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Class 11
Chemistry

Chapter 7
Chemical Kinetics
Handwritten Notes

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CH 07 : CHEMICAL BONDING

Chemical Reactions

Chemical reactions are dynamic processes in which matter and energy change continously. Different chemical reactions occur at a variety of rates from rapid to very slow. Types of reactions: fast reaction, slow reaction, moderate reaction.

Chemical Kinetics

The branch of chemistry which deals with rates of chemical reactions, mechanisms and the factors that affect the rates of chemical reactions is called chemical kinetics.

Rate of Reaction

The change in concentration of a reactant or a product per unit time is called rate of reaction.

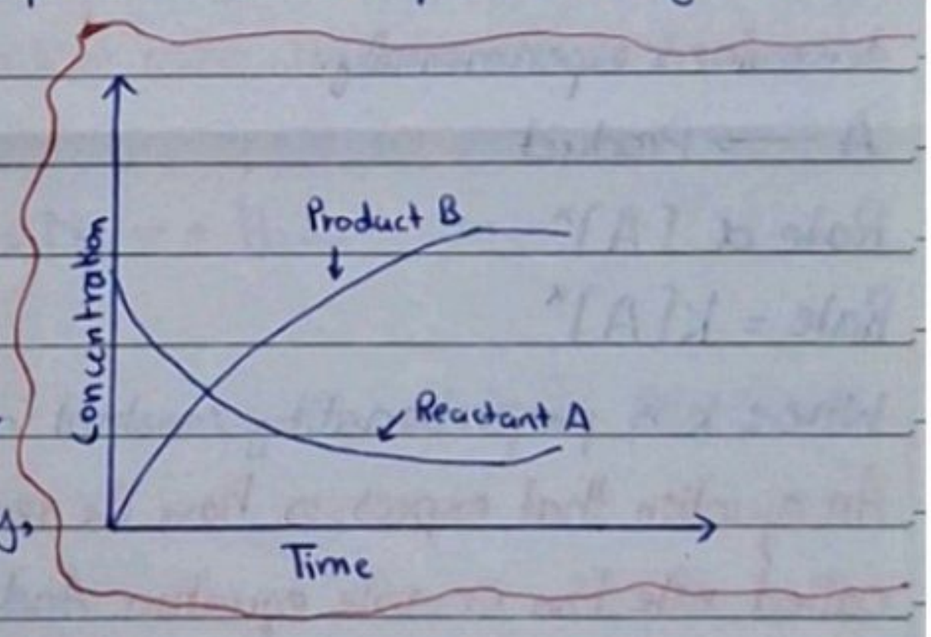
$$\text{Rate} = \frac{\text{Change in Concentration}}{\text{Time taken for change}} = \frac{\Delta C}{\Delta t}$$

The concentration of reactant decreases and concentration of products increases with the passage of time. Unit of rate of reaction $mol dm^{-3} s^{-1}$

Example: The change in concentration of reactants and products can be represented by the general reaction:

$$A \longrightarrow B$$

The slope of graph for both is steeper in the beginning. This indicate rapid decrease or increase in concentration of reactant or product respectively. The rate of reaction is never uniform. As the concentration of reactants decrease continously, the rate of reaction also decrease continously.



Mathematical Representation

If dx is very small change in concentration of product in a very small interval dt than rate can be express as:

$$\text{Rate} = \frac{dx}{dt}$$

For above general reaction:

$$\frac{dx}{dt} = -\frac{d[A]}{dt}$$

$$\frac{dx}{dt} = +\frac{d[B]}{dt}$$

The negative sign indicate a decrease in concentration of the reactant A, whereas the positive sign indicate the increase in concentration of product B.

Types of Rate of reaction

- The rate of reaction b/w two specific time intervals is called the average rate of reaction. The average rate of reaction over any time interval can be determined by the difference b/w the measurement times.

$$\text{Average rate} = \frac{\Delta x}{\Delta t} = \frac{x_2 - x_1}{t_2 - t_1}$$

- The rate of reaction at a particular instant of time is called the instantaneous rate of reaction. The instantaneous rate of reaction is determined from the slope of tangent to the curve at that time.

$$\text{Instantaneous rate} = \frac{dx}{dt}$$

Rate Law

Experimental studies on rate of reaction shows that the rate of chemical reaction is propotional to the molar concentration of reactants each raised to a power. The value of which is determined experimentally.

$A \longrightarrow$ Product

$\text{Rate} \propto [A]^x$

$\text{Rate} = K[A]^x$

Where K is proportionality constant and is known as rate constant.

