

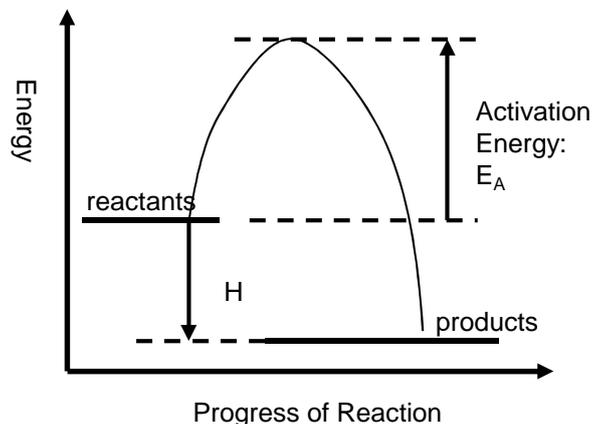
9. Introduction to Kinetics

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

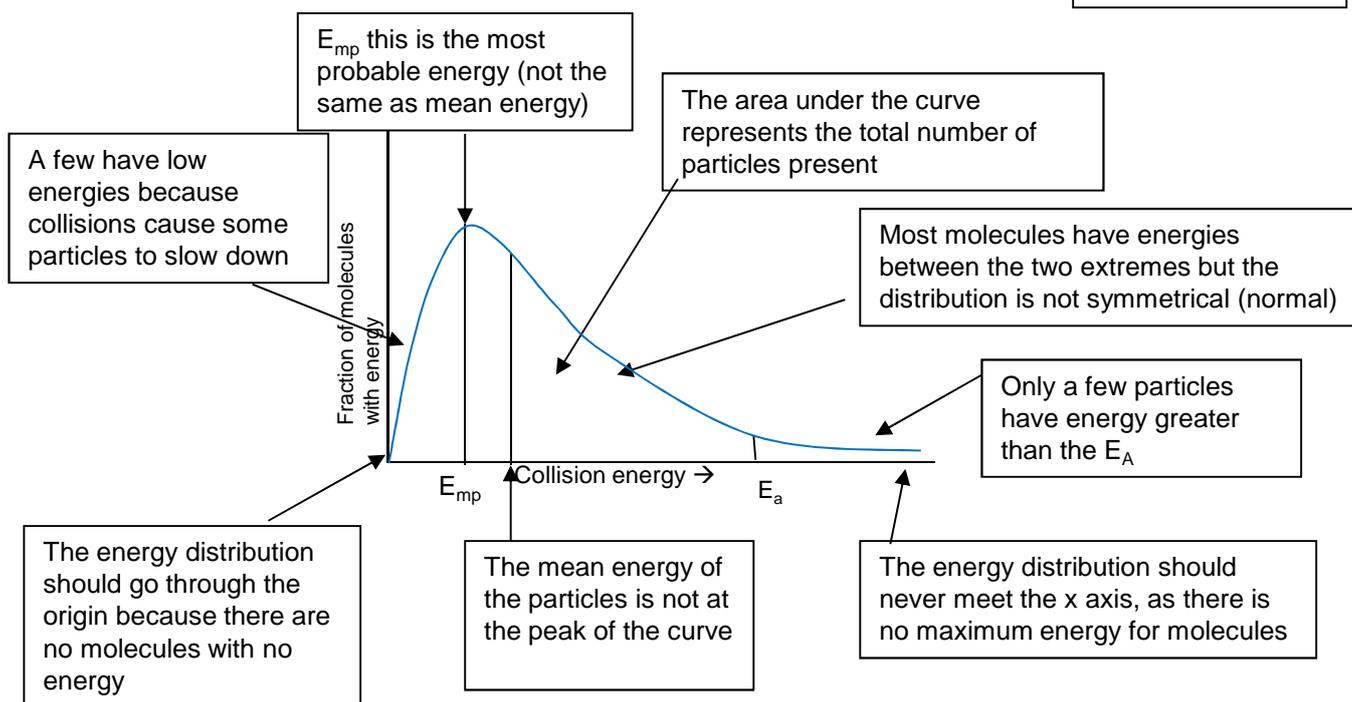
The **Activation Energy** is defined as the **minimum** energy which particles need to collide to start a reaction



