RATE OF REACTION : REVERSIBLE REACTIONS

Rate of reaction measures how the concentration of the reactant or product changes per unit time.

$$\text{Rate of reaction} \propto \frac{1}{\text{time}}$$

$$\frac{1}{\text{Large value for time}} = \text{slow rate of reaction}$$

$$\frac{1}{\text{small value for time}} = \text{fast rate of reaction}$$

Example: $A \longrightarrow B$

Given:
Initial conc = $2 mol/dm^3$
Final conc = $0.2 mol/dm^3$

$\text{Rate} \propto [A]$ → Remember that [ ] represents concentration

$$\text{Rate} = \frac{k \Delta [A]}{\Delta t}$$

$$\Delta [A] = 0.2 - 2$$
$$= -1.8$$

↳ Ignore the - sign and express rate as a positive term

KINETIC / MOLECULAR COLLISIONS THEORY...

States that...

For a reaction to take place, the reactant particles must collide with enough energy (activation energy) to break existing bonds and with the correct orientation, to bring reactive sites closer together so new bonds are made

- Succesful collisions are required to convert reactants to products
- If number of collisions increases ⟶ the rate of reaction increases.

Activation energy is the minimum amount of energy required to convert reactants to products

OR

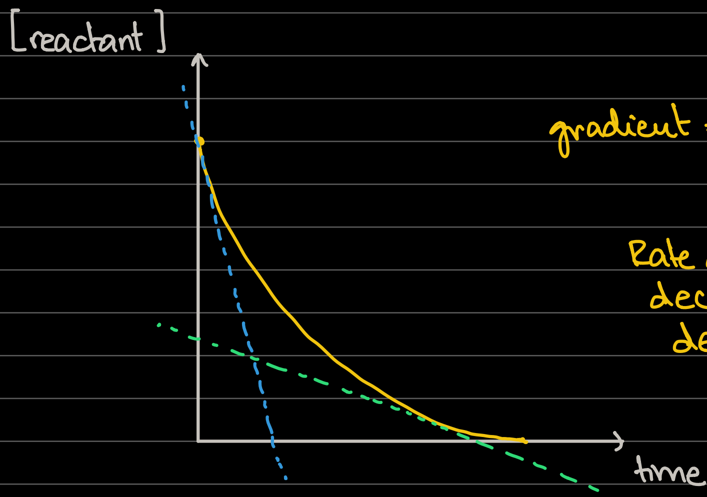
Minimum amount of energy that colliding particles must possess in order to react.

FACTORS AFFECTING RATE

1. Concentration

As the concentration of one or more reactants increases, the frequency of collisions increases and rate increases

- Rate is fastest at the start of the reaction as the conc. of the reactants is the highest



gradient = $\frac{\Delta y}{\Delta x}$ = rate of reaction

Rate decreases over time, as the reactant conc decreases → and as collision frequency decreases

2. Pressure

- Only reactions involving gases will be affected by changes in pressure

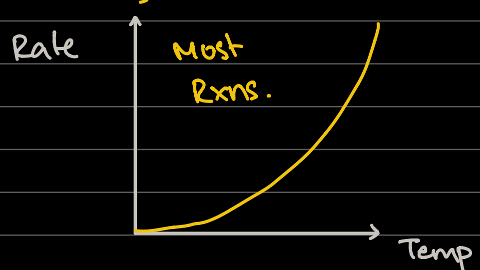
$$\left[\text{Pressure} \propto \frac{1}{\text{Volume}} \right] \rightarrow \text{Boyle's Law}$$

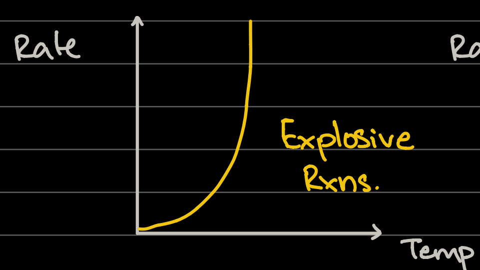
Increase pressure → Volume decreases → Particles are closer together → Frequency of collision increases → Rate of Rxn increases

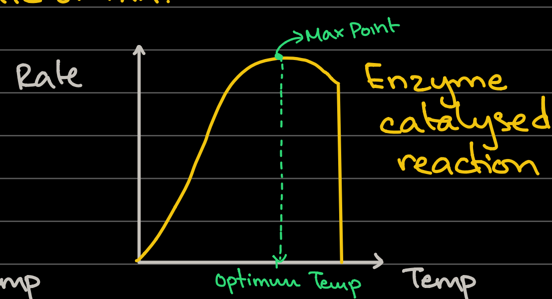
3. Temperature

- An increase in temperature increases the kinetic energy of all particles
- The particles move faster with more energy and collide more frequently
- Therefore, rate increases

- **Roughly** → 10°C rise in temperature doubles the rate of rxn.







