 of the sodium hydroxide was required.
Calculate the percentage of calcium carbonate in the eggshell.

1 Calculate the number of moles of sodium hydroxide used in the neutralisation reaction with the HCl, this will tell us how much of the HCl was unused in the reaction with the eggshell:-

Equation for the reaction is $NaOH + HCl \rightarrow NaCl + H_2O$

moles NaOH = concentration x volume in dm^3 = 0.15 x 0.025 = 0.00375 moles

Acid and alkali are in a 1:1 ratio, so there must be 0.00375 moles of acid left over in 25 cm^3.
However, the sample came from a 250 cm^3 volume, so there must be 0.0375 moles of acid in that
2 Calculate how many moles of acid were used to react with the eggshell:-

Initial number of moles of acid added to the shell = 1.00 x 0.040 = 0.040 moles

There were 0.0375 moles left over, so there must have been 0.04 – 0.0375 = 0.0025 moles of acid used in the reaction with the eggshell.

3 Equation for calcium carbonate reaction is: $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$
so the ratio for $CaCO_3$ and HCl is 1:2. This means that if there are 0.0025 moles of acid reacted with the eggshell, there must have been 0.00125 moles of calcium carbonate in the 0.135g of eggshell.

4 Calculate the mass of calcium carbonate in the eggshell using the equation mass = moles x M_r

mass = 0.00125 x 100 = 0.125g

5 % of calcium carbonate in eggshell = mass of calcium carbonate/mass of eggshell x 100

= 0.125/0.135 x 100 = 92.6%

Atom economy and percentage yield

These relate to the products in a chemical reaction. If products are formed other than the one needed, then these are wasted. A very efficient reaction has a high **atom economy** and **percentage yield**.

$$\text{Atom economy} = \frac{\text{mass of required product}}{\text{total mass of reactants}} \times 100$$

$$\%\ \text{yield} = \frac{\text{mass of product obtained}}{\text{maximum theoretical mass}} \times 100$$

Percentage error and significant figures

In Chemistry, any error in results is estimated from the uncertainties in the equipment used, eg, burette, pipette or thermometer. Manufacturers often quote uncertainties on each piece of equipment. Where this is missing, you can quote the margin of uncertainty as a half of the smallest division on the apparatus (multiplied by two as a beginning and end reading are often taken). The table below shows how uncertainty is calculated using uncertainties quoted on apparatus by the manufacturer: -

Equipment	Estimate of Uncertainty	Value measured in experiment	% Uncertainty
25 cm^3 pipette	± 0.06 cm^3	25.00 cm^3	0.06/25.00 x 100 = 0.24%
50 cm^3 burette	± 0.10 cm^3	24.30 cm^3	0.10/24.3 x 100 = 0.41%
250 cm^3 flask	± 0.20 cm^3	25.00 cm^3	0.20/25 x 100 = 0.80%
Balance	± 0.01g	1.51g	0.01/1.51 x 100 = 0.87%

The calculation made is:-

% uncertainty or error = Estimate of error/Value measured by that piece of equipment x 100

Once you have the percentage error for each piece of equipment, you add them together and have a total % error. (If one of these is around three times larger than the others, then you can ignore the smaller ones at AS level.)

This total % error is applied to your final value and you will get a range of possible values. The number of significant figures for any value is important. If you have an error between 0.1% and 1%, then a sensible number of significant figures to use is 3.

Hopefully you know how to express a number to significant figures (sig figs). If not, here are some basic rules: -

1 If you have zeros to the left of the first number that is not a zero, then those zeros are npt significant. (Usually applies to numbers that start with 0.000…..)
2 If you have zeros between numbers, they are significant, eg 7007 has 4 sig figs.
3 Zeros to the right of a decimal point that have a number in front of it are significant.

Examples: -

0.000081 has **two sig figs.**

307.14 has **five sig figs.**

7.006 has **four sig figs.**

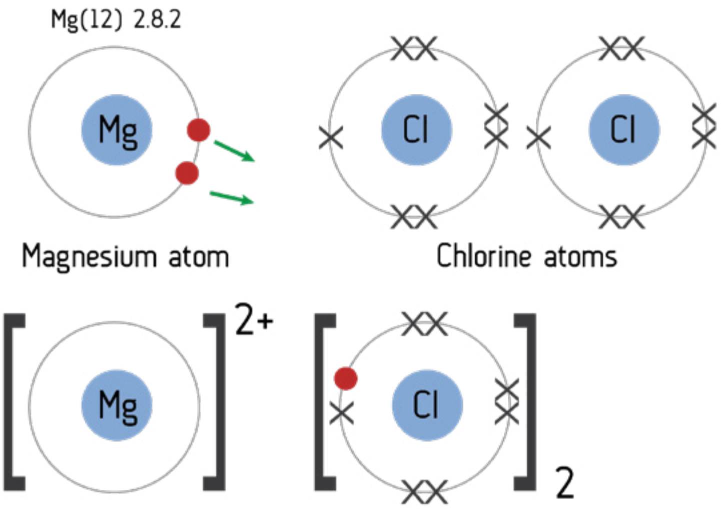
1.4 Bonding

Chemical Bonding

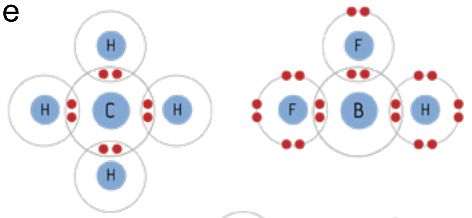
GCSE Chemistry taught us that only a few elements exist as atoms here on Earth. The rest exist bonded together with other atoms to form molecules of differing types, depending on how they bond. There are three main ways in which atoms bond, which you came across at GCSE – **ionic, covalent and metallic**. In the following descriptions, the bonds are shown by ‘dot and cross’ diagrams. Only the outer electrons are shown and the ones from different atoms are represented either as crosses or dots.

Ionic bonding is where one atom donates one or more electrons to another, resulting in the formation of a cation (positive ion) and an anion (negative ion). These ions are strongly attracted to each other because of the opposite electrical charges and the resulting compounds form a solid lattice with high melting point.

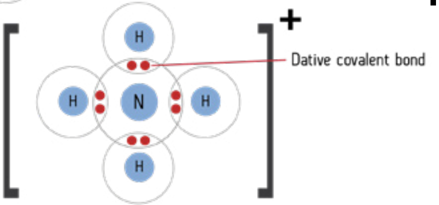
Energy is required when ions are formed, but this is more than paid back by the electrical attraction that is between the cation and anion.

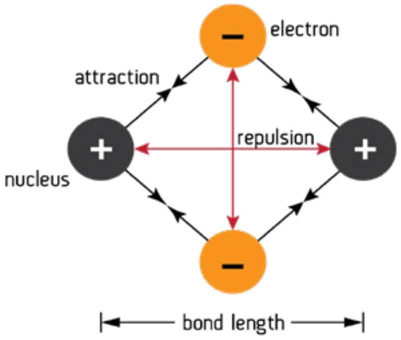


Covalent boding is where each atom gives one electron to the shared pair of electrons. Each electron in the bond has opposite spin, ie, they don’t spin in the same direction.



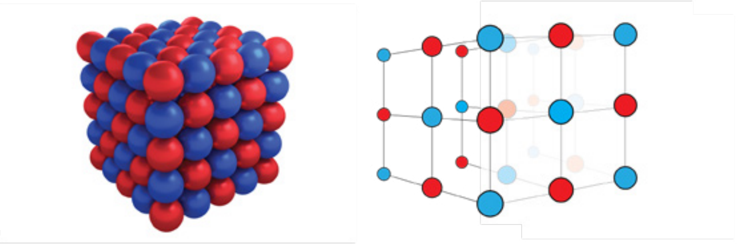
Co-ordinate or dative bonding is a **covalent bond** where both electrons in the bond come from the same atom. You can see in this diagram of the ammonium ion (NH_4^+) that two electrons in one of the bonds comes from one of the hydrogen atoms.





At AS level, you need to be sure that you understand the role of electrical attraction and repulsion between protons and electrons in a **covalent bond**. Electrons in the bond repel each other, but this repulsion is overcome by the attraction between the electrons and the protons of **both** nuclei. If atoms get too close together, then the inner electrons and the nuclei will repel each other, so the bond length is determined by all of these factors. As mentioned previously, the electrons in a bond have opposing spins so as to minimise repulsion.

The cations and anions in an **ionic bond** are arranged so that each anion is surrounded by a certain number of cations and vice versa so that there is maximum attraction obtained and also minimum repulsion.



Electronegativity and polarity of bonds

In a hydrogen molecule, the shared electrons in the single covalent bond are shared evenly between the two hydrogen atoms. If you have a molecule where the atoms are not the same, eg HCl, then the electron pair is not shared evenly between the two atoms, leading one atom in the molecule to be slightly more negative than the other. This is shown using the δ^+ and δ^- symbols above the atoms:-

$$\overset{\delta^+}{\mathrm{H}} \text{ —— } \overset{\delta^-}{\mathrm{Cl}}$$

This type of bond is said to be **polar**. The majority of covalent bonds are polar, unless the atoms are the same or have the same effect on the shared electrons.

Co-ordinate bonds are always polar because it is one of the atoms that donates both electrons and is the one that has most right over the electrons.

The polarity in bonds is determined by a concept called **electronegativity**. This can be very simply explained as the ‘pulling power’ over the bond electrons that the atoms in a covalent bond have.

The difference in electronegativity determines whether a bond is polar or not. The largest difference in electronegativity leads to the most polar bonds.

Here is a chart showing the Pauling **electronegativity scale**, the one most commonly used. This need not be learnt as any required information will be given to you.

Metals in the transition area have an electronegativity value of around 1.6.

Covalent bonds that are polar are said to have some ionic character because they don’t share electrons equally. The larger the difference in electronegativity, the greater the ionic character. Eg, HCl is said to have 19% ionic character.

IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
H 2.1							He –
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne –
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar –
K 0.8	Ca 1.0	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr –
Rb 0.8	Sr 1.0	In 1.7	Sn 1.8	Sb 2.0	Te 2.1	I 2.5	Xe –
Cs 0.7	Ba 0.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn –

Intermolecular forces

Definitions

Intermolecular forces are those that occur **between** molecules.

Intramolecular forces are those that occur **within** molecules.

Intermolecular forces determine physical properties of compounds and the intramolecular forces determine chemical properties, or how the compound reacts.

These type of forces occur between **covalent molecules**.

As covalent compounds are generally soft solids, liquids and gases, you can imagine that intermolecular forces are very weak. **This is because these type of substances have low melting and boiling points due to the fact that their intermolecular forces require very little heat energy to break them. However, the forces within the molecules (covalent bonds) are very strong and require a high temperature to break them.**

Ionic solids need extremely high temperatures to break the force of attraction between the ions.

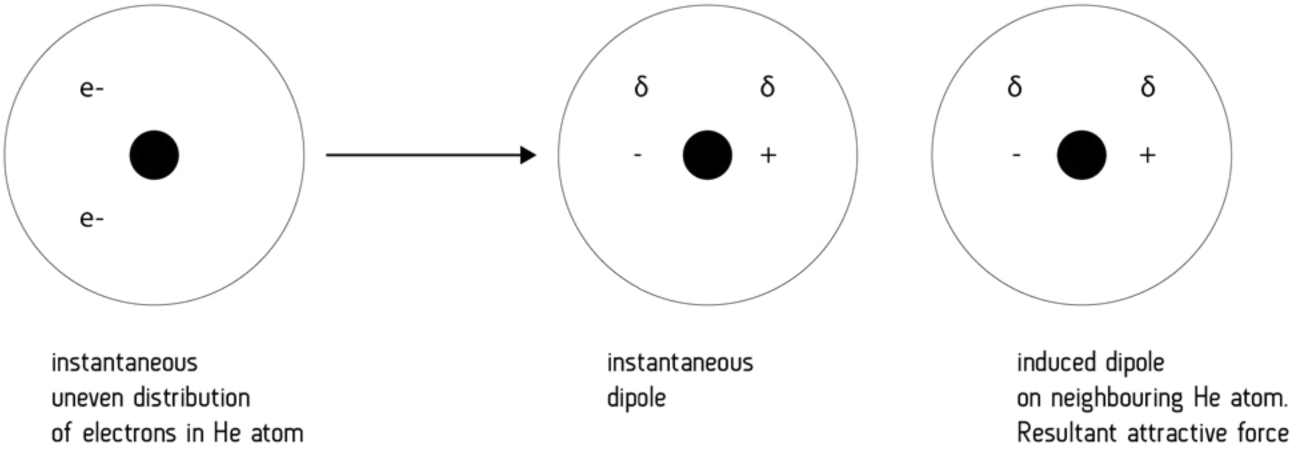
Types of intermolecular forces

Induced dipole-dipole interactions

These are the **weakest** type of intermolecular bond.

All types of intermolecular bond are caused by electrical interaction between opposite charges. Molecules are neutral, so how can this happen?

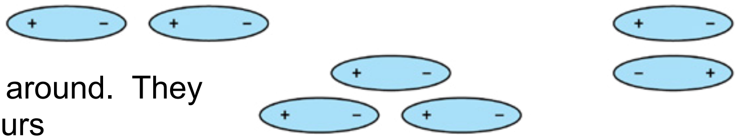
It's because they all contain protons and electrons and in **polar** molecules, this causes a **dipole** as previously mentioned. In non-polar molecules, a dipole can still be formed. This is because electrons are constantly moving around the nuclei so that sometimes they are on one side only and cause a temporary dipole. This causes a dipole in a neighbouring molecule as the electrons move to the δ^+ side of the molecule. This is shown for He atoms in the diagram below: -



This is an example of **van der Waals forces**.

Dipole-dipole interactions

These occur between polar molecules and are exactly the same as the induced kind, but do not rely on the fact that electrons move around. They are already polar, so the dipole interaction occurs instantaneously.



This is another example of **van der Waals forces**.

Van der Waals forces are very weak, around 3kJ mol^{-1}.

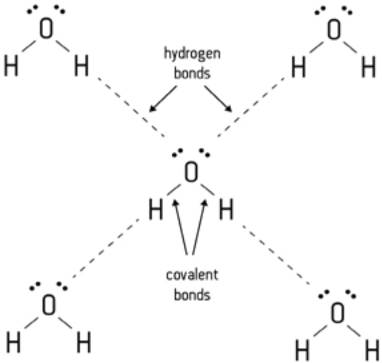
Hydrogen bonding

This is the strongest of the intermolecular forces.

It only happens between molecules that contain hydrogen atoms bonded to **fluorine, oxygen** and **nitrogen – atoms with high electronegativities and lone pairs.**

Although it is the strongest, it is still relatively weak compared to the covalent bond, at 30kJ mol^{-1} compared to 300kJ mol^{-1} for covalent bonds.

Hydrogen bonding in water



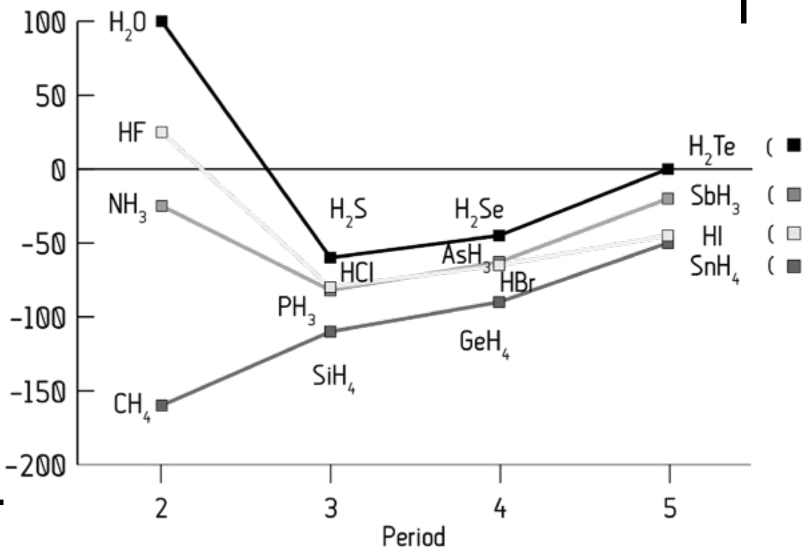
The hydrogen atoms are the δ$^+$ side of the water molecule, with two lone electron pairs on the oxygen atom being the δ$^-$ side.

There is attraction between the oxygen of one molecule and one of the hydrogens of two other molecules. The small size of the hydrogen atom allows the two of them to closely approach the oxygen, forming strong bonds and a tetrahedral hydrogen-bonded structure. The site of attraction to the oxygen atom are the two lone pairs. Note that the hydrogen bonds connecting the two molecules are longer than the internal covalent bonds in the molecules.

Effect of hydrogen bonding on boiling points

As intermolecular forces increase, so do boiling temperatures and they should show a general increase down a group. Look at Group 4 in the diagram, boiling temperatures steadily increase from methane to tin hydride.

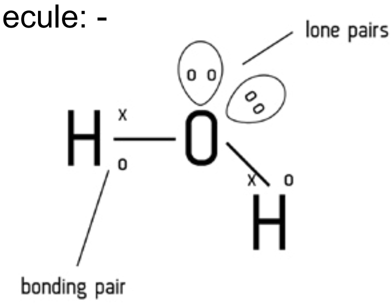
This pattern is completely broken in groups 5, 6 and 7 due to the presence of nitrogen, oxygen and fluorine at the top of these groups. Hydrogen bonding within these molecules forces the boiling points far higher than would be expected with only van der Waals forces.



Shapes of Molecules

Covalent molecules and complex ions have fixed shapes if they have two atoms or more. The shape is determined by the number and type of electron pairs that are around the central atom, eg around the oxygen in H_2O.

These electron pairs can be **bonding pairs** that are electrons shared between two atoms and forming the covalent bond. They can also be **lone pairs** – spare electrons that are present in the outer shell of the central atom and are not involved with the covalent bonding. Both types of bond can be seen in the water molecule: -



All electron pairs repel each other and the shape that is formed is the one that allows the pairs to keep as far away from each other as possible so that repulsion is minimised. Bonding pairs are not as close to the central atom as lone pairs are, they are spread out between the two bonding atoms. Because of this, lone pairs repel more than bonding pairs and this leads to the following sequence of repulsion for electron pairs: -

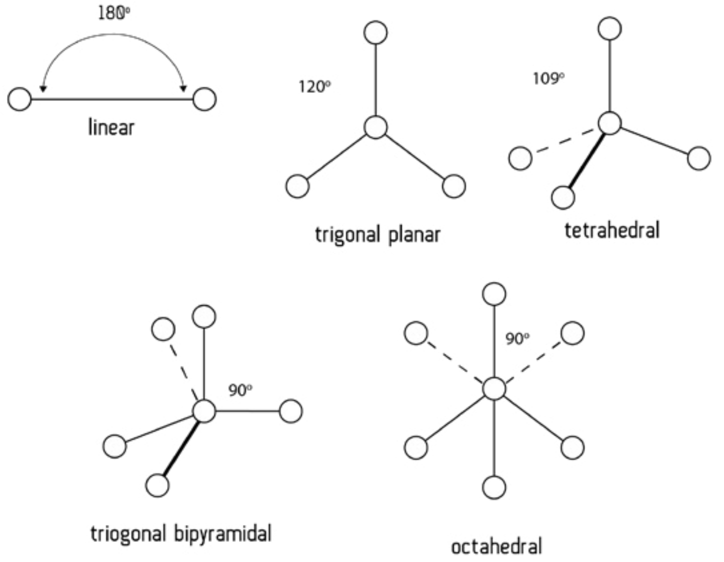
lone pair – lone pair > lone pair – bonding pair > bonding pair – bonding pair

So, in the water molecule, with two lone pairs and two bonding pairs the repulsion between the two lone pairs is greater than that between the lone pair and the bonding pair, so the molecule is squashed into a v-shape. We will see more about this in the next section.

The VSEPR (Valence Shell Electron Pair Repulsion) Theory makes deciding the shapes of simple molecules fairly straightforward. The valence shell is the one where bonding occurs (ie, the outer shell).

Your first step is to count the number of lone pairs and bonding pairs around the central atom. This can help provide the general shape of the molecule and then the repulsion sequence shown above is applied to the number of lone and bonding pairs in order to determine the final shape. Here are the shapes that are formed when you have the following number of pairs: -

Number of electron pairs	Shape	Bond Angle	Examples
2	linear	180°	$BeCl_2$
3	trigonal planar	120°	BF_3
4	tetrahedral	109.5°	CH_4
5	trigonal bipyramid	90° /120°	PCl_5
6	octahedral	90°	SF_6



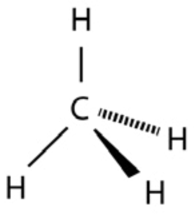
If you're asked to draw any of the shapes, this is the best way to show them.

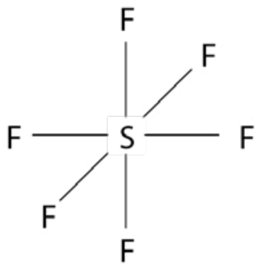
These shapes can be distorted depending on how many lone pairs and bonding pairs are surrounding the central atom.

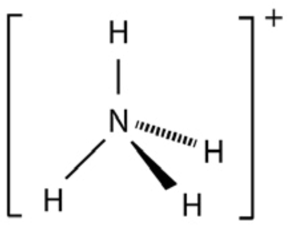
With water, as there are four pairs of electrons surrounding the central atom, you'd expect a tetrahedral shape as with methane. However, because there are two lone pairs, the 109° between the two bonding pairs will be reduced to around 104° by the two lone pairs.

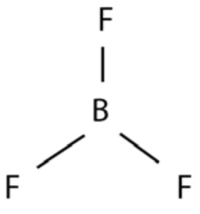
Similarly, for NH_3, there are four pairs of electrons, one of which is a lone pair, so the 109° you'd expect for a tetrahedral shape is reduced to around 107° due to the presence of the single lone pair. (Larger angle than for water as there's only one lone pair repelling.)

You have to learn all of the bond angles associated with the shapes described in the table, as well as the shapes of BF_3, CH_4, NH_4^+ and SF_6 – see below. You also need to predict and explain the shapes of other simple molecules and ions having up to six electron pairs around the central atom.









1.5 Solid Structures

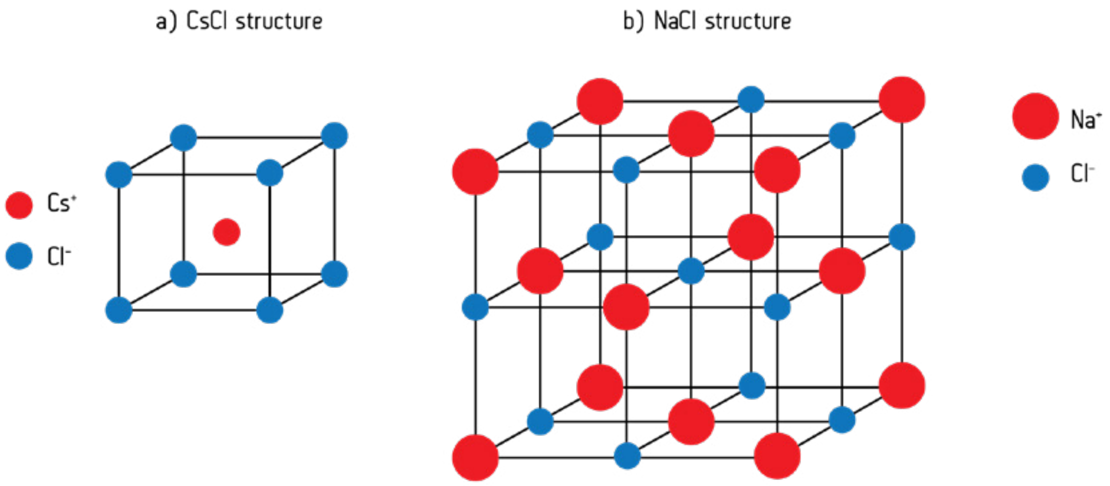
Ionic crystals – sodium chloride and caesium chloride

Both of these solids are made up of oppositely charged ions packed around each other. This maximises attraction between the ions and minimises repulsion, ensuring maximum bond energy.

In sodium, each cation is surrounded by six anions and each anion is surrounded by six cations.

In caesium, the number surrounding each is eight. This is because the Cs^+ cation is larger than that of Na^+, so has more room to accommodate a greater number of anions.

