



Higher Chemistry

HSN11100
Unit 1 Topic 1

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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

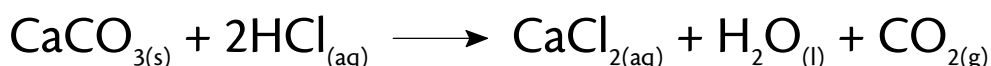
The rate of a reaction is usually found experimentally by measuring how fast a reactant is used up or how fast a product is formed.

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.

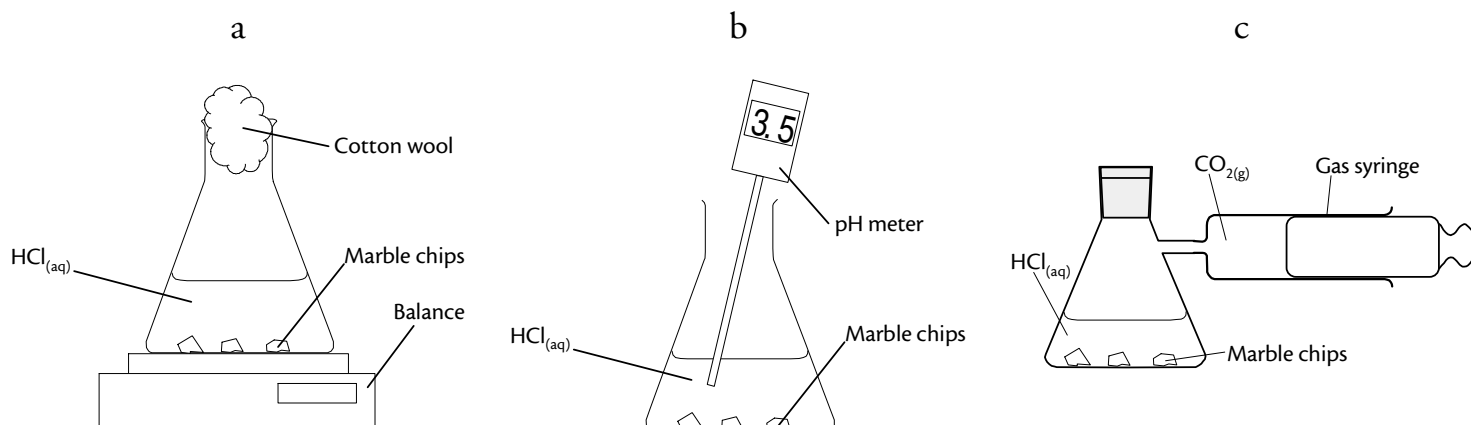
We studied the reaction between marble chips (calcium carbonate) and dilute hydrochloric acid.



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.

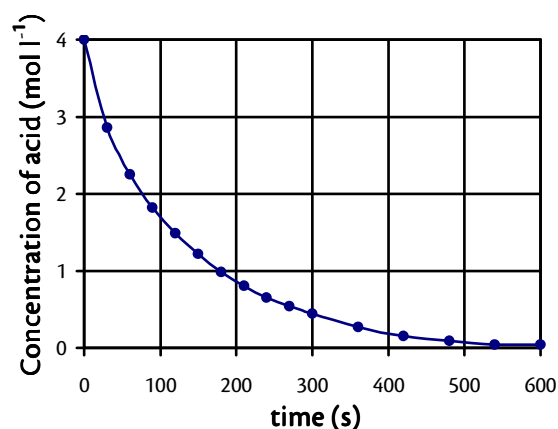
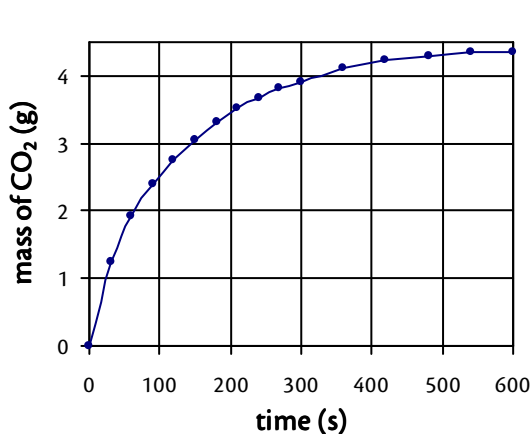
The diagrams indicate how this might be done.



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:

- a. from mass of carbon dioxide produced:

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

- b. 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.

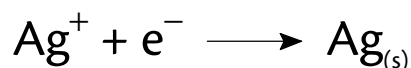
Freezers slow down the rate of decomposition of food so that it can be kept for months.

