



Higher Chemistry

HSN11000
Unit 1 – All Topics

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Topic 1 – Reaction Rates

Rates

From Standard Grade you should know that:

- reaction rates are dependent on
 - the concentration of the reactants;
 - particle size;
 - temperature
- catalysts speed up reactions but are not used up during the reaction
- the concentration of reactants in solution is measured in units of moles per litre written as:

mol/litre or mol litre⁻¹ or mol l⁻¹

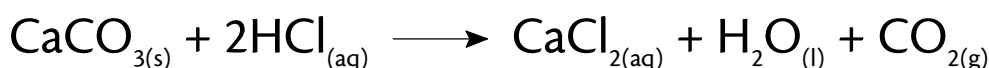
The rate of a reaction is usually found experimentally by measuring how fast a reactant is used up or how fast a product is formed.

This could involve measuring:

- the rate of mass loss or increase in volume if a gas is a product.
- a change in pH if, for example, an acid is being neutralised.
- the rate at which a colour develops or disappears – this is done using an instrument called a colorimeter.

Rate is defined as the change in concentration of reactants or products in unit time.

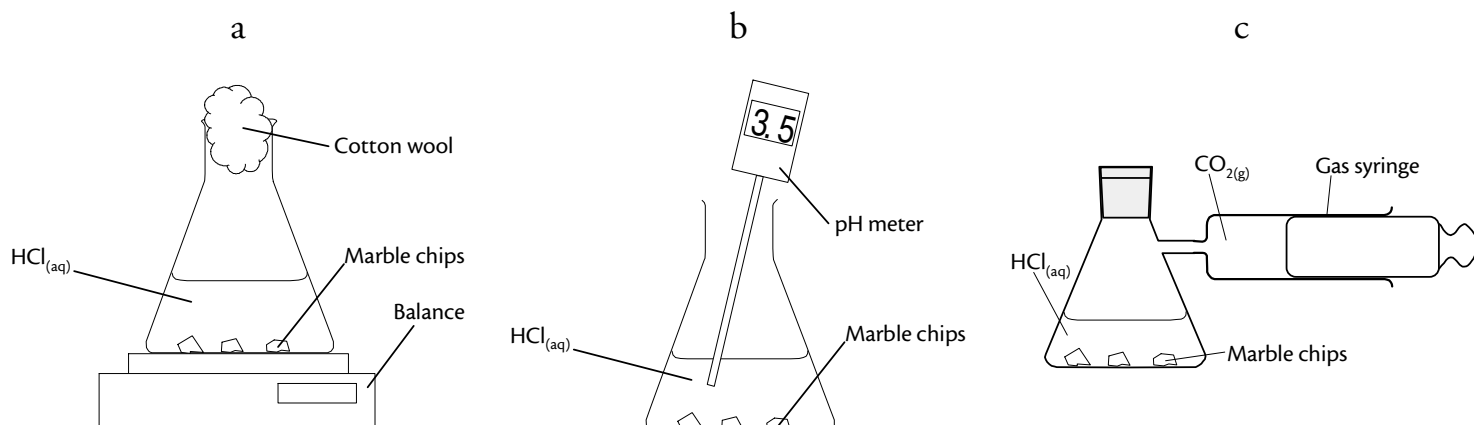
We studied the reaction between marble chips (calcium carbonate) and dilute hydrochloric acid.



The reaction can be followed in a number of ways:

- by measuring the mass loss of the flask as the carbon dioxide is produced and escapes from the flask.
- by measuring the fall in concentration of acid as the reaction proceeds.
- by collecting and measuring the volume of carbon dioxide produced.

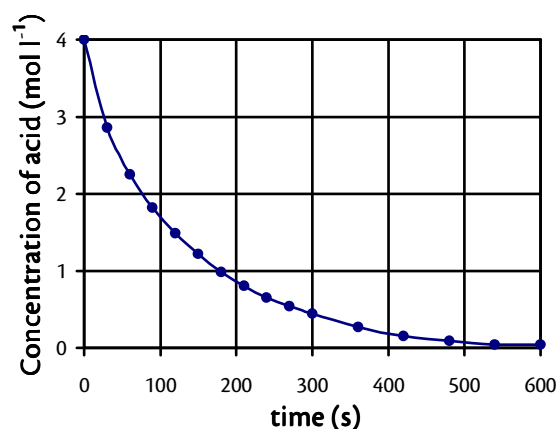
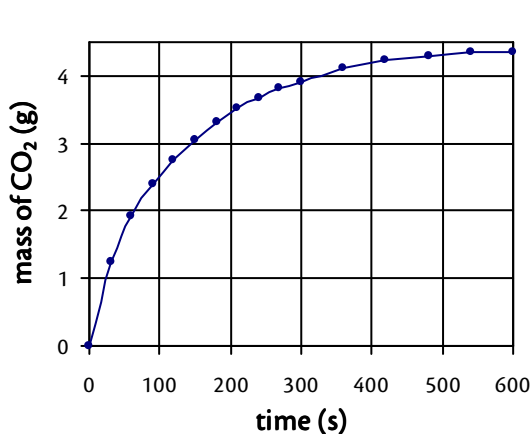
The diagrams indicate how this might be done.



The following table contains results obtained using methods (a) and (b):

| Time (s) | Mass of flask and contents (g) | Decrease in mass (g) | Concentration of acid (mol l ⁻¹) |
|----------|--------------------------------|----------------------|--|
| 0 | 149.00 | – | 4.00 |
| 30 | 147.75 | 1.25 | 2.86 |
| 60 | 147.08 | 1.92 | 2.25 |
| 90 | 146.60 | 2.40 | 1.82 |
| 120 | 146.24 | 2.76 | 1.49 |
| 150 | 145.94 | 3.06 | 1.22 |
| 180 | 145.68 | 3.32 | 0.98 |
| 210 | 145.48 | 3.52 | 0.80 |
| 240 | 145.32 | 3.68 | 0.65 |
| 270 | 145.19 | 3.81 | 0.54 |
| 300 | 145.08 | 3.92 | 0.44 |
| 360 | 144.89 | 4.11 | 0.27 |
| 420 | 144.77 | 4.23 | 0.15 |
| 480 | 144.70 | 4.30 | 0.09 |
| 540 | 144.65 | 4.35 | 0.04 |
| 600 | 144.65 | 4.35 | 0.04 |

The results can be plotted on graphs:



Both graphs show the rate is fastest at the beginning of the reaction and decreases with time until the reaction stops. It is difficult to measure the rate at any one time as the rate is constantly changing. However we can work out the average rate over a period of time. This is done using the loss of mass or change in acid concentration over a certain time interval. We can calculate the average rate over the first 30 seconds of the reaction:

from mass of carbon dioxide produced:

$$\text{Average rate} = \frac{\text{loss of mass}}{\text{time interval}} = \frac{1.25\text{g}}{30\text{s}} = 0.042\text{gs}^{-1}$$

from the change in acid concentration:

$$\begin{aligned} \text{Average rate} &= \frac{\text{decrease in acid concentration}}{\text{time interval}} \\ &= \frac{(4.00 - 2.86)\text{mol l}^{-1}}{30\text{s}} = 0.038 \text{ mol l}^{-1} \text{ s}^{-1} \end{aligned}$$

Note that the two rates that we calculated refer to the same reaction but the units in which rate is measured vary. It is extremely important that the correct units are always used. We will now look in more detail at the factors that affect rates of reaction.

Effect of Concentration on Reaction Rate

Persulphate oxidation of iodide ions

This is a prescribed practical which means that you can be asked about it in the Higher exam.

The Formation of Colloidal Sulphur from Thiosulphate ions

This is not a prescribed practical.

For both of these reactions a graph of rate against concentration is a straight line showing that the rate is directly proportional to concentration.

Effect of Temperature on Reaction Rate

We studied the oxidation of oxalic acid by potassium permanganate at different temperatures. This is a prescribed practical.

The reaction between thiosulphate ions and dilute hydrochloric acid can also be used and gives the same shape of graph. These reactions show a marked increase in rate as the temperature is increased.

Very roughly the rate of a chemical reaction is doubled for every 10°C rise in temperature.

Collision Theory

The collision theory attempts to explain these experimental observations.

Before a reaction can occur the reactant molecules must collide. This is the basis of the Collision Theory. The collision provides the energy to break bonds in the reactant molecules and then new bonds can be formed to make the product molecules. All that we have discovered about the effect of concentration, particle size and temperature can be explained by the Collision Theory.

Concentration

The more concentrated the reactants the more collisions there are going to be between the reactant molecules and hence the faster the reaction.

Particle size

In a reaction involving solids the smaller the particle size the larger the surface area presented to the other reactant. This increases the chance of collision and so increases the reaction rate. Because it is so finely divided (very small particle size), dust in a flour mill can present a high explosion risk (an explosion is a very fast reaction). For this reason, extractors remove dust from the air.

Temperature

The temperature of a substance is simply a measure of the average kinetic energy of its molecules.

At a low temperature, molecules are moving slowly so have a low KE.

At a high temperature, molecules are moving quickly so have a high KE.

We discovered that increasing the temperature causes a very marked increase in the rate of a reaction. At first we might think this is because there is an increase in the number of collisions at the higher temperature. However it can be shown that a 10°C rise in temperature hardly increases the number of collisions yet we know that the rate roughly doubles.

It can also be shown that rates of reactions are very slow compared to the number of collisions actually happening. (This makes sense because if all collisions were successful and led to a reaction happening then there would be no slow reactions). So if 2 colliding molecules are moving slowly they will have a 'soft' collision. They will simply bounce off each other without reacting. If 2 colliding molecules are moving fast enough they will have a 'hard' collision in which bonds will break and allow the reaction to happen. Clearly there must be a minimum speed (or KE) of collision at which the reaction can just happen. This minimum necessary Kinetic Energy is called the Activation Energy.

If the temperature of a reaction is raised the molecules have a higher Kinetic Energy. This means that a higher proportion of collisions will have the Activation Energy needed to react. This is why the rate increases so markedly with temperature. There are many examples of the effect of temperature on rates, such as:

Cooking at higher temperatures reduces the time needed significantly because the rate of cooking increases.

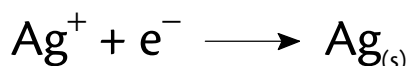
Freezers slow down the rate of decomposition of food so that it can be kept for months.

Light as a supplier of the Activation Energy

Heating the reaction is a common way of supplying the activation energy. However, with some chemical reactions, light can be used to increase the number of particles with energy greater than the activation energy. Such reactions are called photochemical reactions.

Photography

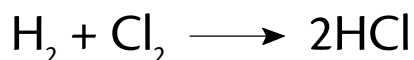
Light hitting a photograph film provides the activation energy for this reaction:



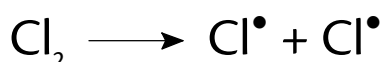
Hydrogen and chlorine

When hydrogen and chlorine are mixed together in the dark, nothing happens.

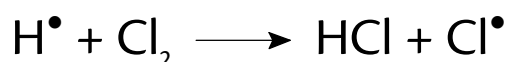
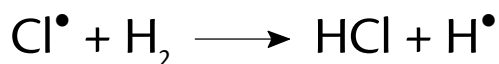
However, as soon as ultra violet light is shone on the mixture there is an explosive reaction forming hydrogen chloride:



The light provides the activation energy for the dissociation of some of the chlorine molecules (note • means an unpaired electron):



The chlorine atoms then attack a hydrogen molecule and a very fast chain reaction results:

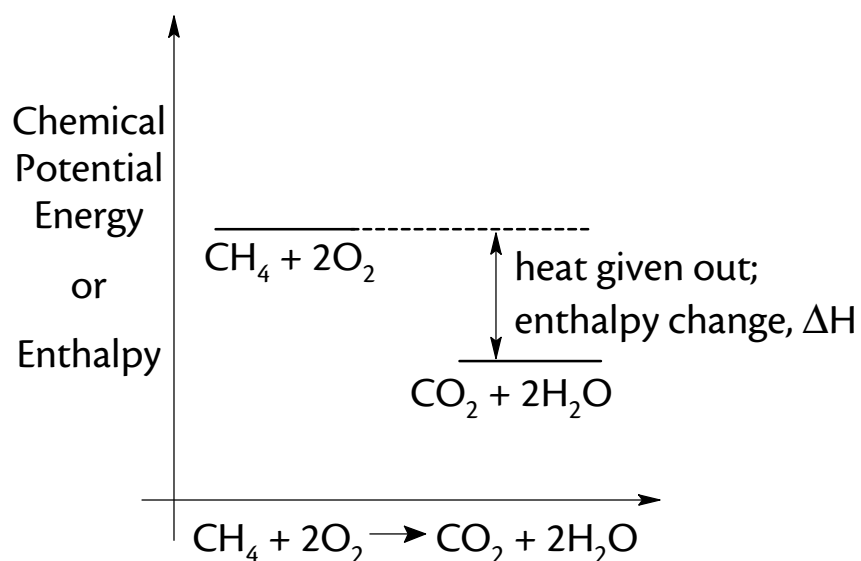


and so on...

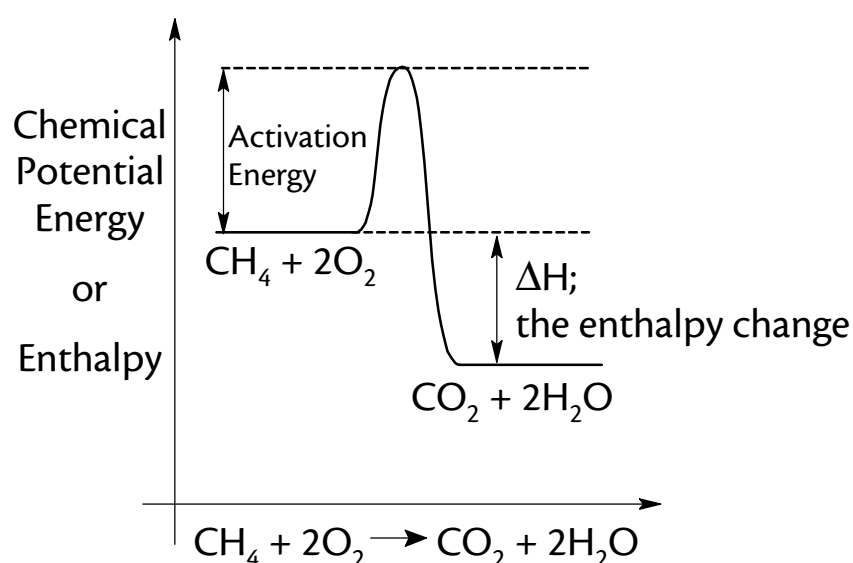
Potential Energy Diagrams

Before we go further with our work on Activation Energy we need to think about exothermic and endothermic reactions.

During an exothermic reaction (eg burning methane) some of the chemical potential energy in the reactant molecules is released as heat energy. This means that the product molecules contain less potential energy than the reactant molecules. During an endothermic reaction heat energy is absorbed from the surroundings and so the product molecules have more potential energy than the reactant molecules. We can illustrate these ideas on graphs, using an exothermic reaction as an example:



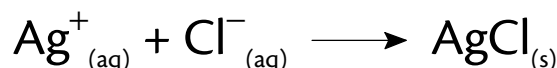
The difference in potential energy between the reactants is called the enthalpy change for the reaction and has the symbol, ΔH . We will meet this again later. We can now incorporate the idea of Activation Energy onto these Potential Energy diagrams.