Note: enzymes work best at an optimum temperature (35°C to 45°C).
At higher temperatures, enzymes are denatured (their structure is destroyed)

MAXWELL-BOLTZMANN DISTRIBUTION

In a gaseous reaction, how frequently the particles collide depends on 3 factors

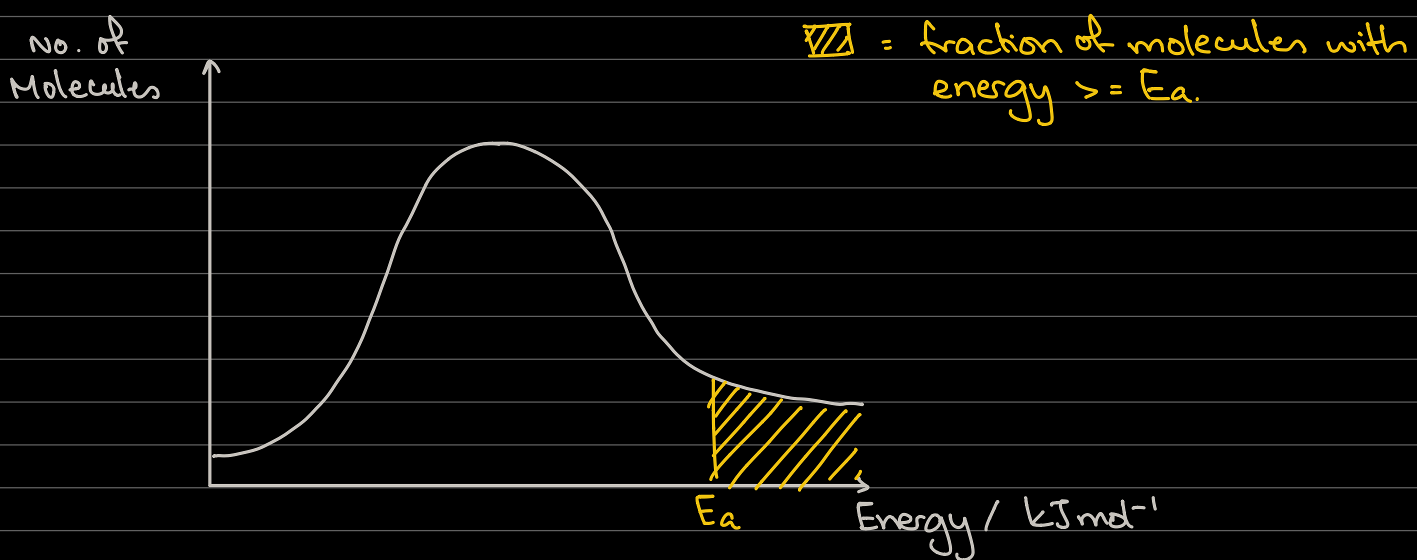
(i) the size (radius) of the molecules:
As size increases, greater chances of collision → rate should increase

(ii) the mass of the molecules
As mass increases, the particles slow down → rate decreases

(iii) the temperature
As temperature increases, kinetic energy increases → more frequent energetic collisions → rate increases

Points i and ii cancel each other out. So rate is only affected by changes in temperature (due to collisions)

