Introduction to kinetics and equilibria

Collision theory, rates of reaction and how to measure them, Maxwell-Boltzmann distributions, catalysts, dynamic equilibrium, and the effect of conditions on the position of equilibrium.

Collision theory and rate

For a reaction to occur, particles must **collide** with at least the **activation energy**, E_a (the minimum energy needed to start a reaction), and with the correct orientation. Most collisions do not result in reaction.

The **rate of reaction** is the change in concentration of a reactant or product per unit time (mol dm^{-3} s^{-1}).

Factors affecting the rate

Factor	Effect and explanation
Concentration (or pressure of a gas)	More particles per unit volume, so more frequent collisions and more successful collisions per second
Surface area of a solid	More particles exposed, so more collisions per second
Temperature	Particles move faster so collide more often, but mainly a **much greater proportion** have energy $\geq E_a$
Catalyst	Provides a different route with a lower activation energy

Calculating rate

- From the **time taken**: rate $\propto 1/t$.
- From a **graph**: the rate at a given time is the **gradient of the tangent** to the concentration–time (or volume–time) curve at that time. The **initial rate** is the gradient at $t = 0$.

NOTE

Rates of reaction practicals: marble chips and acid (measure the volume of gas or the loss in mass), the decomposition of hydrogen peroxide with manganese(IV) oxide, and sodium thiosulfate with acid (time for a cross to disappear).

Note Academy

Maxwell–Boltzmann distribution

The distribution shows the number of molecules with each energy at a given temperature.

- The curve starts at the origin (no molecules have zero energy), rises to a peak and falls, but **never touches the axis**.
- The area under the curve is the total number of molecules, and is the same at all temperatures.
- E_a is marked on the energy axis. The area to its right is the number of molecules able to react.

Raising the temperature: the peak moves to the right and is lower; the curve is flatter. The area beyond E_a increases a lot, so a much greater proportion of molecules can react.

> **A small rise in temperature increases the rate mainly because a larger fraction of collisions have energy greater than or equal to E_a, not because of the increase in collision frequency.**

Catalysts

A **catalyst** speeds up a reaction without being used up, by offering an alternative reaction route of **lower activation energy**. On the diagram, mark a second E_a to the left; more molecules have energy above it, though the distribution of energies is the same.

A reaction profile shows enthalpy against progress. A catalysed route has a **lower peak**, and if the catalyst forms an intermediate, two lower peaks with a dip between them. The enthalpy change ΔH is unchanged.

Catalysts make industrial processes more **sustainable** because they work at lower temperatures (less energy used, fewer emissions) and can allow reactions with a **higher atom economy**.

Dynamic equilibrium

Many reactions are **reversible** (⇌). In a closed system the reaction reaches **dynamic equilibrium** when:

- the **rate of the forward reaction equals the rate of the reverse reaction**, and
- the **concentrations** of reactants and products **stay constant**.

Both reactions are still happening.

Le Chatelier's principle

If a system at equilibrium is subjected to a change, the position of equilibrium shifts to **oppose** the change.

Note Academy

Change	Shift
Increase in concentration of a reactant	Towards the products
Increase in pressure	Towards the side with fewer moles of gas
Increase in temperature	In the **endothermic** direction
Decrease in temperature	In the **exothermic** direction
Catalyst	No change in position (the rates of both directions rise equally)

TRY IT

For $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H = -92$ kJ mol^{-1}, predict the effect of high pressure and of high temperature on the yield of ammonia.

High pressure shifts the equilibrium to the right (4 moles of gas to 2), increasing the yield. High temperature shifts it to the left (the endothermic direction), reducing the yield.

Compromise conditions

Industrial processes balance the yield and the rate. In the Haber process (about 450 °C, 200 atm, iron catalyst) a lower temperature would give a better yield but too slow a rate, and a higher pressure would give more ammonia but would be costly and a safety risk. A compromise is used.

NOTE

Demonstrations of equilibria: the NO_2/N_2O_4 system in a syringe (brown NO_2 is favoured at higher temperature), and the iodine chlorides ICl and ICl_3.

Note Academy