Maxwell Boltzmann Distribution

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

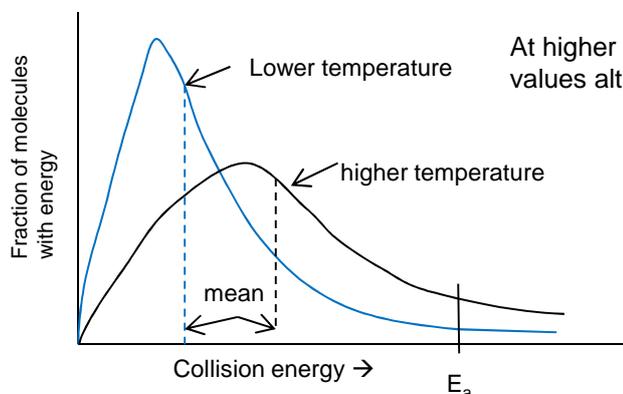


Q. How can a reaction go to completion if few particles have energy greater than E_a ?

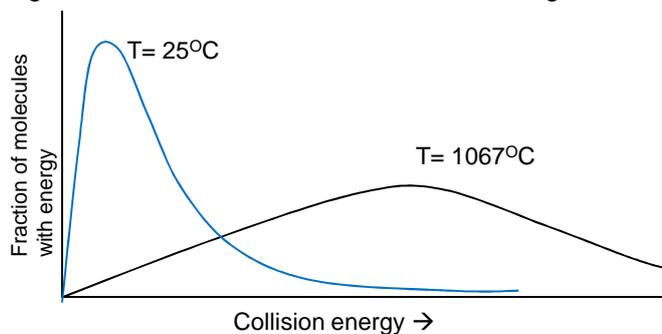
A. Particles can gain energy through collisions

Increasing Temperature

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



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



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

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

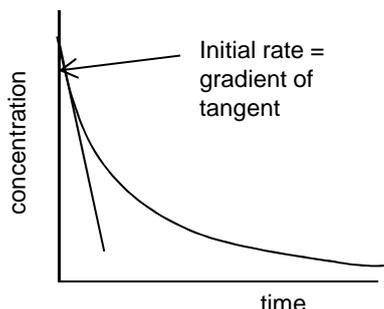
Measuring Reaction Rates

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

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. $\text{Na}_2\text{S}_2\text{O}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{SO}_2 + \text{S} + \text{H}_2\text{O}$
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**.

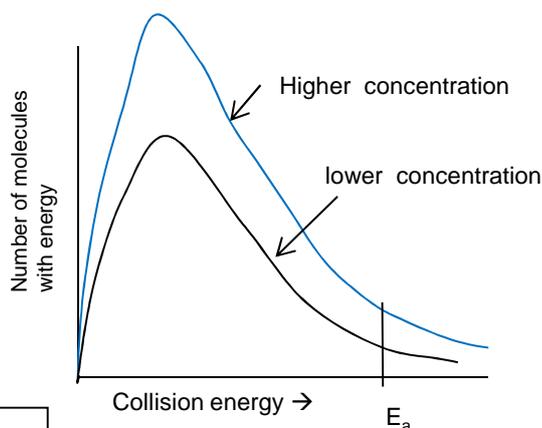
Effect of Increasing Concentration and Increasing Pressure

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.

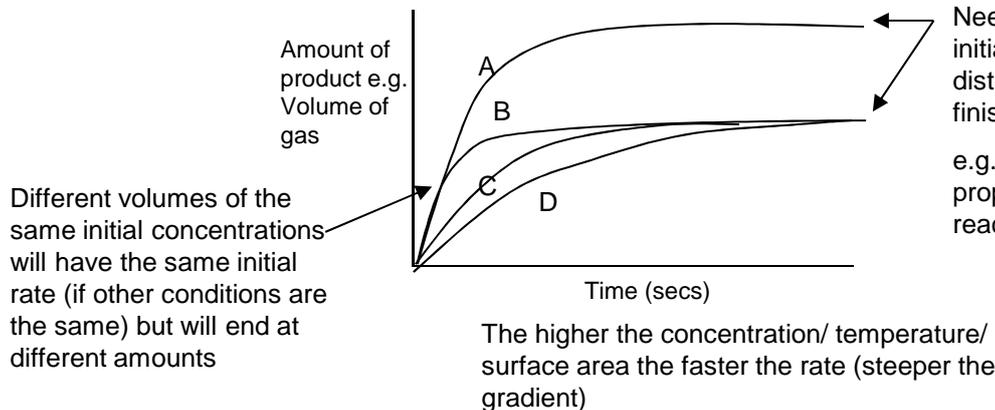
If concentration increases, the shape of the energy distribution curves do not change (i.e. the peak is at the same energy) so the E_{mp} and mean energy do not change

They curves will be higher, and the area under the curves will be greater because there are **more** particles



More molecules have energy $> E_a$ (although not a greater proportion)

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

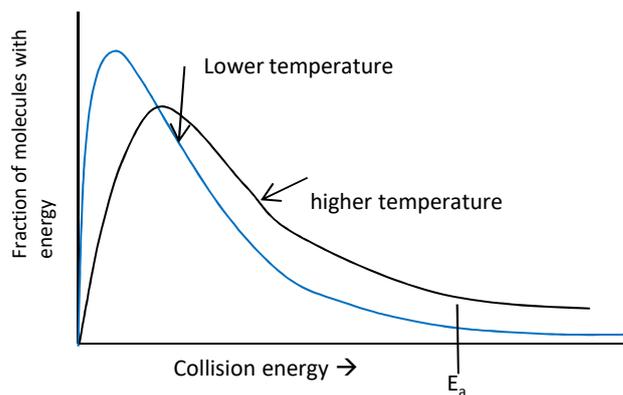
Different volumes of the same initial concentrations will have the same initial rate (if other conditions are the same) but will end at different amounts