An equation that expresses how the reaction rate is related to the concentration of reactants is called rate law or rate equation. And rate constant is defined as, the rate of reactions when molar concentration of each reactant is unity. It is also known as velocity constant.

$\text{Rate} = K[A]^x$

When $[A] = 1$

$\text{Rate} = K$

Rate constant provide a link b/w concentration of reactants and rate of reaction. Every reaction has its own characteristic rate constant. Value of rate constant change with temperature

Order of Reaction

Order of reaction may be defined as the number of molecules of reactants participating in the rate determining-step. In multiple step reactions the slowest step is called rate determing step

$aA + bB \longrightarrow cC + dD$

$\text{Rate} \propto [A]^x[B]^y$

$\text{Rate} = K[A]^x[B]^y$

In above equation 'x' is the order of reaction with respect to 'A' and exponent 'y' is the order with respect to 'B'. The sum 'x+y' is the overall order of reaction.

Order of reaction may also be define as the sum of all the exponents to which the molar concentration terms in the rate equation are raised.

'x' and 'y' may not be the same as 'a' and 'b'. The order of reaction for particular species cannot be predicted by looking at the balanced chemical equation. It can only be determined experimentally.

Example: $2NO_2 + O_3 \longrightarrow N_2O_5 + O_2$

Experimental study shows that:

Rate = $K[NO_2][O_3]$

Order = 1+1 = 2

The order with respect to NO_2 is one. Whereas stiochiometric coefficient is two.

Types of Order of Reactions

-Zero Order Reactions

A reaction that is independent of the concentration of reactant molecules is called zero order reaction.

Example: Decomposition of Ammonia, $2NH_{3(g)} \longrightarrow N_{2(g)} + H_{2(g)}$

Rate = $K[NH_3]^0$.

- Phochemical reactions e.g. Photosynthesis.
- Enzyme catalytic reactions.

- First Order Reactions

A reaction whose rate of reaction directly propotional to the first power of concentration of single reactant molecule is called first order reaction. Rate = $K[A]^1$.

Example: · Thermal decomposition of dinitrogen pentaoxide. $2N_2O_{5(g)} \longrightarrow 2N_2O_{4(g)} + O_{2(g)}$

Rate = $K[N_2O_5]^1$.

All radioactive decays are first order reaction.

- Second Order Reactions

A reaction for which sum of exponents of rate equations is two is called second order reaction.

Rate = $K[A]^2$ Or Rate = $K[A]^1[B]^1$

Example: Reaction of nitrogen monoxide with ozone. $NO_{(g)} + O_{3(g)} \longrightarrow NO_{2(g)} + O_{2(g)}$

Rate = $K[NO][O_3]$

- Third order reaction

A reaction for which sum of exponents of rate equation is three is called third order reaction.

Rate = $k[A]^3$ Or Rate = $k[A]^2[B]^1$ Or Rate = $k[A]^1[B]^1[C]^1$

Example: Reaction of nitrogen monoxide with oxygen. $2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$

Rate = $k[NO]^2[O_2]$ Order = 2+1 = 3

- Fractional order reaction

A reaction for which sum of exponents of rate equation is in fraction is called fractional order reaction. Rate = $k[A]^1[B]^{1/2}$

Example: Reaction b/w H_2 and Br_2. $H_{2(g)} + Br_{2(g)} \longrightarrow 2HBr_{(g)}$

Rate = $k[H_2][Br_2]^{1/2}$ Order = $1 + 1/2 = 3/2$

- Pseudo order reaction

A bimolecular reaction for which solvent is in excess and its concentration remains constant and does not take part in rate determining step is called pseudo first order reaction.

Example: Hydrolysis of tertiary butyl bromide $(CH_3)_3C-Br_{(l)} + H_2O_{(excess)} \longrightarrow (CH_3)_3C-OH_{(l)} + HBr_{(g)}$

Rate = $k[(CH_3)_3C-Br]$

Determination of Reaction Order and Rate law

The effect of change in concentration of reactants on reaction rates cant be deduced from a chemical equation. Order of reactions can be only calculated experimentally.

- Method of Inital rates

In this method an experiment is designed in which the concentration of one reactant is changed while everything elese is kept constant. The concentration of one of the reactants is changed systematically and the initial rate of reaction on every change is determined.

- Half life method for Determining rate constant

The half life ($t_{1/2}$) of a reaction is the time it ~~constant~~ takes for the concentration of a reactant is reduced to half.