The Activation Energy is an 'energy barrier' that must be overcome before reactant molecules can change into product molecules. It is the size of the Activation Energy that controls the rate of a reaction.

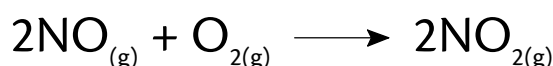
If the Activation Energy is low, many molecules will have enough energy to overcome the barrier and the reaction will be fast, for example:

- a. Precipitation reactions are very fast.



The attraction of the 2 oppositely charged ions to form solid silver chloride has a very low activation energy because no bonds need to be broken. The reaction is instantaneous.

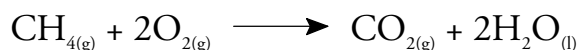
- b. The colourless gas nitrogen monoxide combines very quickly with oxygen to form brown nitrogen dioxide.



Even although in this case bonds need to be broken, the activation energy must be very low.

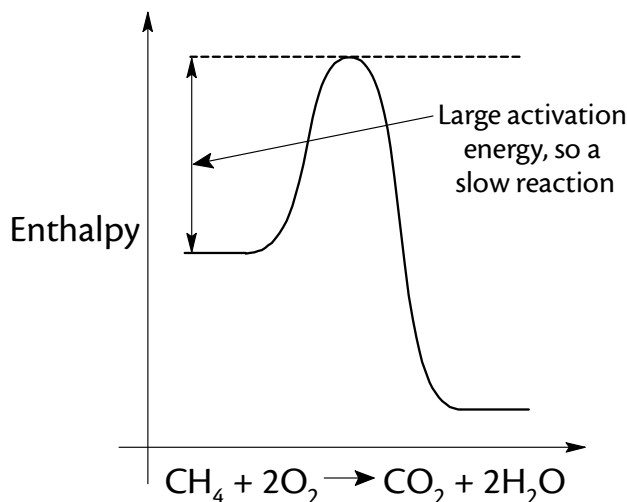
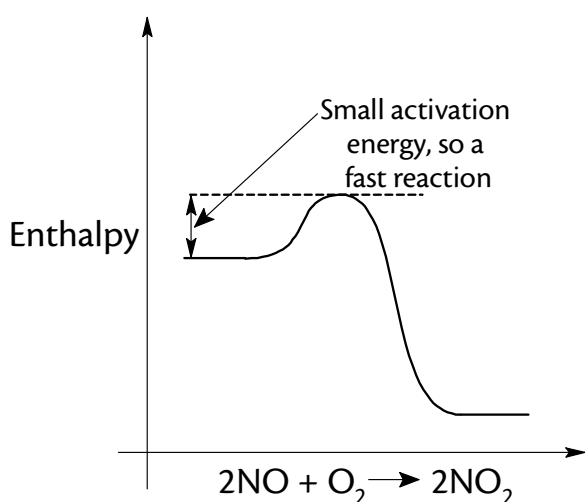
If the activation energy is high, few molecules will have sufficient energy to overcome the energy barrier and the reaction will be slow.

The reaction between methane and oxygen is an interesting example.



This is a very exothermic reaction. About 850kJ of energy are released for every mole of methane that is burned. Yet at room temperature, methane and oxygen can be mixed and the rate of reaction is so slow that we can effectively say that the rate is zero. The reason is that the activation energy is so high that no molecules possess enough energy to overcome the barrier. When we light a Bunsen with a match we are giving the molecules enough energy to overcome the barrier – we are supplying the activation energy. Once started, the energy given out in this exothermic reaction keeps it going.

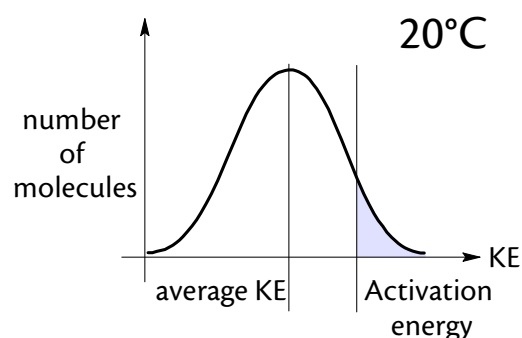
The Potential Energy diagrams below help illustrate this:



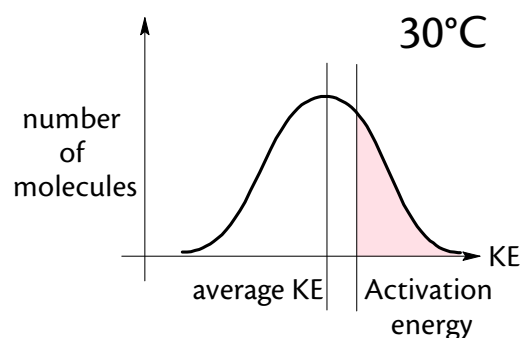
Energy Distribution and the Activated Complex

If all the molecules of a gas at 20°C were to have their KE measured at an instant, a spread of energies would be observed.

The overall pattern remains the same with time but, due to collisions, the energies of the individual molecules change constantly.



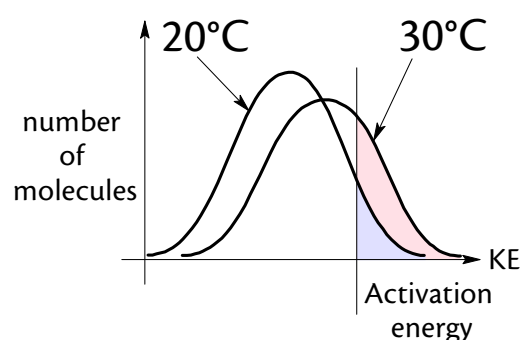
If the measuring process is repeated at a higher temperature (30°C) the graph is of a similar shape but is shifted to the right, i.e. a higher average kinetic energy.



Now superimpose the 2 graphs and label the minimum KE necessary for reaction as E_a , the activation energy.

This clearly shows that at 20°C only a few molecules have energy greater than E_a .

At 30°C many more molecules have energy greater than E_a .



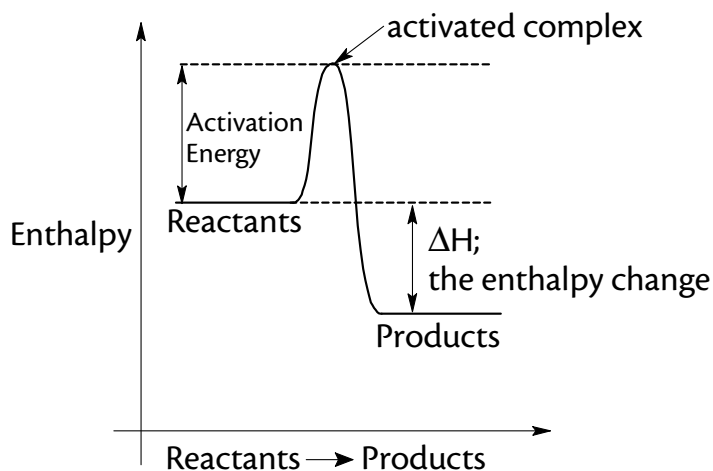
At the higher temperature the total number of collisions does not increase much. However a much higher proportion of the collisions produce the necessary activation energy and so reaction can happen.

Activation Energy and the Activated Complex

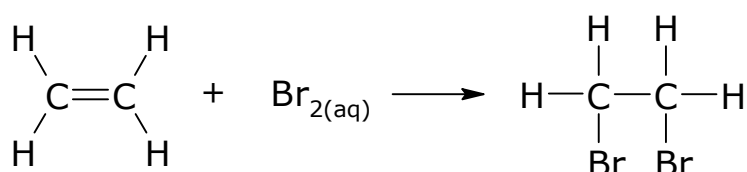
We now look at the case when a collision is hard enough to allow reaction to occur. When two molecules react the first thing that happens as a result of the collision is that they join to form a species called the activated complex. The activated complex is very unstable and exists for only a very short time. The activated complex requires energy for its formation because there may be bonds in the reactants to be weakened or broken (or charged particles to be brought together). This necessary energy comes from the Kinetic Energy of the colliding molecules and is stored as Potential Energy in the bonds of the activated complex. The energy needed to form the activated complex is the activation energy that we met earlier.

ie if the energy available from the collision is less than the activation energy, the activated complex cannot be formed and so no reaction can occur.

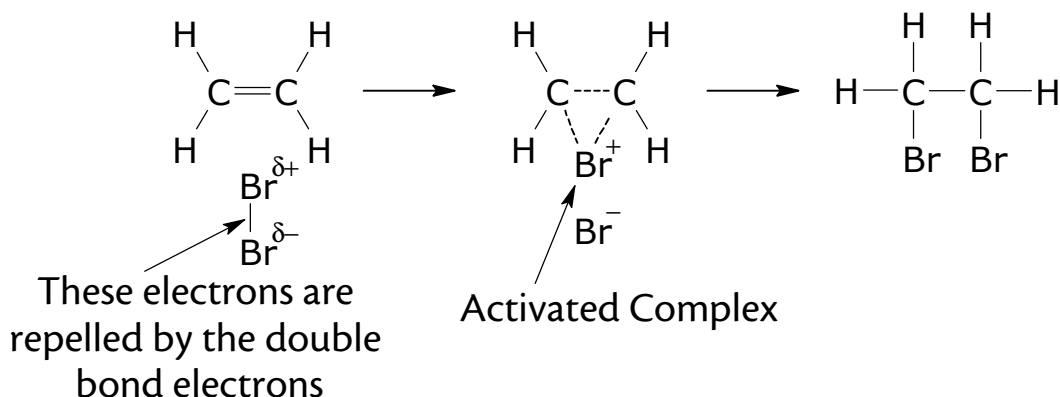
Once formed the activated complex breaks up either reforming the reactants or forming new products. If it breaks up into new products the energy given out can be greater or less than the activation energy. These correspond respectively to exothermic and endothermic reactions. This is shown for an exothermic reaction in the diagram.



The addition of bromine to ethene gives a good illustration of the idea of activated complex.



The reaction is believed to occur as follows:



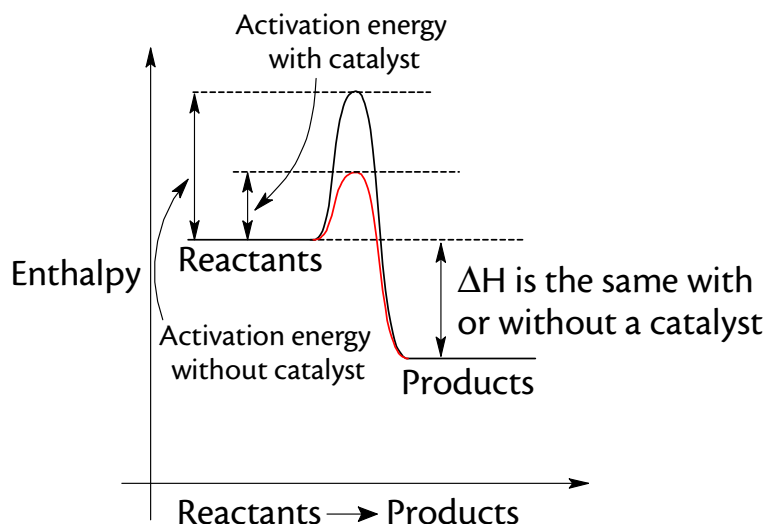
The Effect of Catalysts on Reaction Rate

A catalyst is a substance that alters the rate of a chemical reaction without itself undergoing any permanent chemical change.

Because it is not used up, the amount of catalyst is usually small compared to the other reactants. Catalysts are usually used to speed up reactions but can be used to slow down reactions. In these cases they are called inhibitors. Inhibitors are used:

- in rubber to increase its stability
- in antifreeze to slow down rusting
- to stabilise monomers for polymerisation (eg styrene)

A catalyst works by providing an alternative pathway between the reactants and products. This alternative route has a lower activation energy than the route without the catalyst and so the reaction is speeded up. This is shown for an exothermic reaction on the diagram:



Note that ΔH for the reaction is the same whether a catalyst is used or not.

Types of Catalyst

Homogeneous catalysts are in the same physical state as the reactants.

Heterogeneous catalysts are in a different physical state from the reactants.

The most common heterogeneous catalysts are solid catalysts used to catalyse reactions involving gases. Usually these catalysts are transition metals and many are important industrially. A common everyday example of a heterogeneous catalyst is the catalytic convertor fitted to car exhausts. They catalyse:

- the oxidation of CO to CO_2
- the oxidation of unburned hydrocarbons to CO_2 and H_2O
- the reduction of nitrogen oxides (NO_x) to N_2

(See Standard Grade notes, Topic 6, for more on this)

This table gives other examples of heterogeneous catalysts.

| Catalyst | Process | Reaction | Importance |
|--------------------|--------------------------------|--|--|
| Vandium (V) oxide | Contact | $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$ | Manufacture of sulphuric acid |
| Iron | Haber | $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ | Manufacture of ammonia |
| Platinum | Catalytic oxidation of ammonia | $4\text{NH}_3 + 5\text{O}_2 \rightleftharpoons 4\text{NO} + 6\text{H}_2\text{O}$ | Manufacture of nitric acid |
| Nickel | Hydrogenation | Unsaturated oils + $\text{H}_2 \longrightarrow$ saturated fats | Manufacture of margarine |
| Aluminium silicate | Catalytic cracking | Breaking down long-chain hydrocarbon molecules | Manufacture of fuels, and monomers for the plastics industry |

We carried out 2 experiments on catalysts.

- Homogeneous Catalysis:** In this experiment the aqueous Co^{2+} ion is in the same physical state as the reactants (ie in solution) and acts as a catalyst. Hydrogen peroxide was added to a solution of potassium sodium tartrate (Rochelles Salt). When the mixture was heated to boiling only a very little oxygen was given off. The hydrogen peroxide and Rochelles Salt solution were again made up, but this time sufficient cobalt (II) chloride was added to give a distinct pink colour due to

Co^{2+} ions. This mixture was heated gently – after a short time the pink colour was replaced by an intense green. This shows that the Co^{2+} ions are becoming involved in the reaction. At this stage a vigorous evolution of oxygen occurred. As the evolution stopped the green faded and was replaced by the original pink. This shows clearly the regeneration of the Co^{2+} catalyst.

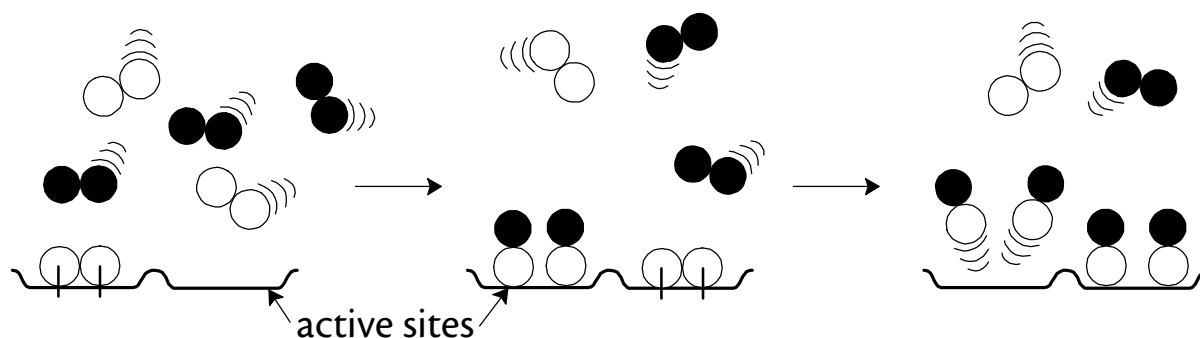
2. **Heterogeneous Catalysis:** The solid manganese dioxide catalyst is in a different physical state from the liquid H_2O_2 .