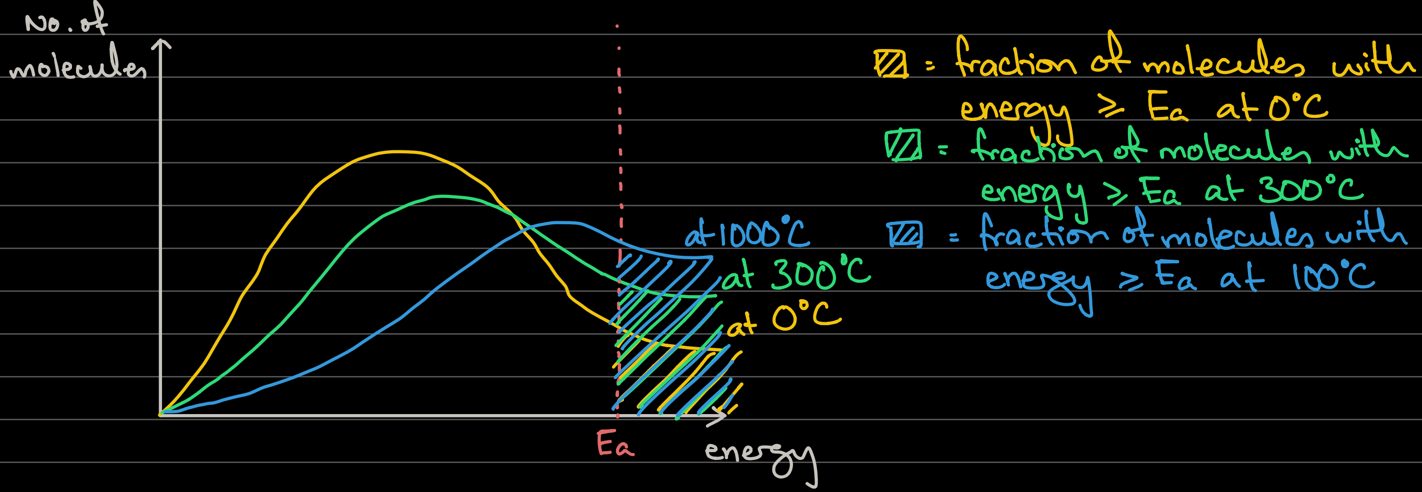
- The Maxwell-Boltzmann Distribution shows how many molecules in a sample can have different amounts of energies.



- There are very few molecules with very low energy
- Most molecules have a moderate amount of energy, which is the most probable energy
- There are very few molecules with very high energy values.

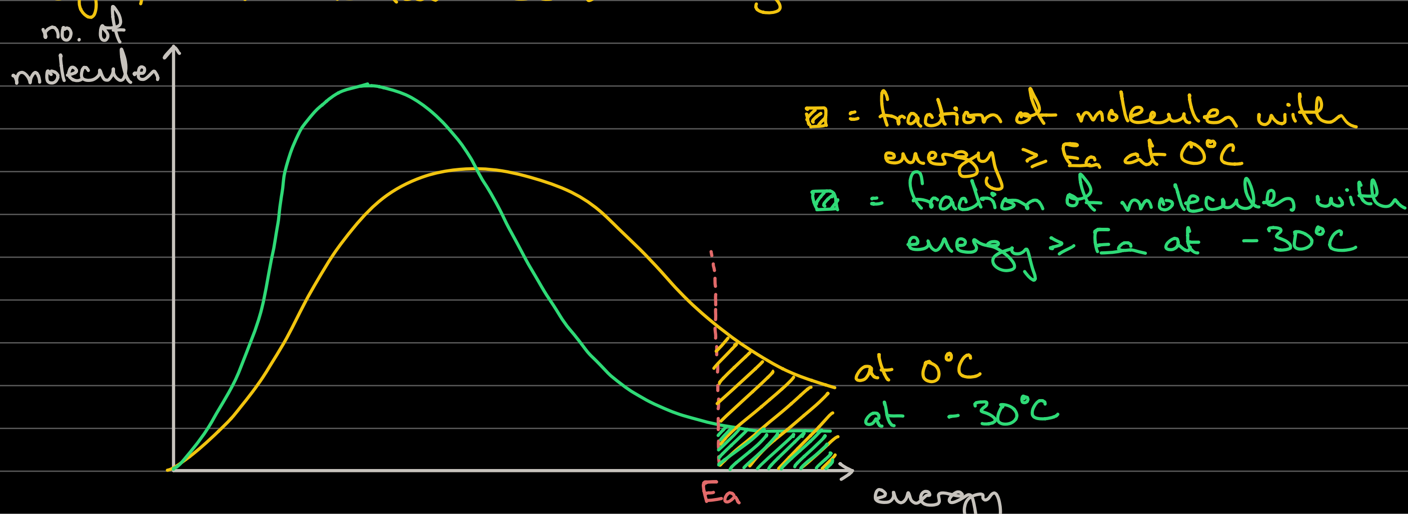
- The line Ea marked shows the high activation energy for a particular reaction and the shaded area shows the fraction of molecules that have activation energy ≥ Ea.

