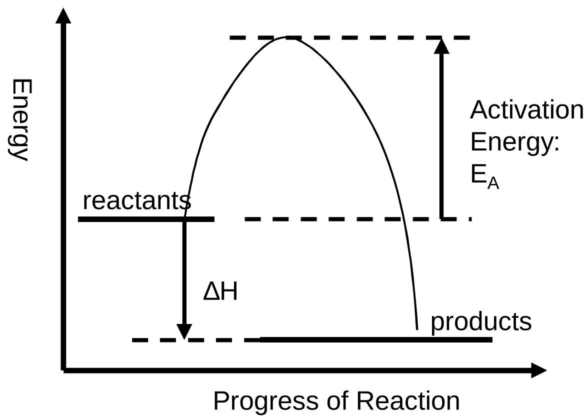
1.5 Kinetics

Collision theory

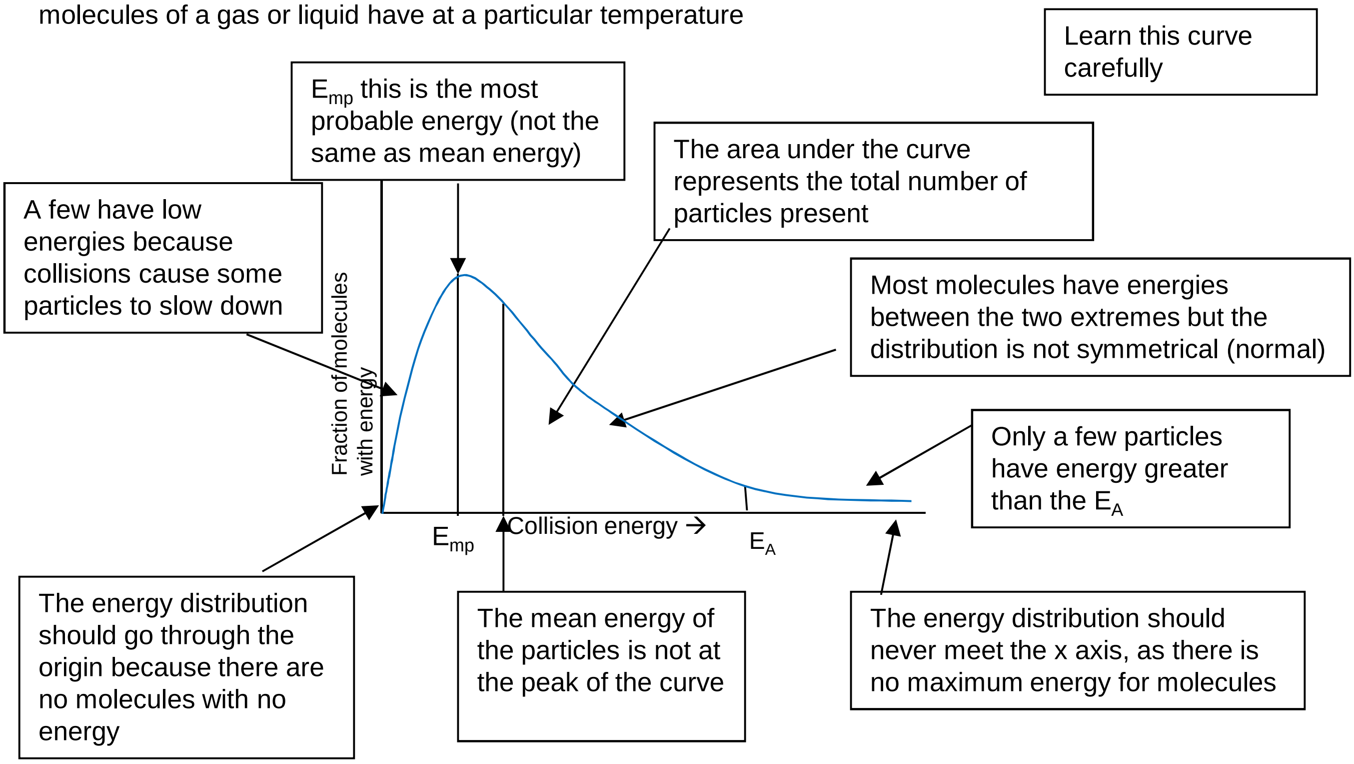
Reactions can only occur when collisions take place between particles having sufficient energy. The energy is usually needed to break the relevant bonds in one or either of the reactant molecules.
This minimum energy is called the **activation energy**.



The **activation energy, E_A,** 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



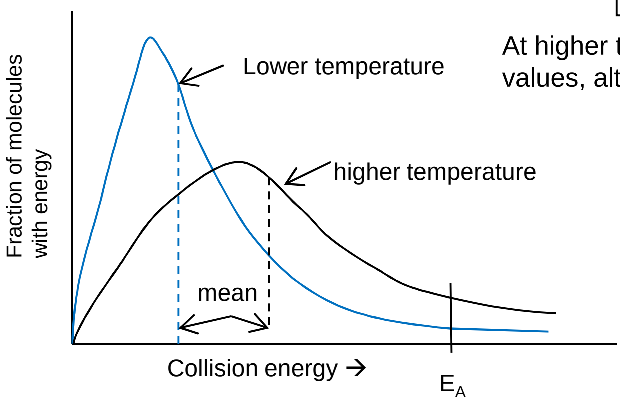
Q. How can a reaction go to completion if few particles have energy greater than E_A?

