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 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.

- $E_{mp}$, this is the most probable energy (not the same as mean energy).
- The area under the curve represents the total number of particles present.
- Most molecules have energies between the two extremes but the distribution is not symmetrical (normal).
- Only a few particles have energy greater than the $E_A$.
- The mean energy of the particles is not at the peak of the curve.
- The energy distribution should never meet the x axis, as there is no maximum energy for molecules.

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 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$_2$S$_2$O$_3$ + 2HCl → 2NaCl + SO$_2$ + S + H$_2$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

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.

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.