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

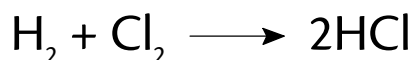
Light hitting a photograph film provides the activation energy for this reaction:



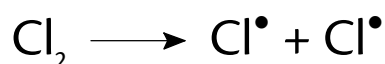
Hydrogen and chlorine

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

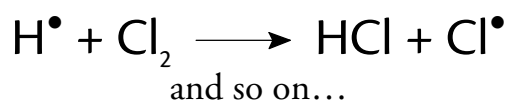
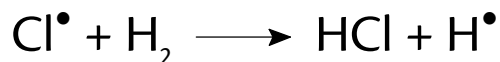
However, as soon as ultra violet light is shone on the mixture there is an explosive reaction forming hydrogen chloride:



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



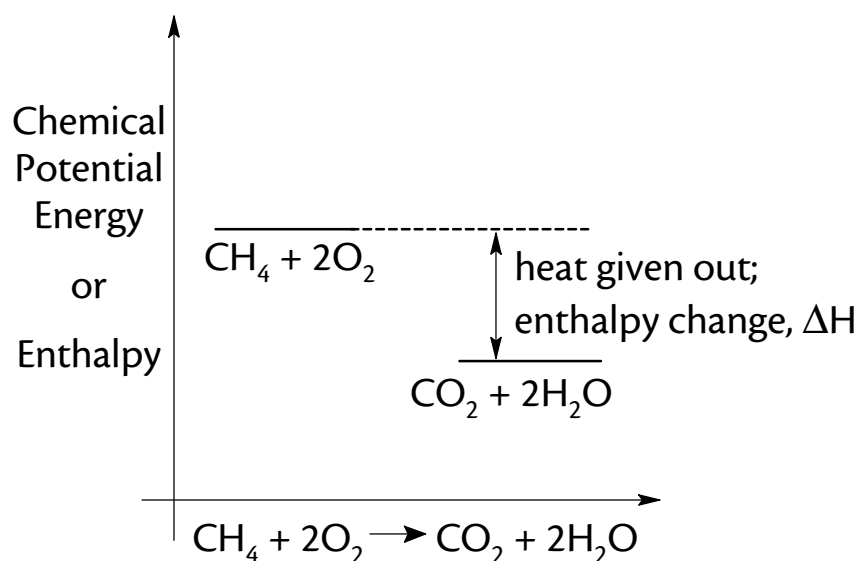
The chlorine atoms then attack a hydrogen molecule and a very fast chain reaction results:



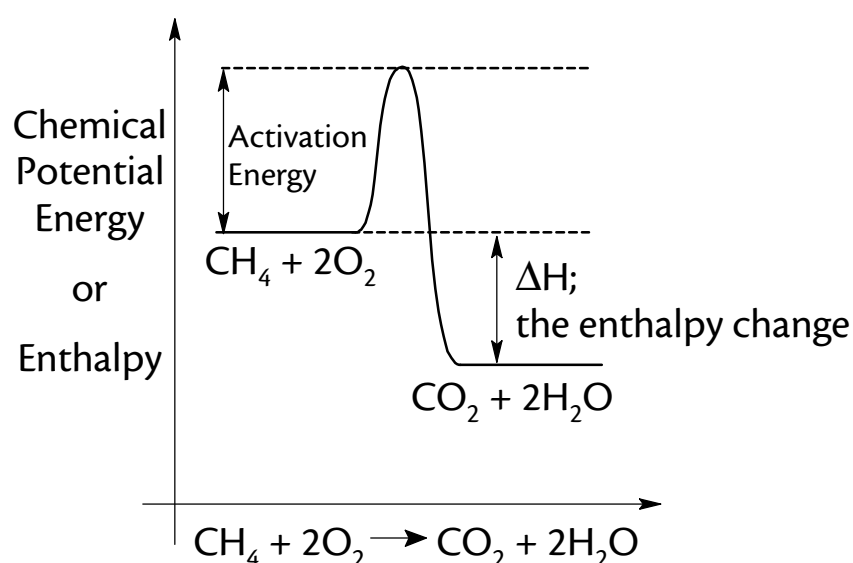
Potential Energy Diagrams

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:



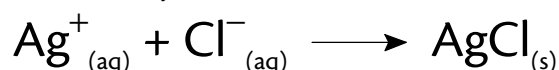
The difference in potential energy between the reactants is called the enthalpy change for the reaction and has the symbol, ΔH . We will meet this again later. We can now incorporate the idea of Activation Energy onto these Potential Energy diagrams.



