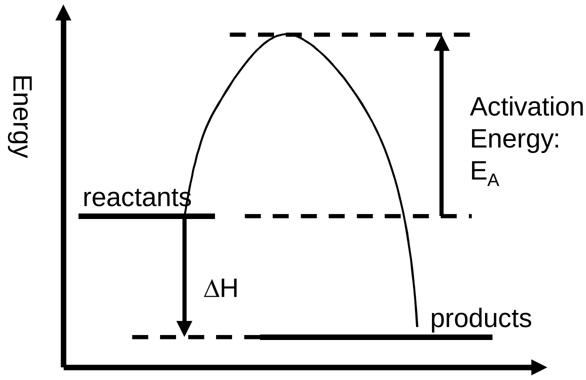
3.2.2. Reactions Rates

Collision theory

Reactions can only occur when collisions take place between particles having sufficient energy. The energy is usually needed to break the relevant bonds in one or either of the reactant molecules.
This minimum energy is called the Activation Energy

The **Activation Energy** is defined as the **minimum** energy which particles need to collide to start a reaction



Effect of Increasing Concentration and Increasing Pressure

At higher concentrations(and pressures) there are **more particles per unit volume** and so **the particles collide with a greater frequency** and there will be a **higher frequency of effective collisions**.

Note: If a question mentions a **doubling** of concentration/rate then make sure you mention **double** the number of particles per unit volume and **double** the frequency of effective collisions.

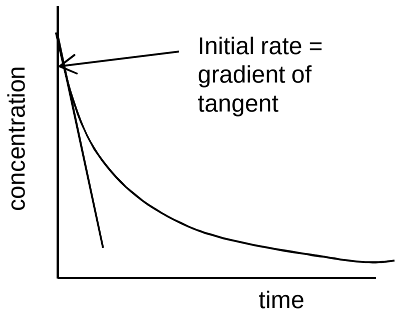
Measuring Reaction Rates

The rate of reaction is defined as the **change in concentration** of a substance **in unit time**
Its usual unit is mol $dm^{-3}s^{-1}$

When a graph of concentration of reactant is plotted vs time, the **gradient** of the curve is the rate of reaction.

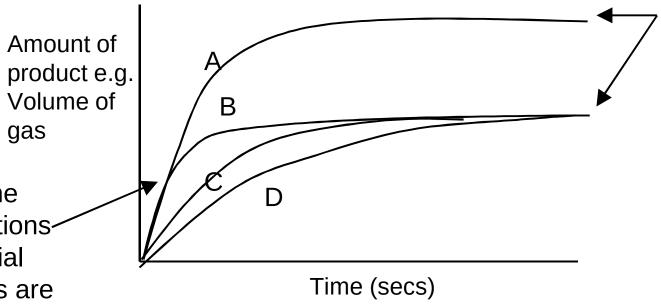
The **initial rate** is the rate at the start of the reaction where it is fastest

Reaction rates can be calculated from graphs of concentration of reactants **or** products



In the experiment between sodium thiosulphate and hydrochloric acid we usually measure reaction rate as **1/time** where the time is the time taken for a cross placed underneath the reaction mixture to disappear due to the cloudiness of the Sulphur . $Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2 + S + H_2O$
This is an approximation for rate of reaction as it does not include concentration. We can use this because we can assume the amount of Sulphur produced is **fixed and constant**.

Comparing rate curves



Need to calculate/ compare initial moles of reactants to distinguish between different finishing volumes.

e.g. the amount of product is proportional to the moles of reactant

Different volumes of the same initial concentrations will have the same initial rate (if other conditions are the same) but will end at different amounts

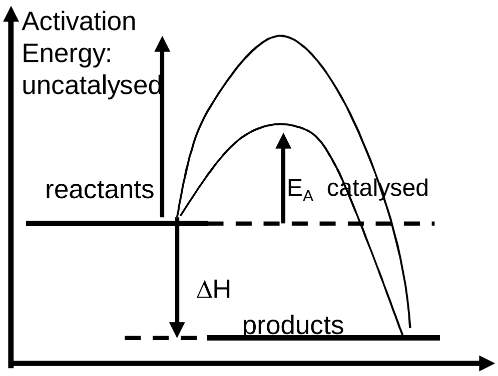
The higher the concentration/ temperature/ surface area the faster the rate (steeper the gradient)

Effect of Catalysts

Definition: Catalysts increase reaction rates without getting used up.

Explanation: They do this by **providing an alternative route or mechanism** with a **lower activation energy so** more molecules have energy above activation energy

Comparison of the activation energies for an uncatalysed reaction and for the same reaction with a catalyst present.



A **heterogeneous catalyst** is in a different phase from the reactants

A **homogeneous catalyst** is in the same phase as the reactants

Heterogeneous catalysis

Heterogeneous catalysts are usually solids whereas the reactants are gaseous or in solution. The reaction occurs at the surface of the catalyst.

