

Rates of reaction | Topic Notes

- The reactions between acidified potassium permanganate and ammonium iron (II) sulfate are very rapid. However the reaction between oxalic acid and the permanganate is very slow, 30 minutes to go to completion.
- **The rate of reaction is the change in concentration per unit time of any one reactant or product.**
- **Average rate = $\frac{\text{total volume of Oxygen given off (cm}^3\text{)}}{\text{time for reaction to complete (secs)}} \times 100$**
- The rate of reaction at a particular instant is the instantaneous rate of reaction. To find the instantaneous rate you volume (Y) against time (X) on a curve and at the instant to be measure, draw a tangent to the curve. Find 2 points on the tangent and find the slope of it.
- Instantaneous rate of reaction = slope of tangent

Factors affecting rates of reactions

1. Nature of reactants

- Reactions that do not involve bond breaking but simply the coming together of oppositely charged species in a solution are usually fast at room temperature. For example $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}$ precipitate
- Reactions that involve the breaking of covalent bonds are slower to take place at room temperature.
- For example acidified sodium dichromate and ethanal is much slower than acidified sodium dichromate and ammonium iron (II) sulfate solution.

2. Particle Size

- The smaller the particle size the faster the reaction.
- This is exemplified with the reaction of dilute hydrochloric acid and marble chips. If the marble chips are powdered the rate at which CO₂ is released increases hugely, if the marble chips were big lumps it would bubble CO₂ at a much steadier rate. **CaCO₃ + 2HCl → CaCl₂ + H₂O + CO₂**
- Very finely divided particles may cause a dust explosion for example when lycopodium powder is blown over a candle in a coffee tin, the force of the explosion can lift the lid high into the air. This is a problem in flour mills, coal mines etc..

3. Concentration

- Changing the concentrations of reactants in a chemical reaction alters the rate of reaction.

This is shown in the following experiment:

To study the effect of concentration on the rate of reaction using sodium thiosulfate and hydrochloric acid.

- Use a graduated cylinder to pour 100 cm³ of sodium thiosulfate 0.2 M into a conical flask. Place the conical flask onto a white sheet of paper with a mark
- Using another graduated cylinder pour in 10cm³ HCl.
- Start the stopclock and watch the yellow sulfur precipitate reach a stage that the cross is no longer visible,
- Stop clock and note time taken.
- Repeat using 80cm³ thiosulfate and 20cm³ water - 80% of 0.2 molar which 0.16 molar solution, repeat with 0.12 molar solution, 0.08, 0.04, 0.02.
- Plot time taken on Y and concentration on X. **Rate of reaction is proportionate to 1/time**, if necessary plot rate on Y axis and concentration on X axis.
- As concentration increases rate increases

- As concentration increases time decreases

4. Temperature

- The cooler it is the slower the reaction, fridges keep food fresh by postponing chemical reactions.
- Repeat the experiment above using 0.05 molar thiosulfate at different temperatures, 15, 20, 30, 40, 50, 60, 70. Heat the conical flask to the temperature with the thiosulfate before adding the acid.
- As temperature increases the rate increases
- As temperature increases time decreases

Catalysts

A catalyst is a substance the ALTERS the rate of a reaction but is not consumed in the reaction.

Negative catalysts or inhibitors slow down the rate, e.g. Glycerine added to hydrogen peroxide to slow down rate of decomposition.

Properties:

- **Catalysts are recovered chemically unchanged at the end of an experiment.** For example if the mass of manganese dioxide is measured before being used in hydrogen peroxide's decomposition, it will be the same mass afterwards.
- **Catalysts tend to be specific.** They may catalyse one reaction but may not have the same effect on a similar one. Biological catalysts are enzymes produced by living cells and are extremely specific. Catalase in the liver decomposes hydrogen peroxide into oxygen as H_2O_2 is highly toxic in living

cells. Also Lysozyme breaks down cell walls of bacteria and help protect us from infection.

- **Catalysts need only be present in very small amounts.** Increasing amount of catalyst doesn't necessarily increase the rate of reaction.
- In the case of equilibrium reactions catalysts **help the reaction achieve equilibrium more quickly. it doesn't affect the position of the equilibrium or the final composition of the mixture in the reaction.**
- **Action of a catalyst may be destroyed by certain substances called catalytic poisons.** E.g. Lead poisons catalysts in catalytic converters, arsenic inhibits actions of certain enzymes in the body.

Types of Catalysis:

- **Homogenous catalysis**

This is catalysis in which both the reactants and catalyst is in the same phase. e.g. Iodine snake. Potassium iodide solution is added to washing up liquid and hydrogen peroxide. Potassium iodide catalyzes decomposition of hydrogen peroxide into water and oxygen. The catalyst and reactants are both liquids.

- **Heterogenous Catalysis**

When the reactants and catalyst is in different phases. I.e. there is a boundary between the reactants and catalysts. The decomposition of hydrogen peroxide (liquid) catalyzed by manganese dioxide (solid).