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.

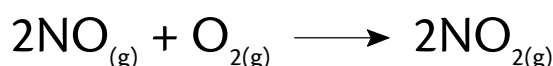
If the Activation Energy is low, many molecules will have enough energy to overcome the barrier and the reaction will be fast, for example:

- 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.

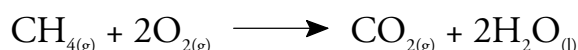
- b. The colourless gas nitrogen monoxide combines very quickly with oxygen to form brown nitrogen dioxide.



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

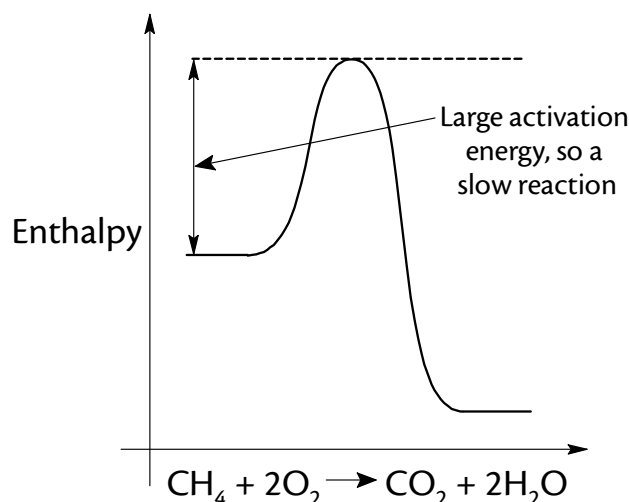
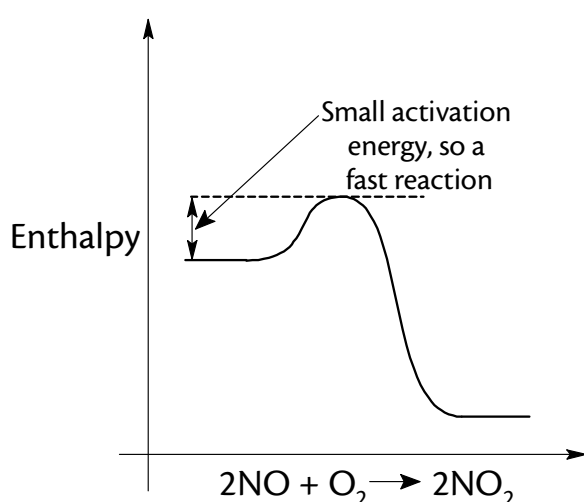
If the activation energy is high, few molecules will have sufficient energy to overcome the energy barrier and the reaction will be slow.

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.

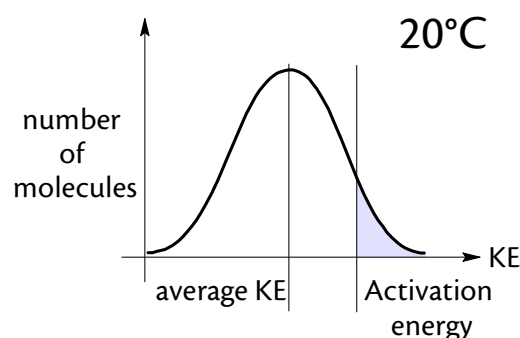
The Potential Energy diagrams below help illustrate this:



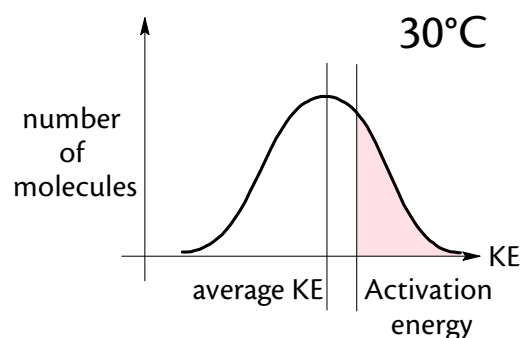
Energy Distribution and the Activated Complex

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.



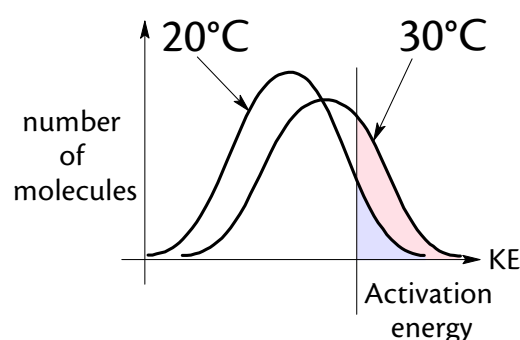
If the measuring process is repeated at a higher temperature (30°C) the graph is of a similar shape but is shifted to the right, ie a higher average kinetic energy.