Crystal co-ordination numbers are 6:6 for NaCl and 8:8 for CsCl

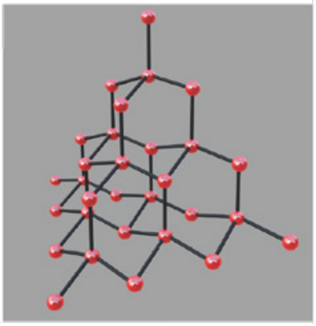


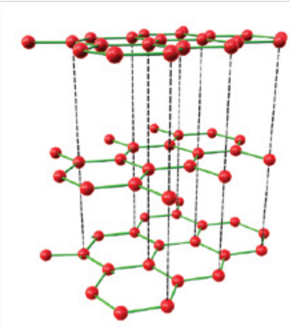
Covalent compounds – giant structures – diamond and graphite

Diamond and graphite are two forms of carbon, which is able to form four covalent bonds. In diamond, the carbon bonds strongly in a tetrahedral formation to form a giant 3-D structure.

In graphite, only three bonds are made by each carbon atom, making hexagonal layers (monolayers – only one atom thick) that are held together by weak forces.

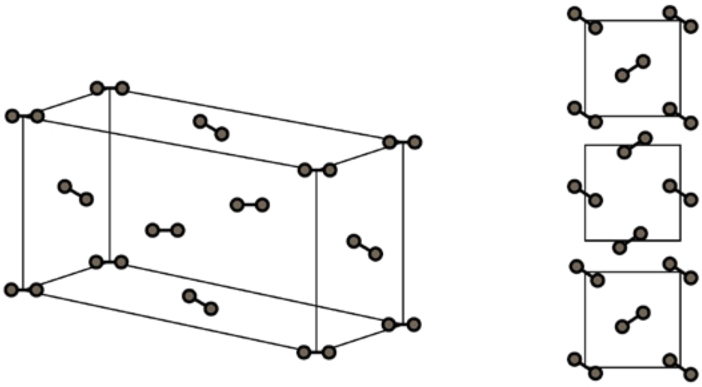
diamond



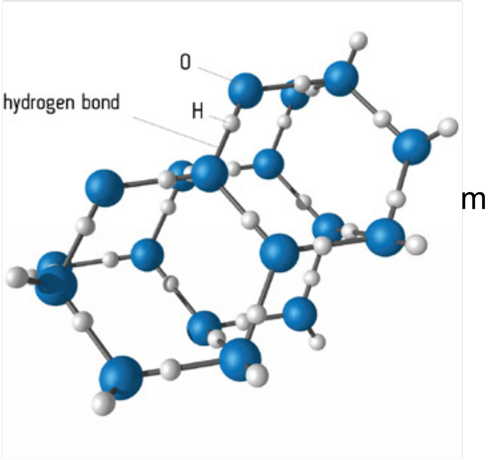


graphite

Covalent compounds – simple structures – iodine and ice



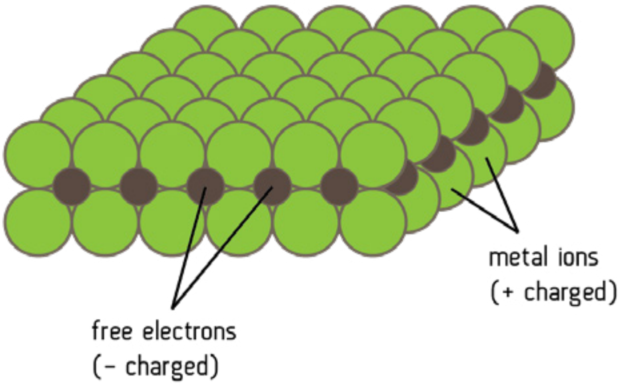
If you could look down through the top of the iodine structure on the left, you would see that the I_2 molecules are positioned in layers as shown in the diagram on the right. Each molecule and layer is held together by weak intermolecular forces. Of course, the covalent bond between the two iodine atoms is very strong.



In ice, you can see that hydrogen bonds hold the water molecules together in a large tetrahedral structure. The strong bonding in the water molecule are polar covalent.

Metallic bonding

Metallic structure is unusual in that the metal atoms become cations and 'squeeze' out their electrons so that they are **delocalised** and form an 'electron sea' around the metal ions. The interaction between the two holds them together in a uniform shape



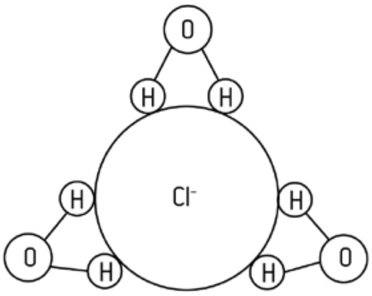
Physical properties of the different structures

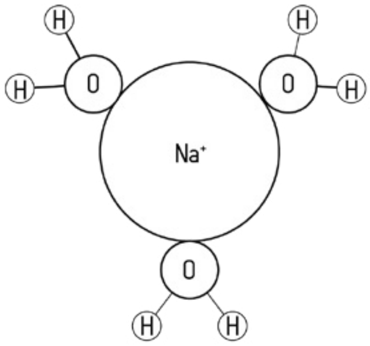
Ionic solids

- hard, brittle and high melting points due to the strong ionic bonds.

- don’t conduct electricity as solids, but when molten or dissolved in water they conduct due to the ions being mobile when voltage is applied.

- some are soluble in water (most chlorides are soluble). Solids will only dissolve if it is energetically favourable to do so. It takes a lot of energy to break the ionic bonds, so there needs to be some ‘payback’ if this is to happen. If the ions of the salt can be surrounded by the water dipoles, then a large amount of energy is given back as hydration energy, so a solution can be made.





Covalent solids

Giant covalent solids: -

- high melting points, insoluble in water (strong covalent bonds to break and no ions to interact with water dipoles)

- diamond is very hard because each carbon atom is bonded to four others, which forms a 3D structure.

- graphite is softer as it has a weaker layer structure, so it’s useful as a lubricant as the layers slide over each other.

- graphite conducts electricity as there is one spare electron for each carbon atom and these become delocalised in the layers.

- iodine is also soft and volatile as the units of iodine are held together by van der Waals forces.

Metals

- conduct electricity and heat due to the electron delocalisation. Electrical conductivity increases with the number of delocalised electrons per atom. Al is a better conductor than Na.

- hardness of metals depends on the number of electrons delocalised per atom, the more delocalised electrons you have, the harder the metal.

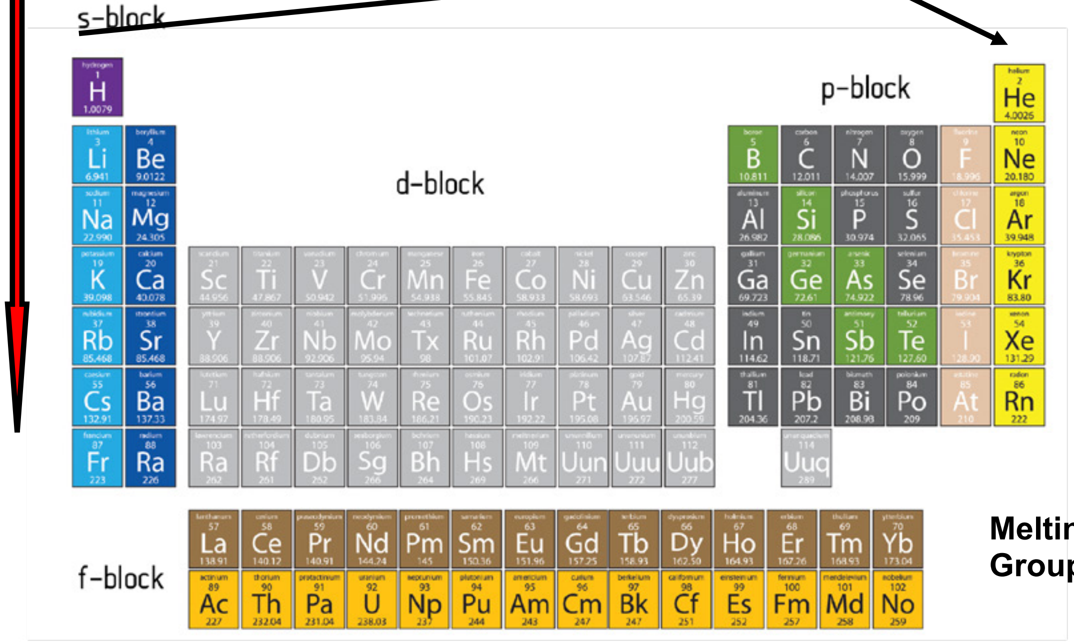
1.6 The Periodic Table

Melting points decrease down Group 1

Melting points of elements increase up to Group 4 and then decrease down to Group 7

s-block elements are reducing—they accept electrons and form cations easily

p-block elements are oxidising—Groups 6 and 7 give off electrons and form anions easily



The oxides of sblock elements are acidic.

The oxides of pblock elements are basic.

Melting points decrease up Group 7

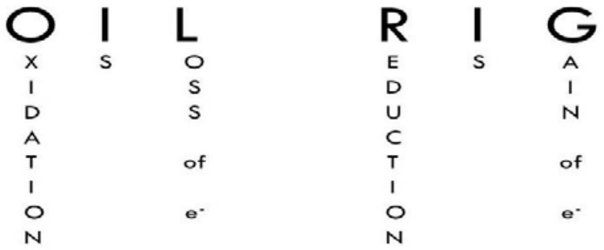
Ionisation energy and electronegativity increases across a period and up a group

Elements are arranged by increasing atomic number. There are 8 vertical **groups** and 7 horizontal **periods**. Elements in the same group exhibit similar properties because they have the same number of electrons in their outer shells. This outer electron number corresponds to the group number. Valency rises with group number up to 4 and then falls to 8 minus the group number.
Melting points vary as they do because of the increase in electrons for metallic bonding from groups I to III, then peak at Group 4 due to the strong covalent bonds. They decrease then because of the diatomic molecules formed in Groups 6 and 7.

iv

Redox

Redox is reduction and oxidation which occurs in many chemical reactions. **Oxidation** is loss of electrons and **reduction** is gain of electrons in the redox reaction. You probably remember OILRIG: -



Eg, the formation of magnesium oxide: -

$$Mg + \frac{1}{2}O_2 \rightarrow Mg^{2+} + O^{2-}$$

The Mg is oxidised, losing two electrons and the O is reduced, gaining two electrons. Both have to happen in the same reaction as electrons need to be **transferred** somewhere.

An **oxidising agent** is a species that accepts electrons, thereby helping oxidation. It becomes reduced itself in the process.

A **reducing agent** is a species that donates electrons, thereby helping reduction. It becomes oxidised itself in the process.

Oxidation Numbers

These are a useful tool for working out what has become oxidised and reduced in a redox reaction. This is a fairly simple process with reactions like the one shown above, but can get more complicated the more complex the reactants become. Each element within a compound can be assigned an oxidation number and if the number changes as a product, then oxidation or reduction has occurred.

Rules for assigning oxidation numbers: -

1 All elements have an oxidation number of zero (including diatomic molecules like H_2)

2 Hydrogen is 1 unless it's with a Group 1 metal, then it's -1

3 Oxygen is -2 (unless it's a peroxide or reacted with fluorine, then it's -1).

4 Group 1 and 2 elements are 1 and 2 respectively.

5 Group 6 and 7 elements are -2 and -1 respectively.

6 Oxidation numbers of elements in a compound or ion must add up to zero or the ion's charge.

Worked example

Work out the oxidation numbers of all of the elements in H_2SO_4
H = 1 (x 2 atoms, so total for the H's is 2)
O = -2 (x 4 atoms, so the total for O's is -8)
S is therefore 6, as 6 + 2 (from the hydrogens) is 8, which cancels out the -8 from the oxygens.

s-block elements – trends in properties of Groups 1 and 2

Both groups form oxides with oxygen or air: -

$4Na + O_2 \rightarrow 2Na_2O$
$2Mg + O_2 \rightarrow 2MgO$

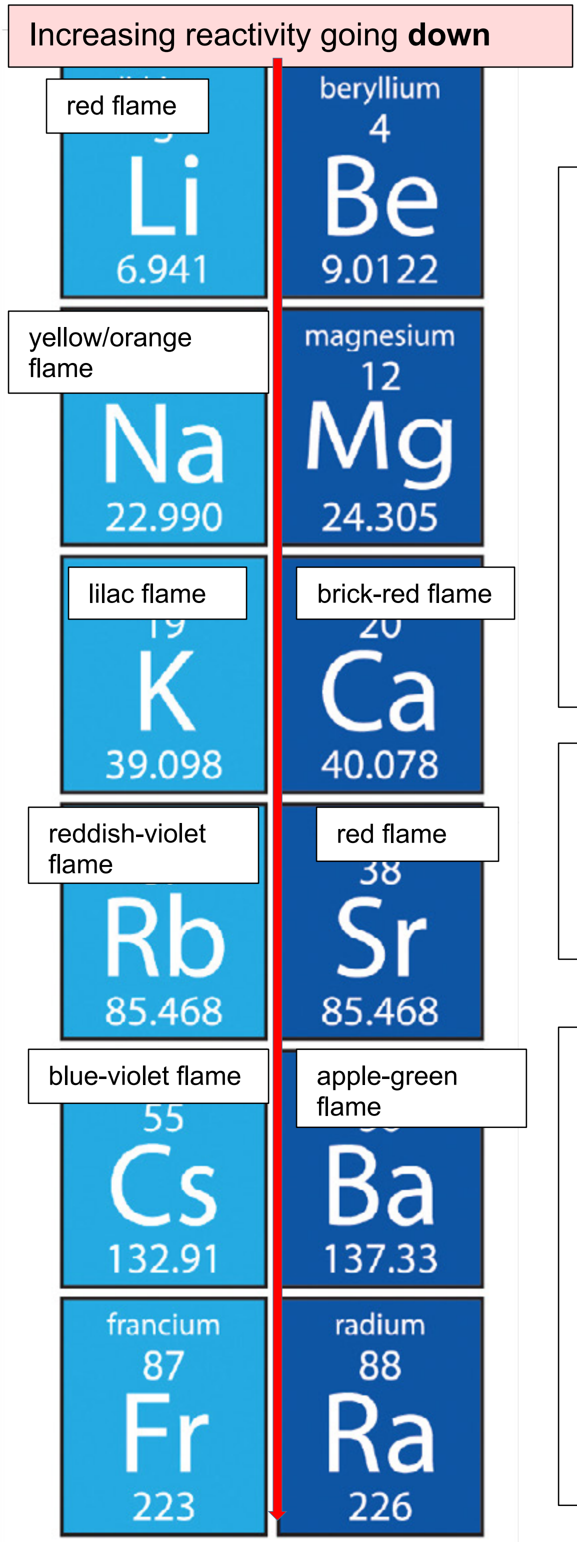
When reacting with water, Group 1 and 2 metals form hydroxides:-

$Na + H_2O \rightarrow NaOH + \frac{1}{2}H_2$
$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$

Magnesium reacts very slowly with water and forms an oxide with steam.

Oxides/hydroxides are basic and react with acids to form a salt and water.

All Group 1 salts are soluble in water.



Solubility of Group 2 salts: -

Hydroxides – $Mg(OH)_2$ is insoluble in water, but solubility **increases *down* the group.**

Sulphates – $BaSO_4$ is insoluble, but solubility **decreases going *down* the group.**

Carbonates – all Group 2 carbonates are insoluble.

Nitrates - all Group 2 nitrates are soluble

Thermal stability – Group 2 carbonates and hydroxides can be decomposed by heat. They become more stable to heat as you descend the group.

Calcium carbonate is important in both living and inorganic systems, such as rocks. **Calcium phosphate** is an essential component of bone tissue.

Calcium and **magnesium** ions are also essential for the biochemistry of living systems, eg chlorophyll and the operation of muscles etc.

The solubility of salts and the flame colours shown on the names of the elements above are very important in qualitative analysis, ie, when trying to identify an unknown salt.

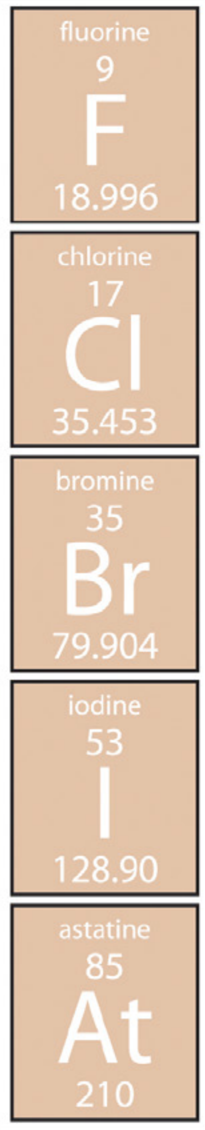
The halogens – Group 7

These are the most electronegative elements.
They react to form anions with an oxidation state of -1. The fact that they have been reduced is shown in the following reaction: -

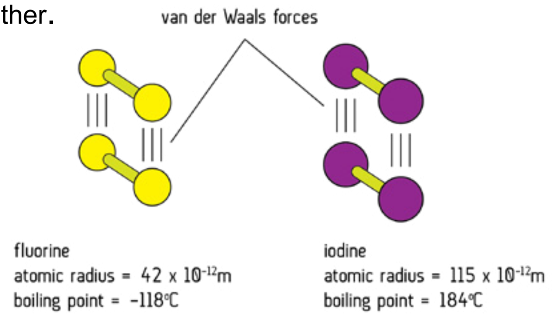
$2Na + Cl_2 \rightarrow 2Na^+ + 2Cl^-$
oxidation 0 0 1 -1
numbers

Oxidation number for chlorine has gone down, therefore reduction. For sodium, it's gone up, therefore oxidation.

Reactivity of the halogens reduces going down the group. This corresponds with the fact that their oxidising power is reduced as the group is descended. (Less able to attract electrons due to the size of the atom – less effect from the positive nucleus on the valence shell).
They are able to displace halide ions from salts if the halide ion is lower down the group than the halogen: -
$Cl_2\ (0) + 2Br^-(-1) \rightarrow 2Cl^-(-1) + Br_2\ (0)$
Cl is reduced Br is oxidised. Cl is the oxidising agent.



Melting points increase *down* the group.
This is because the intermolecular forces become stronger as the atom gets bigger. There are more electrons involved in the induced dipole-dipole interactions that create the force holding the molecules together.



Identification of halide ions.
If you react halide ions with silver nitrate solution in dilute nitric acid, different coloured precipitates of the silver halide are formed.

Halide ion	Colour of Precipitate	Does it dissolve in aqueous ammonia?
Chloride	White	Yes
Bromide	Cream	No
Iodide	Pale yellow	No

This is an important test in the identification of inorganic ions.

Chlorine and fluoride ions in water treatment.
Chlorine gas is added to drinking water to kill dangerous bacteria and viruses such as cholera and typhoid, thereby preventing the outbreak of serious diseases. It forms the following equilibrium in water: -

$$Cl_2 + H_2O \leftrightarrow HOCl + HCl$$

It needs to be added is concentrations below 1 part per million (ppm) in order to be beneficial.

Fluoride is said to prevent tooth decay in children by strengthening tooth enamel and preventing cavity formation. It is also said to strengthen bones, which helps prevent osteoporosis. Again, it only has beneficial effects when added below 1 ppm.

There is controversy around the addition of both chlorine and fluoride to public water supply as some people object to having their supply interfered with. However, the addition of chlorine has virtually eliminated cholera, so benefits outweigh the problems.

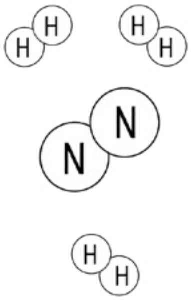
1.7 Simple Equilibria and Acid-Base Reactions

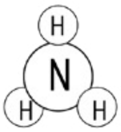
Reversible reactions and dynamic equilibrium

We know that in a chemical reaction, reactants produce products. If magnesium is burnt in air, it forms magnesium oxide and the reactants change completely to produce the product. Some reactions do not do this. They are reversible and as reactants form products, products change back into reactants at the same time. These reactions are **reversible** and are indicated be the ⇋ sign.

Here is an example where nitrogen and hydrogen react to form ammonia in the Haber Process. At the same time, the ammonia decomposes to form nitrogen and hydrogen.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

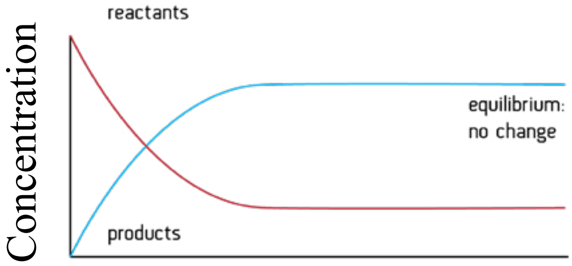




If this reaction is at **equilibrium**, then it means that the forward and reverse reactions are balanced, so you can't **see** anything happening.

However, if you could see things at a molecular level, you would see that the system is moving constantly. The reactants are being converted into products **at the same rate** as the products are converted back into reactants.

This is called **dynamic equilibrium** and the forward and reverse reactions are happening **at the same rate**. There is no overall change in concentration of the reactants and products.



The graph shows what happens to the concentrations of both reactants and products from the beginning of the reaction when the reactants are first mixed. After equilibrium is reached, the concentrations remain constant.

Le Chatalier’s principle

The **position of equilibrium** in an equilibrium mixture refers to the **proportion of reactants to products**. It is possible to change the position of an equilibrium so that there are more products than reactants (known as moving the equilibrium to the right). This is useful to chemical manufacturers as they may be able to influence how much product they are able to make.

These factors can change the position of an equilibrium: -

Changing the concentration of one of the reactants or products

Changing the temperature

Changing the pressure in reactions that involve gases

NB A catalyst **cannot** affect the position of an equilibrium, but may speed up how quickly the reaction reaches equilibrium.

We can decide how each of these factors can affect the position of equilibrium by using **Le Chatalier’s principle,** which states **if a system at equilibrium is subjected to a change, the equilibrium tends to shift so as the minimise the effect of the change.**

Effect of concentration

When chlorine gas is dissolved in water the following equilibrium happens - chloride, hypochlorite and hydrogen ions are formed: -

$$Cl_2(g) + H_2O(l) \rightleftharpoons Cl^-(aq) + ClO^-(aq) + 2H^+(aq)$$

When potassium chloride is added to the equilibrium mixture, the equilibrium will move to the left, in order to remove the chloride ions added, thereby increasing the concentration of the reactants.

We can say that if the concentration of reactants is increased, the equilibrium shifts to the right and more products are formed.

Effect of pressure

Changing pressure only has an effect when it is gases that are reacting together. As the pressure of a gas depends on the number of molecules in a given volume of gas, increasing the number of molecules increases the pressure of the gas. (The more molecules of gas, the more collisions, so greater pressure.)

If we go back to the Haber Process equilibrium: -

$$N_2\,(g) + 3H_2\,(g) \leftrightharpoons 2NH_3\,(g)$$

we can see that four moles of reactants react to give two moles of products, so there is greater pressure on the left hand side.

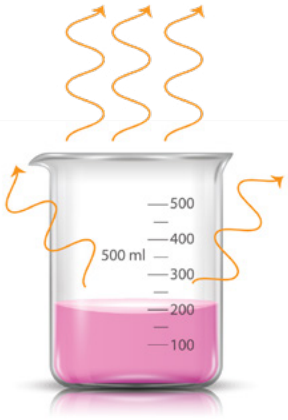
If the pressure is increased for this reaction, then the equilibrium will move to the side where there is **less** pressure, ie the right hand side.

If the pressure is decreased for this reaction, then there will be less ammonia produced as the equilibrium will move to the side where there is more pressure.

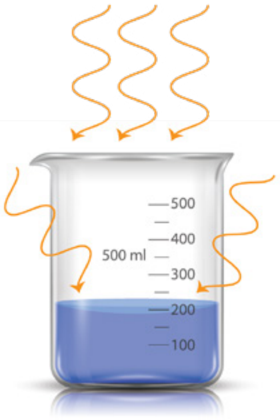
Effect of temperature

The effect of any temperature change on the equilibrium of a reversible reaction depends on whether it is an exothermic or endothermic reaction.

If the forward reaction is exothermic, the reverse reaction is endothermic and vice versa.



in an exothermic reaction, energy is released into the surroundings as heat. As a result, the temperature of the surroundings increases.



in an endothermic reaction, energy is absorbed from the surroundings. As a result, the temperature of the surroundings drops.

Again, let us consider the reaction between hydrogen and nitrogen in the Haber process. The forward reaction is exothermic as it has a negative enthalpy change, meaning the reverse reaction is endothermic: -

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g) \quad \Delta H = -92\ \text{kJ mol}^{-1}$$

If the temperature is increased, the system will try and get rid of this change by reducing the surrounding temperature. The system will therefore move to the endothermic side, so the temperature will drop. This means that increased temperatures will reduce the yield of ammonia.

If the temperature is decreased, the system will try and increase it by shifting to the exothermic side, which will increase the temperature. This will increase the yield of ammonia.