- **Autocatalysis**

One of the products of the reaction catalyzes the reaction. So when potassium permanganate is added to ammonium iron (ii) sulfate, the first few drops were decolorized slowly but subsequent drops were decolorized more rapidly because the reaction was catalyzed by Mn^{2+} ions formed in the reaction.

Mechanisms of Catalysis

1. The intermediate formation theory

- Arrhenius suggested that a catalyst works by forming an intermediate compound. One of the reactants works by combining with the catalyst to form an intermediate compound, may only exist for a short period and can be difficult to detect.



- The iodine snake experiment shows the intermediate formation theory. It is catalyzed by presence of I⁻ ions.
- One of the hydrogen peroxide molecules reacts with I⁻ to form an intermediate IO⁻ compound. $H_2O_2 + I^- \longrightarrow H_2O + IO^-$
- The intermediate then reacts with another hydrogen peroxide molecule to form the products and regenerate the catalyst. $H_2O_2 + IO^- \longrightarrow H_2O + O_2 + I^-$
- Overall reaction is $2H_2O_2 \longrightarrow 2H_2O + O_2$

2. Surface Adsorption theory.

- This explains most **heterogenous catalysis**.
- **Adsorption refers to the accumulation of substances at the surface of another substance.**
- The formation of water on platinum (platinum if finely divided catalyzes formation of water).

- The hydrogen and oxygen molecules settle on the surface of the platinum, the increased concentration of the molecules on the surface of the catalyst makes it more likely that the molecules will collide and react with each other and that a chemical reaction will occur.
- They are held on surface by temporary bond of the vacant D orbitals of platinum and the molecules.
- The oxygen and hydrogen molecules then react to form water molecules on surface of platinum
- Desorption is when the products leave the surface of the catalyst. The more finely divided the catalyst the better as it has an increased surface area over which adsorption can take place.

Catalytic Converters:

- Exhaust fumes from motor vehicles are a major source of air pollution. Exhaust fumes contain Carbon monoxide (from incomplete combustion of fuel hydrocarbons), Nitrogen Monoxide (fuel burned in air at high temperatures oxidizes the nitrogen in air slightly to form NO_x compounds), Nitrogen dioxide and unburned hydrocarbons.
- CO is colorless, odorless and tasteless and is highly poisonous
- NO_x compounds are highly toxic and contribute to acid rain.
- Unburned hydrocarbons can cause smog
- A catalytic converter is fitted to the exhaust system and converts environmentally harmful gases into harmless gases.
- Thin coating of Platinum, Palladium and Rhodium on a ceramic or metal 'honeycomb' inside a stainless steel case.
- The catalysts are spread over the surface of the honeycomb with a huge surface area.
- $2\text{CO} + 2\text{NO} \xrightarrow{(\text{Pt/Pd/Rh})} 2\text{CO}_2 + \text{N}_2$
- Forms carbon dioxide and nitrogen and water.

Collision theory and activation energy:

- For a reaction to occur the reacting particles must collide with each other.
- A collision only results in the formation of products if a certain minimum energy is exceeded in the collision. This is an effective collision.
- When an effective collision occurs bonds are broken and new bonds are formed, bringing about the formation of products.
- The rate of reaction depends on both the number of collisions of reacting particles per second and the fraction of these collisions which are effective.
- The number of effective collisions leads to formation of products.
- The activation energy is the minimum energy colliding particles must have in order for a reaction to occur and effective collisions to occur.
- When molecules with low energies collide they simply bounce apart without a reaction taking place, molecules with higher energies collide and a chemical reaction can occur. Heat energy causes particles kinetic energy to increase and this explains why higher temperatures lead to faster rates of reactions.
- If a large activation energy is required only a small number of molecules will have enough energy to pass over the barrier per second - slower reaction rate.
- If a small E_a energy is required the rate is faster. (Reaction profile diagrams)
- **Nature of reactants:** Only a small amount of E_a required for merely oppositely charged species colliding together as opposed to energy required to break covalent bonds.
- **Particle size:** The smaller particles have a greater surface area over which collisions can take place, more collisions increase the chance of effective collisions
- **Concentration:** If concentration increases number of particles and collisions increase.

- **Catalyst:** A catalyst works by providing an alternative reaction pathway which requires a lower activation energy, therefore reacting molecules need less energy for effective collisions.

To monitor rate of production of oxygen from hydrogen peroxide using manganese dioxide as a catalyst:

- Hold conical Flask of hydrogen peroxide sideways (50 cm³ of 20 volume H₂O₂), with stopper and delivery tube. The manganese dioxide is in the neck of the flask. tilt the flask so that the hydrogen peroxide comes into contact with it.
- Every 30 seconds read the volume of gas produced in the graduated cylinder in the water trough to which the delivery tube leads to.
- Plot volume of O₂ against time (Y against X).
- Average rate is the volume of gas given off over the total time for the reaction to complete in cm³ a second.
- Instantaneous rate is found by getting the slope of the tangent to the point of interest.