Homogeneous catalysis

When catalysts and reactants are in the same phase, the reaction proceeds through an intermediate species.

Benefits of Catalysts

Catalysts speed up the rate of reaction. This means that the use of a catalyst may mean lower temperatures and pressures can be used.
This can save energy costs as there is reduced energy demand for providing high temperature and less electrical pumping costs for producing pressure.
This can mean fewer CO_2 emissions from burning of fossil fuels,

Catalysts can enable different reactions to be used, with better atom economy and with reduced waste, or fewer undesired products or less use of hazardous solvents and reactants.

Catalysts are often enzymes, generating very specific products, and operating effectively close to room temperatures and pressures

Techniques to investigate rates of reaction

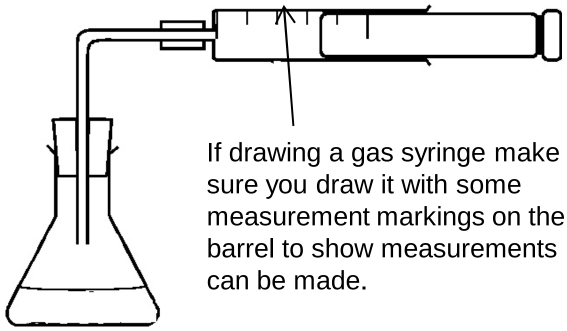
There are several different methods for measuring reactions rates. Some reactions can be measured in several ways

measurement of the change in volume of a gas

This works if there is a change in the number of moles of gas in the reaction. Using a gas syringe is a common way of following this.

$(CH_3)_2C{=}CH_2(g) + HI(g) \rightarrow (CH_3)_3CI(g)$

$HCOOH(aq) + Br_2(aq) \rightarrow 2H^+(aq) + 2Br^-(aq) + CO_2(g)$



If drawing a gas syringe make sure you draw it with some measurement markings on the barrel to show measurements can be made.

Measurement of change of mass

This works if there is a gas produced which is allowed to escape. Works better with heavy gases such as CO_2

$HCOOH(aq) + Br_2(aq) \rightarrow 2H^+(aq) + 2Br^-(aq) + CO_2(g)$

Titrating samples of reaction mixture with acid, alkali, sodium thiosulphate etc

Small samples are removed from the reaction mixture, quenched (which stops the reaction) and the titrated with a suitable reagent.

$HCOOCH_3(aq) + NaOH(aq) \rightarrow HCOONa(aq) + CH_3OH(aq)$ The NaOH could be titrated with an acid

$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$ The H^+ could be titrated with an alkali

$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$ The I_2 could be titrated with sodium thiosulphate

Colorimetry.

If one of the reactants or products is coloured then colorimetry can be used to measure the change in colour of the reacting mixtures

$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow 2H_2O(l) + I_2(aq)$

The I_2 produced is a brown solution

Measuring change in electrical conductivity

Can be used if there is a change in the number of ions in the reaction mixture

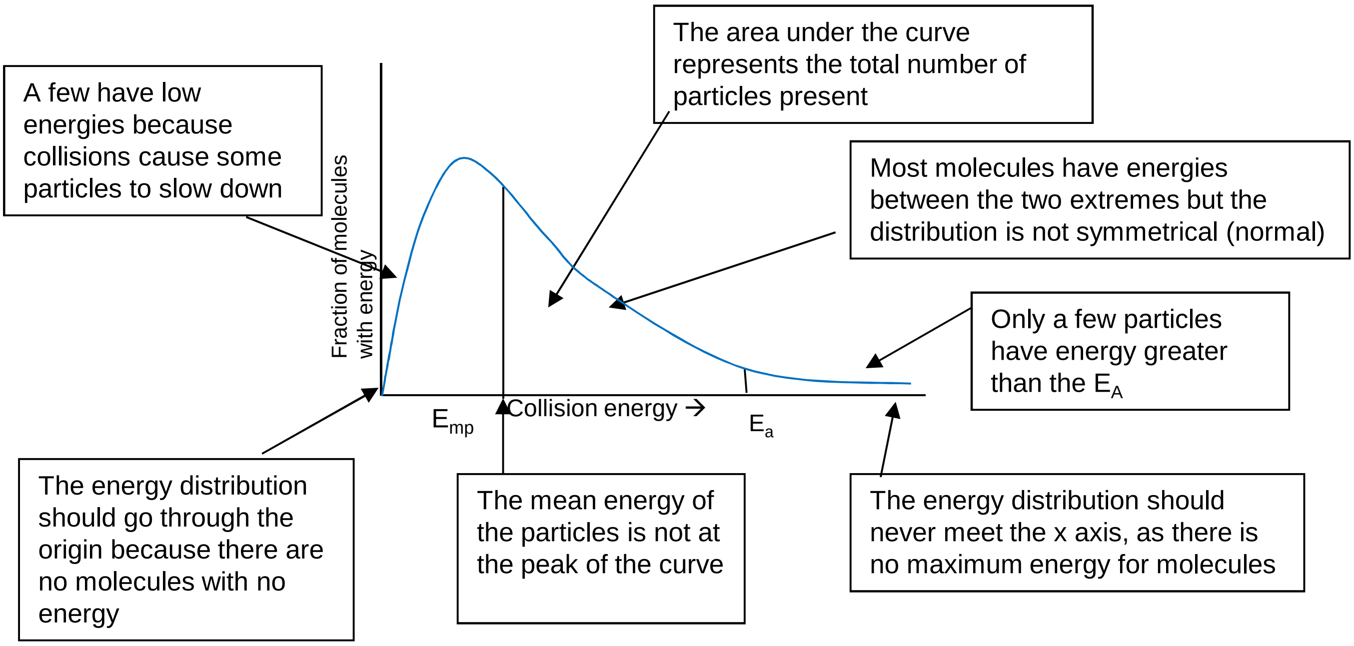
$HCOOH(aq) + Br_2(aq) \rightarrow 2H^+(aq) + 2Br^-(aq) + CO_2(g)$