Ideal conditions for ammonia production are therefore high pressure and low temperature. A compromise has to be reached, however as high pressures increase production costs and low temperatures make the reaction too slow.

Reaction rate is increased by the use of a catalyst (doesn’t affect the position of the equilibrium, just gets it there faster) and a slightly higher temperature.

The equilibrium constant

If you allow a reversible reaction to reach equilibrium and then measure the equilibrium concentrations of everything, you can combine these concentrations into an expression known as an equilibrium constant, K_c.

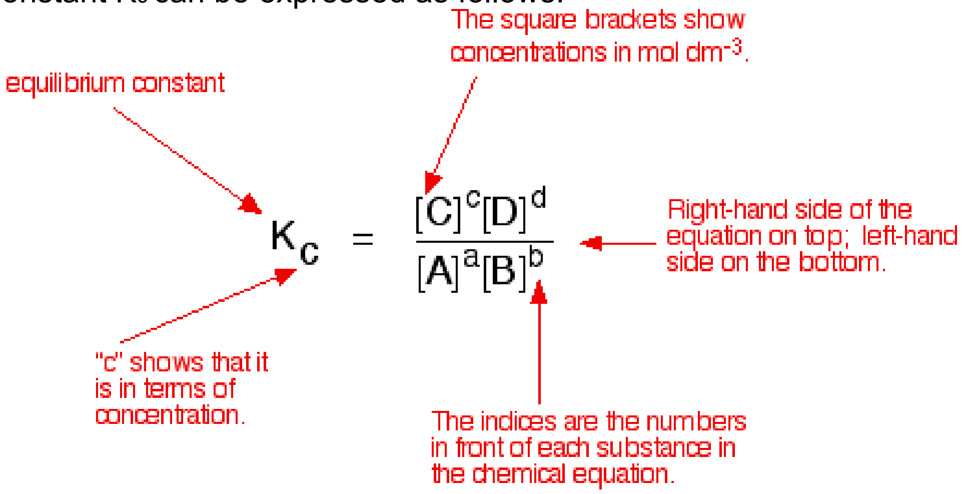
The equilibrium constant always has the same value (provided you don't change the temperature), irrespective of the amounts of reactants and products you started with. It is also unaffected by a change in pressure or whether or not you are using a catalyst.

It is important for you to note that only a change in temperature can change K_c for an equilibrium.

If we look at the following equilibrium: -

$$aA + bB \leftrightharpoons cC + dD$$

the equilibrium constant K_c can be expressed as follows: -



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

The square brackets show concentrations in mol dm^{-3}.

equilibrium constant

Right-hand side of the equation on top; left-hand side on the bottom.

"c" shows that it is in terms of concentration.

The indices are the numbers in front of each substance in the chemical equation.

Worked Example

For the equilibrium: -

$$2SO_2\,(g) + O_2\,(g) \leftrightharpoons 2SO_3\,(g)$$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

and the units are: - $\dfrac{\text{mol dm}^{-3}\ \text{mol dm}^{-3}}{\text{mol dm}^{-3}\ \text{mol dm}^{-3}\ \text{mol dm}^{-3}}$

and they cancel out to leave: - dm^{3} mol^{-1}

If the mixture contains the following concentrations at a certain temperature, calculate K_c at that temperature: -

$[SO_2] = 2.75 \times 10^{-3}$mol dm^{-3} $[O_2] = 4.00 \times 10^{-3}$ $[SO_3] = 3.25 \times 10^{-3}$ mol dm^{-3}

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(3.25 \times 10^{-3})^2}{(2.75 \times 10^{-3})^2\,(4.00 \times 10^{-3})}$$

$$= 3.49 \text{ dm}^3 \text{ mol}^{-1}$$

If you're asked to calculate the concentration of one of the reactants or the product, eg SO_2, just rearrange the equation and find the square root of the answer.

Acids and Bases

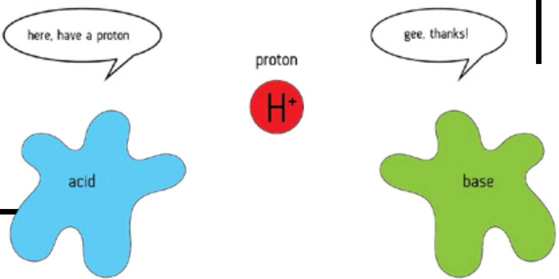
If you look at the formulae of all acids, you will see that they all have something in common – the hydrogen ion, H^+. Here are some examples: -

Hydrochloric acid	HCl
Sulfuric acid	H_2SO_4
Nitric acid	HNO_3
Ethanoic acid	CH_3COOH

They all split up (dissociate) into their ions in water, releasing H^+ ions, eg, for sulfuric acid:

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$

An acid is therefore defined as a proton (H^+) donor.



A base is a compound that accepts protons from an acid.

Here are some common bases (some are **alkalis** because they're soluble in water. All of these have the hydroxide, OH^- ion).

Calcium hydroxide	$Ca(OH)_2$
Sodium oxide	Na_2O
Ammonia	NH_3

Strong and weak acids

You have to be able to tell the difference between **strong and weak** and **concentrated and dilute**.

Concentrated acid is one that contains a lot of acid and a small amount of water in a given volume (think about what you have to do with concentrated fruit squash). **Dilute acid** contains a lot of water and a small amount of acid in a given volume.

Strong acids differ from **weak acids** in the number of H^+ ions that can be donated by an acid. As mentioned above, acids dissociate into H^+ and the anion. If the acid is dissociated completely so that all of the H^+ ions are available for reaction, then it is a strong acid. If it only dissociates slightly, meaning there are very few H^+ ions available, then it is a weak acid.

Dissociation of acids can be represented by the following equation: -

$$HA\ (aq) \rightleftharpoons H^+\ (aq) + A^-\ (aq)$$

For strong acids, the equilibrium is far over to the right, so the acid is totally dissociated. The concentration of hydrogen ions is therefore the same as the concentration of the acid, eg HCl.

A weak acid does not fully dissociate, in fact, as the hydrogen ions and anions are formed, they are just as quickly converted back into the acid. The equilibrium lies more to the left and for ethanoic acid, shown below, only around four in every thousand ethanoic acid molecules dissociate into ions:-

$$CH_3COOH\ (aq) \leftrightharpoons CH_3COO^-\ (aq) + H^+\ (aq)$$

The hydrogen ion concentration is much less than the concentration of the acid.

Definitions

An acid is a proton donor.

A base is a proton acceptor

A strong acid is one that fully dissociates in solution.

A weak acid is one that only partially dissociates in aqueous solution

Bases can be classified as strong or weak. An example of a weak base is ammonia, NH_3 and a strong base is sodium hydroxide, NaOH.

Here's something for you to think about – what's the difference between a concentrated solution of a dilute acid and a dilute solution of a concentrated acid?

Back to basics

Before we move on to talking about the pH scale, you have to make sure that you can remember the basics about acids, bases and salts.

A salt is formed when the hydrogen ion of an acid molecule is replaced by the cation from the base, ie a **neutralisation reaction**, eg:-

$$\begin{array}{llll} HCl & + KOH & \rightarrow KCl & + H_2O \\ \text{acid} & + \text{base} & \quad\ \text{salt} & + \text{water} \end{array}$$

When acids react with carbonates (also bases), they form a salt + water + carbon dioxide.

The salts formed from different acids are named according to which acid formed them, so

Chlorides (Cl^- ions) come from **hydrochloric** acid

Sulphates (SO_4^{2-} ions) come from **sulfuric** acid

Nitrates (NO_3^- ions) come from **nitric** acid

Ethanoates (CH_3COO^- ions) come from **ethanoic** acid

The pH scale

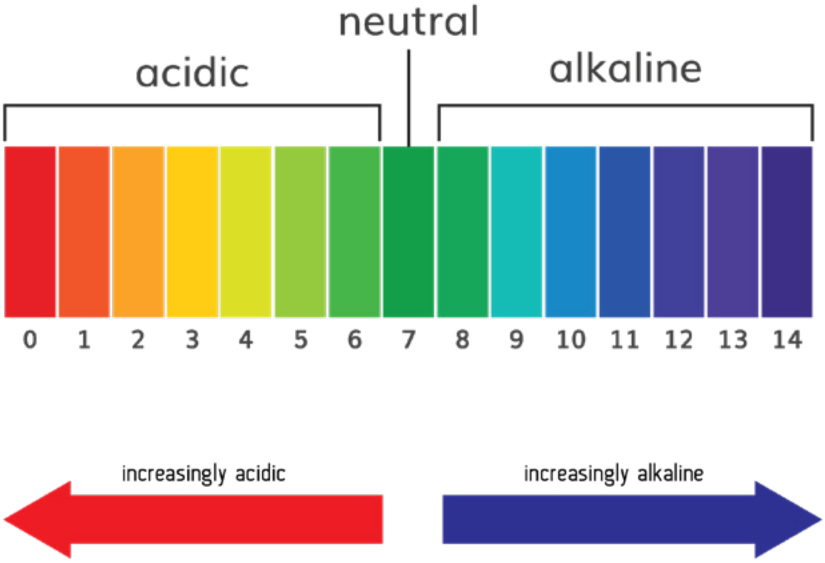
The strength of an acid is dependent upon its concentration of hydrogen ions. Weak acids only contain very small concentrations of hydrogen ions (some around 0.000001 mol dm^{-3}), so it makes these concentrations difficult to imagine.

A Danish chemist came up with a solution to the problem at the beginning of the 20th century when he suggested that the pH scale be used as a measure of acidity. He defined pH as: -

$\mathrm{pH} = -\log [\mathrm{H^+}]$ with $[\mathrm{H^+}]$ being the concentration of hydrogen ions in mol dm^{-3}

The negative sign in the equation to calculate pH means that as hydrogen ion concentration decreases, it's pH number increases and vice versa. Anything with a $\mathrm{H^+}$ concentration of less than 10^{-7} mol dm^{-3} has a pH of more than 7 and is known as an alkali. The converse is true for acids.

The diagram below shows the pH scale that you have probably been seeing since KS3, showing the Universal Indicator colours for each of the different pH numbers.



Perhaps you could use this to work out the puzzle given above?

Worked example

pH can be calculated from knowing $[\mathrm{H^+}]$ and vice versa.

Calculate the pH of a solution of 0.030 mol dm^{-3} of nitric acid.

Nitric acid is fully dissociated as it is a strong acid, so $[\mathrm{H^+}]$ is 0.030 mol dm^{-3}

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

$= -\log 0.030 = 1.5$

Calculate the hydrogen ion concentration of a solution of hydrochloric acid of pH 1.25.

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

$1.25 = -\log [\mathrm{H^+}]$

$\log [\mathrm{H^+}] = -1.25$

$[\mathrm{H^+}] = \text{antilog } -1.25$
$= 0.56$ mol dm^{-3}

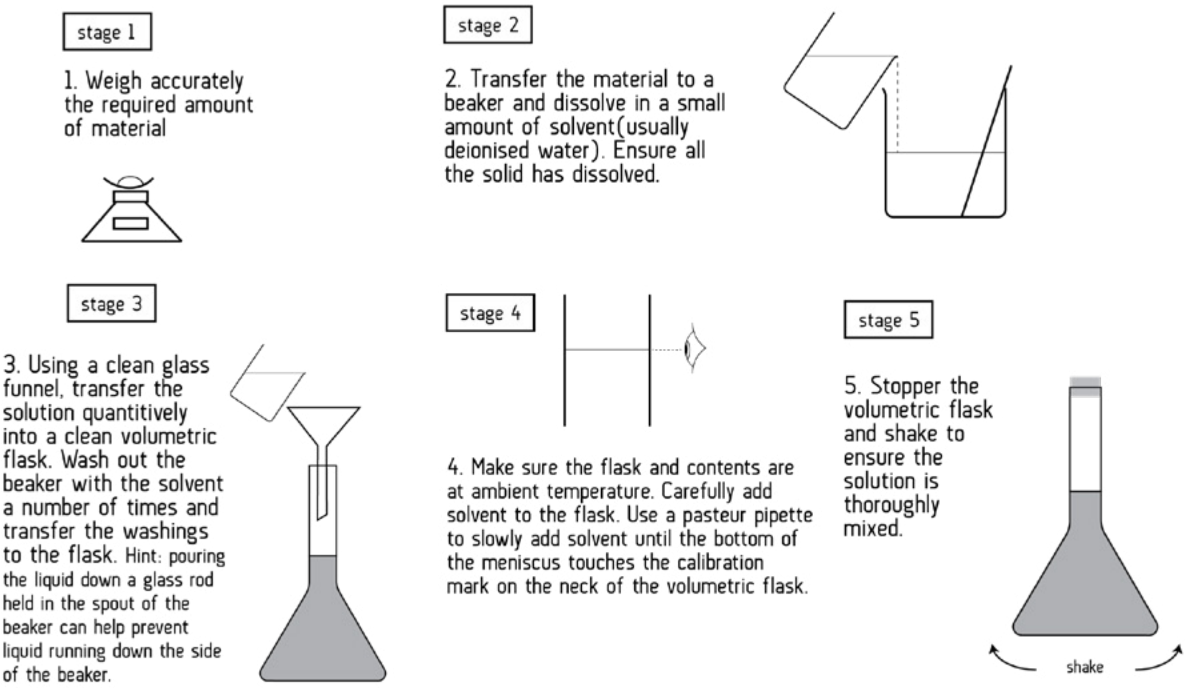
Acid-base titrations

Titrations are a type of volumetric analysis where a solution of known concentration is reacted with a solution of unknown concentration and the reacting volumes used to work out the unknown concentration. In an acid-base or neutralisation reaction, the precise moment of neutralisation is measured using an indicator.

In order to know the exact concentration of the one solution, a standard solution must be used or one that has been standardised using a standard solution.

Making a standard solution

You have to know the exact concentration of a standard solution; ie exactly how much solute is dissolved in a fixed amount of solvent. A standard solution is made using what's known as a primary standard. This is a reagent that can be weighed easily and which is so pure that it's mass is truly a representative of the number of moles contained in that mass.



1. Weigh accurately the required amount of material

2. Transfer the material to a beaker and dissolve in a small amount of solvent(usually deionised water). Ensure all the solid has dissolved.

3. Using a clean glass funnel, transfer the solution quantitively into a clean volumetric flask. Wash out the beaker with the solvent a number of times and transfer the washings to the flask. Hint: pouring the liquid down a glass rod held in the spout of the beaker can help prevent liquid running down the side of the beaker.

4. Make sure the flask and contents are at ambient temperature. Carefully add solvent to the flask. Use a pasteur pipette to slowly add solvent until the bottom of the meniscus touches the calibration mark on the neck of the volumetric flask.

5. Stopper the volumetric flask and shake to ensure the solution is thoroughly mixed.

Here are the features of a primary standard: -

1 Extremely pure

2 Very stable (low reactivity)

3 Doesn't absorb water easily (not very hygroscopic)

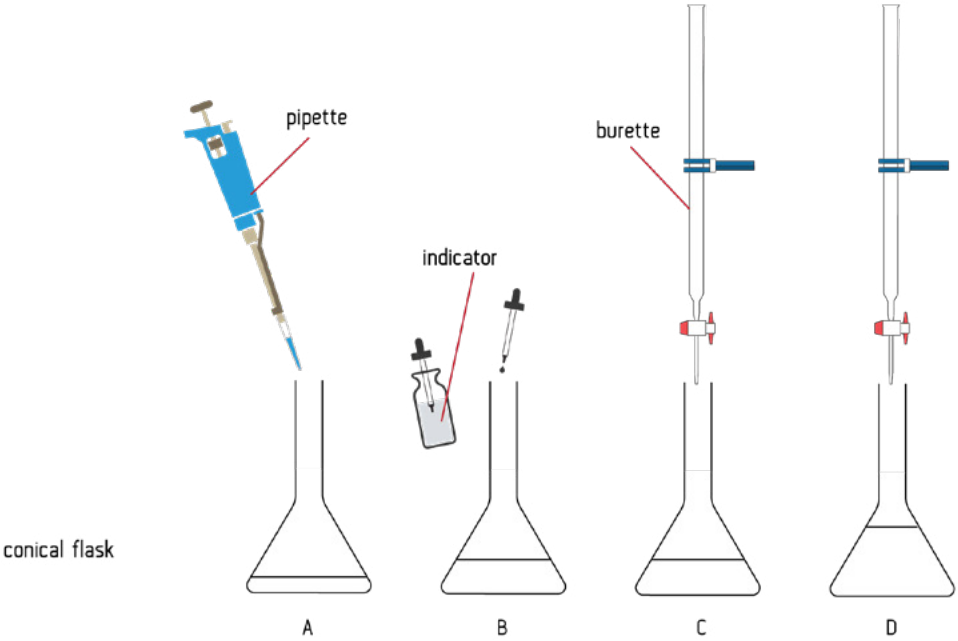
4 High M_r in order to minimise weighing errors

I often ask my students why sodium hydroxide is a poor primary standard. Do you have any ideas?

Carrying out a titration

The series of diagrams below show the steps in performing a titration.

The first step is to fill the burette, usually with an acid. Use a small funnel, making sure that the tip is filled. Remove the funnel after filling and read the level of the acid.



A – use a pipette to add a measured volume (usually 25 cm^3) of the other liquid, in this case alkali, to a conical flask.

B – add a few drops of indicator to the solution in the conical flask

C – run acid from the burette to the solution in the flask, swirling as you do so. Stop when the indicator turns colour. This will be your ‘rough’ titration and you know that this is the maximum volume you need to add from the burette.

D – repeat the titration, this time adding the acid dropwise when you near the volume you got in C until the indicator just turns colour. This is the end-point of your titration.

Record the volume of acid used (the titre).

Repeat until you have at least two readings that are within 0.20 cm^3 of each other and calculate a mean titre.

Types of titration

There are examples involving acid-base and back titrations on pages 31 and 32 of this guide.

The third type of calculation that you need to know about is called a **double titration**.

This uses the concept that different indicators change colour at different values of pH and can be used to calculate the concentrations of **two different bases** in a solution. The titration is performed in two stages and using two different indicators. One indicator is added at the first stage and the second indicator added at the second stage.

Eg, the concentrations of a mixture of NaOH and Na_2CO_3 can be discovered by titrating with hydrochloric acid. The first indicator used will be phenolphthalein (changes at pH 9 from pink to colourless) and the second will be methyl orange (changes at pH 4 from yellow to orange-pink).

In the first stage (phenolphthalein) titration, the following happens:

$NaOH + HCl \rightarrow NaCl + H_2O$

$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$

In the second stage (methyl orange) titration the following happens:

$NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$

So the second titre gives moles of $NaHCO_3$
Which is equal to the moles of Na_2CO_3, because that is where the $NaHCO_3$ came from!

and then the moles of NaOH = moles of HCl in first titre minus the moles of Na_2CO_3.

The concentrations of both can then be calculated.

Worked example

A solution contains both sodium hydroxide and sodium carbonate. 20.0 cm^3 of this solution needed 14.40 cm^3 of 0.700 mol dm^{-3} hydrochloric acid to decolourise phenolphthalein. After adding a few drops of methyl orange, a further 4.50 cm^3 of the acid was needed to turn the indicator from yellow to orange. Calculate the concentrations of both sodium solutions in mol dm^{-3}

moles HCl used in the first stage = volume x concentration = 0.020 x 0.700
=0.014 moles

This is how many moles of OH^- ions **and** CO_3^{2-} ions there are in the solution.

moles HCl used in the second stage = volume x concentration = 0.0045 x 0.700
= 0.00315 moles

This is how many moles of CO_3^{2-} ions there are in the solution as the number of moles of HCO_3 is equal to the number of moles of CO_3^{2-}.

$$\text{concentration of } CO_3^{2-} = \frac{0.00315}{0.025} = 0.126 \text{ mol dm}^3$$

number of moles of OH^- = 0.014 – 0.00315 = 0.0109

$$\text{concentration of } OH^- = \frac{0.0109}{0.025} = 0.436 \text{ mol dm}^{-3}$$

Chemistry AS Unit 2
Energy, rate and the chemistry of carbon compounds

2.1 Thermochemistry

You already know from GCSE that heat is either produced (exothermic) or taken in (endothermic) during a chemical reaction.

One of the most obvious exothermic reactions is the burning of a fuel to give us heat energy. You also learnt that fuel contains chemical energy (a form of potential energy). These are the two types of energy that will be dealt with in this topic. You will learn at an atomic level how chemical energy and heat energy are linked.

When chemicals react with one another, bonds have to be broken in the reactants and new ones made in the products (reactants + products = **chemical system**). Chemical energy is therefore changed due to this bond-breaking and bond-making and this energy is exchanged between the system and its surroundings as heat. The heat energy that is exchanged is referred to as **enthalpy, H**.

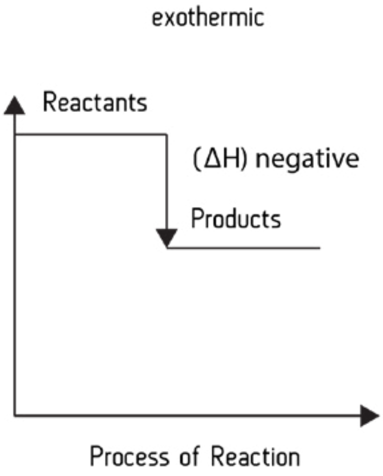
Enthalpy can't be measured, but a **change in enthalpy, ΔH**, can easily be measured. Because it's energy, then its units are **joules, J,** or **kilojoules, kJ**.

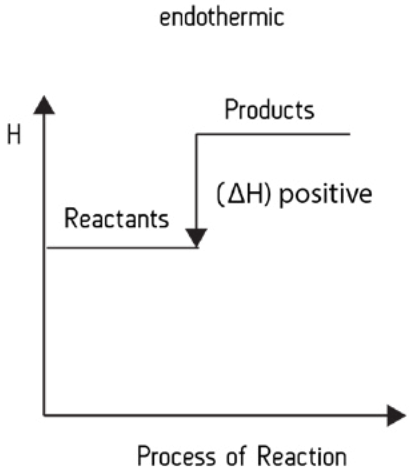
The equation for enthalpy change is: -

$$\Delta H = H_{products} - H_{reactants}$$

If we think about how this relates to an **exothermic reaction**, we must remember that heat is given out to the surroundings, so the enthalpy of the reactants is greater than the enthalpy of the products, so ΔH is negative.

For an **endothermic reaction**, heat is absorbed from the surroundings, so the enthalpy of the products is greater than the enthalpy of the reactants, so ΔH is positive. This can be represented by energy profile diagrams: -





Standard conditions

Enthalpy changes for reactions depend on conditions, so if they are to be compared, then enthalpy change is measured when fixed or **standard conditions** are used. The standard conditions are: -

- all substances in their standard states
- a temperature of 298K (25°C)
- a pressure of 1 atmosphere (101,000 Pa)

The symbol for a standard enthalpy change is ΔH^{θ}

Standard enthalpy change of formation, $\Delta_f H$

Definition – enthalpy change when one mole of a substance is formed from its elements in their standard states under standard conditions. Eg, the standard enthalpy change of formation of sulfur dioxide is represented as: -

$$S(s) + O_2(g) \rightarrow SO_2(g) \quad \Delta_f H = -296.4 \text{ kJ mol}^{-1}$$

If an element like O_2 (g) is being formed from the element O_2 (g), then $\Delta_f H$ is zero as there is no chemical change. So we can say that **all elements in their standard state have a standard enthalpy change of formation of 0 kJ mol^{-1}.**

Standard enthalpy change of combustion, $\Delta_c H$

Definition – enthalpy change when one mole of a substance is completely combusted (burnt) in oxygen under standard conditions, eg the standard enthalpy change of combustion of ethane is given by: -

$$C_2H_6(g) + 3\tfrac{1}{2} O_2(g) \rightarrow 2\,CO_2(g) + 3\,H_2O(l) \qquad \Delta_c H = -1560 \text{ kJ mol}^{-1}$$

Enthalpy change of reaction. $\Delta_r H$

Definition – enthalpy change in any reaction **between the number of moles of reactants shown in the equation for the reaction**.