A solid lump of manganese dioxide was added to hydrogen peroxide – oxygen was given off. However when powdered manganese dioxide was used the evolution of oxygen was much faster. This experiment shows:

- only a trace of catalyst is needed
- finely divided (powdered) catalyst is more effective because it provides a larger surface area on which the reaction can occur.

How do heterogeneous catalysts work?

In the decomposition of hydrogen peroxide using solid manganese dioxide as catalyst we saw that the reaction is fastest when the catalyst has a large surface area. This is because the reaction happens at active sites on the surface of the catalyst. Molecules of reactant are adsorbed at these active sites. The working of a heterogeneous catalyst is shown below:



Adsorption

Molecules of one or both reactants form bonds with the catalyst. This weakens the bonds within the molecules.

Reaction

The molecules react on the catalyst surface. The angle of collision is more likely to be favourable since one of the molecules is fixed.

Desorption

The product molecules leave the catalyst and the vacant site can be occupied by another reactant molecule.

Catalyst poisons

Some substances react with catalysts and prevent them doing their job. Such substances are called catalyst poisons. They are preferentially adsorbed at the active sites. This prevents the reactant molecules being adsorbed and makes the catalyst ineffective.

An example is carbon monoxide, which poisons the iron catalyst in the Haber Process. Also, hydrogen sulphide poisons the vanadium catalyst in the Contact Process for the manufacture of sulphuric acid. These poisoning gases must be removed before they react with the catalyst (eg Cars with catalytic converters must use unleaded petrol because lead would poison the platinum/rhodium/palladium catalyst and stop it working).

Even with these precautions, impurities remaining in the reactants mean that industrial catalysts must be regenerated or renewed from time to time.

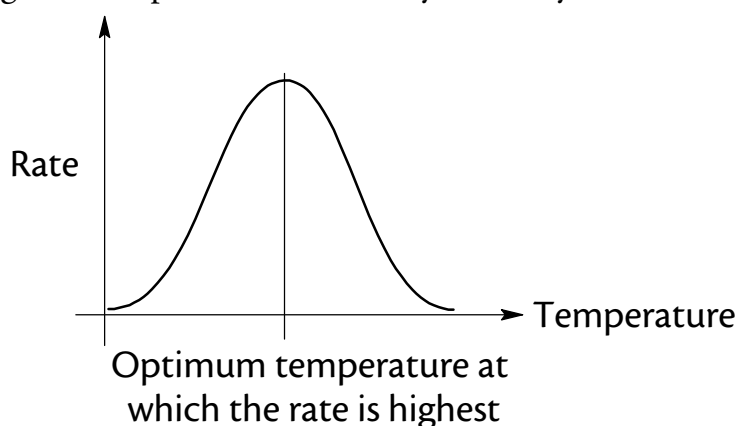
Enzymes

Catalysts that work in biological systems are called enzymes. They catalyse the reactions that happen in the cells of plants and animals.

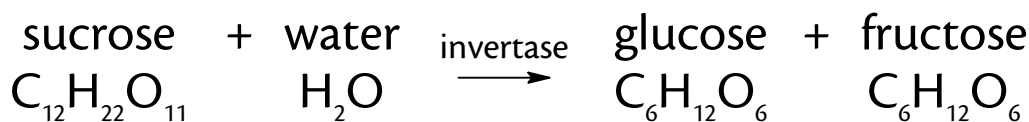
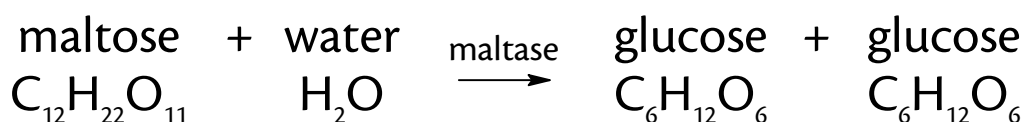
- yeast contains enzymes that convert carbohydrates into alcohol
- amylase is an enzyme that hydrolyses starch
- catalase is an enzyme that helps decompose hydrogen peroxide

Enzymes are proteins, which are very complicated large molecules. The 3 dimensional shape of the molecule is very important to its function as an enzyme. The shape can be destroyed (the protein is said to be denatured) by changes in temperature and pH so enzymes work most effectively at certain optimum temperatures and pH.

The graph of rate against temperature for an enzyme catalysed reaction would be:



Enzymes are very specific; this means that one enzyme catalyses only one reaction. For example, maltose and sucrose are both disaccharides but they are hydrolysed to monosaccharides by different enzymes. Maltose is hydrolysed to glucose by maltase. Sucrose is hydrolysed to glucose and fructose by invertase. This reaction is important in the sweet industry.



Enzymes in our bodies can be poisoned by arsenic, cyanide and carbon monoxide. This prevents the enzyme doing its job and you know the result of that!

Topic 2 – Enthalpy Changes/The Mole

Enthalpy Changes

This part of the unit studies the energy changes which happen in chemical reactions. We have seen that energy changes are nearly always evident when a reaction happens we will only study the heat energy changes in chemical reactions. All substances contain energy which in previous years we have called 'chemical energy'. This energy can be equated to a 'heat content' or enthalpy (symbol H). During all chemical reactions the enthalpy of the substances changes from that of the reactants to that of the products. ie H_r becomes H_p .

It is agreed by convention that the Enthalpy Change ΔH must be equal to the enthalpy of the reactants subtracted from that of the products.

ie
$$\Delta H = H_p - H_r$$

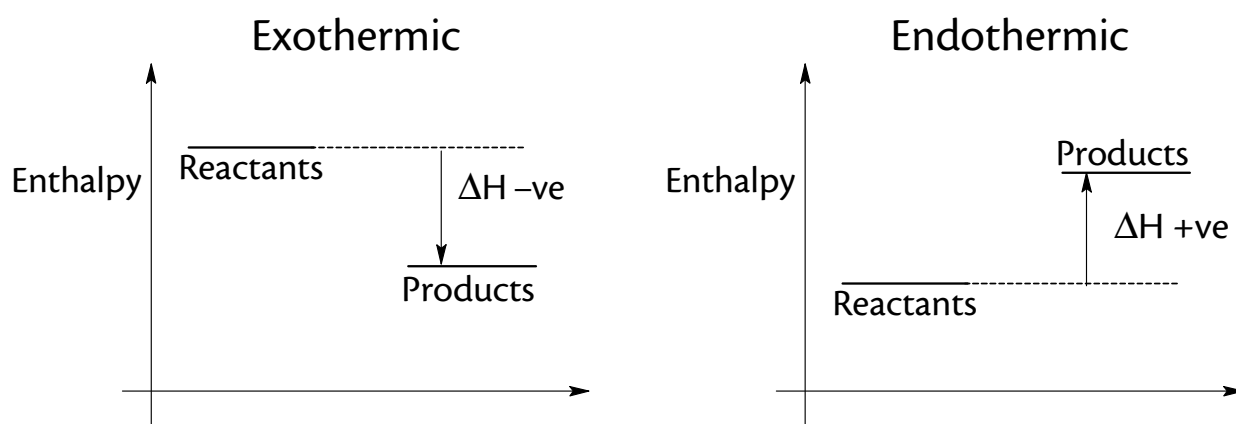
There is no way of measuring the enthalpy of any single substance directly. For this reason we can only discuss enthalpy changes in reaction and this can be measured as an amount of heat given out (exothermic reaction) or taken in (endothermic reaction). Obviously, these amounts of heat energy released or absorbed must be dependent on the quantity of substances reacting so we must define the enthalpy changes in terms of energy changes (kilojoules give convenient numbers) per amount of substance (ie the mole).

Units of enthalpy and enthalpy change are kJ mol^{-1} .

Potential Energy Diagrams

We can represent the level of enthalpy held by reactants and products on a 'Potential Energy Diagram'. We have seen these earlier.

Using these it is easier to help define the direction (sign) of ΔH



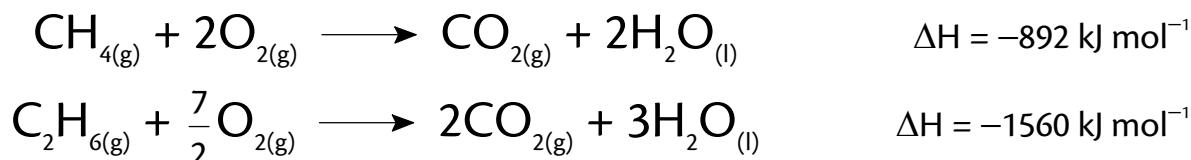
Exothermic Reactions: If, in the process reactants to products, the chemicals release some of their enthalpy in the form of heat then the products must have lower enthalpy. It stands to reason that $H_p - H_r$ must be negative, (ie ΔH is $-ve$).

Endothermic reactions: The converse is true and ΔH must be $+ve$. Endothermic reactions must proceed with an absorption of heat energy from the surroundings, which must therefore cool down.

Some ΔH Definitions

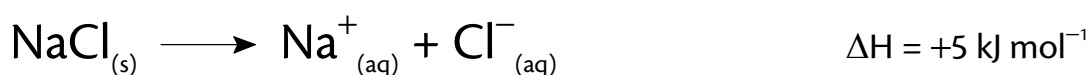
These are very important and must be learned and understood. Note that ΔH values are quoted as energy changes per mole of substance and it must be understood in each individual case what substance is involved (it is not always a reactant, or a product – it can be either!)

Heat of Combustion (Enthalpy of combustion) is the heat energy given out when one mole of a substance burns completely in oxygen. Here, all equations must be written and balanced with the balancing number of the substance burned being 1.



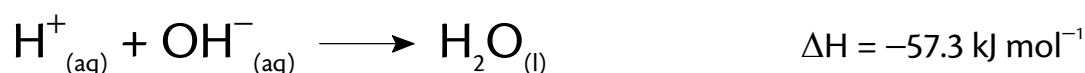
N.B. In tables of values of heats of combustion the negative sign is often missed out. They are always exothermic!

Enthalpy of solution is the enthalpy change when 1 mole of solute is completely dissolved.



Enthalpy of neutralisation is the heat energy released when 1 mole of water is formed by neutralisation of an acid with a base.

This always involves the reaction of a mole of $\text{H}^+_{(aq)}$ with one mole of $\text{OH}^-_{(aq)}$.



Ionisation Energy

We will be referring to this later in the unit so it is defined here. It is the energy required to remove one mole of electrons from one mole of particles (atoms or ions) in the gas state.



It is very important that all of these definitions be learned and fully understood! Note that the state of the particles involved is very important – the ionisation energy is the energy involved in removing the electrons from the atoms only in the gas state and the equation must show this!

Experimental Determination of Enthalpy Changes

Many chemical reactions require complicated methods for calculating the enthalpy changes but a simple determination can be done in the laboratory – the enthalpy of combustion of alkanols can be determined by heating water with burning alcohol and measuring the temperature rise. The energy from the flame is that which is absorbed (ignoring heat losses for the purpose of simplifying the calculations!) and this can be calculated from a formula:

$$\text{Energy absorbed (kJ)} = C \times m \times \Delta T$$

where: C = Specific heat of water, $4.18 \text{ kJ kg}^{-1} \text{ }^\circ\text{C}^{-1}$

m = Mass of water in kg

ΔT = Temperature rise of water in $^\circ\text{C}$

If this is the heat energy absorbed by the water from a known mass of alcohol we can work out the heat energy from 1 mole.

The Mole – The Avogadro Constant

We are used to thinking of the mole as the relative atomic mass of an element or the formula mass of a compound in grams, for example:

| 1 mole of | Weights |
|--|---------|
| aluminium (Al) | 27g |
| sulphur (S) | 32g |
| oxygen atoms (O) | 16g* |
| oxygen molecules (O ₂) | 32g* |
| water (H ₂ O) | 18g |
| sodium chloride (NaCl) | 58.5g |
| sodium sulphate (Na ₂ SO ₄) | 142g |

*Note: It is important to know precisely what type of particle is being considered.

The definition of a mole is that amount of substance that contains the same number of elementary particles as 12g of carbon-12.

The usefulness of the mole in chemistry is that all the above contain the same number of elementary particles (atoms, molecules or 'ionic units' depending on the substance being considered). This number has been calculated from the results of many different experiments and has been shown to be 6.02×10^{23} . It is known as the Avogadro constant, L. You should be able to do the following types of question based on this.

Example 1

What is the mass of 0.25 moles of nitrogen gas?

The formula of nitrogen gas is N₂ so the formula mass is 28 amu.

1 mole of nitrogen weighs 28g

so 0.25 moles of nitrogen weighs $28 \times \frac{0.25}{1} = 7\text{g}$

Example 2

How many moles of carbon dioxide are in 4.4g of the gas?

The formula of carbon dioxide is CO_2 so the formula mass is 44 amu.

44g is the mass of 1 mole of CO_2
 so 4.4g is the mass of $1 \times \frac{4.4}{44} = 0.1$ moles of CO_2

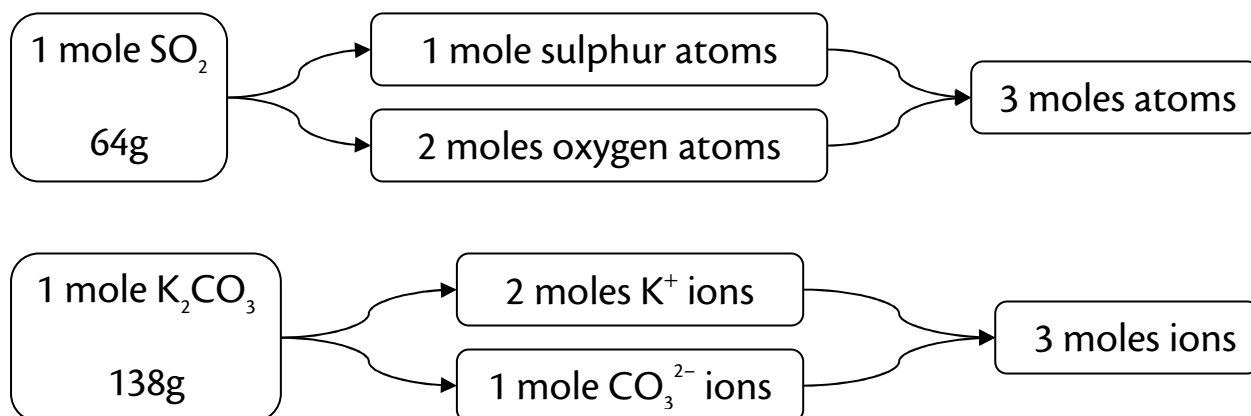
We must always be very careful about the particles we are dealing with.

Consider:

1 SO_2 molecule contains 3 atoms
 so 1 mole of SO_2 molecules contains 3 moles of atoms

1 $(\text{K}^+)_2\text{CO}_3^{2-}$ 'formula unit' contains 3 ions
 so 1 mole of $(\text{K}^+)_2\text{CO}_3^{2-}$ 'formula units' contains 3 moles of ions

This is illustrated below:

**Using the Avogadro's Constant**

We now know that a mole contains 6.02×10^{23} elementary particles. This figure is called the Avogadro Constant. We must be able to do problems involving this number and some examples are given:

Example 3

How many atoms are in 0.69 g of lithium?