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 .



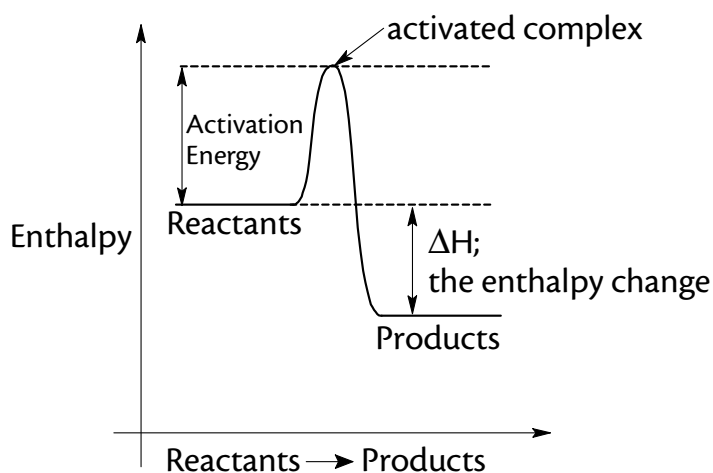
At the higher temperature the total number of collisions does not increase much. However a much higher proportion of the collisions produce the necessary activation energy and so reaction can happen.

Activation Energy and the Activated Complex

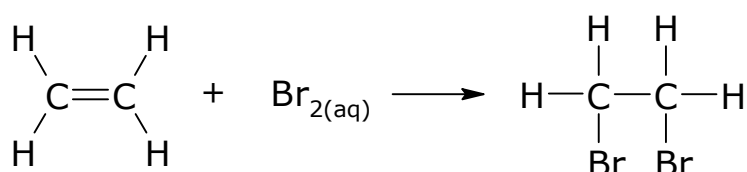
We now look at the case when a collision is hard enough to allow reaction to occur. When two molecules react the first thing that happens as a result of the collision is that they join to form a species called the activated complex. The activated complex is very unstable and exists for only a very short 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.

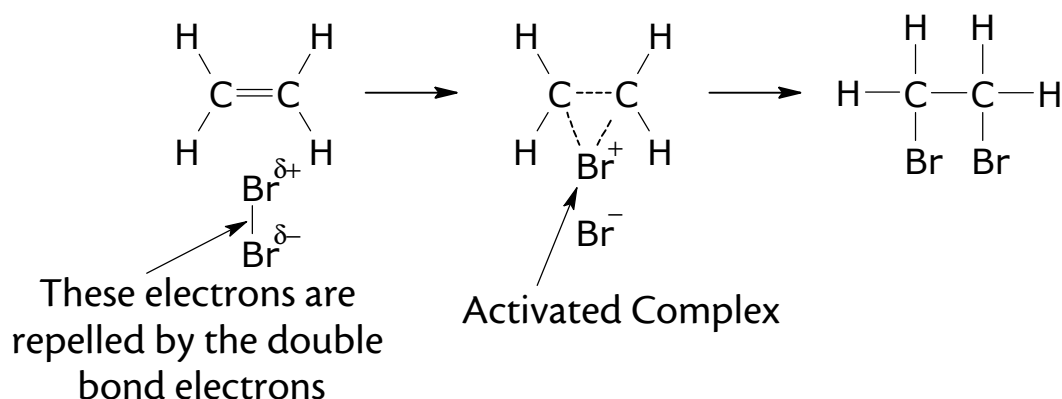
Once formed the activated complex breaks up either reforming the reactants or forming new products. If it breaks up into new products the energy given out can be greater or less than the activation energy. These correspond respectively to exothermic and endothermic reactions. This is shown for an exothermic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