EFFECTS OF TEMPERATURE ON THE MAXWELL-BOLTZMANN DISTRIBUTION



- At higher temperatures, there is an increase in the proportion of molecules with energy greater than or equal to activation energy
- So the number of effective collisions increase, and the rate of reaction increases.
- Area under the curve stays constant as this represents the total number of molecules.
- The average energy of the particles increases, as all particles gain kinetic energy at higher temperatures ; hence the curve shifts to the right
- So at higher temperatures, there is a greater proportion of molecules that has energy at least equal to the Ea.

When the temperature is lowered... the peak shifts leftwards and increases in height, while the tail decreases in height.



EFFECTS OF CATALYSTS ON MAXWELL-BOLTZMANN DISTRIBUTION

Catalyst:

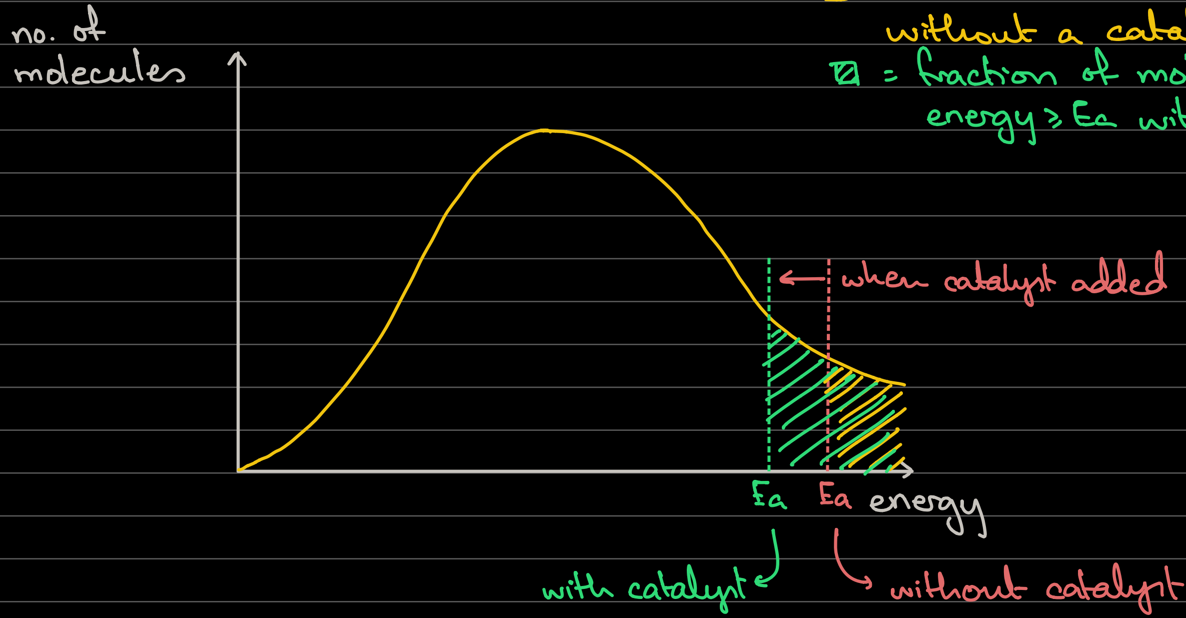
A substance that speeds up the rate of a reaction without getting consumed in the reaction.

How it works:

The catalyst works by providing an alternate pathway with a lower activation energy.