The relative atomic mass of Li is 6.9 amu so 1 mole of Li has mass 6.9g.

6.9g (1 mole) of lithium contains 6.02×10^{23} atoms
 So 0.69g of lithium contains 6.02×10^{22} atoms

Example 4

How many molecules are in 3g of water?

Water, H₂O, has formula mass 18 amu, so 1 mole of water weighs 18g.

18g of water (1 mole) contains 6.02×10^{23} molecules

So 3g water contains $6.02 \times 10^{23} \times \frac{3}{18}$ molecules
 $= 1.003 \times 10^{23}$ molecules

Example 5

How many atoms are in 2.2g of carbon dioxide gas?

Carbon dioxide (CO₂) has formula mass 44 amu, so 1 mole has mass 44g.

Now 1 CO₂ molecule contains 3 atoms

So 1 mole of CO₂ molecules contains 3 moles of atoms

ie. 44g of CO₂ molecules contains $3 \times 6.02 \times 10^{23}$ atoms

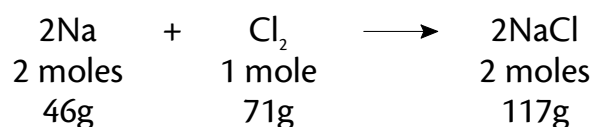
So 2.2g of CO₂ molecules contains $3 \times 6.02 \times 10^{23} \times \frac{2.2}{44}$ atoms
 $= 9.03 \times 10^{22}$ atoms

We now revise calculations from equations that we did in Standard Grade.

As well as problems of the sort just done, you need to be able to tackle questions in which one of the reactants is in excess.

Example 6

What mass of sodium chloride is formed when 4.6g of sodium burns in 5g of chlorine?

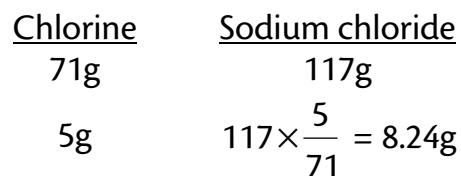


From the equation:

46g of sodium reacts with 71 g of chlorine

So 4.6g reacts with 7.1 g of chlorine

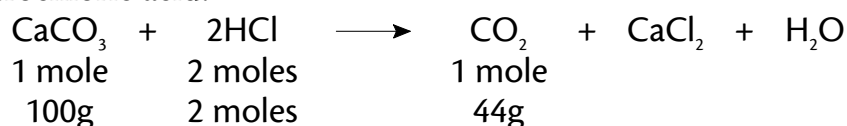
So, if all the 4.6g of sodium were to react we would need 7.1 g of chlorine. However we have only 5g of chlorine, so all the sodium cannot react. The sodium is in excess. The mass of sodium chloride formed is calculated using the chlorine, the reactant not in excess.



So 8.24g of sodium chloride are formed

Example 7

What mass of carbon dioxide is formed when 20g of calcium carbonate reacts with 500ml of 1 mol l⁻¹ hydrochloric acid?



Moles of HCl:

1 mol l⁻¹ means: 1000ml contains 1 mole of HCl
 so 500ml contains 0.5 moles of HCl

From the equation:

100g of calcium carbonate reacts with 2 moles of HCl so

$$\begin{array}{l}
 20\text{g of calcium carbonate reacts with } 2 \times \frac{20}{100} \\
 = 0.4 \text{ moles HCl}
 \end{array}$$

So we have worked out that 20g calcium carbonate reacts with 0.4 moles HCl, but we have been given 0.5 moles of HCl, so the acid is in excess. This means we must calculate the mass of carbon dioxide from the reactant not in excess, ie the calcium carbonate.

| Calcium Carbonate | Carbon Dioxide |
|-------------------|--|
| 100g | 44g |
| 20g | $44 \times \frac{20}{100} = 8.8\text{g}$ |

So the mass of carbon dioxide formed is 8.8g

Gas Molar Volume

This simply means the volume of a mole of a gas. The volume of a gas is very dependent on temperature and pressure. So when gas molar volumes are stated, the conditions of temperature and pressure are often quoted. However, we will ignore these at this level. Molar volumes can be calculated from density measurements (See 'New Higher Chemistry', page 50). We found, by experiment, the volume of 1 mole carbon dioxide gas. A flask was weighed empty (ie. with the air evacuated) and weighed again when filled with carbon dioxide gas. The exact volume of the flask was found by measuring how much water it could hold.

Results

| | | | |
|------------------------------------|---|--------|----|
| Mass of empty flask | = | 107.38 | g |
| Mass of flask + carbon dioxide | = | 108.37 | g |
| So mass of carbon dioxide | = | 0.99 | g |
| Volume of flask (ie volume of gas) | = | 570 | ml |

Calculation of Molar Volume

0.99g of carbon dioxide occupy 570 ml

So 44g (1 mole) of carbon dioxide occupy 25333 ml

So we have found that the molar volume of carbon dioxide is 25.3 litres per mole (1 mol^{-1})

The experiment was repeated with other gases and their molar volumes were:

Nitrogen = $25333 \text{ ml mol}^{-1}$

Oxygen = $25333 \text{ ml mol}^{-1}$

Experiments of this sort with other gases have shown that the molar volume of all gases is the same as long as the temperature and pressure are the same for each. At 20°C and 1 atmosphere pressure the molar volume of any gas is just over 24 litres per mole (1 mol^{-1}). It seems surprising that 1 mole of any gas occupies the same volume – it certainly is not true for liquids and solids. In a gas, however, the molecules are far apart so the volume of the gas is not dependent on the size of the molecules. In a gas the molecules occupy only about 0.1 % of the total volume – the rest is empty space!

So the molar volume of all gases is the same and it contains 6.02×10^{23} molecules

Avogadro deduced from this that:

“Equal volumes of all gases, under the same conditions of temperature and pressure, will contain the same number of molecules.”

This is known as Avogadro’s Hypothesis. The following examples illustrate the use of Molar Volume and Avogadro’s Hypothesis.

Volumes of Gases in Reactions

Example 8

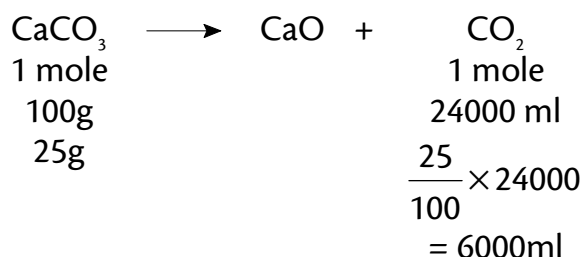
What volume of oxygen is required for the complete combustion of 4 litres of methane?



8 litres of oxygen are required

Example 9

What volume of carbon dioxide is produced by roasting 25g of chalk (calcium carbonate)? The molar volume is 24 l mol^{-1}



Example 10

- a. How many moles of copper (II) chloride are present in a solution that contains 13.45g of the salt?
- b. What is the maximum volume of chlorine which could be obtained by electrolysis of this solution? Take the molar volume as 24 l mol^{-1} .

(a) Formula mass of CuCl_2 :

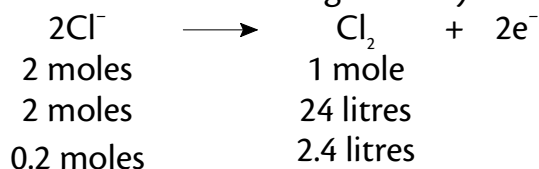
$$\begin{aligned} 1 \times \text{Cu} &= 63.5 \\ 2 \times \text{Cl} &= 71 \\ \text{total} &= 134.5 \text{ amu} \end{aligned}$$

134.5g of CuCl_2 is 1 mole so 13.45g of CuCl_2 is 0.1 mole

(b) Although we have just calculated that we have 0.1 moles of CuCl_2 we have 0.2 moles of chloride ions. This is because each 'formula unit' of CuCl_2 contains 2 chloride ions.

| | |
|---|-----------------------------|
| 1 mole of CuCl_2 contains | 2 moles of chloride ions |
| So 0.1 mole of CuCl_2 contains | 0.2 moles of chloride ions. |

The equation for the formation of chlorine during electrolysis is:



So the maximum volume of chlorine is 2.4 litres

Example 11

If 300 cm^3 of a gas weigh 0.55g, what is the formula mass of the gas? The molar volume is 24 l mol^{-1} .

| | |
|--|---------------------------------|
| 300 cm^3 of the gas weighs | 0.55g |
| So 24000 cm^3 (1 mole) of the gas weighs | $0.55 \times \frac{24000}{300}$ |
| | = 44g |

1 mole of the gas weighs 44g so the formula mass is 44 amu.

Example 12

What is the density of butane in g l^{-1} if its molar volume is 22 l mol^{-1} ?

Butane has formula mass 58 amu, so 58g butane occupies 22 litres.

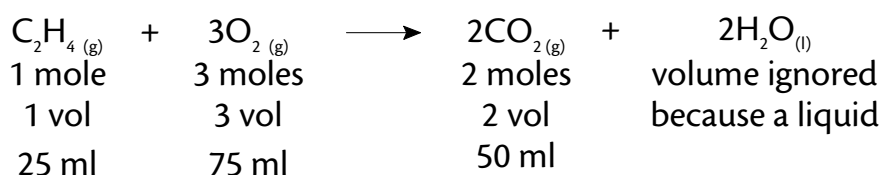
| | |
|-----------------------|---|
| 22 litres weighs | 58g |
| So 1 litre will weigh | $58 \times \frac{1}{22} = 2.64\text{g}$ |

The density of butane is 2.64 g l^{-1} .

Composition of Gas Mixtures

Example 13

If 25ml of ethene are burned in 100ml of oxygen, what would be the composition of the resulting gas mixture?



Volume of CO₂ produced = 50ml

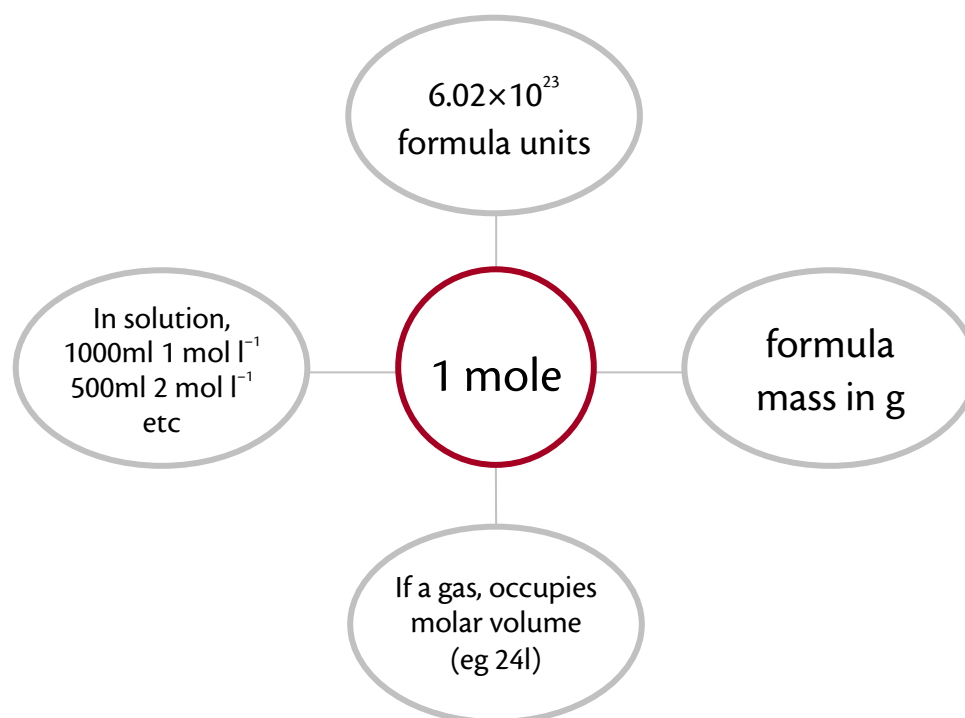
Volume of oxygen used = 75ml

Volume of oxygen left = 100 – 75 = 25ml

The composition of the final gas mixture is 50ml carbon dioxide and 25ml of oxygen.

Summary of Mole Relationships

The following diagram summarises the relationships any question about moles will rely on. Note that this diagram is not yet complete, since there are new facts about the mole to be covered further on.



Topic 3 – Patterns in the Periodic Table

The Periodic Table

The modern periodic table is based on that first drawn up by the Russian chemist, Mendeleev, in about 1870. He listed the known elements in order of increasing atomic mass and then arranged them so that those with similar chemical properties fell into the same vertical column. He left gaps for elements not yet discovered, like germanium, and predicted their properties with accuracy. The periodic table that we use is very similar to Mendeleev's but has all the elements arranged in order of their Atomic Number. The vertical columns are called groups and the horizontal rows are called periods. Make sure you know the work on the periodic table covered at Standard Grade.

We are now going to see how the structures of the elements affect physical properties.

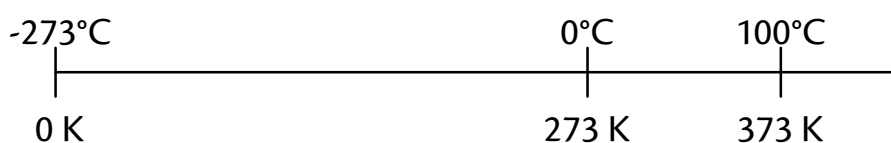
Melting Points and Boiling Points of the Elements

Look at the melting and boiling points (in °C) of the elements in the table below. There is a very large range of values but they can quite easily be put into 5 groups. The state in which the element exists at room temperature is also given.

| | | | | | | | | |
|----------------------------|----------------------------|-----------------------------|-----------------------------|----------------------------|--------------------------|--------------------------|---------------------------|--------------------------------|
| H -259 -253 gas | | | | | | | | 1 He -270 -269 gas |
| Li 180 1340 solid | | Be 1280 2500 solid | B 2030 3700 solid | C 3500 3900 solid | N -210 -196 gas | O -219 -183 gas | F -220 -188 gas | Ne -249 -246 gas |
| Na 98 883 solid | Mg 650 1110 solid | Al 660 2400 solid | Si 1410 2500 solid | P 44 280 solid | S 119 445 solid | Cl -101 -34 gas | Ar -189 -186 gas | |
| K 63 760 solid | Ca 850 1440 solid | | | | | | | |

Key: symbol, m.pt. (°C), b.pt. (°C), state

A very similar table is on page 4 of your Data Book but note that the temperatures are given on the Kelvin scale. The relationship between degrees Celsius and Kelvin is shown below.



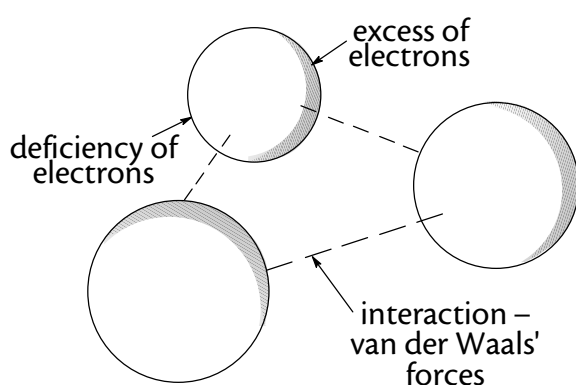
By studying the bonding in each group of elements we can explain the range of melting points. The melting point temperature of a solid is a measure of the amount of energy needed to break the bonds which hold the basic particles (atoms or molecules) together. So high melting points indicate strong bonds are being broken.