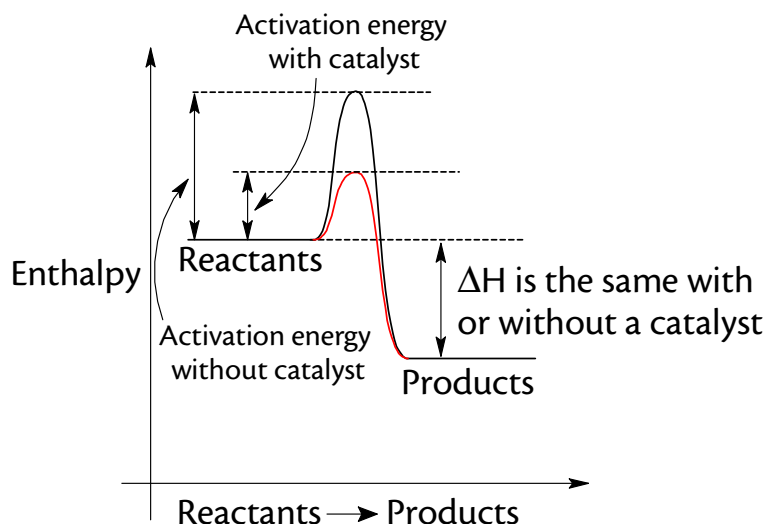
The Effect of Catalysts on Reaction Rate

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.

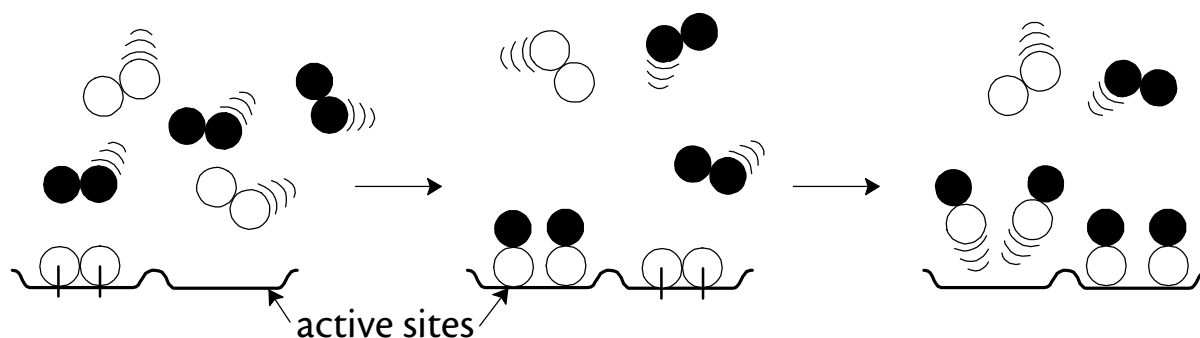
2. **Heterogeneous Catalysis:** The solid manganese dioxide catalyst is in a different physical state from the liquid H_2O_2 .

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.

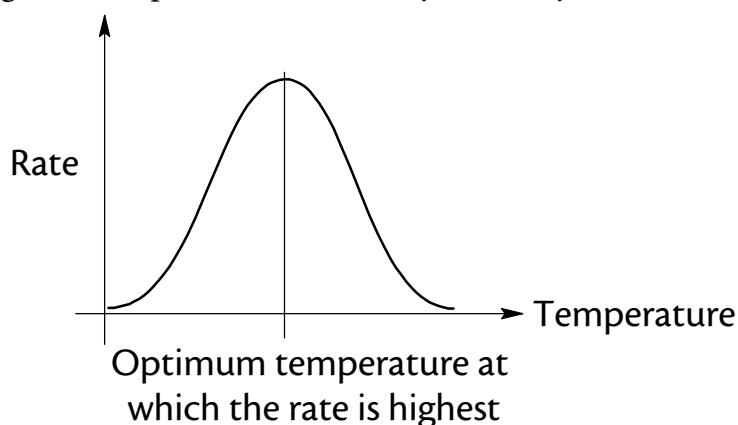
Enzymes

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

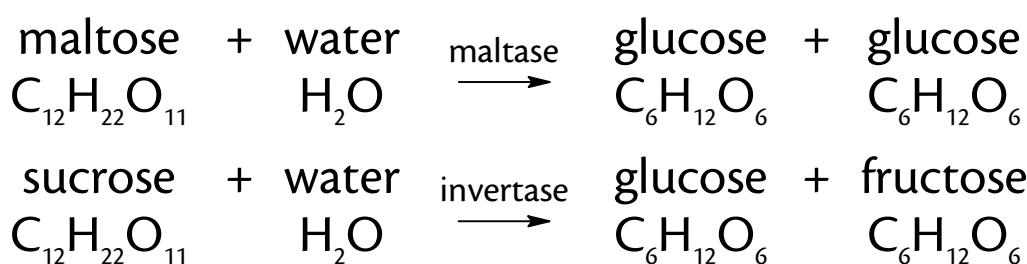
- yeast contains enzymes that convert carbohydrates into alcohol
- amylase is an enzyme that hydrolyses starch
- catalase is an enzyme that helps decompose hydrogen peroxide

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!