The standard enthalpy change for a chemical reaction is calculated from the standard enthalpies o formation of all the reactants and products involved. The symbol for the **standard** enthalpy change of reaction is **$\Delta_r H^{\theta}$**. The equation used to calculate this enthalpy is: -

$$\Delta_r H^{\theta} = \Sigma\Delta_f H \text{ (products)} - \Sigma\Delta_f H \text{ (reactants)} \qquad \Sigma = \text{‘total or the sum of’}$$

Worked example

Calculate the standard enthalpy change of reaction for: -

$$2H_2S(g) + SO_2(g) \rightarrow 3S(s) + 2H_2O(l)$$

given the following information

Substance	$H_2S(g)$	$SO_2(g)$	$S(s)$	$H_2O(l)$
$\Delta_f H^{\theta}$/kJ mol^{-1}	-20.2	-297	0	-286

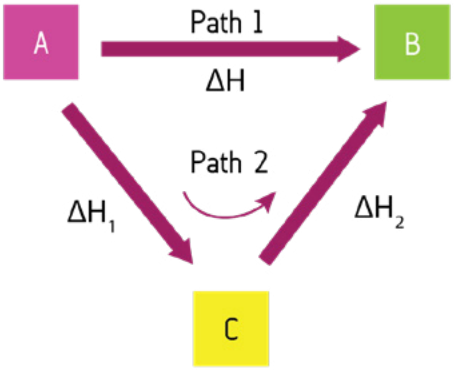
$$\begin{aligned}\Delta_r H^{\theta} &= \Sigma\Delta_f H \text{ (products)} - \Sigma\Delta_f H \text{ (reactants)}\\ &= (0 + (2 \times -286)) - ((2 \times -20.2) + -297)\\ &= -572 - (-337.4)\\ &= -234.6 \text{ kJ mol}^{-1}\end{aligned}$$

Hess's Law

In some reactions, products can be formed by different routes. There's a method that's based on the conservation of energy that can be used to calculate the enthalpy change of a reaction if it can't be measured directly. This method is called **Hess's Law**.

Definition – the total enthalpy change of a reaction is independent of the route taken from the reactants to the products.

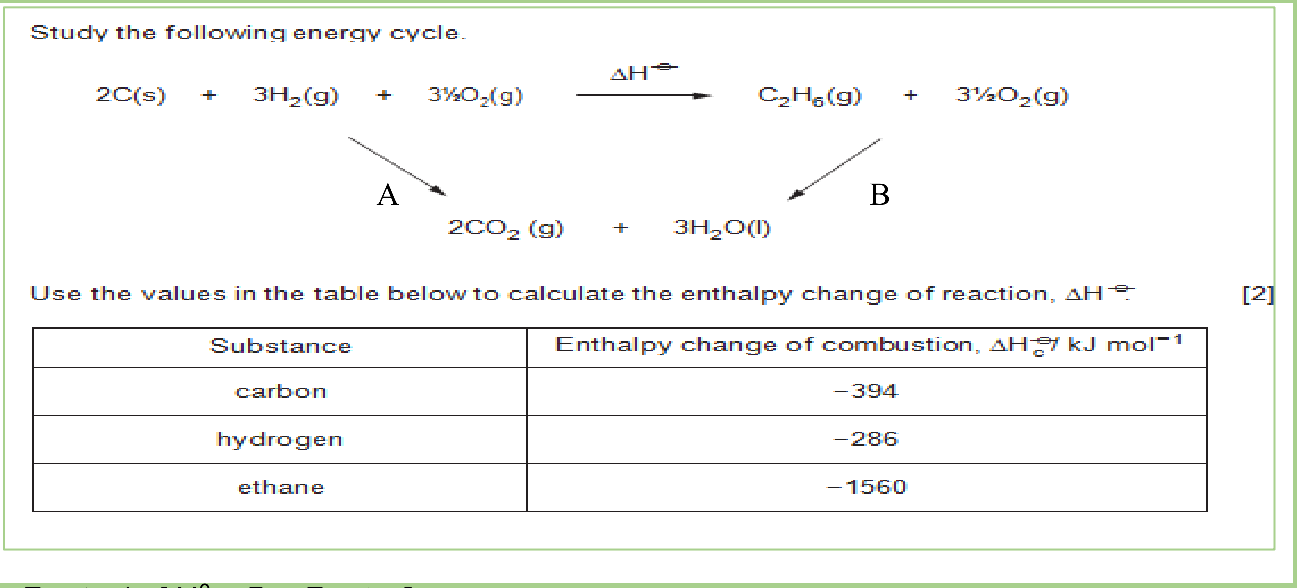
In the following diagram, Path I shows a direct route for converting reactants to products and Path II shows an indirect route via the formation of an intermediate, C.



Hess's law states that the total enthalpy is independent of the route, so Path I must equal Path II:

$\Delta H = \Delta H_1 + \Delta H_2$

Worked example



Study the following energy cycle.

$$\begin{tikzcd}
2C(s) + 3H_2(g) + 3\frac{1}{2}O_2(g) \arrow[rr, "\Delta H^\ominus"] \arrow[dr, "A"'] & & C_2H_6(g) + 3\frac{1}{2}O_2(g) \arrow[dl, "B"] \\
& 2CO_2(g) + 3H_2O(l) &
\end{tikzcd}$$

Use the values in the table below to calculate the enthalpy change of reaction, $\Delta H^\ominus$. [2]

Substance	Enthalpy change of combustion, $\Delta H_c^\ominus$/ kJ mol^{-1}
carbon	−394
hydrogen	−286
ethane	−1560

A = Route 1, ΔH^θ + B = Route 2

A = (2 x -394) + (3 x -286) = -788 + (-858) = -1646 kJ mol^{-1}

B = -1560 kJ mol^{-1}

ΔH^θ = A – B

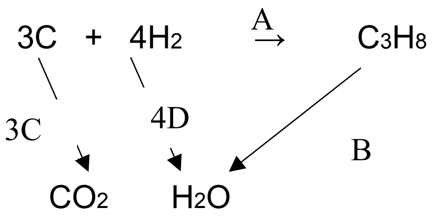
= -1656 – (-1560)

= -86 kJ mol^{-1}

As we saw from the previous example, enthalpy changes of combustion can be uses to calculate an overall enthalpy change for a reaction. Enthalpy changes of formation can also be used. The question will tell you if you need to use enthalpies of combustion or formation.

If the cycle diagram is not given to you, use the following tips to help you draw the arrows: -

If you're burning something in oxygen, it forms oxides, **so combustion products of the reactants and products will be listed below the reaction equation.** Then draw arrows from the equation to the oxides below it, eg,

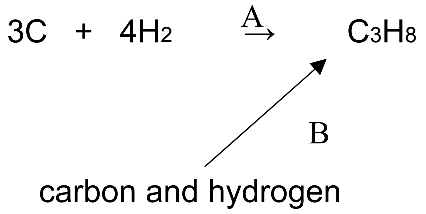


A + B = 3C + 4D, where

A = ΔH^θ, B = $\Delta_c H$ for propane,

C = $\Delta_c H$ for carbon and D = $\Delta_c H$ for hydrogen

When the reactants and products are being formed from their common elements, the arrows will go from the common elements up to the equation, eg: -



Now we have the situation where:
A = B
With B representing enthalpy change of formation instead of combustion. (Remember that carbon and hydrogen have 0 value for $\Delta_f H$ as they are elements in their standard states)

Worked example

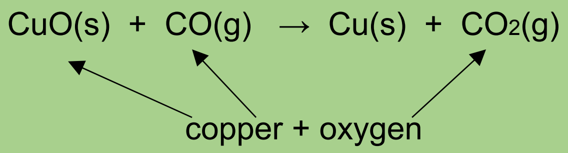
Copper(II) oxide can be reduced to copper by carbon monoxide: -

$$CuO(s) + CO(g) \rightarrow Cu(s) + CO_2(g) \quad \Delta_f H = -126 \text{ kJ mol}^{-1}$$

Calculate the enthalpy change of formation of CuO given that: -

$\Delta_f H(CO) = -111$ kJ mol^{-1} and $\Delta_f H(CO_2) = -394$ kJ mol^{-1}

Write the cycle for these reactions, remembering that it's enthalpy change of **formation**: -



$\Delta_f H$ for Cu = 0, CuO = ?,
CO = -111 kJ mol^{-1}
CO_2 = -394 kJ mol^{-1}

$? + (-111) + (-126) = -394$

$$? = -394 - (-111) - (-126) = -157 \text{ kJ mol}^{-1}$$

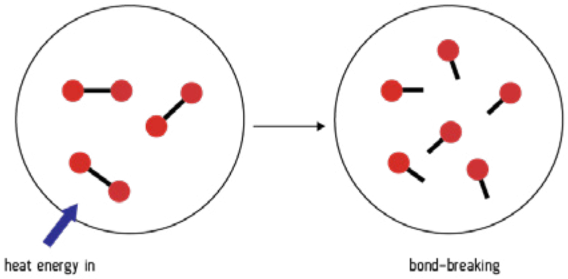
Bond enthalpies

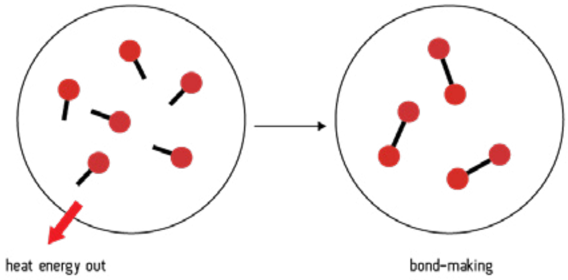
Definitions

Bond enthalpy - the amount of energy needed to break a covalent bond during a chemical reaction.

Average bond enthalpy – the average value of the enthalpy required to break a given type of covalent bond in the molecules of a gaseous species. ie, calculated using a wide range of compounds. These are used in calculations and won't be as accurate as using actual bond enthalpies, but they give a good indication, so are extensively used.

When considering reactions, **breaking bonds** requires energy, so it's **endothermic** and always positive. **Making bonds** releases energy, so it's **exothermic** and always negative: -





Calculations involving bond energies

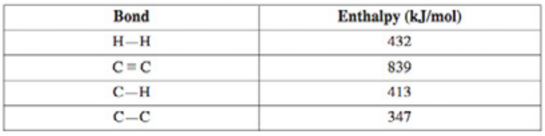
There are four steps that need to be followed in order to be successful: -

- draw out the molecule so that you can see the bonds
- calculate the energy needed to break all of the bonds in the reactants (positive values)
- calculate the energy released when bonds are formed in the products (negative values)
- add the enthalpy changes together

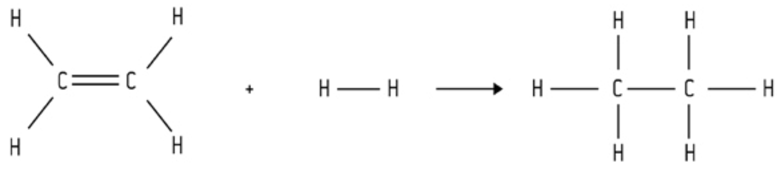
Worked example

Calculate the standard enthalpy change of reaction for the hydration of ethene, using the average bond enthalpies given.

$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$



Bond	Enthalpy (kJ/mol)
H–H	432
C=C	839
C–H	413
C–C	347



Bonds broken: -

2 x C-H = 2 x 413 = 826

= -2478

2 x H-H = 2 x 432 = 864

1690

Bonds made: -

6 x -413

1 x -346 = -346

-2824

$\Delta H = \Sigma(\text{bonds broken}) + \Sigma(\text{bonds formed})$

$\Delta H = 1690 + (-2824) = -1134 \text{ kJmol}^{-1}$

Calculating energy changes

It isn't possible to measure the enthalpy (heat content) of a system, so what has to be measured is the energy released to or taken out of the surroundings. A thermometer measures any change in temperature and enthalpy can be calculated from this, the mass and specific heat capacity of the contents of the colorimeter used for the reaction.

The equation for the amount of heat transferred (q) is given below: -

$q = mc\Delta T$ where

m = mass of the solution in the colorimeter

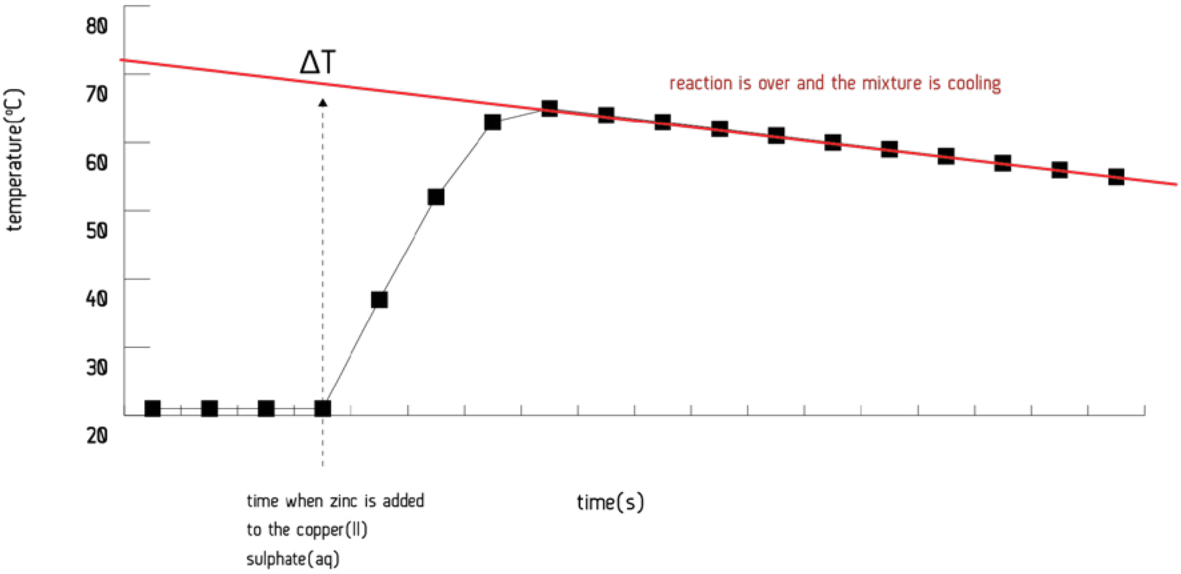
c = specific heat capacity of the solution

ΔT = change in temperature

We also assume that: -

- all of the heat is exchanged with just the solution
- the solution has the same specific heat capacity as water (you will be given this, 4.18 $Jg^{-1}K^{-1}$)
- the density of the solution is 1 g cm^{-3} (so the mass is always the same as the final volume in the colorimeter)

The following graph shows how readings are taken during an experiment to measure the enthalpy of a reaction where zinc is added to copper sulphate: -



The temperature of the copper sulphate is taken every 30 seconds for 90 seconds and then the zinc is added to it. The temperature is then taken every thirty seconds until the temperature begins to drop and shows a clear fall. The maximum temperature is discovered by extrapolating the graph back to the mixing time.

If we want to calculate the enthalpy change of a reaction per mole, we have to use the equation: -

$$\Delta H = \frac{-q\ (mc\Delta T)}{n}$$

where n = number of moles that have reacted

Worked example

4g of magnesium were added to 25.0 cm^3 0f 1.00 mol dm^{-3} copper sulphate solution in a polystyrene cup. The maximum temperature change was calculated to be 48.5° C. Calculate the enthalpy change for the reaction: -

$$Mg(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$

(Assume that the density of the solution is 1gcm^{-3} and its specific heat capacity, c, is 4.18Jg^{-1}K^{-1})

$q = mc\Delta T$

$q = 50 \times 4.18 \times 48.5 = 5068.25$ J

$$\text{moles of Mg} = \frac{4.0}{24} = 0.0334 \text{ moles}$$

moles $CuSO_4$ = volume x concentration = 0.05 x 1 = 0.05, so Mg is not in excess and is used in the calculation.

$$\Delta H = \frac{-q}{n} = \frac{-5068.25}{0.0334} = -151{,}744 \text{ J mol}^{-1}$$

$$= 151.7 \text{ kJ mol}^{-1}$$

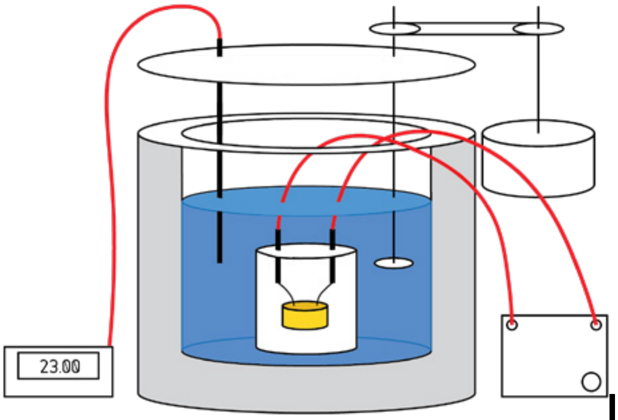
Specified practical work

There are two practical investigations that you have to carry out, determining the enthalpy change of combustion of a fuel and indirect determination of an enthalpy change.

Methods for both investigations are detailed in your laboratory book, but you should make sure that you accurately measure any liquids using a burette or appropriate sized pipette. Accuracy is key to these investigations, so you should be aware of how to measure everything as accurately as possible.

The value will always be less than the book value because some of the energy that is transferred during any reaction is lost to the surroundings because of poor insulation.

You should also be aware that a bomb calorimeter can be used to give an experimental value for combustion that is closer to the book value.



2.2 Rates of reaction

It is important that manufacturers know the rate of a chemical reaction and how to change it (increase or decrease). They would want to increase the rate of a useful reaction in order to obtain the maximum product in the smallest time. They would also want to decrease the rate of a reaction that was unwanted.

Definition

Rate of reaction is the change in concentration of a reactant or product per unit time.

Equation:

For a reaction: - $\textbf{rate} = \dfrac{\textbf{change in concentration}}{\textbf{time}}$ $\textbf{units} = \dfrac{\textbf{mol dm}^{-3}}{\textbf{s}} = \textbf{mol dm}^{-3}\textbf{s}^{-1}$

Other values can be measured, eg mass or volume, with the corresponding units used instead of mol.

Rates of reaction were covered extensively at GCSE, so you should remember the following points:

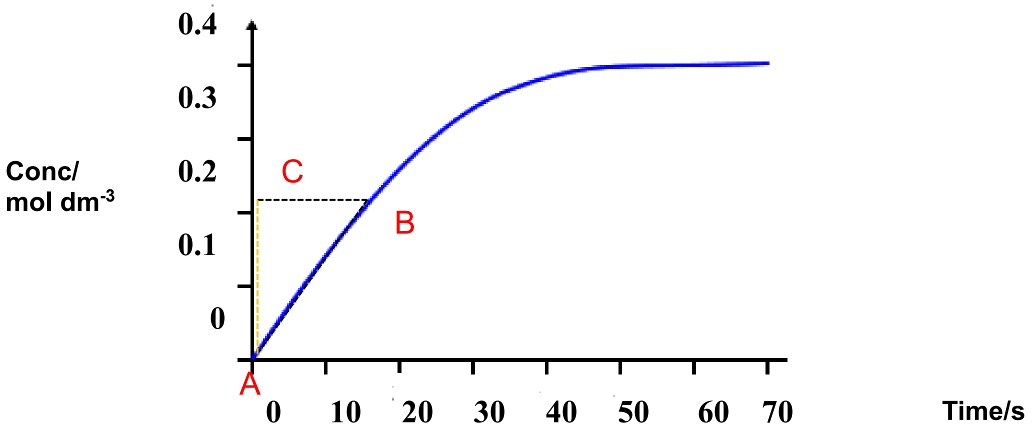
- the rate is fastest at the beginning of a reaction as each reactant is at its highest concentration.

- the rate slows down as the reaction proceeds because the concentration of reactants decreases.

- the rate is zero when the reaction stops. This is when one reactant has been used up.

Measuring and calculating rates of reaction

Rates are measured by measuring the concentration of a reactant or product over a certain period of time, eg measuring the volume of a gas (and finding out its concentration) or measuring the concentration of an acid or alkali during a titration (done by taking out samples and titrating them to find out their concentration at that point). A graph is drawn of the results and this is used to find the initial rate of reaction. The initial slope or gradient of the line is found and used to calculate the rate (concentration/time):-



To find the gradient at point B on the line, draw a horizontal line from C to B and then a vertical line from A to C.

From the graph:

$$\text{Rate} = \frac{\text{change in concentration}}{\text{time}} = \frac{AC}{CB} = \frac{0.20 - 0.00}{15} = \frac{0.20}{15} = 0.0133\ \text{mol dm}^{-3}\text{s}^{-1}$$

If you have a curve where the concentration is falling, the same process would be followed.

As we need to know which of the reactants are responsible for how quickly a reaction proceeds, we need to find out the relationship between the initial rate of reaction and the concentrations of the reactants. A series of experiments is therefore performed in which the concentration of only one reactant is changed at a time.

The table below gives some experimental data for the reaction between propanone and iodine in acid solution:-

Experiment	Initial concentrations / mol dm^{-3}			Initial rate / 10^{-4} mol dm^{-3}s^{-1}
	Iodine	Propanone	Hydrogen ions	
1	0.006	0.6	0.6	1.50
2	0.006	0.12	0.6	3.00
3	0.012	0.6	0.6	1.50

In experiments 1 and 2, the only thing that is changed is that the propanone concentration is doubled, this doubles the initial rate. In experiments 1 and 3, the concentration of iodine is doubled and this has no effect on the initial rate of reaction.

This means that the concentration of propanone is directly proportional to the initial rate of reaction.

Collision theory – factors determining reaction rates

We know from GCSE that the factors that can affect the rate of a reaction are: -

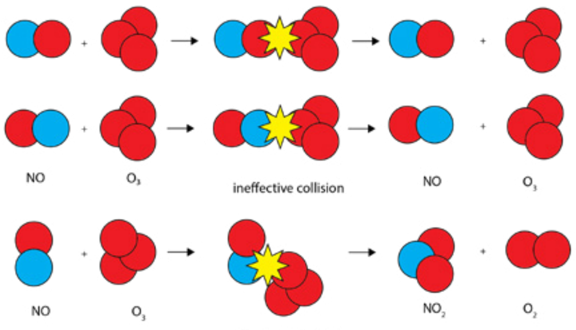
- surface area of a solid
- concentration of a solution
- temperature of the reaction
- a catalyst
- pressure of gaseous reactions
- light (in some light sensitive reactions, eg photosynthesis)

We use **collision theory** to help us explain how these factors affect a reaction's rate: -

For a chemical reaction to occur, the reacting molecules have to collide with the correct force and direction in order to react.

We can see this shown effectively by the diagram of nitrogen monoxide and ozone molecules attempting to react on the next page.

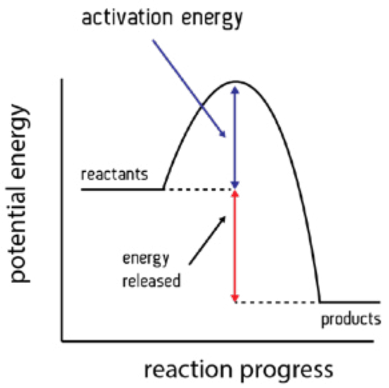
The first two attempts are obviously approaching from the wrong direction. They do collide with force, but do not react. The third one approaches from a different direction, so we see a reaction.



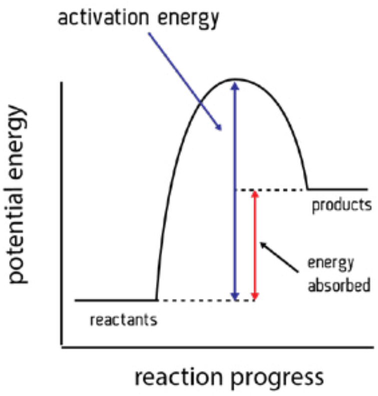
Any factor that can increase the chance of successful collisions will increase the rate of a reaction. The minimum energy required for the reaction to occur is called the **activation energy.**

Energy profiles for exothermic and endothermic reactions

The following diagrams are known as energy profiles. They compare the enthalpy of reactants with products for both exothermic and endothermic reactions.



exothermic reaction



endothermic reaction

In the **exothermic reaction,** the reactants lose energy and heat is given out to the surroundings. The activation energy is shown with the blue arrow, it shows that although energy is ultimately given out, energy must be supplied initially in order to break bonds and get the reaction started.

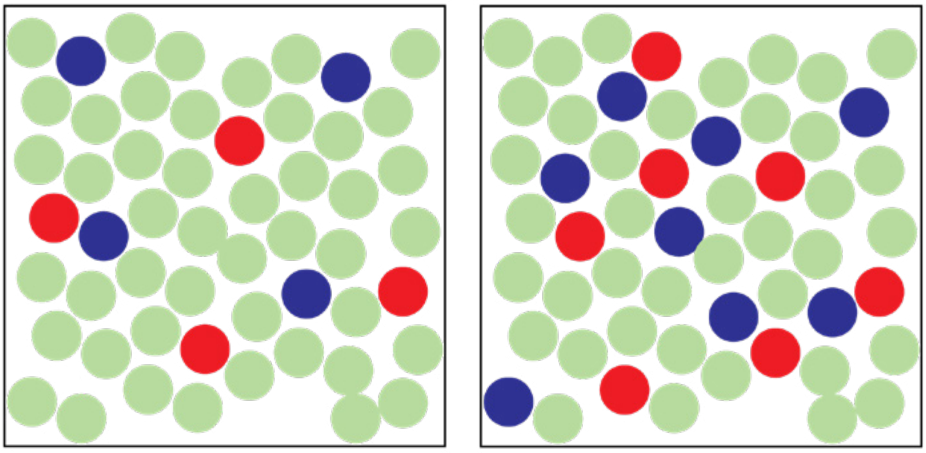
This diagram also helps to explain why a **negative ΔH** is obtained with an exothermic reaction. The products have less energy than the products and the excess energy is lost from the reaction as heat.