The relationship b/w half life and rate constant depend upon order of the reaction.

$[t_{1/2}]_n \propto \frac{1}{a^{n-1}}$: Where n = Order of reaction.

Effect of temperature on the rate of reaction

Rate of reaction $\propto$ Temperature

- Effect of increase in temperature

According to the collision theory, the rate of a reaction is propotional to the number of collisions among the reactant molecules. An increase in kinetic energy of reactant

molecules increases the collision frequency i.e. the number of effective collisions and hence the reaction rate. Only effective collisions bring about the reaction.

- Effective collision and Activation Energy.

For a collision to be effective, molecules must posses the activation energy and must be properly oriented. At ordinary temperature, very few molecules possess this enery of activation.

- Arrhenius Equation

Arrhenius (1889) studied the effect of temperature on reaction rates. He found that the effect of temperature on rate of reaction is given by the following equation. This equation is known as Arrhenius equation.

$$k = Ae^{-Ea/RT}$$

k = Rate constant

A = Arrhenius constant

e = the base of natural log.

Ea = Activation energy

R = General gas constant

T = Absolute temperature

Therefore, rate constant k varies with the temperature. It increases with temperature which in turn increases rate of reaction.

Mechanism of a Chemical Reaction

The rate equation for a reaction is very useful because it provide information about mechanism of reaction. The path followed by the reactants in forming the products in a chemical reaction is called mechanism. A reaction may occur in a single step or in many steps. When the reaction proceeds through two or more steps, one of the step is the slowest. The rate of the slowest step determines the overall rate of reaction. The slowest step of a reaction mechanism which determines the overall rate of reaction is called as rate determing step. This is because it places a limit on the rate at which the overall reaction can occur. No reaction can proceed slower than the rate-determing step. All other steps of the reaction are generally fast.

Example: $2NO_{2(g)} + F_{2(g)} \longrightarrow 2NO_2F_{(g)}$

Rate = $k[NO_2][F_2]$

$NO_{2(g)} + F_{2(g)} \longrightarrow NO_2F_{(g)} + F$ (Slow Step)

$NO_{2(g)} + F_{(g)} \longrightarrow NO_2F_{(g)}$ (Fast Step)

Thus, the rate equation is determined by the slow step of this reaction

Energy of Activation

The minimum amount of energy which is required to start a reaction.

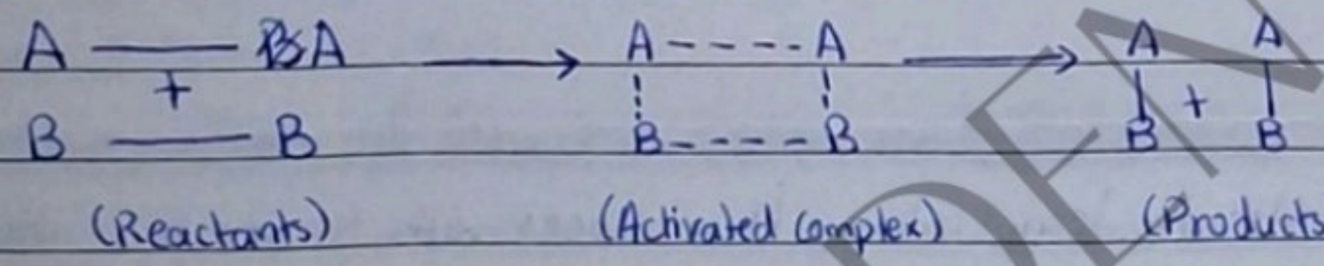
- Collision Theory

Collision theory has been proposed to explain the observed kinetics of reactions. For a chemical reaction to occur, the combining atoms or molecules must collide with one another. The effective collision can only take place only if the energy of colliding particles is high eneough to overcome the repulsion b/w electrons around the particles. Have a proper orientation, it means that at the time of collision the atoms which are required to make new bonds should collide with each other.

The minimum amount of energy, in addition to the average K.E, which the particles must posses for effective collisions is called activation energy. Thus, the rate of reaction depend upon its energy of activation. The greater the activation energy, the lesser will be the rate of reaction.