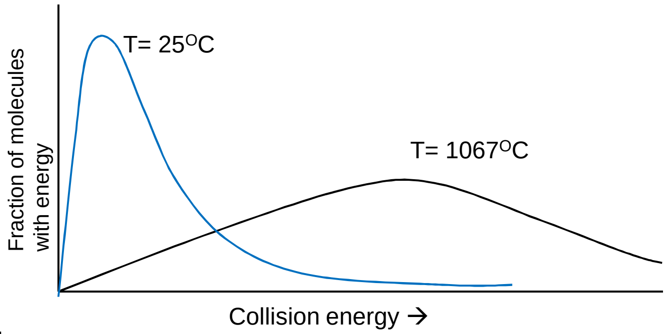
A. Particles can gain energy through collisions

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 higher 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.

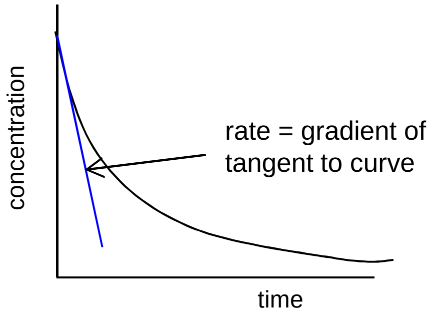
Measuring reaction rates

The rate of reaction is defined as the **change in concentration** of a substance **in unit time.**
The 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, by drawing a tangent to the curve (at different times) and calculating the gradient of the tangent.



In the experiment between sodium thiosulfate and hydrochloric acid we usually measure reaction rate as **1/time.** The time is the time taken for a cross placed underneath the reaction mixture to disappear due to the cloudiness of the sulfur . $Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2 + S + H_2O$
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 sulfur produced is **fixed and constant**.

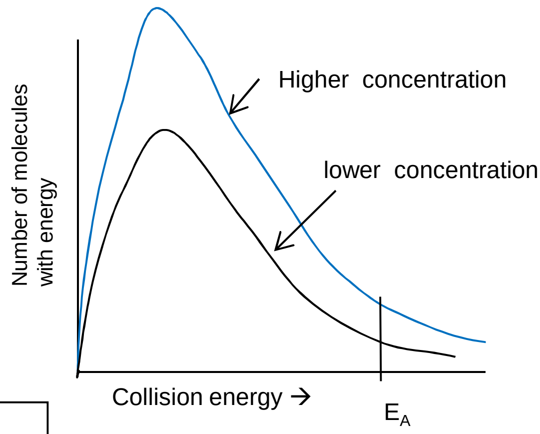
Effect of increasing concentration and increasing pressure

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.

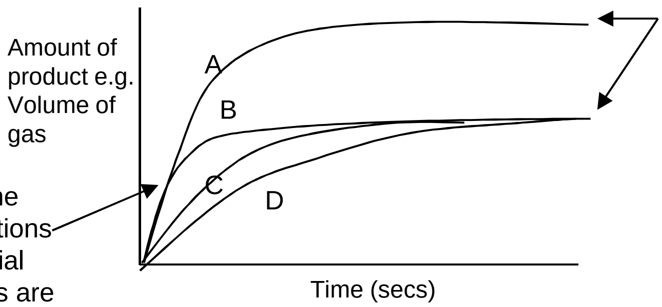
If concentration increases, the shape of the energy distribution curves do not change (i.e. the peak is at the same energy) so the E_{mp} and mean energy do not change.

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

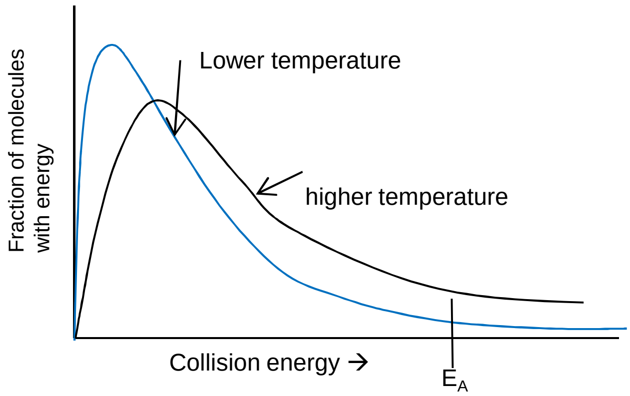
Different volumes of the same initial concentrations will have the same initial rate (if other conditions are the same) but will end at different amounts

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. The pariticles 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

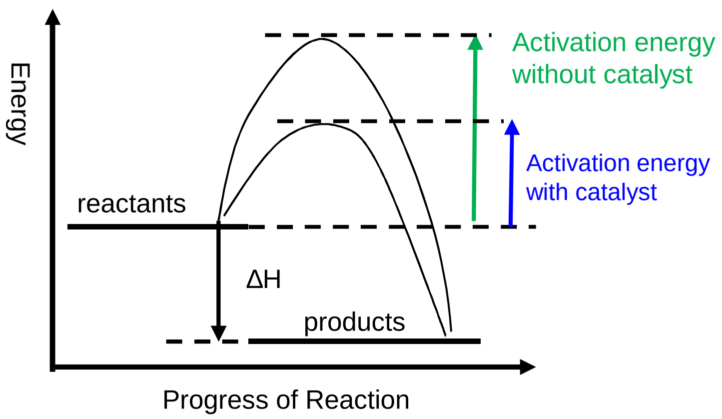
Increasing surface area will cause successful **collisions to occur more frequently** between the reactant particles and this increases the rate of the reaction.

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.



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.