1. Noble Gases

Helium atoms have only 2 electrons. They fill the 1st shell and this is a stable arrangement. All the other noble gases have 8 electrons in their outer shells. We know that this is a stable arrangement. Because the atoms are already stable, they don't join with each other. They exist as separate single discrete atoms – they are monatomic.

Although they have very low melting points, the Noble gases can be obtained in the solid state. This means that there must be some force holding the atoms together. The force is called van der Waals force and it arises as follows:

The electrons in an atom are constantly in motion resulting in uneven distribution of the electrons round the atom. This causes temporary dipoles in which one side of the atom is slightly negative and so the other side becomes slightly positive. These temporary dipoles attract each other (see diagram).

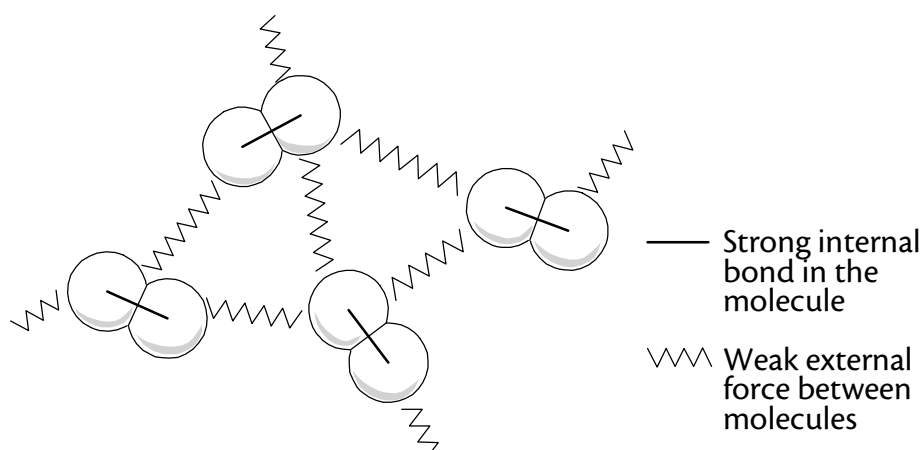


This attraction is called van der Waals force. The electrons are always in motion so the dipoles are constantly changing but they are always present. The more electrons in an atom, the larger the resulting dipole, so the larger the van der Waals force. This means more energy will be needed to overcome the force so the higher the melting point. We can see this effect if we look down the noble gas group – the increasing number of electrons in the atoms causes melting points to increase.

Note: Van der Waals forces are weaker than all other forms of bonding.

2. The Diatomic Gases (2 atoms to a molecule)

They exist as discrete diatomic molecules. Each molecule contains two atoms held together by a covalent bond, hence N_2 , O_2 etc. In the solid state the molecules are held together by van der Waals forces.



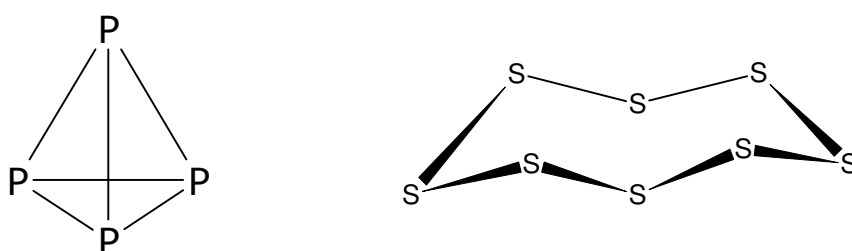
The size of the van der Waals force and hence the melting point depends on the number of electrons in the molecule, so the bigger the molecule, the bigger the Van der Waals force. Check this trend in the diatomic gases.

Note: Van der Waals forces are important only in the solid and liquid states. In the gas state the molecules are too far apart to experience any attraction.

3. Phosphorus and Sulphur

Nitrogen and phosphorus are in the same group, but they have very different melting points. This would suggest different structures. Similarly we would expect oxygen and sulphur to have differences in their bonding because they have very different melting points.

Both phosphorus and sulphur do exist as discrete (separate) molecules but they are not diatomic like N_2 and O_2 . Phosphorus has P_4 molecules and Sulphur S_8 molecules as shown.

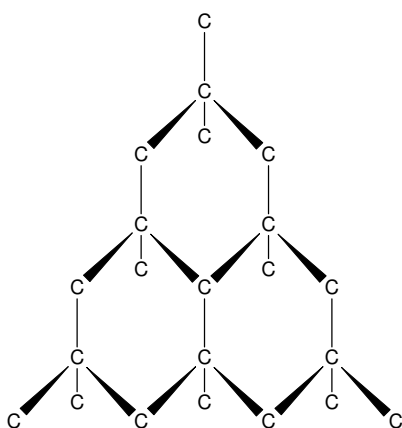


In the solid these molecules pack in layers held together by van der Waals forces. Because the molecules are bigger, with more electrons, the van der Waals forces are strong enough to hold the molecules together as a solid at room temperature.

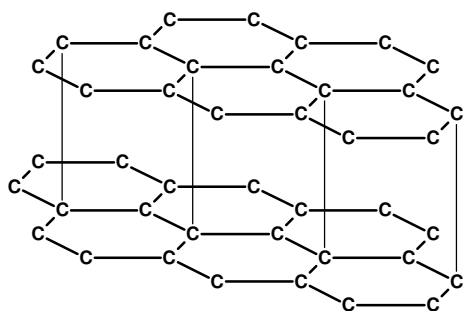
4. Carbon, Silicon and Boron

The element carbon exists in three forms – diamond, graphite and the recently discovered fullerenes. When an element can exist in more than one form it is called polymorphism.

The forms, diamond, graphite and fullerenes are called polymorphs.

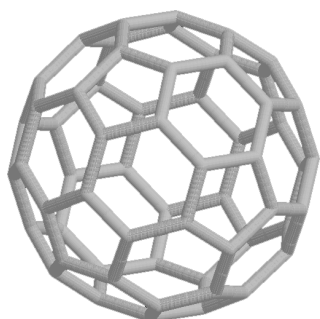


Diamond is a 3-dimensional network of carbon atoms. Each carbon atom is covalently bonded to 4 other carbon atoms that are arranged tetrahedrally round it. This gives a very rigid structure making diamond one of the hardest substances known. There are no discrete molecules in diamond so there are no weak forces. The structure is a covalent network lattice held together by strong covalent bonds. To melt diamond involves breaking these covalent bonds. This requires a lot of energy so the melting point is very high. Note also that all 4 outer shell electrons on each carbon are used in bonding so none is available to let diamond conduct electricity – diamond is a non-conductor.



Graphite is a layered structure. Each carbon is covalently bonded to only 3 other carbon atoms. The result is a hexagonal flat layer held together by strong covalent bonds. As you can see the layers are relatively far apart – too far to be covalently bonded to each other. The layers are held together by relatively weak van der Waals forces. These weak forces allow the layers to slide over each other fairly easily giving graphite a greasy feel. For this reason graphite is used as a lubricant between moving metal parts. More commonly, writing with a pencil involves sliding the graphite layers onto the paper.

As we saw above in graphite, only 3 of carbon's 4 outer shell electrons are used in bonding. These spare electrons are free to move so graphite, unlike diamond, is a conductor of electricity. It finds use as electrodes in dry cells and in industrial electrolyses.



a C_{60} molecule

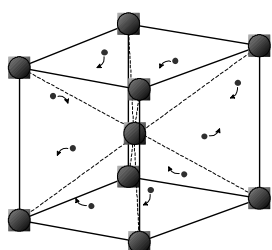
Fullerenes were discovered in the late 1980s. They are a form of carbon in which the atoms join to form large discrete molecules, eg C_{60} and C_{70} . These molecules are spherical in shape and are named after the American, Richard Buckminster Fuller, who developed the geodesic dome. They are at present the subject of a lot of research.

Silicon has a 3-dimensional covalent network lattice similar to diamond so it too has a very high melting point.

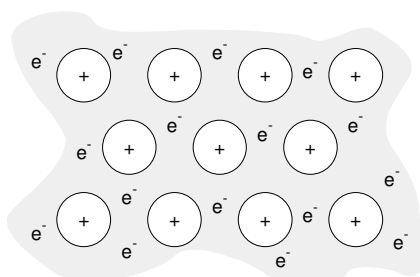
Boron The bonding in boron is complicated but it has a covalent network structure so again a high melting point.

5. The Metals

Metal elements have 1, 2 or 3 electrons in their outer shell and they all have the same basic structure. The outer shell electrons do not remain with the atom but are free to move throughout the whole structure – they are said to be delocalised. The atoms which have lost their electrons effectively become positive ions.



We can think of the metallic structure as being positive ions fixed in place in a lattice with a 'sea' of electrons moving through them. Metallic bonding is the attraction between the positive ions and the sea of electrons.



This attraction is not destroyed by altering the metal structure, so metals are malleable (can be hammered into shape) and are ductile (can be drawn out to form wires).

When a metal is molten these attractions between electrons and positive ions are still present so the process of melting does not break these attractions, so melting points are relatively low. Boiling a metal would separate the ions from the electrons so the attraction

would need to be overcome, so boiling points are very high. As we go down a Group the melting points of the metals decrease. This is because the attraction between the sea of electrons and the positive ions decreases as the size of the ion increases. This decrease in attraction means that the strength of metallic bonding decreases down a group.

In general melting points for Group 2 metals are higher than those of group 1 because group 2 atoms have 2 electrons to contribute to the 'sea' and the positive ions have a 2+ charge. The result is a greater attraction and so stronger metallic bonding in Group 2 than in Group 1.

As we have seen, the 'sea' of electrons is free to move so metals conduct electricity.

Metallic Character of the Elements

By metallic character we mean being shiny, conductors of heat and electricity, malleable and ductile. The free moving 'sea' of electrons is responsible for these metallic properties.

Trends in metallic character

(a) across a period – metallic character decreases.

This is because ionisation enthalpies (see page 10) increase across a period and it therefore becomes more difficult for atoms to release the electrons needed to give the delocalised 'sea'.

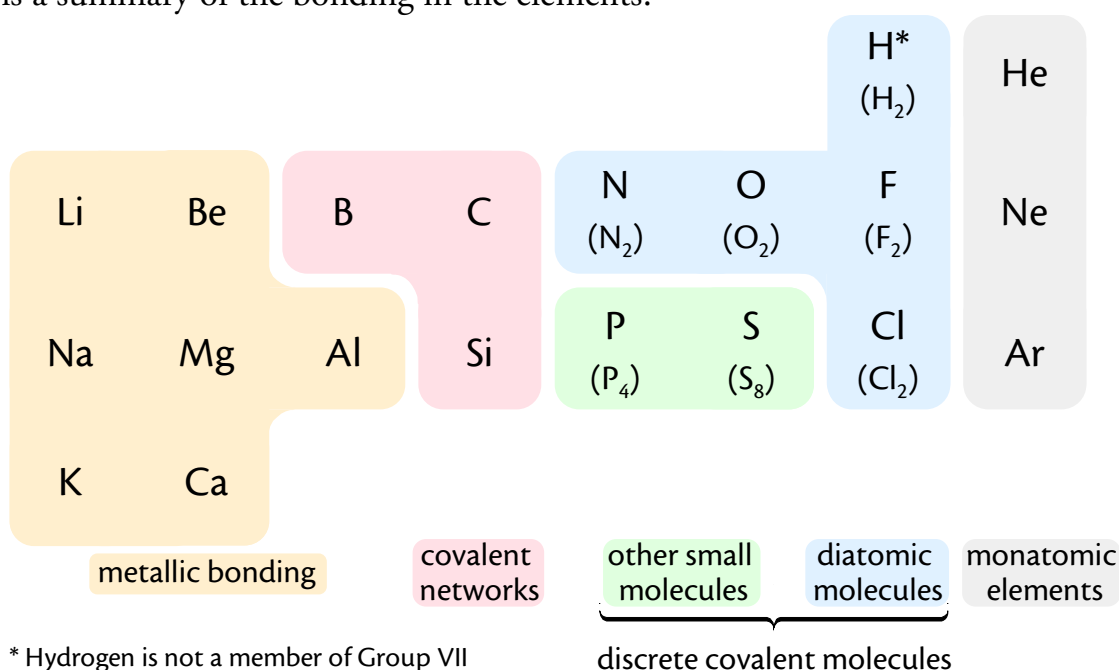
(b) down a group – metallic character increases.

Ionisation enthalpy decreases down a group so increasing the delocalisation of electrons giving increased metallic character.

Note: the stronger the metallic bond the less the metallic character and vice versa.

Taking the two trends together the most metallic elements are found in the bottom left of the periodic table and the least metallic elements at the top right.

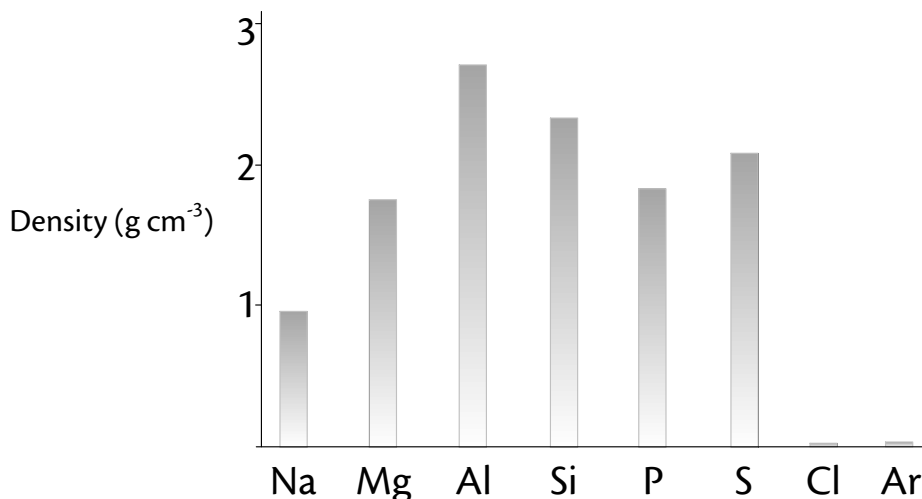
Here is a summary of the bonding in the elements:



We will now try to explain other physical properties of the elements in terms of bonding.

Density

The density of a substance is its mass per unit volume, usually measured in g cm^{-3} . The graph shows the variation in density across a period.



Na, Mg and Al have metallic bonding which is the attraction between the delocalised outer shell electrons and the fixed positive ions. The greater the number of outer shell electrons the greater the charge on the positive ion and so the greater the attraction. This means as we go from Na to Mg to Al the metallic bonding becomes stronger and the ions are pulled more closely together, leading to an increase in density.

Phosphorus and sulphur atoms are heavier than silicon atoms so we might expect their densities to be higher. However silicon is a covalent network of tightly packed atoms whereas the P_4 and S_8 molecules are only loosely held by van der Waals forces. Chlorine and argon are gases at room temperature. The chlorine molecules and argon atoms are well spread out so their densities are very low.