- Example

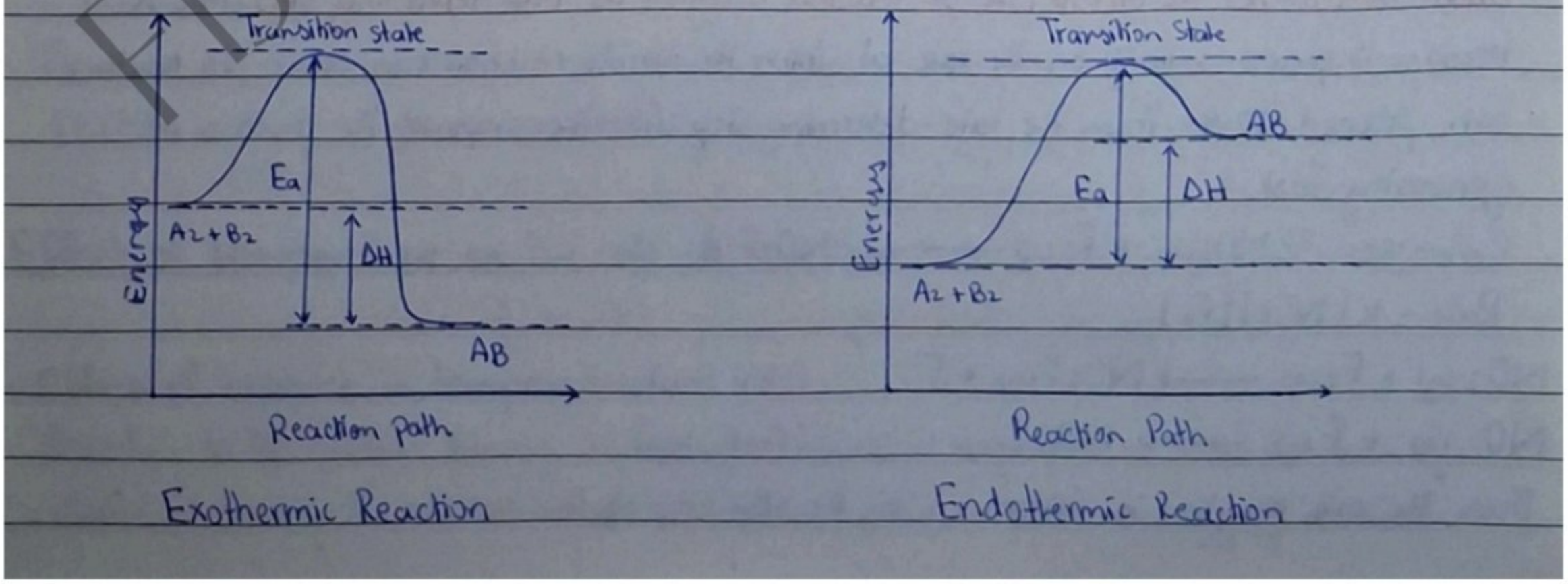
Consider a reaction b/w A_2 and B_2 molecule to form a new molecule AB.



Activated complex is short lived, high energy species which quickly break down to products. This activated complex is also called transition state.

- Explanation

In an effective collision the colliding molecules come close to each other, slow down just before collision. Their K.E decrease and potential energy increase which appear as a hill b/w reactants and products. In both, exothermic and endothermic reactions, activation energy Ea is an energy barriesr which can be crossed over before the products can be formed.



Catalysis

A substance which accelerates a chemical reaction but remains chemically unchanged at the end of reaction is called as catalyst. The name catalysis was coined by Barzelius in 1836

-Features of catalyst

- A catalyst provides a new mechanism for the reaction with low energy of activation.
- Catalyst increases the rate of reaction by decreasing its energy of activation.
- A catalyst has no effect on the total thermodynamic or enthalpy of the reaction. For this reason, a catalyst cannot be used to bring about a chemical reaction, which is not favoured thermodynamically.

Example

In the stratosphere, conversion of an ozone molecule by an oxygen atom into two O_2 molecules occurs. This reaction has higher energy of activation.

$$O_3 + O \longrightarrow 2O_2 \qquad Ea = 17.1\ KJmol^{-1}$$

Chloroflourocarbon compounds diffuse up into the stratosphere. These compounds absorb short wave length ultraviolet light from sun, that breaks carbon-chlorine bonds and produce chlorine atoms. Cl atoms catalyzes the mechanism requiring less energy of activation.

$$O_3 + Cl \longrightarrow 2O_2 + ClO \qquad Ea = 2.1\ KJmol^{-1}$$

$$O + ClO \longrightarrow O_2 + Cl \qquad Ea = 0.4\ KJmol^{-1}$$

Net reaction will be, after combining these two reactions:

$$O_3 + O \longrightarrow 2O_2 \qquad Ea = 2.5\ KJmol^{-1}$$