Maxwell Boltzmann Distribution

Progress of Reaction

The Maxwell-Boltzmann energy distribution shows the spread of energies that molecules of a gas or liquid have at a particular temperature

Learn this curve carefully

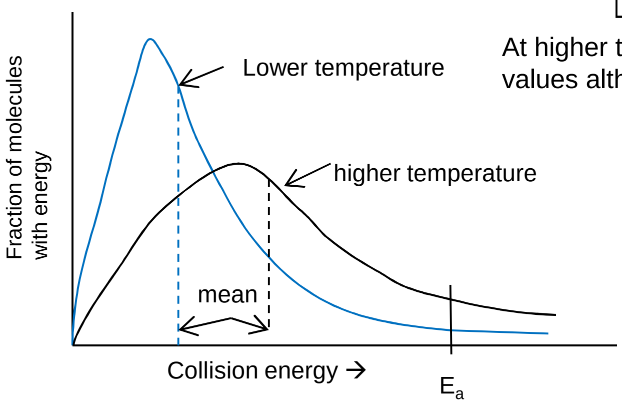


Q. How can a reaction go to completion if few particles have energy greater than Ea?

A. Particles can gain energy through collisions

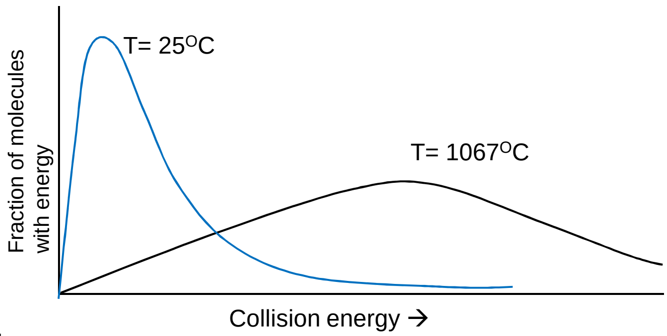
Increasing Temperature

As the temperature increases the distribution shifts towards having more molecules with higher energies



The total area under the curve should remain constant because the total number of particles is constant

At higher temps both the E_{mp} and mean energy shift to high energy values although the number of molecules with those energies decrease

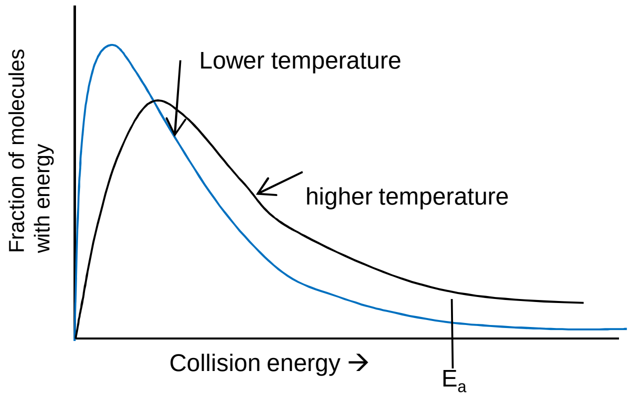


At higher temperatures the molecules have a wider range of energies than at lower temperatures.

Effect of Increasing Temperature

At higher temperatures the energy of the particles increases. They collide more frequently and more often with energy greater than the activation energy. More collisions result in a reaction

As the temperature increases, the graph shows that a **significantly bigger** proportion of particles have **energy greater than the activation energy**, so the **frequency of successful collisions increases**



Effect of Increasing Surface area

Increasing surface area will cause **collisions to occur more frequently** between the reactant particles and this increases the rate of the reaction.

Effect of Catalysts

If the activation energy is lower, **more particles will have energy > E_A**, so there will be a higher frequency of effective collisions. The reaction will be faster