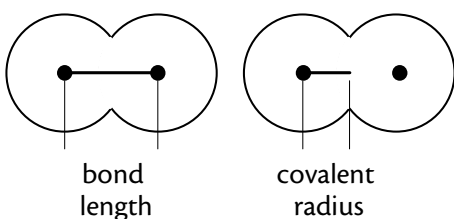
Covalent Radius

The size of an atom is very difficult to measure because atoms do not have a sharp boundary. However an X-ray technique can measure the distance between the nuclei of covalently bonded atoms – this distance is called the bond length.

The covalent radius of an element is half the distance between the nuclei of two of its covalently bonded atoms.

eg the covalent bond length in a chlorine molecule is 198 pm.

(pm = picometre; 10^{-12} metre)



$$\text{So the covalent radius of a chlorine atom} = \frac{198}{2} = 99 \text{ pm}$$

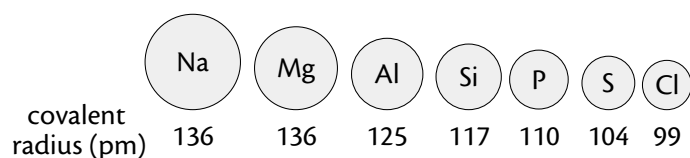
Trends in covalent radii

(a) down a group – covalent radii increase

| | Electron arrangement | Covalent radius (pm) |
|----|----------------------|----------------------|
| Li | 2, 1 | 123 |
| Na | 2, 8, 1 | 157 |
| K | 2, 8, 8, 1 | 203 |
| Rb | 2, 8, 18, 8, 1 | 216 |
| Cs | 2, 8, 18, 18, 8, 1 | 235 |

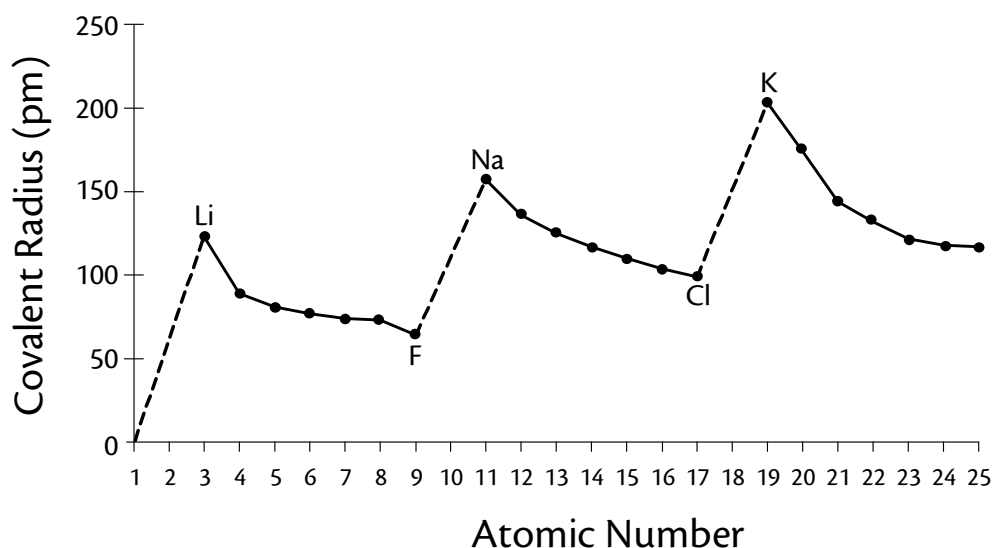
As we go down a group each member has an extra shell of electrons so the covalent radius increases. The positive charge on the nucleus increases down a group which tends to pull the electrons closer but the effect of adding an extra shell outweighs this.

(b) across a period – covalent radii decrease



As we go across a period electrons are being added to the same shell and protons are being added to the nucleus. This increasing positive charge pulls in the outer shell of electrons more closely so the radius decreases.

The graph shows how Covalent Radius varies with Atomic Number:



Bond Lengths from Covalent Radii

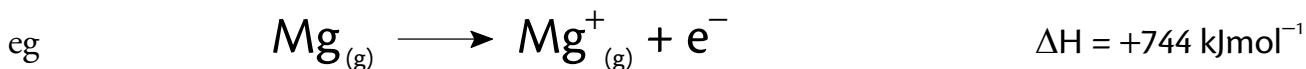
Single bond lengths between atoms of different elements can be found by adding their individual covalent radii.

e.g. the covalent radii of hydrogen and chlorine are respectively 37 and 99 pm.

so the bond length in HCl = 37 + 99 pm = 136 pm

Ionisation Enthalpy

The 1st ionisation enthalpy is the energy required to remove 1 mole of electrons from 1 mole of atoms in the gas state to form 1 mole of ions in the gas state. This is always an endothermic process.



The above equation represents the 1st Ionisation Enthalpy of magnesium. The table below gives values for 1st Ionisation Enthalpies. The values are in kJ mol^{-1} .

| | | | | | | | | |
|-----------|-----------|-----------|-----------|-----------|-----------|------------|------------|-------------------------------------|
| Li 526 | Be 905 | B 807 | C 1090 | N 1410 | O 1320 | F 1690 | Ne 2090 | ↓ decrease down group ↓ |
| Na 502 | Mg 744 | Al 584 | Si 792 | P 1020 | S 1010 | Cl 1260 | Ar 1530 | |
| K 425 | Ca 596 | Ga 577 | Ge 762 | As 953 | Se 941 | Br 1150 | Kr 1350 | |
| Rb 409 | Sr 556 | In 556 | Sn 715 | Sb 816 | Te 870 | I 1020 | Xe 1170 | |

← overall increase along period →

Trends in Ionisation Enthalpies

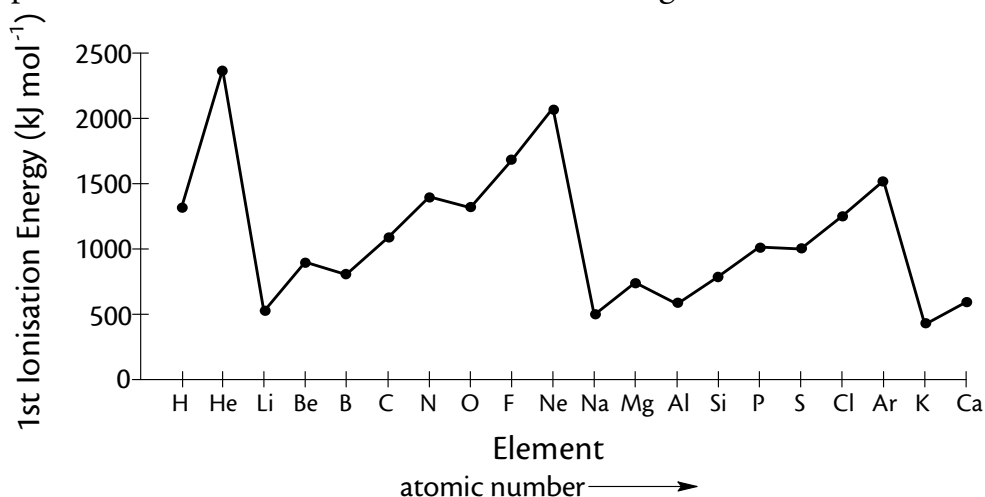
(a) down a group – ionisation enthalpies decrease

As we go down a group the outer shell electron we are removing is progressively further away from the nucleus and so is less tightly held and so easier to remove. However as we go down a group the nucleus is becoming more positive and should hold the outer electron more tightly, making ionisation enthalpies increase. This effect is diminished by the screening effect of the intervening electron shells. The outer shell electron does not feel the full attraction of the positive nucleus – so the increasing size argument wins.

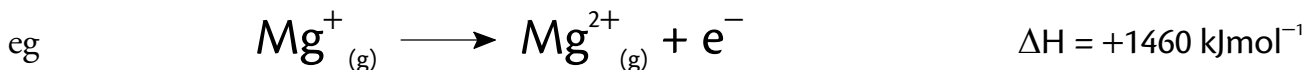
(b) across a period – ionisation enthalpies increase

Across a period the nucleus becomes more positive. This makes the outer shell electron more difficult to remove. Also, across a period the atoms become smaller so the outer electron is closer to the nucleus and so is held more tightly. The result of this trend is that metals have relatively low ionisation enthalpies and can form positive ions but for non metal atoms forming positive ions is energetically impossible.

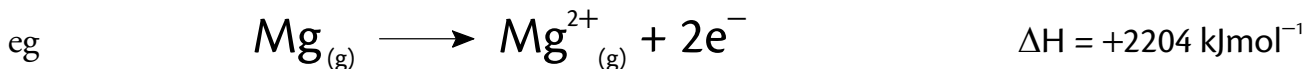
The graph shows the variation of 1st Ionisation Energies with Atomic Number.



The 2nd Ionisation Enthalpy of an element is the energy required to remove the 2nd mole of electrons.



So the total energy to remove 2 moles of electrons from an atom is the sum of the 1st and 2nd Ionisation Enthalpies.



The 2nd Ionisation energy of an atom is always larger than the first because it involves removing an electron from a species that is already positively charged. This table contains data from page 10 of the SQA Chemistry data book.

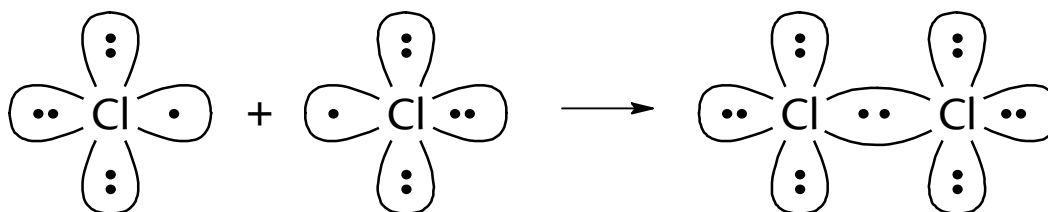
| Element | Symbol | Ionisation Energies (kJ mol^{-1}) | | | |
|-----------|--------|--|--------|-------|--------|
| | | First | Second | Third | Fourth |
| lithium | Li | 526 | 7310 | 11800 | — |
| beryllium | Be | 905 | 1770 | 14800 | — |
| boron | B | 807 | 2440 | 3660 | 25000 |
| carbon | C | 1090 | 2360 | 4640 | 6220 |
| nitrogen | N | 1410 | 2860 | 4580 | 7470 |
| oxygen | O | 1320 | 3400 | 5320 | 7470 |
| fluorine | F | 1690 | 3380 | 6060 | 8410 |
| neon | Ne | 2090 | 3960 | 6140 | 9360 |

Note

1. The large increase from the 1st to 2nd Ionisation energy of sodium. The 1st ionisation energy removes the single outer shell electron from the sodium atom so the 2nd ionisation energy involves breaking into a stable octet of electrons – this requires a lot of energy.
2. With magnesium the large increase in ionisation energy comes once the 2 outer shell electrons of the magnesium atom have been removed. The 3rd ionisation energy breaks into a stable octet.

Bonding in Compounds

Let's start by looking at the covalent bond in the element chlorine



A covalent bond is a pair of electrons shared by 2 atoms. Atoms in a covalent bond are held together by the electrostatic attraction between the negatively charged shared electrons and the 2 positively charged nuclei.



If the two bonded atoms are the same as in a chlorine molecule, then the pair of electrons is shared equally by the two atoms. We call this a non-polar covalent bond.

If the two bonded atoms are different, one nucleus will have a stronger attraction for the shared electrons than the other so the electrons will not be shared equally.

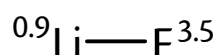
Electronegativity values are useful in predicting how electrons will be shared. Electronegativity is a measure of the attraction an atom involved in a covalent bond has for the electrons of the bond. In hydrogen iodide, H–I, the iodine atom is more electronegative than the hydrogen so the iodine has the greater attraction for the shared electrons. This means the shared pair are attracted nearer to iodine, which as a result becomes slightly negatively charged, δ^- . The hydrogen becomes slightly positive, δ^+ , because the shared electrons have moved nearer the iodine. When the sharing of the bonding electrons is unequal we call it a polar covalent bond.



In hydrogen fluoride, H–F, the difference in electronegativities is greater so this covalent bond is more polar.

In some compounds one atom is so much more electronegative than the other that there is no sharing of electrons at all.

eg in lithium fluoride the electronegativities are:



This difference is so great that the bonding electron originally belonging to lithium is transferred to the fluorine. This forms two ions of opposite charge, Li^+ and F^- . These are attracted to each other – this electrostatic attraction is called the ionic bond.

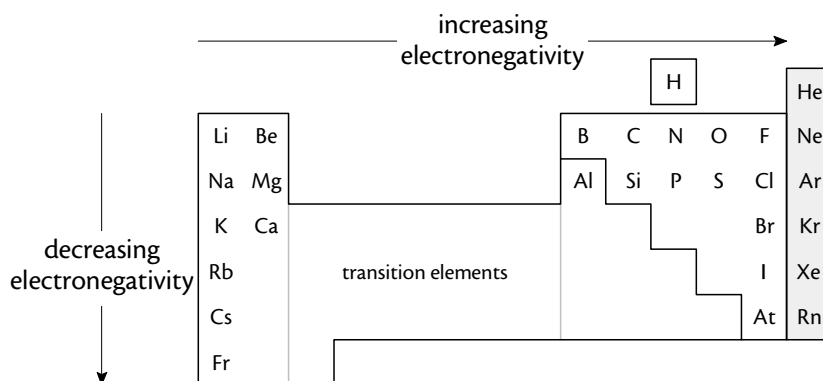
Don't think of non-polar covalent, polar covalent and ionic as 3 completely separate types of bonding. Rather think of them as being on a continuous scale. At one end is non-polar covalent with its equal sharing of electrons, moving on to progressively more and more polar covalent. Eventually the sharing is so unequal that an electron is effectively transferred from one atom to the other forming ions, and therefore ionic bonding.

————— increasing difference
in electronegativity —————>



equal sharing of electrons ————— increasingly unequal
sharing of electrons —————> transfer of
electrons

The diagram below indicates the variation in electronegativity of the atoms.



The main trends are

- increasing electronegativity across a period.
- decreasing electronegativity down a group.

The greater the difference in electronegativity between atoms, the less likely they are to share electrons and form covalent bonds and the more likely they are to form ionic bonds. So the more widely separated atoms are in the Periodic table the more likely they will bond ionically.

e.g. sodium chloride and magnesium oxide are ionic and caesium fluoride is the compound with the greatest ionic character.

Structure and Properties of Compounds

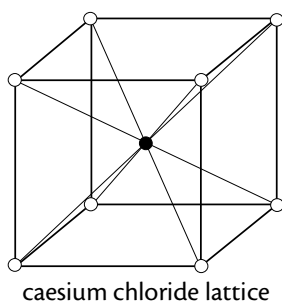
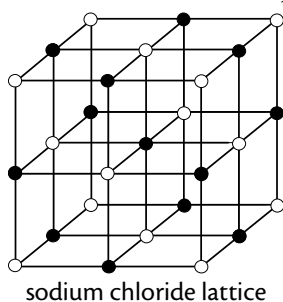
In the previous section we saw that compounds have ionic bonding or covalent bonding. We now must see, just as we did with elements, how the bonding affects the properties.