There is also a **positive ΔH** obtained with an exothermic reaction. The products have more energy than the reactants and energy is absorbed from the surroundings.

Effect of concentration/pressure and particle size on the rate of a reaction

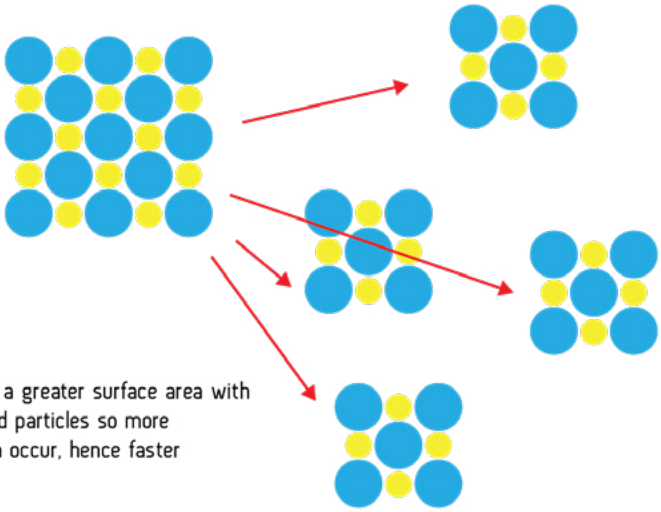
We know that the rate of a reaction increases if the concentration increases. This is because there are more molecules in the same volume, so there is an increase in the number of collisions in a unit of time. There will therefore be a greater chance of successful collisions, ie those that are greater than the activation energy.

For reactions involving gases, increasing the pressure is the same as increasing the concentration. This is because you have more gas molecules per unit area as the molecules are pushed together.



There are more molecules of reactant in the right hand side container, so they are more likely to collide with energy greater than the activation energy.

Smaller particles react more quickly than large particles as the surface are of the solid is increased in small particles.



if we break up this lump into smaller pieces the number of particles has not changed but there are now more 'surface' particles.

there is now a greater surface area with more exposed particles so more collisions can occur, hence faster reaction.

Larer surface area = faster reaction

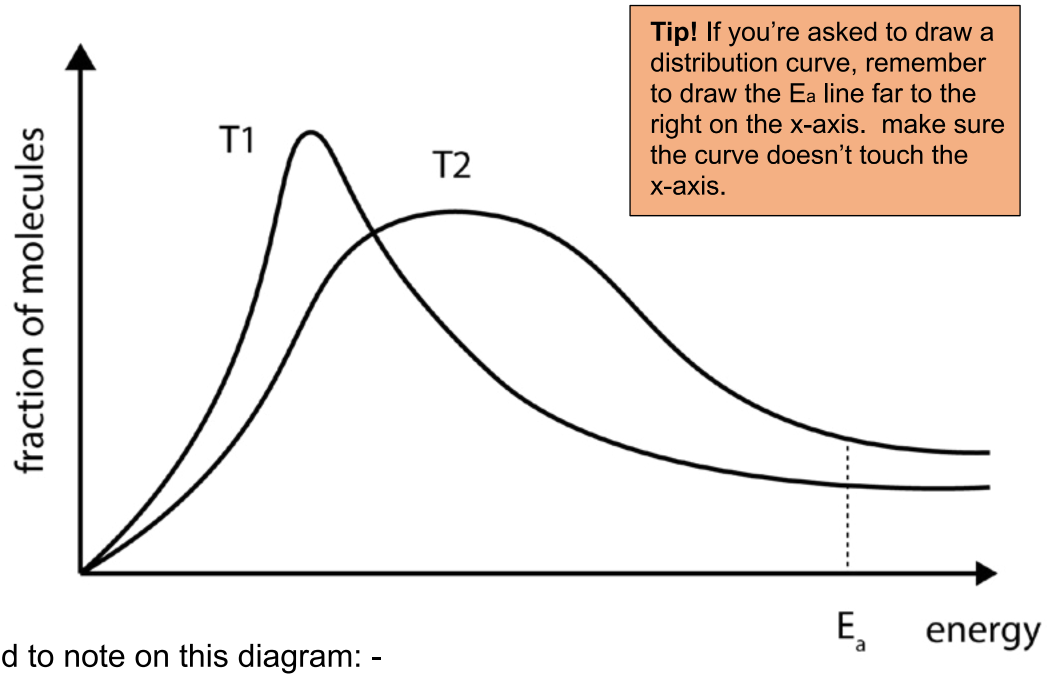
Effect of temperature on rates of reaction

The rate of a reaction increases with an increase in temperature. This is because molecules have greater kinetic energy at higher temperatures so they move a lot faster. More molecules have energy that is greater than the activation energy, so more successful collisions occur in a given time.

The Boltzmann energy distribution curve on the next place shows this. In the diagram, temperature T1 is less than temperature T2.

Tip! If you're asked to draw a distribution curve, remember to draw the E_a line far to the right on the x-axis. make sure the curve doesn't touch the x-axis.

fraction of
molecules



Things that you need to note on this diagram: -

- the curves never touch the energy axis
- at the higher temperature, the peak moves to the right – molecules have **higher energy** but the peak is at a lower height.
- the areas under the two curves are equal to one another.
- only those molecules to the right of the E_a (activation energy) mark on the x-axis are able to react - at the higher temperature, more molecules have enough energy to react, so you get an increase in the rate of reaction.

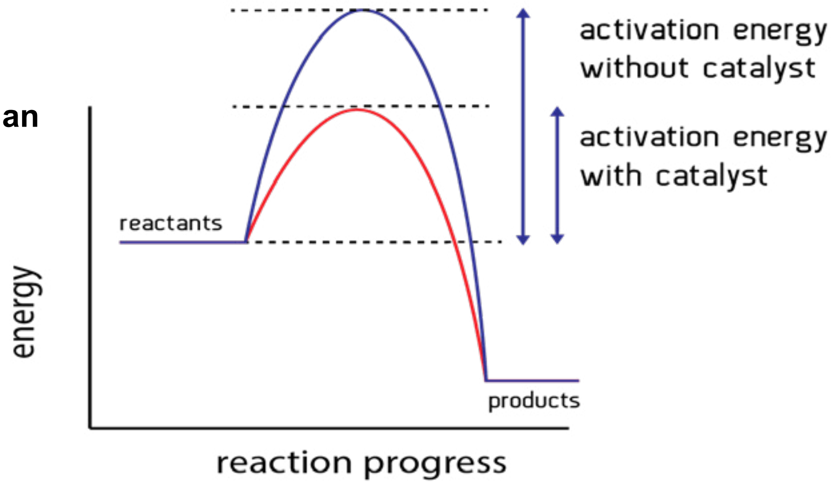
The role of catalysts in changing the rate of a reaction

Definition

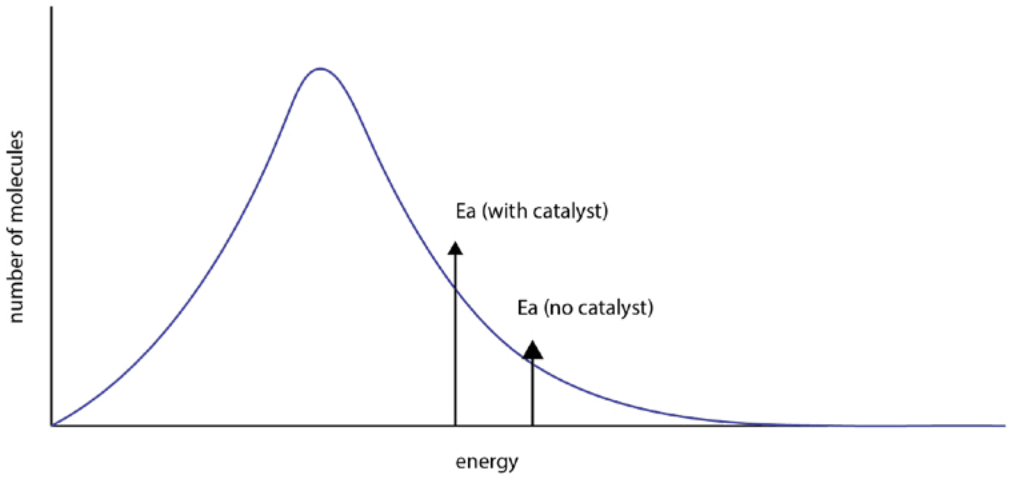
A **catalyst** is a substance that increases the rate of a chemical reaction without being used up in the process. It does this by providing an alternative route of lower activation energy.

In other words, if the activation energy is lower, more particles will have that activation energy, so the reaction will be faster. A catalyst can be recovered at the end of the reaction totally unchanged so that it can be used again.

You can see the **different pathways on an energy profile diagram**:



Whilst the **number of molecules with energy greater than the activation energy can be shown on a distribution curve**: -



NB – a catalyst does not affect the position of an equilibrium. However, equilibrium is reached more quickly as the catalyst increases the rate of forward and reverse reactions by the same amount.

Types of Catalyst

Homogenous

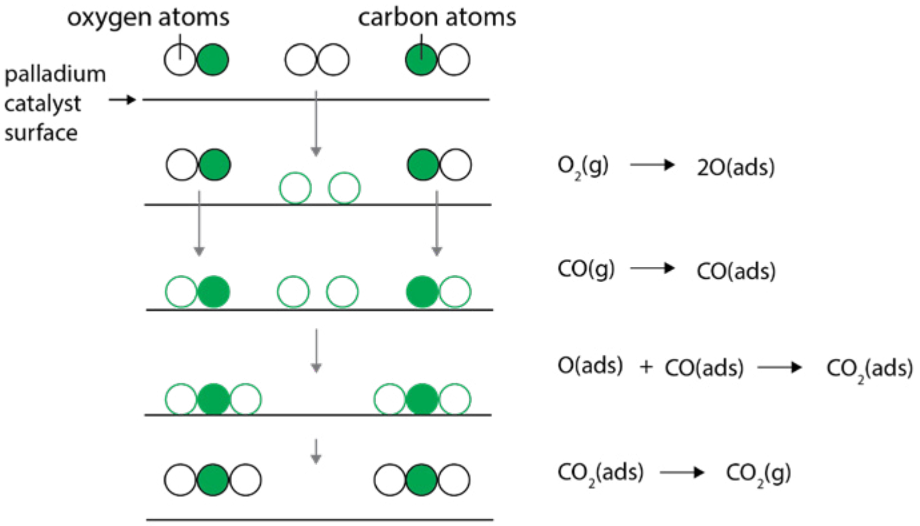
This type of catalyst is in the same phase as the reactants. They take an active part in the reaction rather than being a spectator. The examples below are both in the liquid phase.

Eg, the hydrolysis of sugar into glucose and fructose is catalysed by conc. sulfuric acid and iodide ions can catalyse the decomposition of hydrogen peroxide into water and oxygen.

Heterogeneous

These are in a different phase from the reactants and include those industrial catalysts that you will have heard of during your studies at GCSE. Many of them are transition metals because the d-block metal provides a site for the reaction to take place. Gases are adsorbed onto the metal surface and react. The products are then desorbed from the surface.

This is shown in the diagram which shows how palladium metal catalyses the oxidation of carbon monoxide to carbon dioxide in a catalytic converter:



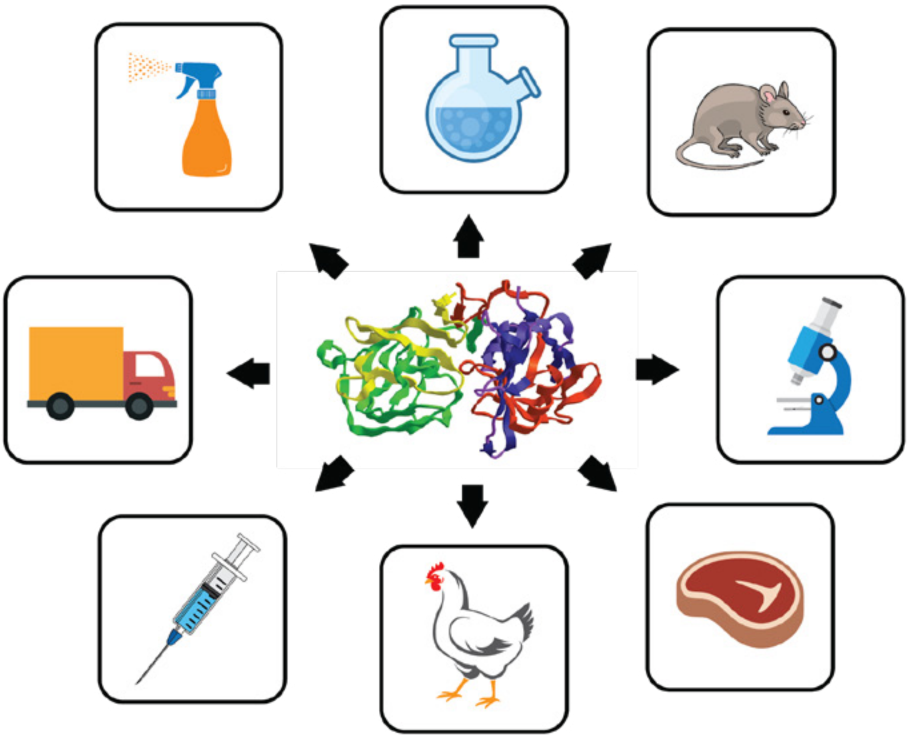
Other examples are the use of iron in the Haber process for ammonia production, vanadium(V) oxide in the Contact process during the manufacture of sulfuric acid and nickel in the hydrogenation of unsaturated oils during margarine production.

Use of catalysts in industry

Most industrial reactions involve catalysts and heterogeneous catalysts are used a lot because they are easy to separate from the products. Because catalysts lower the activation energy of a reaction, then less energy is needed for the molecules to react, thereby saving energy costs. Using less energy is also beneficial to the environment because less fossil fuels are burnt, meaning less carbon dioxide is released into the atmosphere.

New catalysts are being developed all the time, often using new nanotechnology.

Biotechnology companies use **enzymes** when manufacturing detergents and cleaners and in the production of food and drinks.



Enzymes are biological catalysts, you will have studied them at GCSE and you should remember that they work best at or near room temperature or pressure. They are exceptionally efficient and are over 10,000 times more efficient than other catalysts in industry. There are problems however, in that they are affected by temperature and pH and can be rather difficult to be removed from liquid products.

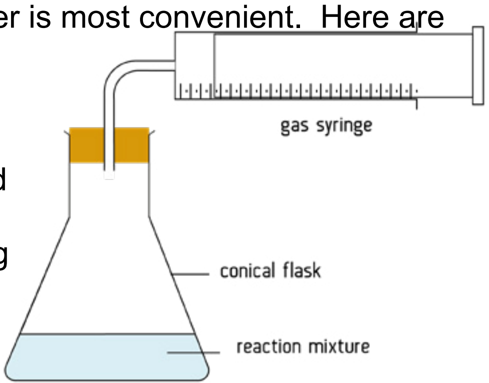
Here are some of the benefits of using enzymes: -

- they don’t harm fabrics and food, so are safe to use.
- they are biodegradable, so disposal is not a problem.
- lower temperatures and pressures can be used, which saves energy and costs.
- pure products are usually formed as there are no side reactions, which means that products do not need to be separated from any side products formed.

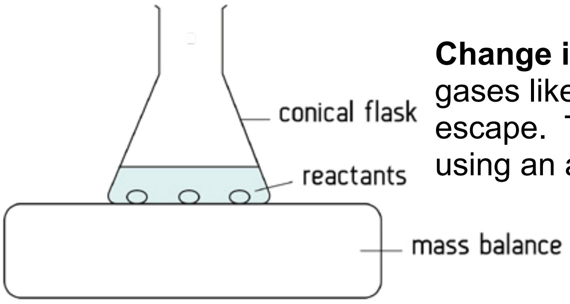
Studying rates of reaction

Rates of reaction can be measured using any change of reactant or product with time. You can make measurements of chemical or physical changes, whichever is most convenient. Here are some methods (that should be carried out at constant temperature): -

Change in volume of a gas. This method can be used for any reaction where gas is produced, eg a reactive metal with an acid will produce hydrogen gas. The gas can be collected and measured accurately using a gas syringe at varying times during the reaction.



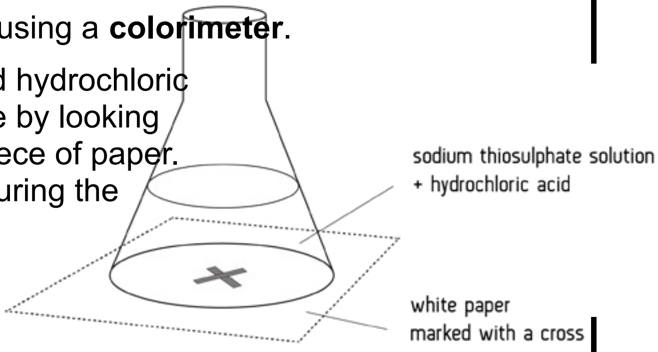
Change in pressure. This can only be used for reactions involving gases. If the number of moles of gas differ between reactants and products, then the pressure will change. This pressure change can be measured at varying times using a manometer.

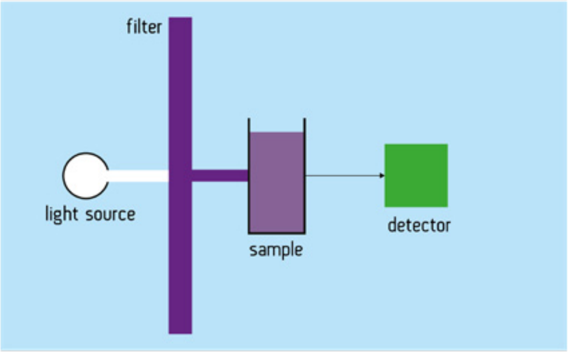


Change in mass. This method is used when one of the heavier gases like CO_2 is released during a reaction and allowed to escape. The change in mass can be measured at varying times using an accurate balance.

Change in colour. A change in colour can be measured using a **colorimeter**.

If you studied the reaction between sodium thiosulfate and hydrochloric acid at GCSE, you may have measured the colour change by looking through the increasingly cloudy solution at a cross on a piece of paper. The colour change is caused by the production of sulfur during the reaction.





A colorimeter can measure the colour change far more efficiently, as it is able to monitor the colour change more accurately – it doesn't depend on the person doing the observing.

Another reaction that can be followed using a colorimeter is the reaction between acidified propanone and iodine. The brown colour of the iodine will fade and a colorimeter can measure the colour change and therefore the change in concentration.

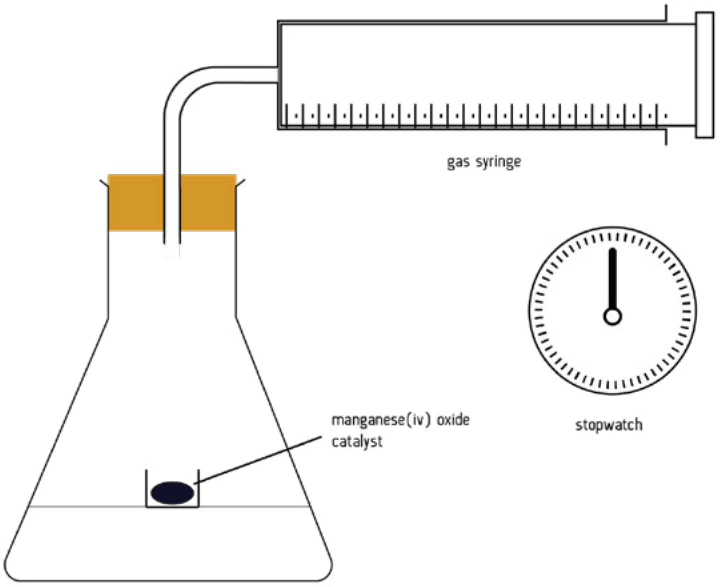
$$CH_3COCH_3\ (aq)\ +\ I_2\ (aq)\ \rightarrow\ CH_3COCH_2I\ (aq)\ +\ HI\ (aq)$$

Practicals in the specification

Gas collection method

You can use this method to measure the rate of any chemical reaction that produces a gas, be it investigating the effect of changing concentration, temperature, particle size or the effect of a catalyst.

When hydrogen peroxide is exposed to certain catalysts, it decomposes rapidly to produce water and oxygen. A typical method of seeing how concentration affects the rate of reaction would be: -



-start the reaction by shaking the catalyst into the hydrogen peroxide and start a stopwatch.

-measure the amount of oxygen given off at constant intervals.

-stop the watch when oxygen is no longer being produced.

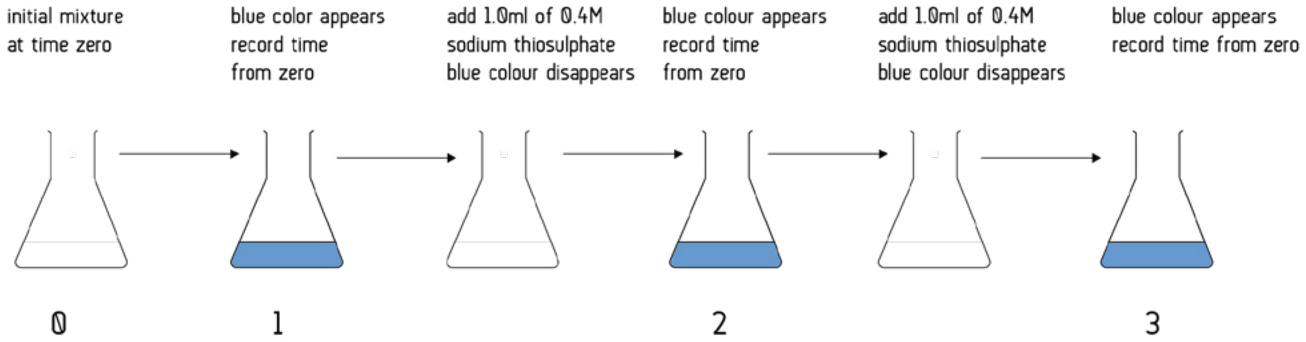
-repeat the experiment with different concentrations of hydrogen peroxide ensuring all other factors are kept constant.

-draw a graph of your results.

Iodine-clock reactions

This is an excellent reaction to use in order to compare the rates of reaction under different conditions. It involves setting up a number of experiments in which initial concentrations are known and the time it takes for each reaction is recorded.

Iodide ions can be oxidised by hydrogen peroxide to iodine and the presence of iodine is indicated using starch solution. A strong blue colour is obtained with even the smallest amount of iodine. if, however, a given amount of thiosulfate ions are present, iodine will react very quickly with it, reforming iodide ions. Therefore, **no blue colour will appear until all of the thiosulfate has been used up**. The time taken for this to happen acts as a type of ‘clock’ to measure the rate of iodide ions being oxidised. This diagram shows what can happen if you continue to add thiosulfate



Equations for the reactions are seen below: -

$$H_2O_{2(aq)} + 2I^-_{(aq)} + 2H^+_{(aq)} \xrightarrow{\text{slow}} I_{2(aq)} + 2H_2O_{(l)}$$

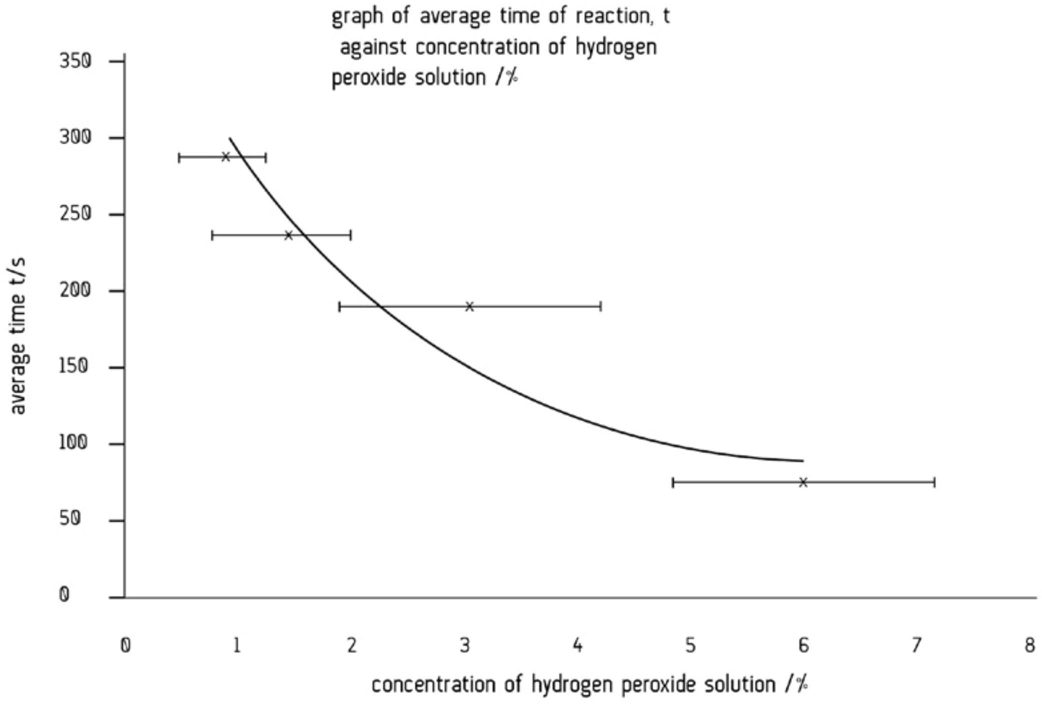
$$2S_2O_3^{2-}{}_{(aq)} + I_{2(aq)} \longrightarrow S_4O_6^{2-}{}_{(aq)} + 2I^-_{(aq)}$$

The temperature has to be kept constant as rates vary a great deal with the slightest change in temperature.

