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.

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

Amount of product e.g. Volume of gas

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).

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.
**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 whereas the reactants are gaseous or in solution. The reaction occurs at the surface of the catalyst.

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

**Heterogeneous catalysis**

**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.

\[
(\text{CH}_3)_2\text{C}=\text{CH}_2(\text{g}) + \text{HI}(\text{g}) \rightarrow (\text{CH}_3)_2\text{Cl}(\text{g})
\]

\[
\text{HCOOH}(\text{aq}) + \text{Br}_2(\text{aq}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{Br}^- (\text{aq}) + \text{CO}_2(\text{g})
\]

**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 CO₂.

\[
\text{HCOOH}(\text{aq}) + \text{Br}_2(\text{aq}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{Br}^- (\text{aq}) + \text{CO}_2(\text{g})
\]

**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.

\[
\text{HCOOCH}_3(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{HCOONa}(\text{aq}) + \text{CH}_3\text{OH}(\text{aq})
\]

The NaOH could be titrated with an acid.

\[
\text{BrO}_3^-(\text{aq}) + 5\text{Br}^- (\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3\text{Br}_2(\text{aq}) + 3\text{H}_2\text{O}(\text{l})
\]

The H⁺ could be titrated with an alkali.

\[
\text{CH}_3\text{COCH}_3(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow \text{CH}_3\text{COCH}_2\text{I}(\text{aq}) + \text{H}^+(\text{aq}) + \text{I}^- (\text{aq})
\]

The I₂ 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.

\[
\text{H}_2\text{O}_2(\text{aq}) + 2\text{I}^- (\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{I}_2(\text{aq})
\]

The I₂ 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.

\[
\text{HCOOH}(\text{aq}) + \text{Br}_2(\text{aq}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{Br}^- (\text{aq}) + \text{CO}_2(\text{g})
\]
**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

- A few have low energies because collisions cause some particles to slow down
- The energy distribution should go through the origin because there are no molecules with no energy
- The mean energy of the particles is not at the peak of the curve
- 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 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

**Progress of Reaction**

Learn this curve carefully

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.

With a lower activation energy more particles have energy greater than the activation energy.