Ionic Compounds

Ionic compounds do not form molecules. The electrostatic attraction between positive and negative ions forms giant 3 dimensional lattice structures. The relative numbers of positive and negative ions is such that the overall charge is neutral.

eg $\text{Ca}^{2+}(\text{Cl}^-)_2$

The energy given out when the lattice is formed is called the lattice energy. This is therefore the energy that must be supplied to separate the ions and break down the lattice it is therefore a measure of the strength of the electrostatic attraction. All ionic compounds are solids at room temperature and generally they have very high melting points. This shows that the electrostatic attraction – the ionic bond – between the ions is very strong. The diagrams below show the structures of NaCl and CsCl. Although they both have similar formulae the structures are different because of the different relative sizes of Na^+ and Cl^- ; and of Cs^+ and Cl^- .



Note: in an ionic compound (e.g. MgCl_2) the formula does not suggest the presence of molecules. It is showing that in the giant crystal lattice there is 1 Mg^{2+} ion for every 2 Cl^- ions.

Covalent Compounds

Covalent bonding in compounds can result in either discrete molecules or covalent network structures.

(a) discrete molecules

Covalent compounds made of discrete molecules have strong covalent bonds within the molecules but relatively weak forces between the molecules. (The weak forces between the molecules are called intermolecular forces and we will look at them in more detail later). When a covalent molecular compound is melted or boiled it is the weak intermolecular forces that are overcome and not the covalent bonds in the molecule. This means melting points and boiling points are relatively low. Covalent molecular compounds can be solid, liquid or gaseous at room temperature;

eg carbon dioxide (g), water (l) and candle wax (s) are all covalent molecular.

(b) covalent network

Both carbon and silicon are in Group 4 and their oxides have formulae CO_2 and SiO_2 . However, as we have seen, CO_2 is a gas at room temperature but SiO_2 is a solid that only melts at 1700°C . This suggests very different bonding in the two compounds. CO_2 consists of discrete molecules so has weak forces between its molecules, so CO_2 exists as a gas above -78°C . Silicon oxide, commonly known as silica, is the main chemical in sand. Its structure is a 3 dimensional covalent network. There are no discrete molecules so melting involves breaking strong covalent bonds. A lot of energy is required so the melting point is very high.

Abrasives

The very strong covalent network structure of silica, SiO_2 makes it very hard. Other substances with strong covalent networks are also very hard.

Diamond, a polymorph of carbon

Silicon carbide, SiC , commonly called carborundum

Boron nitride, BN

Fused alumina, Al_2O_3

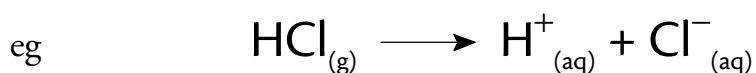
These all have covalent network structures. Because they are very hard they all find use as abrasives, cutting tools or in polishing.

Compounds and Conduction of Electricity

Ionic compounds do not conduct when solid. They do conduct when melted or dissolved in water. This sets the ions free so they can be attracted to the electrode of opposite charge.

Covalent compounds do not conduct when solid or when melted or in solution because they contain no ions.

However there are a few covalent compounds that ionise when dissolved in water. Obviously their solutions will conduct electricity.

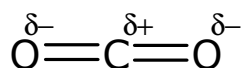


Polar Bonds and Polar Molecules

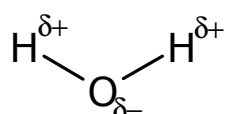
We saw earlier that covalent bonds between different atoms are polar because of the differing electron attracting powers of the atoms, for example:



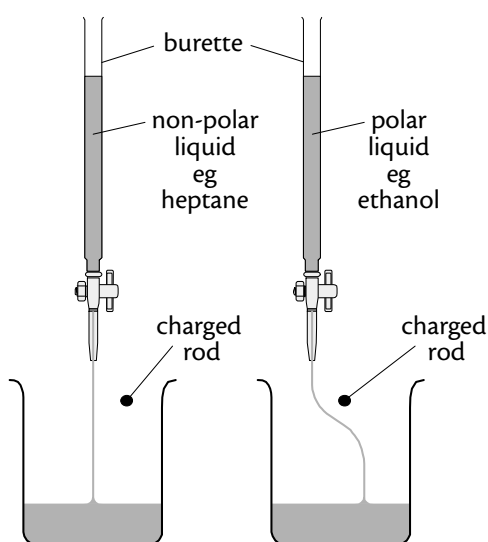
The presence of polar bonds in a molecule does not necessarily mean that the molecule as a whole will be polar. Carbon dioxide has two polar bonds,



but because they are symmetrically arranged the polarity cancels out and as a whole the molecule is non-polar. Water has two polar bonds,

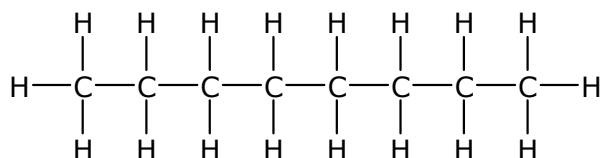


but they are not symmetrically arranged and don't cancel out, so water molecules are polar. The water molecule is said to be a permanent dipole.

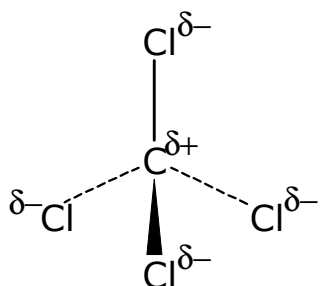
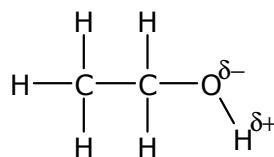


Liquids with polar molecules are easily distinguished from those with non-polar molecules. Polar molecules are attracted to a charged rod but non-polar molecules are not attracted.

Heptane has almost non-polar bonds so the molecules are non-polar.

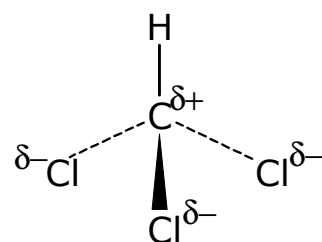


Ethanol has one polar O–H bond so the molecule is polar.



Two molecules worth noting are CCl_4 and CHCl_3 . Molecules of CCl_4 have 4 polar C–Cl bonds but being symmetrically arranged (tetrahedrally) the polarities cancel and the molecule is non-polar because it has no permanent dipole.

CHCl_3 has 3 polar C–Cl bonds and one C–H bond which is almost non-polar. In this case the polarities don't cancel; we have a permanent dipole, so CHCl_3 has polar molecules.



Intermolecular Forces

We now look in more detail at the relatively weak intermolecular forces that exist in covalent molecular compounds.

Van der Waals Forces

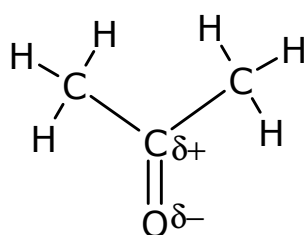
We met them already when we discussed bonding in the elements but they also occur between molecules. They are the weakest of the intermolecular forces but in the absence of any others they are important. The bigger the molecule the bigger the Van der Waals force.

We know that as we go up the alkane series the molecules get bigger so the Van der Waals force between the molecules increases. The result is that more energy has to be put in to overcome this force when melting or boiling the alkanes. This explains why melting and boiling points increase up the alkane series and indeed up every homologous series.

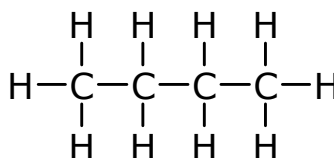
Permanent dipole–permanent dipole attractions

Propanone molecules have a permanent dipole so the molecules are polar. As well as Van der Waals force, the permanent dipole interactions between propanone molecules are an additional electrostatic attraction holding the molecules together.

The example below shows the effect. Both compounds have the same formula mass but the one with polar molecules has the higher boiling point.



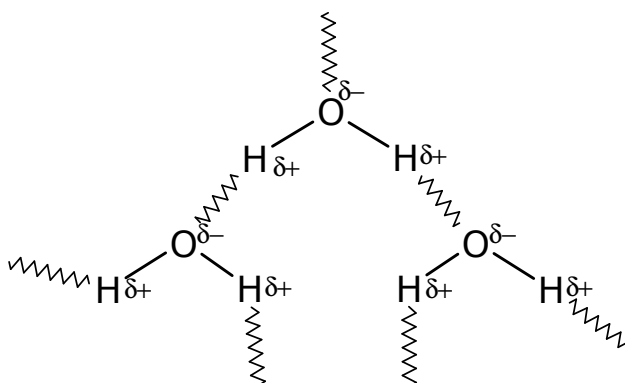
Propanone
formula mass 58
boiling point 56°C



Butane
formula mass 58
boiling point 0°C

Hydrogen Bonds

Hydrogen atoms have a very low electronegativity. If hydrogen is bonded to a very electronegative atom (N, O and F) then the covalent bond will be very polar. Consider water molecules:

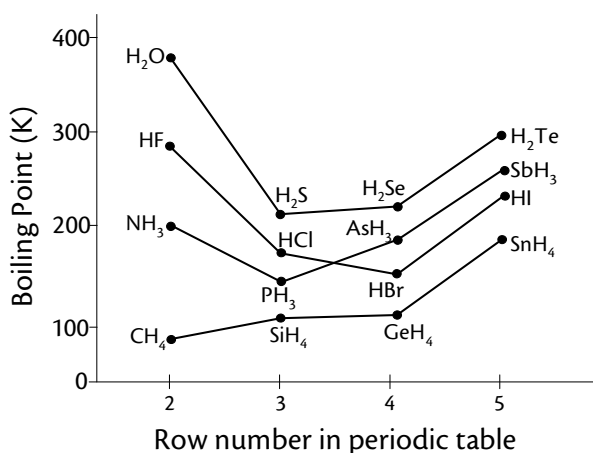


There are relatively strong forces of attraction between the $\delta+$ hydrogen in one molecule and the $\delta-$ oxygen in a neighbouring molecule. These forces are called hydrogen bonds and are additional to Van der Waals forces. Hydrogen bonds are the strongest of the intermolecular forces but they are much weaker than covalent bonds.

Effects of Hydrogen Bonding

Physical Properties of Hydrides

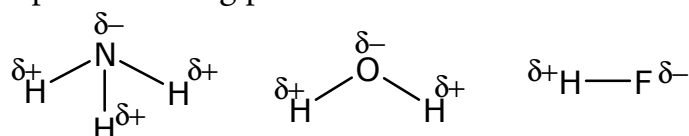
Look at the graph of the boiling points of the Group 4, 5, 6 and 7 hydrides.



Only the boiling points in Group 4 follow the expected trend; as we go down group 4 the hydride molecules become bigger so increasing van der Waals forces resulting in gradually increasing boiling points. In groups 5, 6 and 7 the boiling points of the first members are much higher than expected. This means more energy than expected has to be supplied to separate the molecules, indicating that they are held together by more than just van der Waals forces. The extra force is called hydrogen

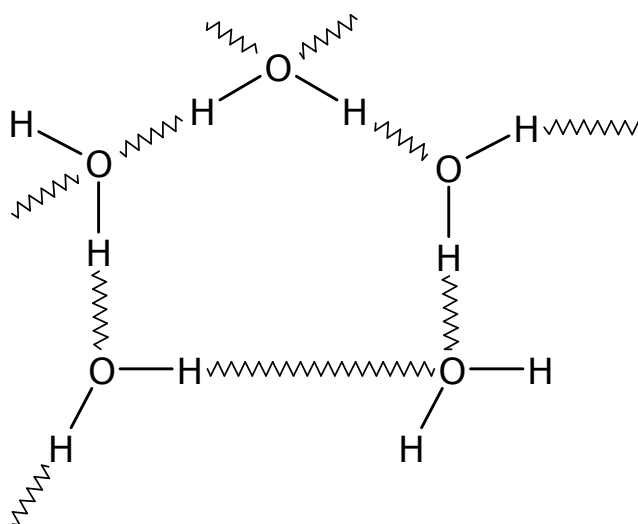
bonds which, remember, is present only in molecules in which hydrogen is bonded to a small electron attracting atom like N, O or F.

The covalent bonds within the molecules are very polar with the result that $H^{\delta+}$ on one molecule attracts $\delta-$ on another molecule. It is this additional bond that gives NH_3 , H_2O and HF higher than expected boiling points.



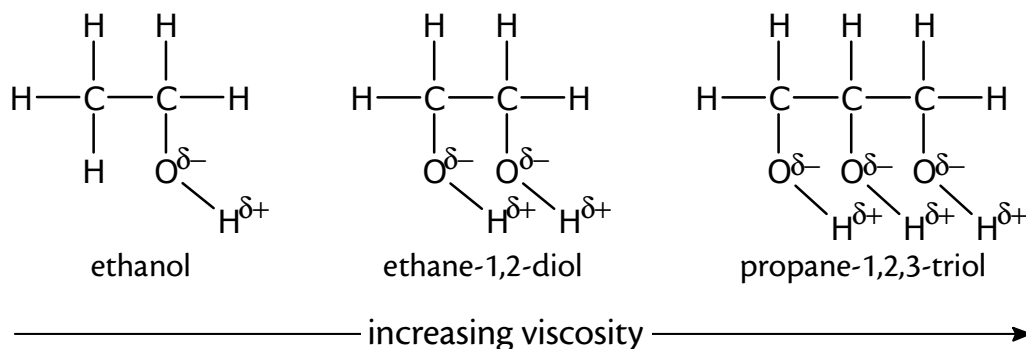
Hydrogen bonding in Ice

Usually when a substance is cooled its molecules/atoms lose kinetic energy and move closer and closer together increasing the density until the substance solidifies. So normally a substance has a greater density in the solid state than in the liquid state. As water is cooled, its density increases as the temperature falls, until 40°C is reached where water has its maximum density. Further cooling causes the molecules to start to move apart, forming hydrogen bonds until it freezes in an open cage like structure. The result is that ice is less dense than water. This is the reason that ice floats on water.



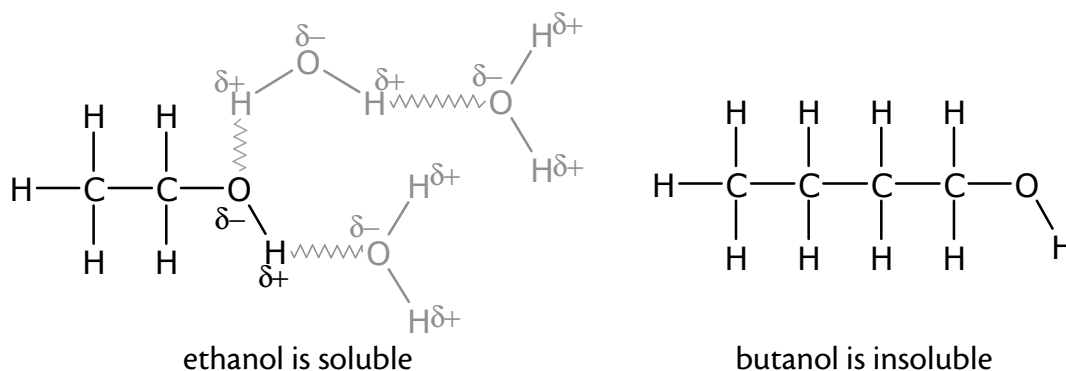
Viscosity

Viscosity is the thickness of a liquid and can be measured by timing how long it takes a ball bearing to fall through the liquid – the more viscous, the longer it takes. The more hydrogen bonds in a molecule the more the molecules will hold together and the more viscous the liquid will be. Hexane, C_6H_{14} , has no hydrogen bonds between its molecules (only Van der Waals forces) so is not very viscous. However, consider the following 3 molecules which have respectively 1, 2, and 3 polar O–H bonds. The more O–H bonds per molecule, the more hydrogen bonds the molecule can make and, therefore, the more viscous the molecule is.