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

Effect of 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

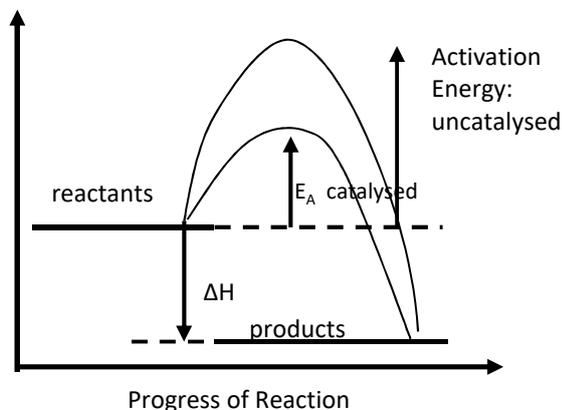
Increasing surface area will cause successful **collisions to occur more frequently** between the reactant particles and this increases the rate of the reaction.

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**

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

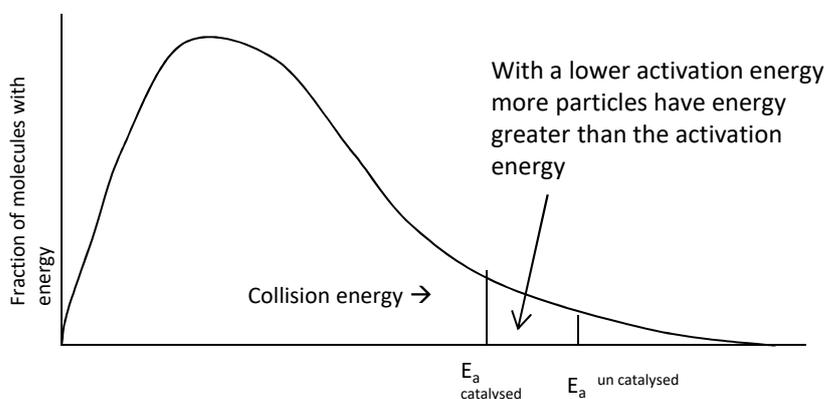


Industrially catalysts speeds up the rate allowing lower temp to be used (and hence lower energy costs) but have no effect on equilibrium

Environmental benefits of Catalysts

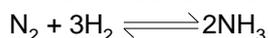
Catalysed reactions can occur at lower temperature so less fuel needed and fewer emissions from fuels. Catalysed reaction enables use of an alternative process with higher atom economy so meaning fewer raw materials needed and less waste products are produced

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



9 Introduction to Equilibrium

Many reactions are reversible



All reversible reactions reach an **dynamic equilibrium** state.

Dynamic equilibrium occurs when **forward** and **backward** reactions are occurring at **equal rates**. The **concentrations** of reactants and products stays **constant** and the reaction is continuous.

We use the expression '**position of equilibrium**' to describe the composition of the equilibrium mixture.

If the position of equilibrium favours the reactants (also described as "towards the left") then the equilibrium mixture will contain mostly reactants.

Le Chatelier's Principle

We use Le Chatelier's principle to work out how changing external conditions such as temperature and pressure affect the position of equilibrium

Le Chatelier's principle states that if an external condition is changed the equilibrium will shift to oppose the change (and try to reverse it).

Effect of Temperature on equilibrium

If temperature is increased the **equilibrium will shift to oppose** this and move in the **endothermic** direction to try and **reduce the temperature** by absorbing heat.

And its reverse

If temperature is decreased the **equilibrium will shift to oppose** this and move in the **exothermic** direction to try and **increase the temperature** by giving out heat.

Typical Exam question: What effect would increasing temperature have on the yield of ammonia?



Exam level answer : must include bold points

If temperature is increased the **equilibrium will shift to oppose** this and move in the **endothermic, backwards** direction to try to **decrease temperature**. The position of equilibrium will **shift towards the left**, giving a **lower yield of ammonia**.

Low temperatures may give a higher yield of product but will also result in slow rates of reaction. Often a compromise temperature is used that gives a reasonable yield and rate

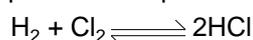
Effect of Pressure on equilibrium

Increasing pressure will cause the equilibrium to shift towards the side with **fewer moles of gas** to **oppose the change** and thereby **reduce the pressure**.

And its reverse

Decreasing pressure will cause the equilibrium to shift towards the side with **more moles of gas** to **oppose the change** and thereby increase the pressure.

If the number of moles of gas is the same on both sides of the equation then changing pressure will have no effect on the position of equilibrium



Typical Exam question: What effect would increasing pressure have on the yield of methanol?



Exam level answer : must include bold points

If pressure is increased the **equilibrium will shift to oppose** this and move towards the side with **fewer moles of gas** to try to **reduce the pressure**. The position of equilibrium will **shift towards the right** because there are 3 moles of gas on the left but only 1 mole of gas on the right, giving a **higher yield of methanol**.

Increasing pressure may give a higher yield of product and will produce a faster rate. Industrially high pressures are expensive to produce (**high electrical energy costs for pumping** the gases to make a high pressure) and the **equipment is expensive** (to contain the high pressures)