▨ = fraction of molecules with energy ≥ Ea without a catalyst

▨ = fraction of molecules with energy ≥ Ea with a catalyst

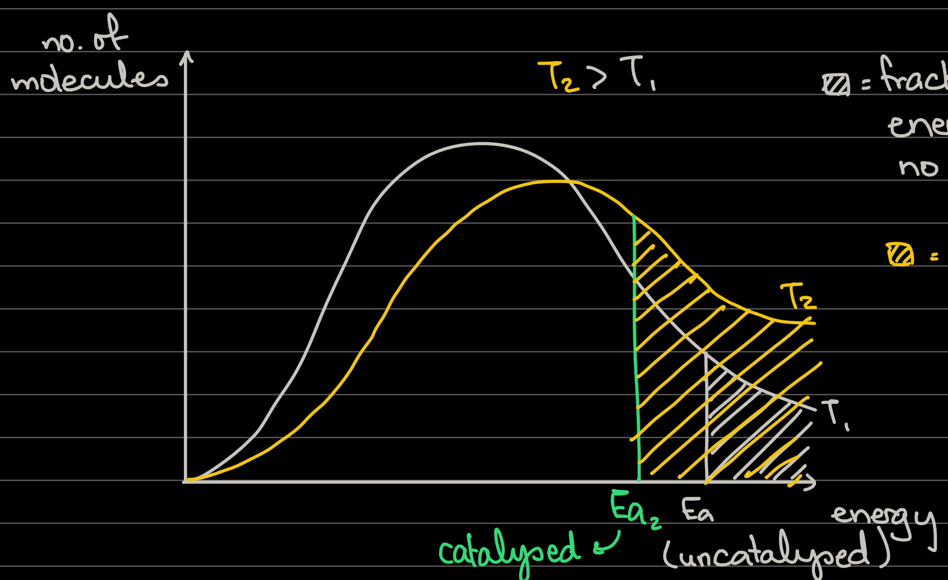


Example Question 1:

Q. What is the effect of an increase in temperature and the use of a catalyst on the Maxwell-Boltzmann distribution? Label appropriately.

▨ = fraction of molecules with energy ≥ Ea with temp T_1 and no catalyst

▨ = fraction of molecules with energy ≥ Ea_2 with temp T_2 and a catalyst



Some other points on catalysts:

- A catalyst increases the rate of both the forward and the backwards reaction.
- A catalysed reaction does not yield more product than one without a catalyst, but it yields the product more quickly
- A catalyst that takes part in a reaction is regenerated
- Catalysts are needed / used in small non-stoichiometric quantities
- A solid catalyst works more effectively when it is in a powdered form as it has a larger surface area for the reaction to take place on

Catalysts

Homogenous Catalysts

Is in the same state or physical phase as the reactants (as the reaction it catalyses)

Heterogenous Catalysts

Is in a different state or physical phase from the reactants

Homogenous Catalyst:

1. Esterification

catalyst

$$CH_3CH_2OH\,(l) + CH_3COOH\,(aq) \xrightleftharpoons{\text{conc. } H_2SO_4} CH_3CO_2CH_2CH_3\,(l) + H_2O\,(l)$$

2. Gas-phase reactions (NOX pollution)

$$NO_2\,(g) + SO_2\,(g) \longrightarrow SO_3\,(g) + NO\,(g)$$

catalyst

from factory emissions

$$NO\,(g) + \tfrac{1}{2}O_2\,(g) \longrightarrow NO_2\,(g)$$ → catalyst regenerated

- NO_2 catalyses the oxidation of SO_2 to SO_3 in the atmosphere

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(l)$$

↳ Acid rain

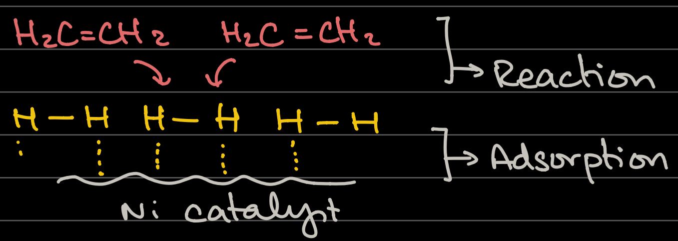
Heterogeneous Catalysts:

1. Cracking → uses $Al_2O_3(s)$ as catalyst
2. Polymerisation → uses $Al_2O_3(s)$ as catalyst
3. Hydrogenation of alkenes → uses $Ni(s)$ as catalyst
4. Haber → uses $Fe(s)$ as catalyst
5. Contact process → uses $V_2O_5(s)$ as catalyst
6. Catalytic Converter in car engines

How do solid catalysts work?

Solid catalysts work by a process known as adsorption
↳ "to loosely attach"

- The catalyst "holds on" to the gaseous reactants which helps in bond breaking and bond making



ENZYMES

- enzymes are biological catalysts
- speed up the rate of a biochemical reaction by providing an alternate route with a lower E_a.

- enzymes are proteins → made up of amino acids
  ↳ Proteins are polymers made up of several thousand amino acid monomer units and folded in special shapes

- Enzymes work best at an optimum temperature of 37°C to 40°C.

- At very high temperatures, their structure and the shape of their active site is destroyed
  ↳ so they stop working

- At very low temperatures, enzymes are inactive, but will work again at optimum temps.

- Enzymes are pH sensitive

- Enzymes are specific in nature, ie. a certain enzyme will catalyse only a specific reaction