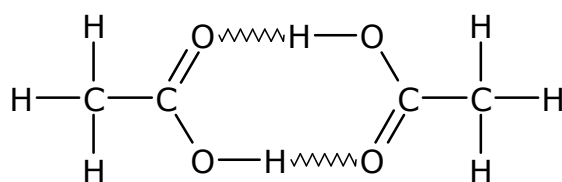
Miscibility with water

In general, organic molecules are insoluble in water. However, small molecules like ethanol, with a polar O–H functional group, are soluble in water because the ethanol molecules can form hydrogen bonds with the water molecules. Larger molecules, like butanol, are insoluble even though they have the same polar group, because the larger non-polar hydrocarbon chain is the dominant influence.



Formula mass

Ethanoic acid has a formula mass of 60. Some methods of determining formula mass give the value as 120 because in solution hydrogen bonds hold the molecules together in pairs.

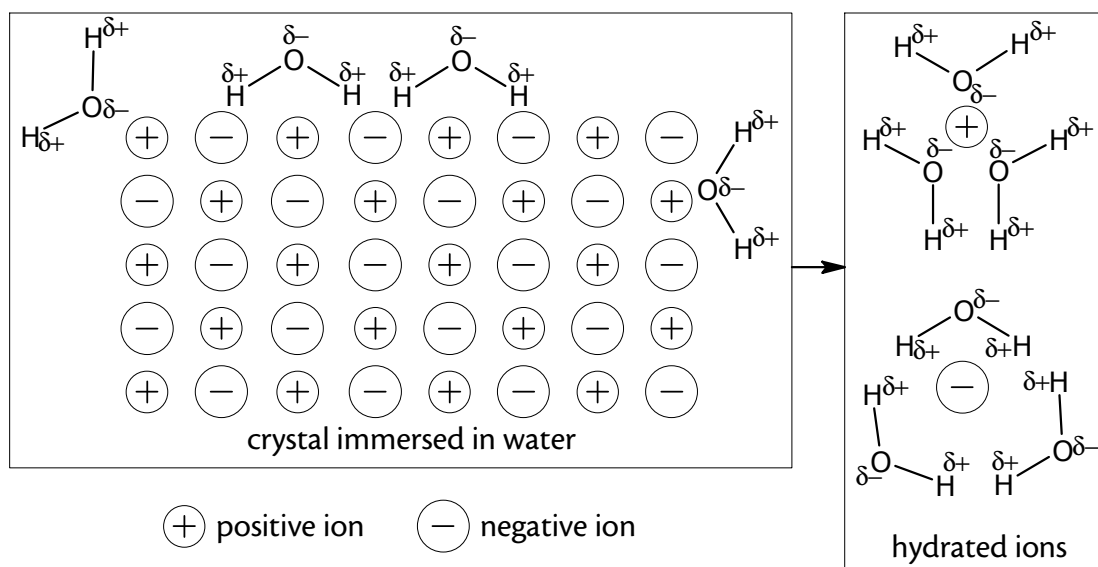


Dissolving

As a general rule, water will be the best solvent for ionic solids and substances with polar molecules. Non-polar solutes are likely to dissolve in non-polar solvents like heptane or tetrachloromethane. It is sometimes stated as 'like dissolves like'.

Water as a Solvent

The diagram shows what happens when an ionic crystal dissolves in water.



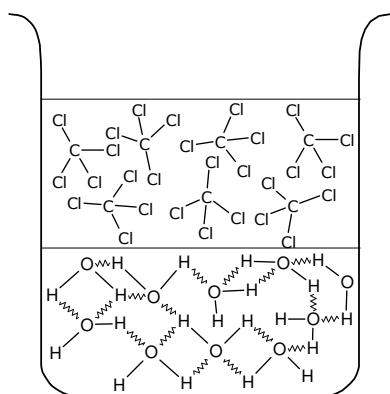
The polar water molecules are attracted to the ions in the crystal lattice. The attraction drags the ions out of the crystal ‘into solution’, where the ions are surrounded by water molecules.

Using sodium chloride dissolving in water as an example, the equation for the above process is:



The (aq) in the equation indicates that the ions are hydrated, ie they are surrounded by polar water molecules, held by the electrostatic attraction of opposite charges.

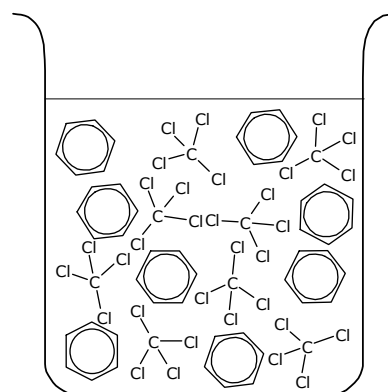
Non-polar compounds, like tetrachloromethane do not dissolve in water.

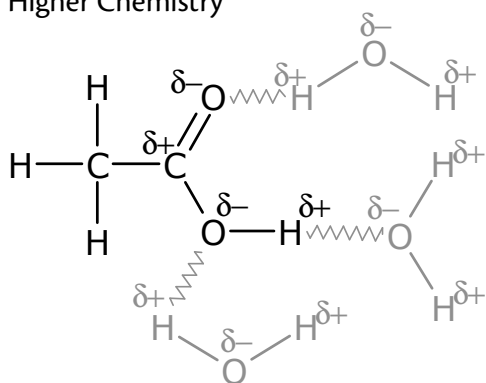


Non-polar molecules cannot hydrogen bond with water molecules and if they were to go into water, they would separate the water molecules and reduce the number of hydrogen bonds. This is energetically unfavourable so they don't dissolve.

Non-polar compounds are miscible with each other because the only attractions present are van der Waals forces and they can exist between different non polar molecules.

eg tetrachloromethane and benzene (2 non-polar molecules) are miscible.

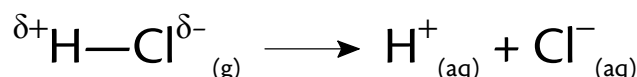




Small polar molecules, like ethanol or ethanoic acid, dissolve in water because the polar functional groups are able to hydrogen bond with water molecules.

However, as we go up their homologous series, the increasing length of the non-polar hydrocarbon chain means that higher members are insoluble in water.

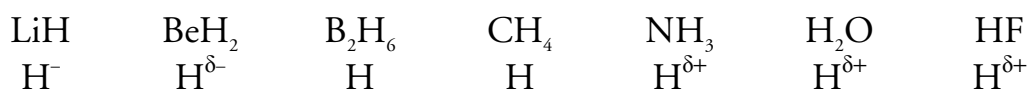
Some polar covalent molecules ionise when they dissolve in water:



Let's now see how our ideas on bonding affect the properties of some compounds of the first 20 elements.

Hydrides

Compounds of the elements with hydrogen are called hydrides. The hydrides of the period 2 elements along with the trend in polarity are shown below.

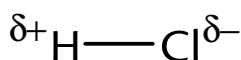


Note the trend from ionic to covalent across the period. This follows from a decreasing difference in electronegativity between hydrogen and the other element as we go from left to right. Most of these compounds are already familiar to you but Li⁺H⁻ containing the hydride ion is probably new. The H⁻ ion is found only in hydrides of elements that have a very low electronegativity.

eg Li⁺H⁻, Na⁺H⁻, K⁺H⁻ etc.

All the ionic hydrides are white solids. When they are melted and electrolysed, hydrogen gas is evolved at the positive electrode confirming the presence of H⁻ ions. As we move right, we pass the non-polar hydrides, CH₄ and SiH₄.

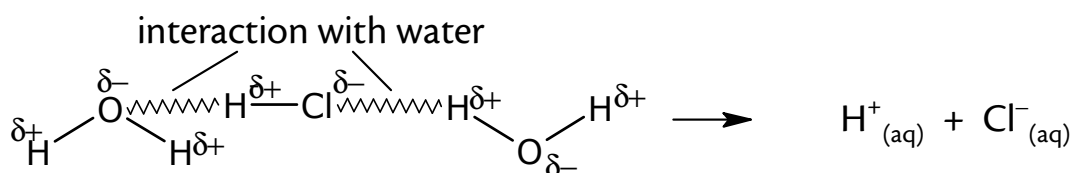
At the right of Periodic Table are the hydrides of the halogens. These are all gases with polar covalent bonding.



In aqueous solution these molecules ionise completely to give acidic solutions.



This happens as follows:



The attraction between the slightly negative oxygen in water and the slightly positive hydrogen in HCl helps break the H–Cl bond.

Oxides

Structure of Oxides

The trend from ionic to covalent bonding is as expected from electronegativities.

| | | | | | | |
|--------------------------------|-------------------------------|-----------------------------|------------------------------|--|--------------------------------|--|
| □ | ionic lattice | □ | covalent network | □ | discrete molecules | |
| $(\text{Li}^+)_2\text{O}^{2-}$ | $(\text{BeO})_n$ | $(\text{B}_2\text{O}_3)_n$ | CO_2 CO | N_2O NO NO_2 | O_2 | F_2O |
| $(\text{Na}^+)_2\text{O}^{2-}$ | $\text{Mg}^{2+}\text{O}^{2-}$ | $(\text{Al}_2\text{O}_3)_n$ | $(\text{SiO}_2)_n$ | P_4O_{10} | SO_2 SO_3 | Cl_2O Cl_2O_7 |

← increasing ionic character increasing molecular character →

Group 1 & 2 Metal oxides (except BeO) form **ionic lattices**. They are solids at room temperature and have high melting points and boiling points. When melted, these ionic oxides conduct electricity.

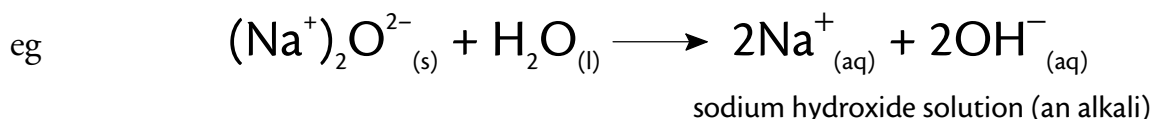
Oxides of Be, B, Al, Si exist as **covalent networks**. They have very high melting points and boiling points but unlike the ionic oxides, covalent network oxides do not conduct electricity when molten. SiO_2 as we have already seen is a very hard substance because the 3-dimensional arrangement of strong covalent bonds in the covalent network is very rigid.

Oxides of C, N, P, S, F, Cl consist of **discrete small molecules**. They have low melting points and boiling points because there are only weak van der Waals forces to be overcome. They do not conduct in the molten state because they are molecular.

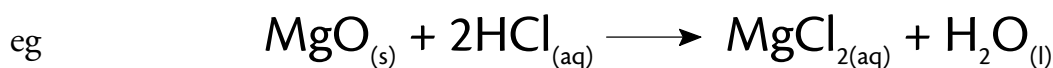
Acid/Base Character of Oxides

This is Standard Grade work but repeating it will do no harm.

Basic oxides are the oxides of metals and, if they are soluble in water, they give alkaline solutions. Basic oxides react with acids. The ionic oxides, Li_2O , Na_2O , MgO are basic oxides. They are soluble in water so they form alkaline solutions.



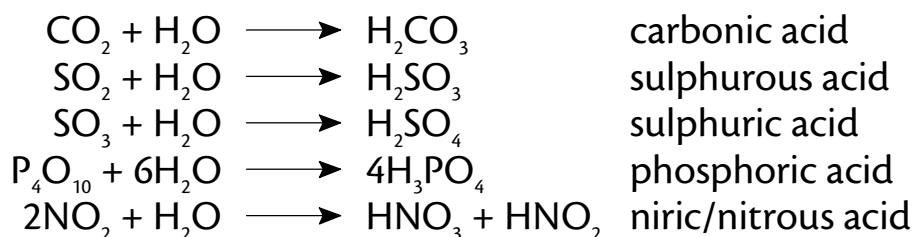
They react with acids to form a salt and water.



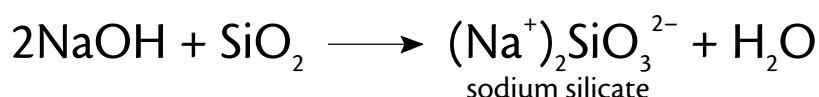
Note: many metal oxides (e.g. CuO) are insoluble in water so do not give alkaline solutions. However they are basic oxides because they react with acid.

Acidic Oxides are the oxides of non-metals and if they are soluble in water they form acidic solutions. Acidic oxides react with alkalis to form salts and water.

The equations below show the acids formed when some acidic oxides dissolve in water.



SiO_2 is insoluble in water so does not give an acid solution but, being an acidic oxide, it reacts with alkalis.



Amphoteric Oxides behave as both an acidic oxide and a basic oxide.

Neutral oxides are oxides which react with neither acid nor alkali. CO , NO and N_2O are neutral oxides.

The properties of these oxides are now summarised:

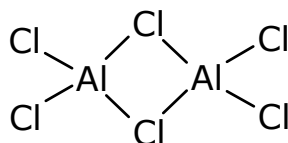
| | | | | | | |
|---|--|--|------------------------------|--|--------------------------------|--|
| basic oxide | amphoteric oxide | acidic oxide | | | | |
| $(\text{Li}^+)_2\text{O}^{2-}$ | $(\text{BeO})_n$ | $(\text{B}_2\text{O}_3)_n$ | CO_2 CO | N_2O NO NO_2 | O_2 | F_2O |
| $(\text{Na}^+)_2\text{O}^{2-}$ | $\text{Mg}^{2+}\text{O}^{2-}$ | $(\text{Al}_2\text{O}_3)_n$ | $(\text{SiO}_2)_n$ | P_4O_{10} | SO_2 SO_3 | Cl_2O Cl_2O_7 |
| <p>→ increasing acidic character</p> <p>← increasing basic character</p> | | | | | | |

Chlorides

Chlorine is very reactive and combines directly with most elements. The bonding (as in the oxides) varies from ionic to covalent across the periodic table. As expected, the metals form ionic lattices and the non-metals form discrete molecules. This again is in line with electronegativities.

| | | | | | | |
|---|--|--------------------------|-----------------|----------------|-------------------------|---------------|
| ionic lattice | discrete molecules | | | | | |
| LiCl | BeCl_2 | BCl_3 | CCl_2 | NCl_3 | OCl_2 | FCl |
| NaCl | MgCl_2 | Al_2Cl_6 | SiCl_4 | PCl_3 | S_2Cl_2 | Cl_2 |
| <p>→ increasing molecular character</p> <p>← increasing ionic character</p> | | | | | | |

The formula of aluminium chloride is surprising, and the fact that it is molecular is surprising. The melting point is only 1900°C and it is a poor conductor when molten which indicates that the bonding in aluminium chloride is likely to be covalent rather than ionic. It appears to exist as Al_2Cl_6 molecules as shown:



Summary of Bond Types and Strengths

This is a very rough guide to the strengths of bonds we have met in this topic.

| Bond Type | Strength (kJ mol^{-1}) |
|-----------------------------------|-----------------------------------|
| Metallic bond | 80 to 600 |
| Ionic bond | 100 to 500 |
| Covalent bond | 100 to 500 |
| Hydrogen bond | 40 |
| Permanent dipole-permanent dipole | 30 |
| Van der Waals force | 1 to 20 |