A method you could use would be: -

- Measure accurately known volumes of acid, thiosulfate solution and iodide solution into a conical flask and add a little starch solution.
- Measure accurately a known volume of hydrogen peroxide into a test tube.
- Quickly pour the peroxide into the conical flask, starting the stopwatch at the same time. Mix thoroughly.
- When the blue colour appears, stop the watch.
- Repeat using different concentrations of peroxide, ensuring the total volume of the mixture is kept constant.
- You should vary the concentration of the peroxide by at least three times in order to ensure a good spread of results.

As the rate of reaction is proportional to 1/time and the total volume is constant for each experiment, concentration of peroxide is proportional to the volume of peroxide used in each experiment. Plotting a graph of 1/time against concentration of peroxide will give the relationship between peroxide concentration and rate.



Precipitation reactions

The reaction between sodium thiosulfate and hydrochloric acid was mentioned previously.

It is the sulfur that is the precipitate being produced. Each thiosulfate ion produces one sulfur atom, so the production of sulfur is proportional to the amount of thiosulfate that was there initially. The cross on paper method is used to calculate how quickly the reaction takes place.

The following method can be used.

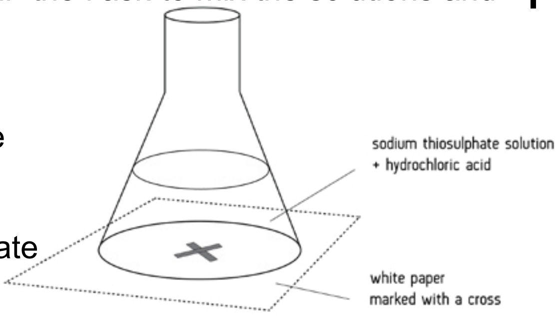
1 Put 50 cm^3 of sodium thiosulfate solution in a flask.

2 Measure 5 cm^3 of dilute hydrochloric acid in a small measuring cylinder.

3 Add the acid to the flask and immediately start the clock. Swirl the flask to mix the solutions and place it on a piece of paper marked with a cross.

4 Look down at the cross from above. When the cross disappears stop the clock and note the time. Record this in the table.

5 Repeat this using different concentrations of sodium thiosulfate solution.



6 Repeat this again using three different concentrations of acid, keeping the volume of thiosulfate constant and the total of the mixture constant.

As rate is proportional to 1/time. Plotting a graph of 1/time against concentration of thiosulfate at constant acid concentration will give the relationship between the concentration of thiosulfate and rate. Plotting a graph of 1/time against the concentration of acid at constant thiosulfate concentration will give the relationship between acid concentration and rate.

2.3 The wider aspects of chemistry

(a) Application of the principles studied to problems encountered in the production of chemicals and of energy

In this topic you will have to apply the principles that you have studied in 2.1 and 2.2 to situations and problems you might find in the production of energy and chemicals. You could be supplied with data relevant to the situation and the marks you gain will depend on how you analyse and evaluate the situation or problem. You may have to carry out calculations, but you will definitely need to have a basic understanding of equilibrium, energetics and kinetics in order to answer the questions reasonably successfully.

Energy

You are probably aware of the increasing worldwide demands for energy. Most problems are caused by the fact that the majority of this is provided by burning fossil fuels, which releases carbon dioxide into the atmosphere and oceans. The level of carbon dioxide in the atmosphere has increased by around 30% in the last 100 years and it is an accepted theory that this contributes to global warming. Oceans are becoming more acidic with serious biological effects. Because the supply of fossil fuels is falling and the consequential increase in price, alternative sources are being sought. Those that interest chemists are nuclear power, biomass and solar energy.

With the use of biomass fuels it is hoped that **carbon neutrality** will be achieved. This means that the carbon dioxide being generated by burning the fuel will be compensated for by that absorbed by the fuel during photosynthesis.

Nuclear power has been used in this country for many years and the work being done at the moment is to try and make it safer. Semiconductors are used in solar power and chemists are trying to increase their efficiency and reliability. There is also much work being done to develop the use of hydrogen as a fuel as it doesn't produce carbon dioxide when it is burnt. Hydrogen doesn't occur naturally on Earth, however, so there is research being done to make it through the solar photolysis of water.

(b) The role of Green Chemistry and the impact of chemical processes

Questions under this topic may supply you with data and information and you will be expected to discuss these and evaluate them in your answer.

Green Chemistry aims to make chemicals and products that we need with as little impact on the environment as possible. In order to do this, the following has to happen: -

- Use as little energy as possible and get this from renewable sources rather than from fossil fuels that will run out. Energy efficiency should be increased.
- Use renewable raw materials such as plant based compounds wherever possible.
- Use methods having high atom economy so that there is little waste.
- Develop better catalysts, eg enzymes, to carry out reactions at lower temperatures and pressures in order to save energy and avoid the expense of construction of strong plants.
- Avoid the use of solvents that are bad for the environment.
- Make products that are biodegradable at the end of their useful lives.
- Avoid the use of toxic materials and ensure that there are no undesirable by products.

2.4 Organic compounds

Organic compounds are those that contain carbon and hydrogen. Some also contain oxygen, nitrogen, sulfur, phosphorous and/or the halogens. There are millions of different organic compounds and there is international agreement on how compounds should be named, which ensures that scientists throughout the world recognise the compound being described.

Naming organic compounds

Before we begin the actual procedure for naming organic compounds, some definitions need to be given: -

A **hydrocarbon** is a compound containing hydrogen and carbon only.

The **functional group** of an organic compound is the atom or group of atoms that gives that compound its characteristic properties.

A **homologous series** is a series of compounds that have the same functional group. You may find it easier to think of the homologous series as a 'family' of compounds.

A **saturated compound** is one that contains no C=C bonds. The term saturated comes from the fact that you can fit no more elements onto the carbon atoms.

An **unsaturated compound** is one that contains C=C bonds. You can fit more elements onto the carbon atoms.

The homologous series studied in this unit are: -

alkanes – these are **saturated hydrocarbons** (the simplest organic compounds)

alkenes – these are **unsaturated hydrocarbons**

halogenoalkanes – as the name suggests, these are alkanes **where one or more hydrogens have been replaced by a halogen.**

primary (1°) alcohols – these compounds contain the functional group -OH.

carboxylic acids – compounds containing the -COOH group as the functional group.

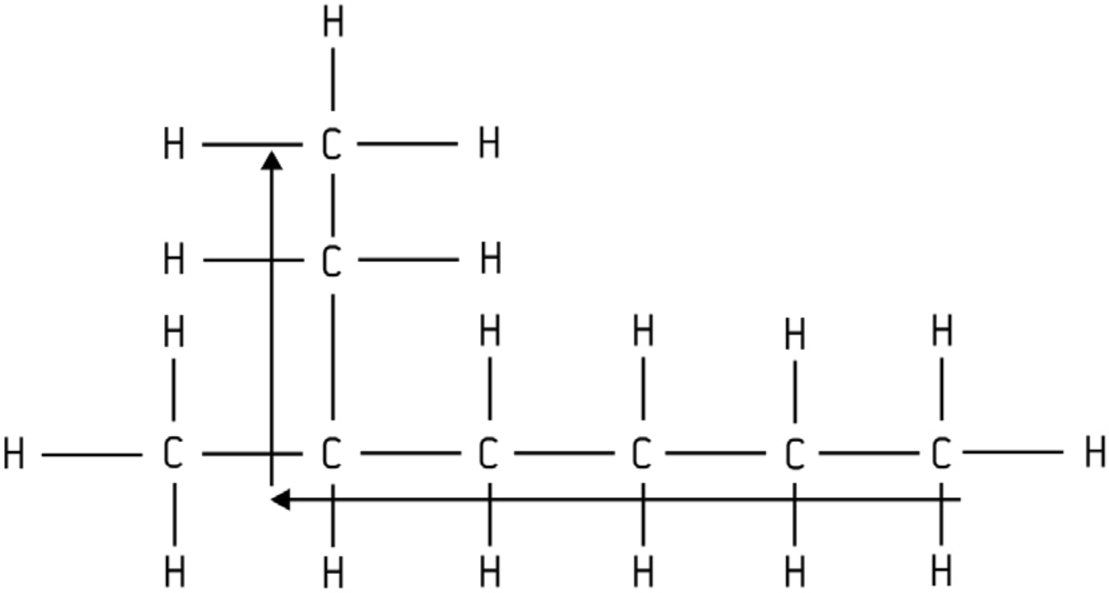
The name also depends on the number of carbon atoms in the molecule. Here are the prefixes that represent the different numbers of atoms: -

Number of carbon atoms	Prefix	Number of carbon atoms	Prefix
1	meth-	6	hex-
2	eth-	7	hept-
3	prop-	8	oct-
4	but-	9	non-
5	pent-	10	dec-

Now we need to learn the **rules for naming organic compounds**.

1. Find the longest continuous carbon chain. **Take care here!** The following compound at first sight might be seen to have a longest chain of six from one side to another, but the longest straight chain incorporates the two carbon atoms that are sticking up, so the longest chain is seven.

The prefix for this compound is 'hept-' as there are seven carbon atoms.



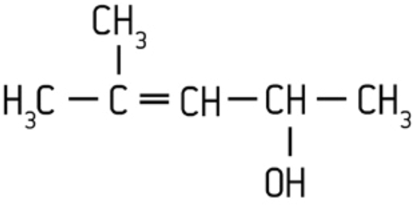
2. Number the carbon atoms in the longest chain. If there is a branch coming off the straight chain, you must start numbering from the end nearest that branch.

3. If you have more than one branch or group that is the same on the molecule, they are incorporated into the name as di, tri etc. NB, a CH_3 group is a methyl group, a CH_3CH_2 group is an ethyl group.

4. When incorporating the branch names, keep them in alphabetical order, ie, ethyl comes before methyl.

Using these rules, the above compound is called 3-methylheptane. (The methyl group is on the number three carbon atom of a straight chain of 7)

Naming functional groups
Alkanes have the suffix – ane
Alkenes have the suffix -ene
Halogenoalkanes are named with a prefix that has the halogen present in it, eg chloro, bromo etc
Alcohols have the suffix -ol
Carboxylic acids have the suffix – oic acid



$H_3C-C(CH_3)=CH-CH(OH)-CH_3$

4-methylpent-3-ene-2-ol

Here's another example: -
- the longest chain here is five, so it is a 'pent-' chain.
- as this is an alcohol, this takes priority when it comes to the lowest number. Start numbering from the right hand side.
- there is a double bond between the 3 and 4 carbon atoms, so this is shown as pent-3-en.
- a methyl group is present on the number 4 carbon atom, hence the 4-methyl in the name.

Types of formula

There are several ways of showing the formula of compounds that you need to know. We have: -
Molecular formula – this shows the number and type of each atom there are in a molecule of a compound. These are the formulae you will have learnt to write at KS3.

Displayed formula – here, you have to show all the atoms and the bonds that are between them, as in the examples on the previous page.

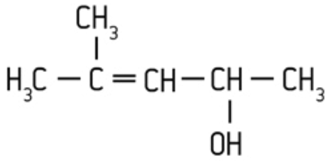
Shortened formula – you have to show the way the atoms are bonded, but don't have to include the bonds. The formula must show exactly what the compound is.

Skeletal formula – all you will see here are the bonds between any carbon atoms in the molecule and any functional groups that may be attached. You won't see the carbon and hydrogen atoms (unless the hydrogen atoms are part of a functional group.

This is how each type of formula would look for 4-methylpent-3-ene-2-ol: -

Molecular formula: $C_6H_{12}O$

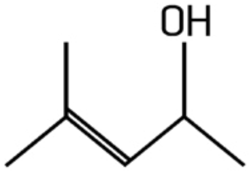
Displayed formula:



$$H_3C-\overset{CH_3}{\overset{|}{C}}=CH-\underset{OH}{\underset{|}{CH}}-CH_3$$

Shortened formula: $CH_3CCH_3CHCH(OH)CH_3$

Skeletal formula:



Homologous series

You should also know some of the properties of homologous series of compounds. As stated previously, they are members of the same 'family', so they :-

1. Can all be represented by a general formula, eg C_nH_{2n+2} for alkanes.
2. Differ from the next one up or down in the series by CH_2.
3. Have similar chemical properties as they have the same functional group.
4. Exhibit a general trend in physical properties as the M_r of the compound varies

Empirical formulae

Definition: this is the formula of a compound with the atoms of the elements in their simplest ratio.

This could also be the molecular formula of the compound, or the molecular formula could be any multiple of the empirical formula.

Eg, the molecular formula of ethene is C_2H_4. The ratio of C:H is 2:4.

Simplest ratio is 1:2, so the empirical formula is **CH_2**

Calculation of an empirical formula

When organic compounds are analysed, you often get the results as masses or percentages of the elements present. These masses or percentages can be used to calculate the empirical formula of the compound.

Example using percentages

A compound has the following percentage composition: C = 40.00%, H = 6.67% and O = 53.33%. Find its empirical formula and its molecular formula if it's M_r is approximately 58.

Compounds present		C	H	O
% of each		40.00	6.67	53.33
Divide by A_r to give molar Ratio		12.0	1.01	16.0
	=	3.33	6.604	3.33
Divide by smallest number	=	1	2	1

Empirical formula = CH_2O

M_r of empirical formula = 30.02

M_r of compound is approximately 58, which is ≈ 2 x 30.02,

So, molecular formula is $C_2H_4O_2$

Example using masses

A sample of hydrocarbon was burned completely in oxygen to form 0.660g of carbon dioxide and 0.225g of water. Find it's empirical and molecular formula if its M_r is approximately 80.

Mass of carbon in the carbon dioxide = 12/44 x 0.660 = 0.180 g

Mass of hydrogen in the water = 2/18 x 0.225 = 0.025 g

Compounds present		C	H
Mass of each		0.180	0.025
Divide by A_r to give molar Ratio		12.0	1.01
	=	0.0150	0.0248
Divide by smallest number	=	1	1.65
Multiply both to get a whole number	=	3	5

Empirical formula = C_3H_5, M_r = 41

So, molecular formula of compound is C_6H_{10}

Isomerism

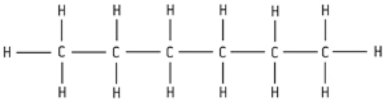
Structural isomerism

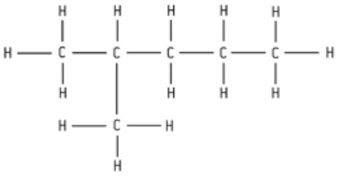
Definition: these are compounds with the same molecular formula but a different structural or displayed formula, ie the way the atoms are arranged. There are three different types that you need to know about:

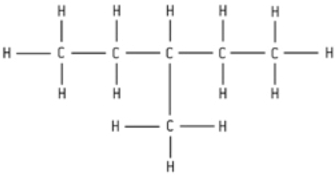
Chain isomerism

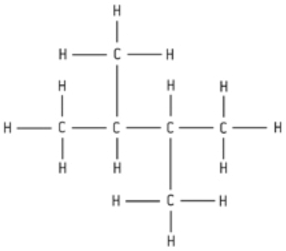
This occurs when the carbon chain within the molecules is arranged differently. This is usually because one isomer has branches instead of a straight chain.

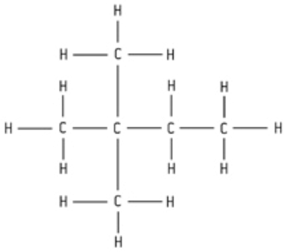
Here are the isomers of hexane: -


Hexane


2-Methylpentane


3-Methylpentane


2,3-Dimethylbutane

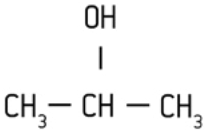

2,2-Dimethylbutane

Positional isomerism

The functional group can appear in different positions on the molecule, known as functional group isomerism. Here are the positional isomers for propanol: -

$CH_3-CH_2-CH_2-OH$

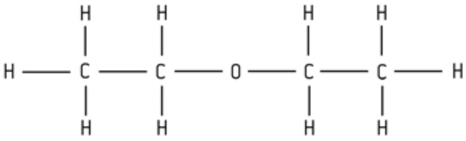
Propan-1-ol

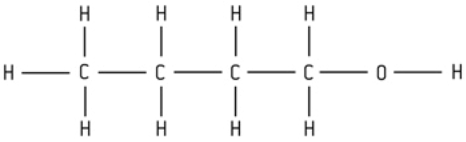

$CH_3-CH(OH)-CH_3$

Propan-2-ol

Functional group isomerism

You can have compounds with the same molecular formula, but different functional


An Ether

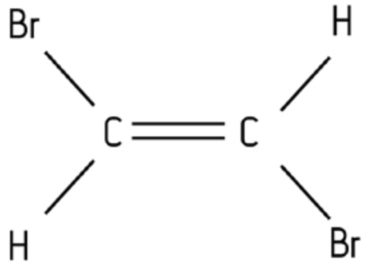

Butanol

groups (usually within those compounds containing oxygen).

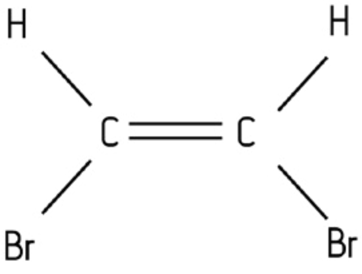
E-Z Isomerism

Definition: This type of isomerism occurs in alkenes because there is restricted rotation about the double bond.

In alkanes, the single bond allows for free rotation of carbon atoms. However, when you have a double bond, the atoms are unable to rotate, meaning they are in fixed positions. This gives rise to isomers as the atoms exist in different places in space, eg 1,2-dibromoethene: -



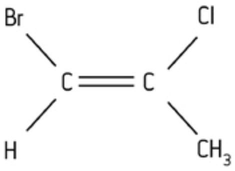
(E)-1,2-Dibromoethene

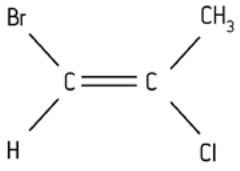


(Z)-1,2-Dibromoethene

Naming *E-Z* isomers

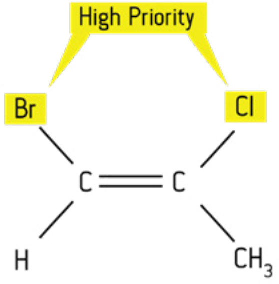
In order to decide which isomer is which, you have to look at the type of atoms directly attached to each of the carbon atoms on either side of the double bond. Look at each carbon separately and work out which atoms on the carbon have the highest atomic number. Then you have to look at how these highest priority atoms or groups are arranged around the double bond. If they are on the same side of the double bond, then you have the *Z* isomer, but if they're on opposite sides, you have the *E* isomer.



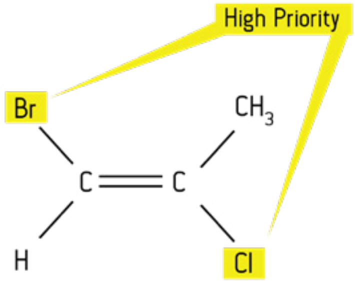


This is quite easy to work out if you have the same atom on both carbon atoms. However, if you have a structure like that shown below, it is rather more complicated:-

You have to look at the atoms/groups on both carbon atoms of the double bond. The left hand carbon has bromine and hydrogen attached to it, the right has chlorine and a methyl group attached to it. The two atoms that have priority are bromine and chlorine as they have higher atomic numbers than methyl and hydrogen. Therefore, the isomers are named as follows: -



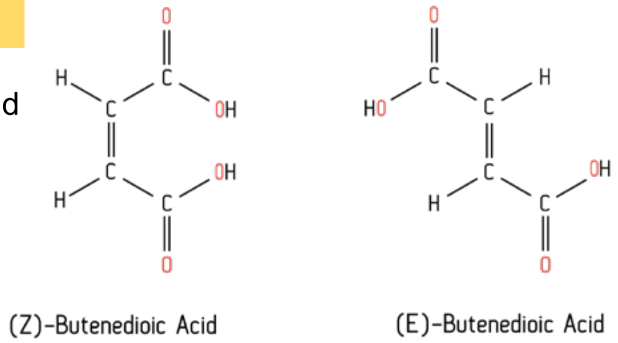
the Z isomer



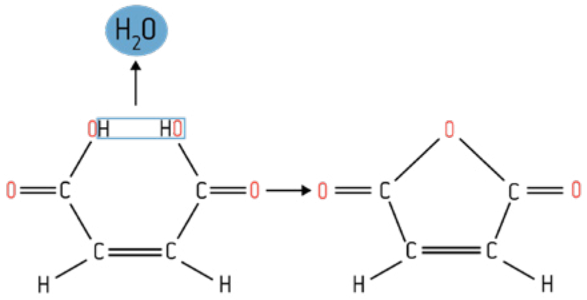
the E isomer

Properties of *E-Z* isomers

The different orientation of the functional groups can mean that *E-Z* isomers can have different physical and chemical properties. For example, butenedioic acid has two isomers:


(Z)-Butenedioic Acid (E)-Butenedioic Acid

The two -COOH groups can interact in the *Z*- isomer, but are too far apart in the *E*- isomer as the carboxyl groups are too far apart.


Dehydration of the (Z)-Isomer of Butenedioic

Physical properties of the two different isomers will also be different, eg boiling point. *E*- isomers tend to pack together better, so they will have stronger intermolecular forces and higher melting and boiling temperatures.

Melting and boiling points of organic compounds

In order to melt any solid or boil any liquid, heat energy needs to be supplied in order to overcome the forces that hold the particles together in that solid or liquid. When we think about the simple covalent compounds that are organic compounds, then the forces that hold them together are **Van der Waals forces**. If we are able to work out the strength of these Van der Waals forces, then we can predict the range of melting and boiling temperatures of different organic compounds.

Hydrocarbons only have induced dipole-induced dipoles between their molecules, so their intermolecular forces are very weak. The longer hydrocarbon chain, the stronger the Van der Waals forces as these dipoles only occur at the surface of the molecule and long chains have greater surface area.

Small molecules are therefore gases at room temperature, larger ones are liquids and the largest are solids.

If an isomer has branching, then this reduces the boiling temperatures as the chains cannot approach each other closely enough in order for them to experience Van der Waals forces.

2.5 Hydrocarbons

Fossil fuels

Definition: fuels that were derived from organisms that lived several million years ago.

We have been reliant upon fossil fuels for our energy needs for centuries and, although other sources are being developed, it is envisaged that these fuels will continue to supply our energy for the foreseeable future.

You need to know both the advantages and disadvantages of the use of fossil fuels: -

Advantages

1. They are available in many forms so can be used for a variety of uses. For example, coal and gas are used in power stations. Crude oil is refined into many different fractions and these are used for varying purposes.
2. Some of the alternative fuels such as solar and wind cannot be used all the time, but fossil fuels are always available.

Disadvantages

1. Fossil fuels are **non-renewable resources** because they take millions of years to form and are being used up very quickly.
2. Carbon dioxide, a **greenhouse gas** is formed during the combustion of hydrocarbons. These gases are responsible for raising the Earth's temperature and the consequential effects of this – rising sea levels and changes to crop suitability.
3. **Acid rain** is rain with a lower than expected pH. It is formed from the oxides of sulfur and nitrogen that are by-products of burning fossil fuels that contain sulfur and nitrogen. Acid rain causes damage to aquatic life, plant life and buildings and also initiates health issues for people with breathing difficulties.
4. Carbon monoxide is formed when **incomplete combustion** of fossil fuels happens. It is extremely poisonous. Incomplete combustion occurs when there is insufficient oxygen available.

Alkanes

The homologous series – a reminder

1. General formula is C_nH_{2n+2}.
2. Each member differs from its neighbour by CH_2.
3. The chemical properties of each member of the series are similar.
4. Their physical properties vary gradually as the size of the molecule increases. The smallest are gases (methane), larger ones are liquids (petrol) and the largest ones (candle wax) ae solids.

Reactions of alkanes

Alkanes are unreactive compounds as they are non-polar and do not have double bonds. They do undergo two important reactions however: -

1. **Combustion**

Alkanes are used as fuels because they burn well in oxygen and produce energy in exothermic reactions. Complete combustion occurs in the presence of sufficient oxygen to produce carbon dioxide and water. Eg, with methane: -

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l)$$

If there is not enough oxygen available, then carbon monoxide is formed due to incomplete combustion. CO is toxic as it can inhibit the transport of oxygen around the body. It also wastes chemical energy in that less energy is produced during incomplete combustion.

Soot is also produced during incomplete combustion and it is this that is responsible for the black smoke that is seen when diesel engines are not burning properly.

TIP! This is one of three reaction mechanisms that you need to understand and learn. **One of them will be on the exam paper!**

2. **Halogenation**

Alkanes react with halogens in the presence of uv light. You need to know the **mechanism** of this reaction, which occurs in three stages: -

Initiation stage

A chlorine molecule needs to be broken. The energy for this comes from uv light.

$$Cl_2 \rightarrow 2Cl^{\cdot}$$

This process is called **homolytic bond fission** where a covalent bond is broken and one electron from the bond goes to each atom. $Cl^{\cdot}$ is known as a **free radical**, which is a species with an unpaired electron.

Propagation stage

Free radicals are very reactive and will take part in **propagation** reactions. These are reactions where the process continues or grows.

$$Cl^{\cdot} + CH_4 \rightarrow CH_3^{\cdot} + HCl$$

$$CH_3^{\cdot} + Cl_2 \rightarrow CH_3Cl + Cl^{\cdot}$$

You will see that a new free radical is formed, the methyl free radical. In the propagation stage each reaction starts with a free radical and this then produces another one so that the **chain reaction** continues.

Termination

The chain reaction continues until two radicals meet in a **termination** stage, eg

$$CH_3^{\cdot} + Cl^{\cdot} \rightarrow CH_3Cl$$

This is an example of a **substitution reaction** where a hydrogen atom in the alkane is replaced by a chlorine atom.

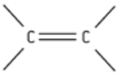
Further substitution can occur when chloromethane takes part in the chain reaction rather than methane, so dichloromethane is eventually made. Trichloromethane can also be made in the same way. This mixture of products being formed can be avoided by limiting the amount of chlorine in the reaction mixture.

This type of reaction is known as a **free radical substitution** reaction.

Alkenes

General formula – C_nH_{2n}

Functional group



Because of the double bond, they are known as **unsaturated hydrocarbons**. They are much more reactive than alkanes because of this.

They're formed when long hydrocarbon chains are **cracked**.

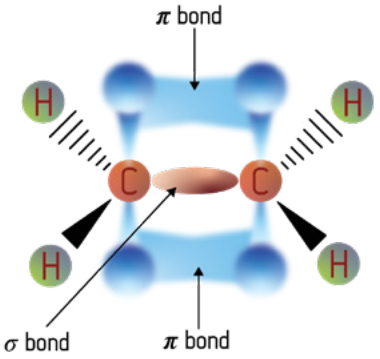
Used to make polymers and as starting materials for a range of organic compounds.

Structure of the double bond

The carbon-carbon double bond in alkenes is made up of two types of bond. The normal bond between carbon and other atoms is called a **sigma** (σ) bond. The second bond in the double bond is **made up of a sideways overlap between the spare p-orbital on both carbon atoms. It's called a pi (π) bond**.

Some people are confused by the π bond and they think that it is actually two bonds. It is, in fact, one bond with two lobes, so the pair of electrons can appear anywhere within those two lobes.

What it does offer is an electron-rich environment that allows certain types of reaction to take place.



Structure of the Double Bond

Electrophilic addition reaction

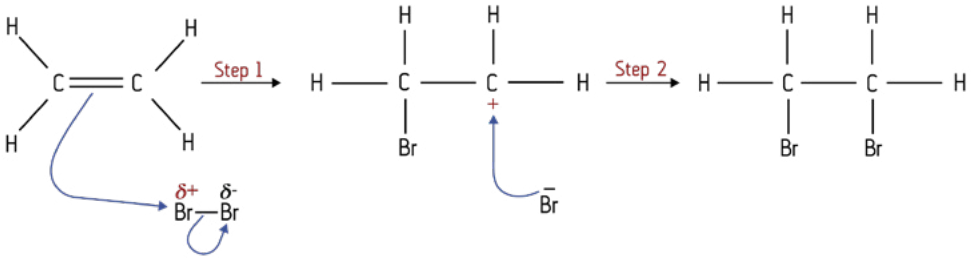
(**Electrophile** = a species that wants to gain electrons because it is electron deficient. It has the ability to accept a lone pair of electrons. **Addition** = something being added to the alkene, so reagents combine to give just one product.)

TIP! This is the second reaction mechanism

This is the mechanism of most reactions of alkenes.

The electron pair in the π-bond, as mentioned previously, gives the alkene a space of high electron density, so this is a good place for attack by an **electrophile**. During the attack, **heterolytic bond fission** occurs. This is when a bond is broken and **both** of the electrons from the bond goes to **one** of the bonded atoms.

Br_2 is non-polar, so a dipole is induced by the negative charge of the π-bond. A bond is formed between one carbon and one bromine, making the second carbon positive. The bromide ion attaches to this positive carbon, called a **carbocation**. Product is 1,2-dibromoethane. . . . . NB – curly arrows denotes the movement of an electron pair.



Other examples of addition reactions

1. Test for alkenes

You know that bromine water decolourises in the presence of alkenes. This is due to the addition reaction shown on page 85, where the brown bromine is added to the alkene and therefore is no longer bromine. The bromo- substituted alkene will be colourless.

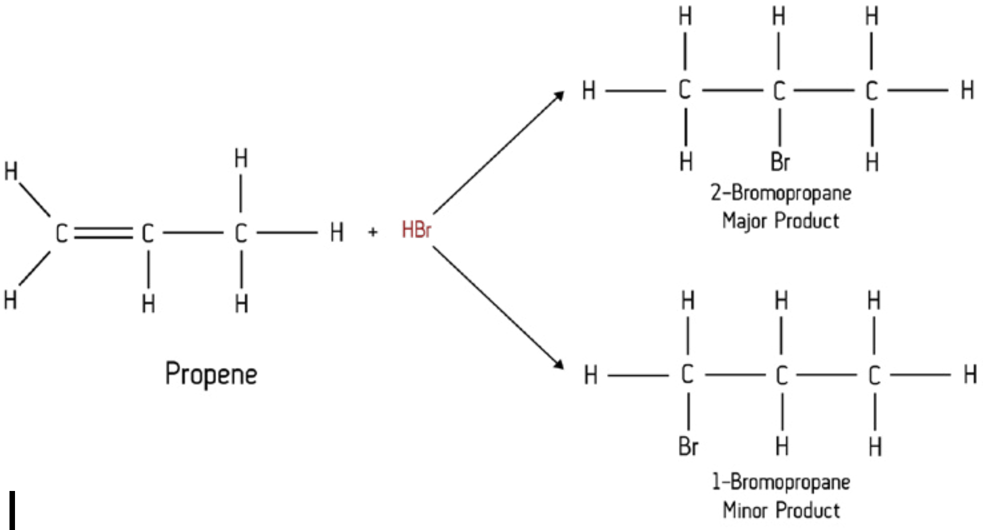
Potassium manganate(VII) is also changed from its purple colour to colourless in the presence of alkenes. Two OH groups are added across the double bond, giving the diol (alcohol with two -OH groups).

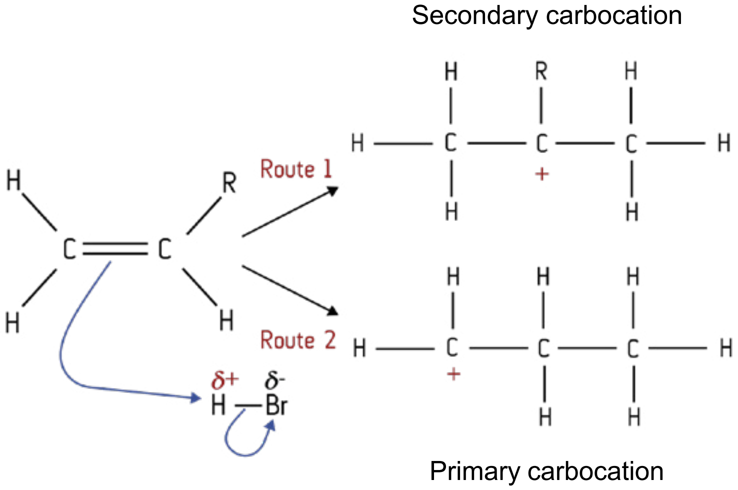
2. Reaction with hydrogen

Nickel is the most commonly used catalyst for this reaction. This **hydrogenation** reaction is important commercially as it converts liquid unsaturated oils into solid, more edible saturated fats. These are used as butter substitutes and spreads.

3. Reaction of propene with hydrogen bromide

Any unsymmetrical alkene can give two products when HBr is added to them, but propene is a convenient example to use: -





2-bromopropane is the major product because the carbocation produced in the first mechanism is more stable. It is called the secondary carbocation as the positive charge is on the second carbon atom.

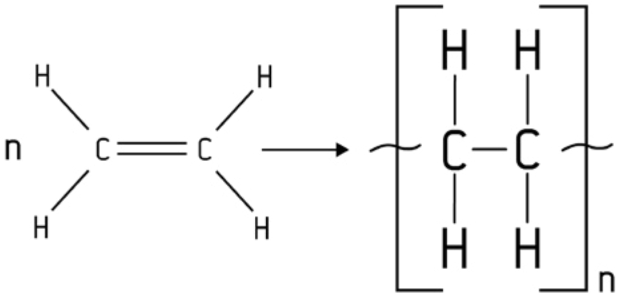
The alternative carbocation is called the primary carbocation. This is less stable as it is more susceptible to attack in that position.

Polymerisation

Definition: the joining of a huge number of **monomer** molecules to make a large **poymer** molecule.

Monomers are small molecules that can be made into a polymer. Alkenes are good examples of monomers as they undergo **addition polymerisation** where the double bond is used to join the monomers together. Nothing is eliminated in this process.

Ethene is polymerised to form poly(e)thene. The following is a representation of the reaction. The n represents the large number of monomers that are joined together in the polymer. Note that you must show the lines sticking out from the bracket to show that the chain continues.



Note that the polymer does not contain double bonds, but it does contain the name of the monomer. The regions inside the bracket is called the **repeat unit** of the polymer.

Polyethene is used to make plastic bags, buckets etc as it is flexible and unreactive. When it was first made it had side branches which meant that the chains couldn't pack together tightly, reducing the number of Van der Waals forces, meaning their melting point was also low.

Catalysts were developed that make polyethene into straight chains. This gives a polythene with higher density and higher melting point. They are used where more rigidity is required and/or the temperature of use is higher.

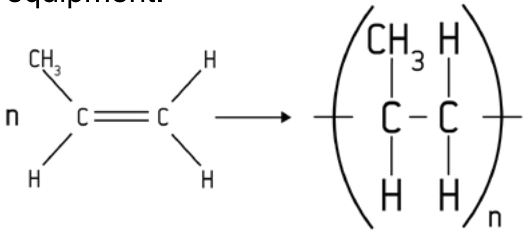
Different polymers can be made using substituted alkenes as the monomer. This makes polymers with a large variety of uses. Here are some that are widely used: -

Polypropene

Monomer = propene

Polymer = polypropene

It's rigid and used in food containers and kitchen equipment.

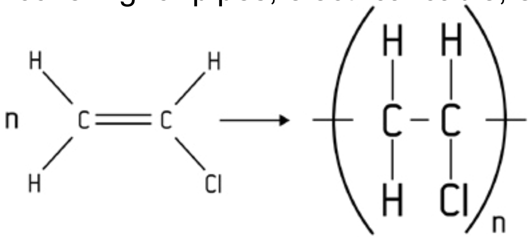


Polychloroethene

Monomer = chloroethene

Polymer = polychloroethene

Former name is PVC, used as a flexible covering for pipes, electrical cable, etc

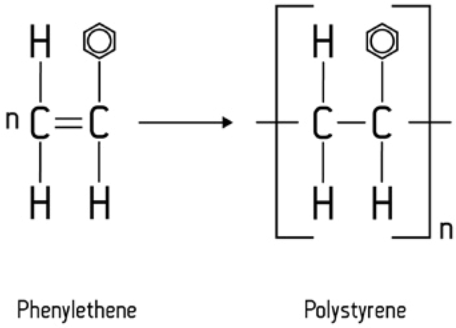


Polyphenylethene

Monomer = phenylethene

Polymer = polyphenylethene

Former name is polystyrene and as it is hard, it is used in many household items needing strength and rigidity. Expanded polystyrene is a good insulator.

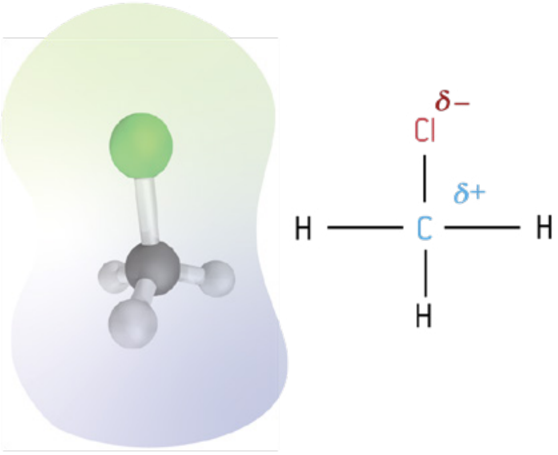


2.6 Halogenoalkanes

Definition: a homologous series where one or more hydrogen atoms in an alkane have been replaced by a halogen atom.

This diagram of chloromethane shows how the more electronegative chlorine atom makes the molecule polar. Chlorine is δ- and the carbon that is attached to the chorine is δ+.

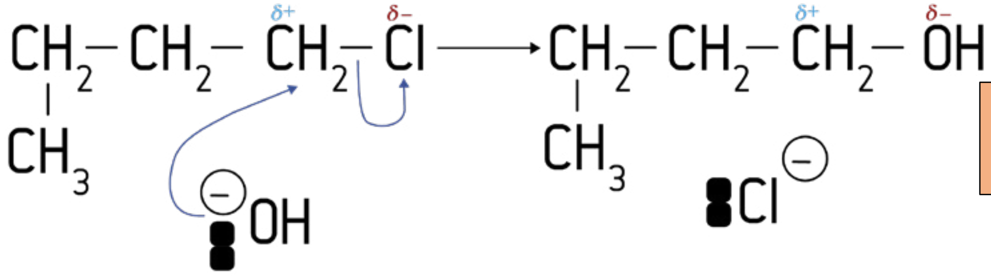
This means that halogenoalkanes are susceptible to attack by electron-rich species via the electropositive carbon atom. This is known as **nucleophilic attack**. Nucleophilic attack leads to **substitution**, where an atom is substituted for another atom or species.



Chloromethane, CH_3Cl

Nucleophilic substitution of 1-chlorobutane

The nucleophile is the hydroxide ion, OH^-, which is provided by sodium hydroxide. It has lone pairs on the oxygen atom, so is therefore a good nucleophile. Here is the reaction mechanism: -



TIP! This is the third reaction mechanism that you need to understand and learn

The lone pair on the hydroxide ion is donated to the δ+ carbon in the chlorobutane, following attack by the nucleophile on the positive atom. Because the lone pair is donated, a bond is formed between the OH^- and the carbon. The carbon-chlorine bond breaks to release the chloride ion. The product is butan-1-ol.

This **nucleophilic substitution** reaction can also happen using the OH^- ion in water. This reaction can therefore be classified as a **hydrolysis** reaction. (This is a reaction with water that produces a new product.) However, the reaction is very slow with water as the concentration of OH^- ions is low in water. In order to achieve hydrolysis, the halogenoalkane is heated under reflux with water or aqueous sodium hydroxide.

Does changing the halogen have an effect on the hydrolysis reaction?

Changing the halogen affects the rate of the reaction. This is due to two factors that have to be considered when we think about an explanation. (NB, only Cl, Br and I are considered): -

1. **Electronegativity**. Chlorine is the most electronegative, which makes the C-Cl bond the most polar out of the three possible. The carbon in the C-Cl bond is the most δ+ out of the three.

2. **Bond strength.** Chlorine is the smallest halogen, so that the C-Cl bond is the strongest and it is this bond that is broken during hydrolysis.

These two factors work in opposition, but because the iodo- compound is hydrolysed most quickly, it must be the bond strength that has the most effect. Even though its carbon atom is the least δ+, it is obvious that the C-I bond is broken easily in order for the reaction to take place.

Testing for halogens in an organic compound

This is relatively simple as hydrolysis of a halogenoalkane produces a halide ion and halide ions can be tested with silver nitrate ($AgNO_3$), following the addition of HNO_3.

The first part of the process is hydrolysis, where the organic compound is heated with aqueous sodium hydroxide solution: -

$$RX + NaOH(aq) \rightarrow ROH + Na^+(aq) + X^-(aq)$$

where R is the alkyl group.

Once $X^-(aq)$ has been produced by hydrolysis, HNO_3 is added in order to remove any NaOH remaining. Then the $AgNO_3(aq)$ can be added to test for the type of halide ion present.

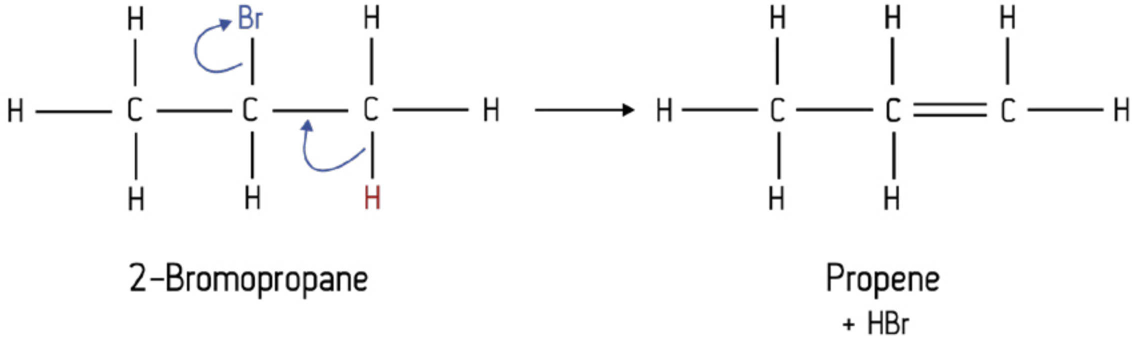
As the colours can be ambiguous with the silver nitrate test, concentrated and dilute ammonia can be used in order to verify the result: -

Wikipedia : Rrausch1974 CC-BY-SA-3.0

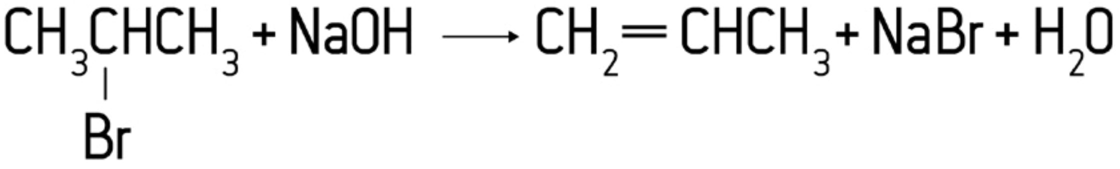
Halogen	Addition of silver nitrate	Addition of ammonia to precipitate formed with silver nitrate
chlorine	white precipitate	dissolves in dilute ammonia solution
bromine	cream precipitate	dissolves in concentrated ammonia solution
iodine	yellow precipitate	does not dissolve in ammonia solution

Elimination reactions

Definition: a reaction that involves the loss of a small molecule in order to produce a double bond. Elimination reactions in halogenoalkanes involves the removal of a hydrogen halide and the formation of an alkene. The hydrogen halide is acidic (eg HCl) and can be removed using an alkali such as NaOH. To avoid hydrolysis/nucleophilic substitution occurring instead of elimination, the alkali must be in an ethanolic solution instead of with water.



If you include the sodium hydroxide in the equation, then it can be written as: -

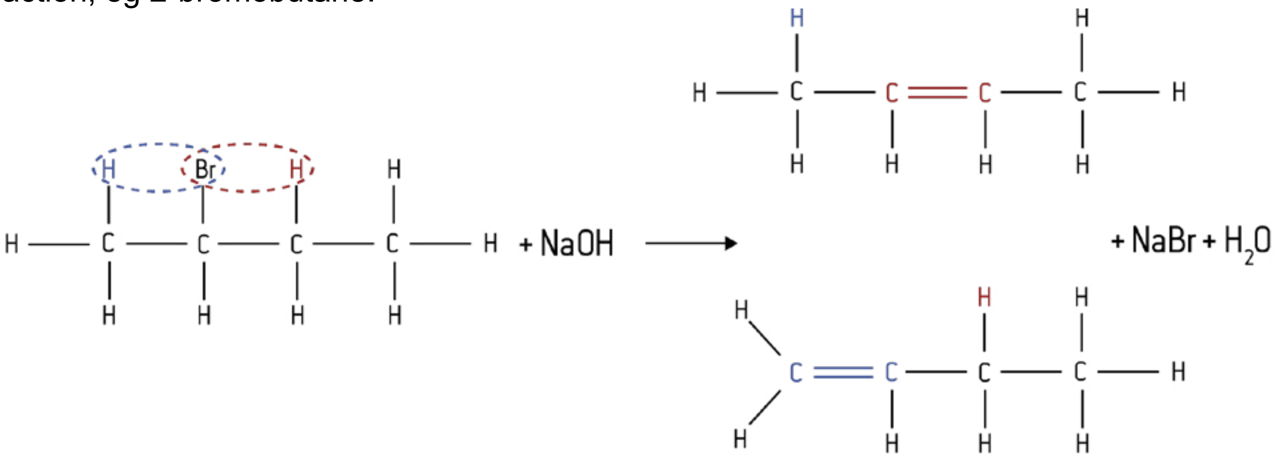


$$\underset{\displaystyle Br}{CH_3\underset{|}{C}HCH_3} + NaOH \longrightarrow CH_2{=}CHCH_3 + NaBr + H_2O$$

If the hydrogen halide is going to be eliminated successfully, it must be attached to a carbon atom next to a carbon that has a hydrogen atom attached to it.

Example

In an unsymmetrical halogenoalkane, more than one alkene can be produced during the elimination reaction, eg 2-bromobutane.



Here, but-2-ene and but-1-ene are formed. You don't need to know which is the more likely of the two to be formed.

Uses of halogenoalkanes

Halogenoalkanes are insoluble in water as they do not have the O-H or N-H needed in order to hydrogen bond with water. Another property is that their boiling points are close to room temperature so that if they are gases they are easily condensed and if they are liquids they are easily vaporised.

These properties make them useful as solvents and as refrigerants:-

1 Solvents

Because they are polar molecules, but are not soluble in water, halogenoalkanes are able to mix with polar and non-polar organic compounds. They are therefore used as degreasing agents and are used as solvents in several organic processes. They are used as dry cleaning fluids.

2 Refrigerants

When a liquid evaporates, it takes in heat, so halogenoalkanes are ideal refrigerants with their boiling points close to room temperature. As they evaporate, heat is taken from the surroundings, thereby cooling it down.

3 Anaesthetics

$CHCl_3$, trichloromethane, used to be used as an anaesthetic. You may have heard of it as it was called ‘chloroform’. Some halogenoalkanes are still used as anaesthetics.

CFCs and the environment

Chlorofluorocarbons (CFCs) are halogenoalkanes that contain both chlorine and fluorine. They were the most commonly used refrigerants and propellants in spray cans. Unfortunately, they were seen to be responsible for making holes in the **ozone** layer, which allow uv rays from the sun to reach the earth’s surface and cause skin cancer. Their use is now tightly regulated and different compounds are now being sought, such as **HFCs (hydrofluorocarbons)**, which do not contain C-Cl bonds and therefore no chlorine free radicals.

Here is the chain reaction that occurs as CFCs affect ozone. It’s similar to the chlorination of alkanes: -

Initiation stage

When the bond between C-Cl breaks, free radicals are formed, this is initiated by the uv radiation in the upper atmosphere. The C-Cl bond is weaker than the C-F and C-H bonds, so it breaks first. Here is the reaction for trichlorofluoromethane: -

$$CFCl_3 \rightarrow Cl\cdot + CFCl_2\cdot$$

Propagation stage

There are several propagation stages that are possible. These include: -

$$Cl\cdot + O_3 \rightarrow ClO\cdot + O_2$$

$$ClO\cdot + O_3 \rightarrow Cl\cdot + 2O_2$$

This is a chain reaction, so a small number of chlorine radicals can decompose several ozone molecules.

Termination stage

You can get several final products, depending on the free radicals that come together. Several different ones can be formed during the propagation stage.

2.7 Alcohols and Carboxylic Acids

These are two of the oxygen-containing homologous series of organic compounds.

Alcohols

Definition: homologous series containing -OH as the functional group.

Ethanol is the most widely used alcohol and is it is the one that it commonly known as ‘alcohol’ in everyday language.

Industrial preparation of ethanol

Ethene reacts with steam, producing ethanol.

Conditions: - Temperature = 300°C, Pressure = 60-70 atm, Catalyst = phosphoric acid

$$CH_2{=}CH_2\ (g)\ +\ H_2O\ (g)\ \leftrightarrows\ CH_3CH_2OH\ (g)\qquad \Delta H\ =\ -45\ kJ\ mol^{-1}$$

The conditions used can be explained using **Le Chatalier’s Principle**: -

Temperature

The forward reaction is exothermic, so yield would be greatest at low temperature (cf Haber Process). Because this gives a slow rate of reaction, a compromise temperature of 300°C is used.

Pressure

Two moles of reactants give one mole of products, so a higher pressure will give a higher yield. This will also increase the rate of a reaction, but remember that high pressures are expensive to maintain.

Catalyst

The catalyst is an inert solid coated with **phosphoric acid**. It increases the rate of a reaction, but doesn’t affect the yield.

These conditions convert around 5% of reactants to products, so the unreacted ethane is recycled back into the reaction chamber.

Fermentation

Definition: an enzyme catalysed reaction that converts sugar to ethanol.

The enzyme that catalyses the reaction is in yeast, so sugar is dissolved in water before the yeast is added. It is then left in a warm place until ethanol is formed. This is how alcoholic drinks are made. Here’s the equation using glucose as an example of the sugar used: -

$$C_6H_{12}O_6\ \rightarrow\ 2C_2H_5OH\ +\ 2CO_2$$

Ethanol can be removed from the aqueous solution by fractional distillation as it has a boiling point of 80°C, much lower than water.

Biofuels

Definition: a fuel that has been produced from a biological source.

Bioethanol is produced by the fermentation of sugars in plants and **biodiesel** is produced from the oils and fats present in the seeds of some plants.

The use of biofuels has advantages and disadvantages.

Advantages

1 They're renewable

The plants that produce biofuels can be grown every year. Waste materials from animals are also used.

2 Greenhouse gases help make them 'carbon neutral'

Biofuels do produce carbon dioxide, but the plants that make them have taken in carbon dioxide during photosynthesis, making them carbon neutral.

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6$$

3 Economic and political security

Countries that do not have fossil fuels are affected by changes in price and availability when these fuels are imported.

Disadvantages

1 Land use

Land being used for crops to create biofuels cannot be used for food crops. Also, forests are being destroyed to create land on which to grow plants for biofuels.

2 Use of resources

Because large amounts of water and fertilisers are needed to grow biofuels, growing them can cause problems due to water shortages in some areas and pollution of water due to fertiliser use.

3 Are they really carbon neutral?

The burning of biofuels and their absorption of carbon dioxide during growth do balance out with carbon neutrality. However, this does not take into account the fuel needed to build factories, transport raw materials and so on.

Dehydration of primary alcohols

A lot of alcohols can be dehydrated to form alkenes. The equation for propan-1-ol is shown below:-

$$CH_3CH_2CH_2OH \rightarrow \underset{\text{propene}}{CH_3CH{=}CH_2} + H_2O$$

this is the reverse of the reaction of alkenes with steam. The most commonly used dehydrating agents are concentrated sulphuric acid or heated aluminium oxide.

A hydrogen atom is removed from one carbon atom and the OH group from the next atom, so a double bond is formed.

Classification of alcohols

Primary (1°), secondary (2°) and tertiary (3°) alcohols are so-called according to how the OH group is attached to the molecule.

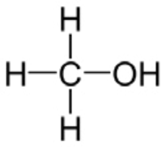
Primary alcohols have their -OH group joined to a carbon that is itself attached to no other or one other carbon.

Secondary alcohols have their -OH group joined to a carbon that is itself attached to two other carbon atoms.

Tertiary alcohols have their -OH group jointed to a carbon that is itself joined to three other carbon atoms.

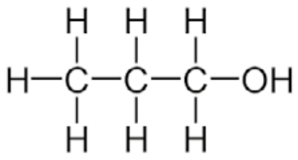
Examples

Methanol



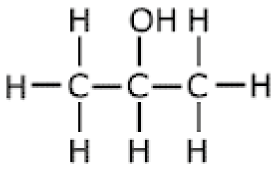
The -OH is joined to a carbon atom attached to no other carbon atoms, so it is a primary alcohol

Propan-1-ol



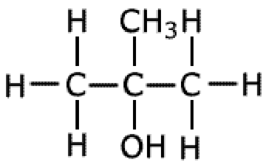
The -OH is joined to a carbon attached to one other carbon, so it is a primary alcohol.

Propan-2-ol



The -OH group is joined to a carbon atom attached to two other carbons and so it is a secondary alcohol.

2-methylbutan-2-ol

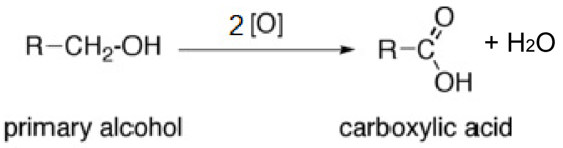


The -OH group is joined to a carbon atom attached to three other carbons and so it is a tertiary alcohol

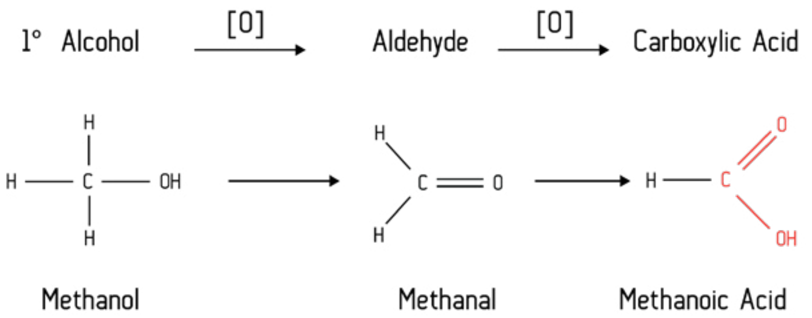
Oxidation of alcohols

Another reaction that many alcohols undergo is oxidation. Usually, acidified potassium dichromate(VI) (also written as $Cr_2O_7^{2-}/H^+$) is the oxidising agent and this is heated with the alcohol.

The product depends on whether the alcohol is primary, secondary or tertiary. In the following equations, the oxidising agent is shown as [O]. If you use this symbol for the oxidising agent, then the equation must be balanced, eg.



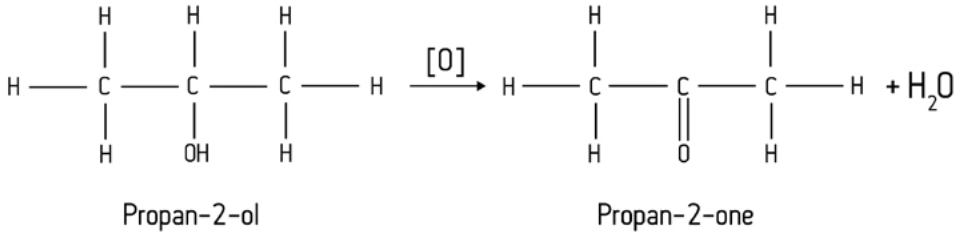
Oxidation of primary alcohols, eg methanol



The **first stage** of the reaction is where two hydrogens are lost. One comes from the -OH group and the other one from the carbon next to it. This leaves a C=O double bond. The product formed here is an **aldehyde**, with the functional group -CHO.

The **second stage** of the reaction sees an oxygen atom added to the aldehyde. The product is a **carboxylic acid**, with the functional group -COOH.

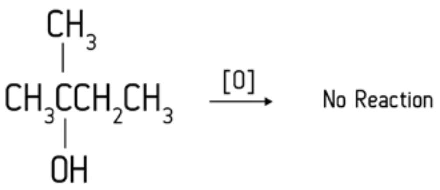
Oxidation of secondary alcohols, eg propan-2-ol



There is only one stage here, which is the same as the first stage in the oxidation of primary alcohols. Two hydrogens are lost and a double bond is formed between the carbon and oxygen.

The resulting compound is called a **ketone** and it has the functional group -C=O.

Oxidation of tertiary alcohols, eg 2-methylbutan-2-ol



$$CH_3C(CH_3)(OH)CH_2CH_3 \xrightarrow{[O]} \text{No Reaction}$$

As there is no hydrogen on the carbon atom adjacent to the -OH group, no reaction can occur.

Summary of alcohol oxidation reactions

Primary to **aldehydes** to **carboxylic acids**

Secondary to **ketones**

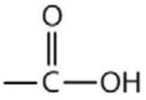
Tertiary no reaction

Test for primary and secondary alcohols

Acidified potassium dichromate changes colour from orange to green in the presence of primary and secondary alcohols. This uses to be the basis of old breathalyser tests when drivers were asked to ‘blow in the bag’. Tertiary alcohols have no effect.

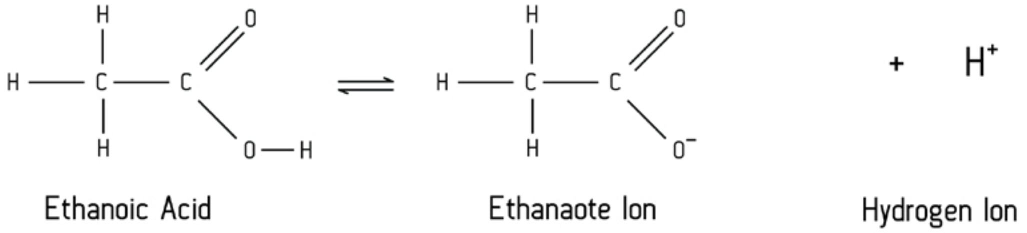
Carboxylic acids

Definition: an homologous series containing -COOH as its functional group. Here is the structure of the functional group: -



$$-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

They are **weak acids**, so only partially ionise in aqueous solution. Eg for ethanoic acid: -



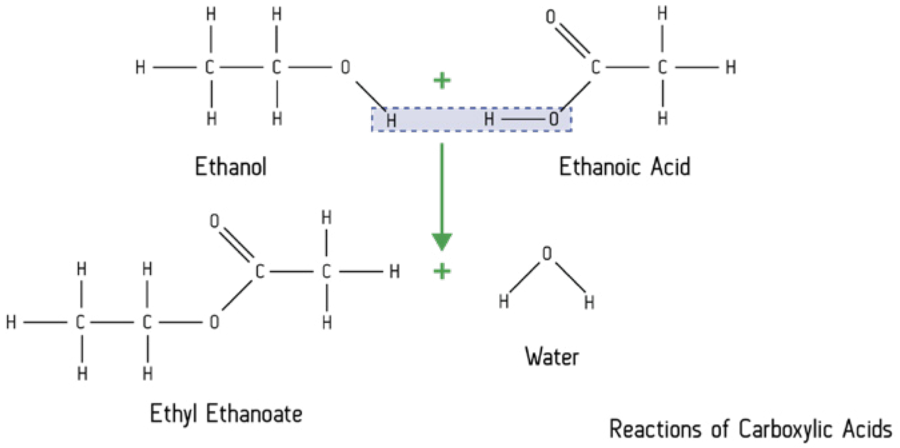
Reactions of carboxylic acids

Esterification

Carboxylic acids react with alcohols when heated to form esters and water.
It is a reversible reaction, catalysed by conc sulphuric acid.
The ester can be separated by distillation.
Eg, the reaction between ethanoic acid and ethanol.

See how a water molecule is formed by removing a hydrogen from the alcohol and a hydroxide from the acid.

Esters have a characteristic sweet, fruity smell.



As acids

In the same way as their inorganic counterparts, carboxylic acids react with alkalis, bases, carbonates and hydrogencarbonates to form salts: -

Acid + Base (or alkali) → Salt + Water

Acid + Carbonate (or hydrogencarbonate) → Salt + Water + Carbon dioxide

The salts formed from carboxylic acid contain the '-anoate ion', eg ethanoic acid gives the ethanoate ion and propanoic acid gives the propanoate ion.

2.8 Instrumental analysis

Before the widespread use of instrumental techniques, chemists used to analyse the nature and quantity of an unknown substance by volumetric and gravimetric analysis. Now, spectroscopic techniques are used to do the same thing.

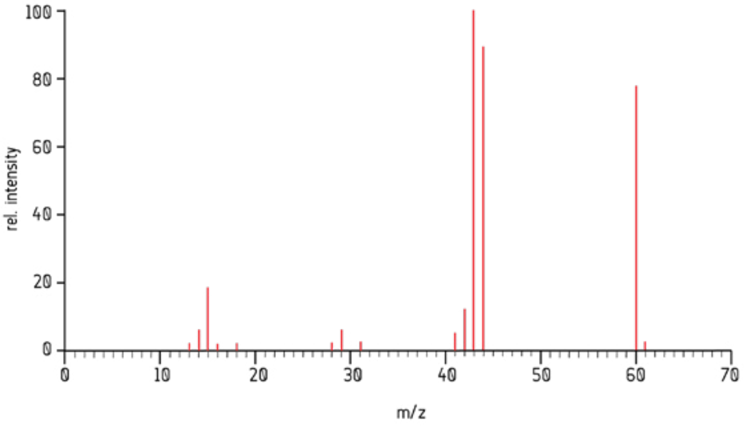
You need to be able to analyse mass, infra-red (IR) and nuclear magnetic resonance (NMR) spectra to help identify the structure of an organic molecule.

Mass spectrometry

In a mass spectrometer, an electron is knocked off molecules of a gaseous sample of an organic compound to produce a positive ion. This is called the **molecular ion,** which is the positive ion formed in a mass spectrometer from the whole molecule. You will often see them referred to as M^+. Molecules also split in the mass spectrometer, forming **fragments,** which are the smaller parts of the molecule and **fragmentation** is the process of producing the fragments. Analysing the patterns given by the molecules and their fragments can give information about the structure of the molecule

Here is a simplified mass spectrum of ethanoic acid (CH_3COOH). Assume that each ion has a charge of +1

The peak with the highest m/z value is that of the molecular ion and it **gives the M_r**, which is 60. There is a large peak at 45, which comes from the $COOH^+$ ion, the peak at 15 is due to the CH_3^+ ions. The peak at 43 is due to an ion made up of CH_3CO^+.

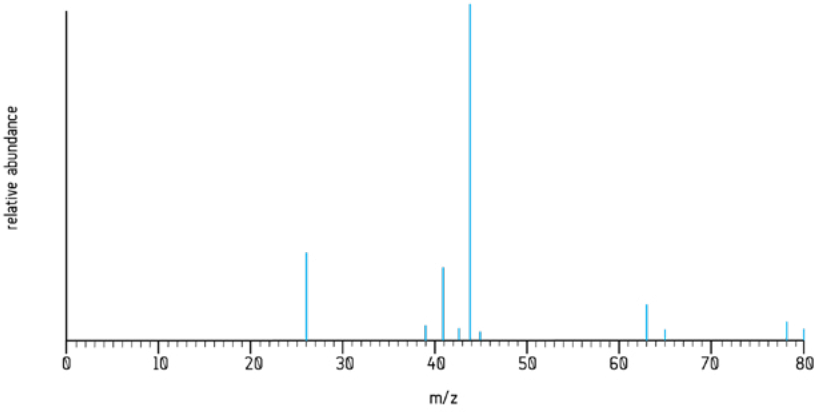


If you have chlorine or bromine in the compound, you will get two peaks for the molecular ion and some of the fragments because you have both halogens existing as isotopes.

This is a simplified mass spectrum of 2-chloropropane.

There are two peaks for the molecular ion, one for the ion that contains chlorine-35 (at m/z = 78) and one for the ion that contains chlorine-37 (at 80).

The peaks at 63 and 65 are due to the loss of a CH_3 fragment which is 15.



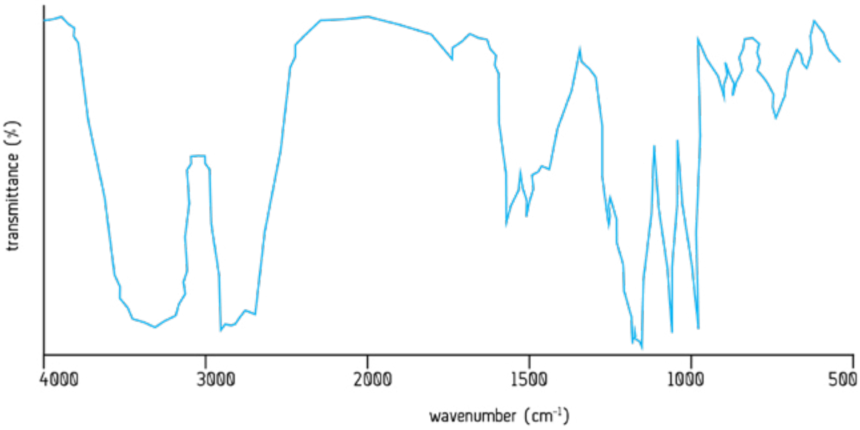
Infrared spectrscopy

Organic molecules absorb energy from the electromagnetic spectrum. Energy in the IR part of the spectrum causes increased vibrations and bending of bonds. Different bonds absorb IR at different values of IR radiation and this absorption is shown on an infra-red spectrum.

The **wavenumber** where **absorption** happens is **characteristic** of that particular bond, so it is useful in identifying the functional group present.

Wavenumbers will be supplied to enable you to answer questions in the examination. Here's a spectrum for propan-1-ol, along with examples of wavenumbers: -

Bond	Wavenumber/cm^{-1}
C-C	650 to 800
C-O	1000 to 1300
C=O	1650 to 1750
C-H	2800 to 3100
O-H	2500 to 3550



You will be looking for something that tries to confirm the functional group of the compound. A lot of the troughs you will see can be ignored, just look for information corresponding to any functional groups you may be required to identity. Here, you will notice that there is no trough between 1650 and 1750, so no C=O group, but there is a strong possibility of a C-O group due to the trough around 1100. There is also a trace between 2500 to 3550, so there must be an -OH group present in the compound.

Nuclear magnetic resonance spectroscopy

Energy can be absorbed by atoms that changes the spin of the nucleus, but you do not need to know why or how this happens. What is important is that the energy absorbed depends on the **environment** that the atom is in, that is, how many and which atoms surround it.

Each absorption appears at a different place on a trace and the **δ** or **chemical shift** value for the peak tells you the energy that has been absorbed by the nucleus. There are two types of nmr spectra that you need to know about, those for ^{13}C and ^{1}H.

Definitions

Environment: the nature of the surrounding atoms/groups in a molecule

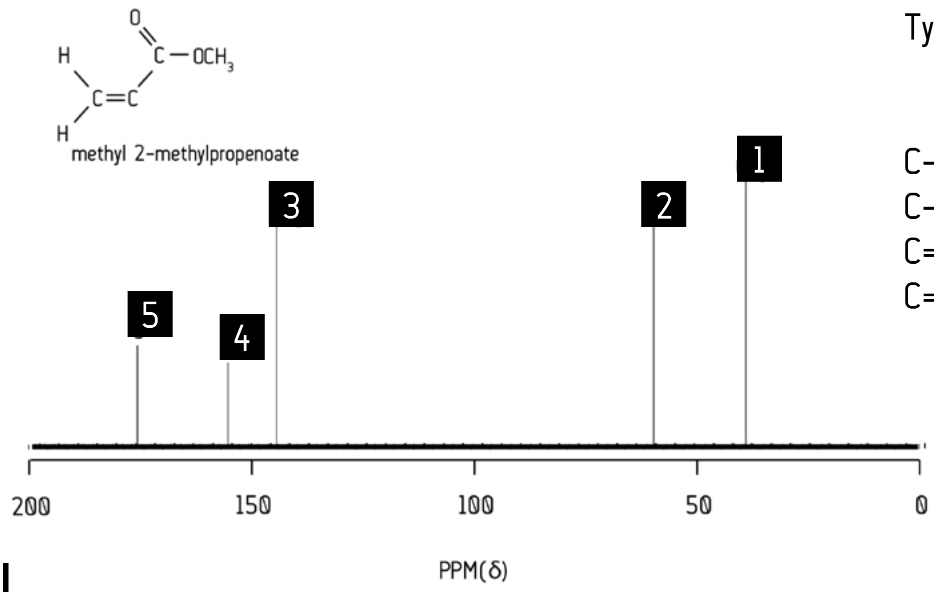
Chemical Shift: a measure of difference in parts per million from the standard of energy of a particular absorption type.

^{13}C Spectroscopy

An atom needs to have an uneven number of protons or nucleons if they are to have a nuclear magnetic resonance, this is why the more usual ^{12}C is not suitable.

All organic compounds contain very small amounts of ^{13}C, so these atoms will be able to absorb energy and produce a spectrum.

Again, you will be given the data you need in order to interpret the spectrum. Here is a spectrum of a fairly complicated molecule: -



Type of carbon	Chemical atom shift/ppm
C-C	5 to 55
C-O	50 to 70
C=C	115 to145
C=O	160 to 220

This is the information that you gain from a spectrum: -

- the number of peaks gives you the number of different carbon environments (in this case 5)
- the chemical shifts of the peaks give you the type of carbon environment.

Carbon number 1 in the spectrum is part of the methyl group that is attached to the carbon in the double bond, it has a **C**-C environment.

Carbon number 2 is part of the other methyl group that's attached to the oxygen, it has a **C**-O environment.

Carbon number 3 is the carbon that is attached to two hydrogens at one end of the double bond. It has a C=**C** environment.

Carbon number 4 is the first carbon from the double bond and it also has a **C**=C environment.

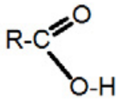
Carbon number 5 is the one that is double bonded to the oxygen atom, it has a **C**=O environment.

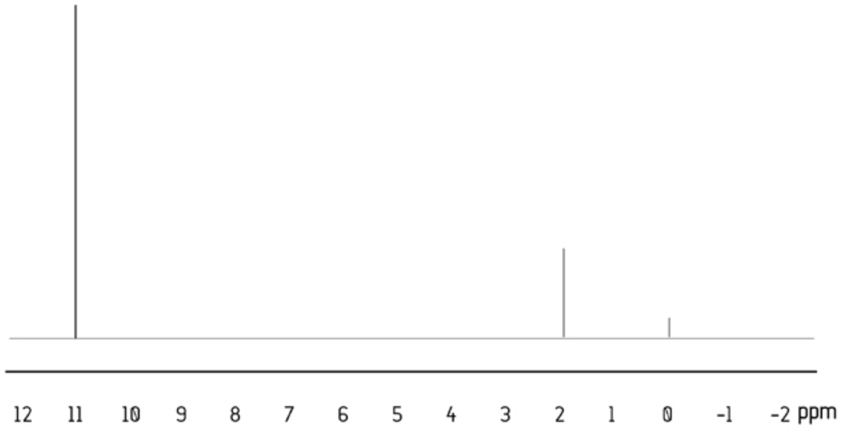
You would not normally have enough information to distinguish between carbons 3 and 4, it is just that the diagram is labelled that way.

^1H Spectroscopy

This is also known as proton spectroscopy. As well as the number and different types of proton environment, this type of spectroscopy also gives information about the **ratio of the numbers** of protons in each environment. (This ratio is shown by the area or height of the peaks, but you will usually be given it in the question.)

Here is a spectrum of an unknown compound that has a molecular formula of $C_2H_4O_2$. The ratio of areas of peaks is 3:1, so there must be three protons in one environment and one in the other.

Type of Proton	**Chemical shift/ppm**
CH_3-C=O	2.0 to 2.5
	11.0



We can see from the molecular formula that there are four protons.
They are in two different environments as there are two peaks.
We have already said that there are three protons in one environment and one in the other because of the ratio of the peaks.
From the chemical shift data, we can see that we have one environment as part of a methyl group and one that is part of an -OH group.

The compound is therefore ethanoic acid, CH_3COOH.