CHEMICAL KINETICS

The branch of physical chemistry which deals with (i) rate of the reaction (ii) factors including the rate of reaction (iii) possible explanation of the rate in terms of reaction mechanism.

We shall not study the rate of such reactions which are very fast (i.e the reaction between $AgNO_3$ solution and NaCl solution is complete in 10^{-4} seconds). We also not study the rate of such reactions which are slow eg H_2 and O_2 react to give H_2O which takes 4 years for its completion. We shall study the rates of such reactions which proceed with a moderate rate. That is,

Decomposition of H_2O_2

(i) $H_2O_2 \longrightarrow H_2O + \frac{1}{2} O_2$

(ii) $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$

(iii) $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

Ethyl acetate.
(ester)

(iv) $2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$.

RATE OF THE REACTION:-

The change in concentration (no. of moles/litre) of the reactant or product per unit time is called rate of the reaction. The unit time is generally taken in one second.

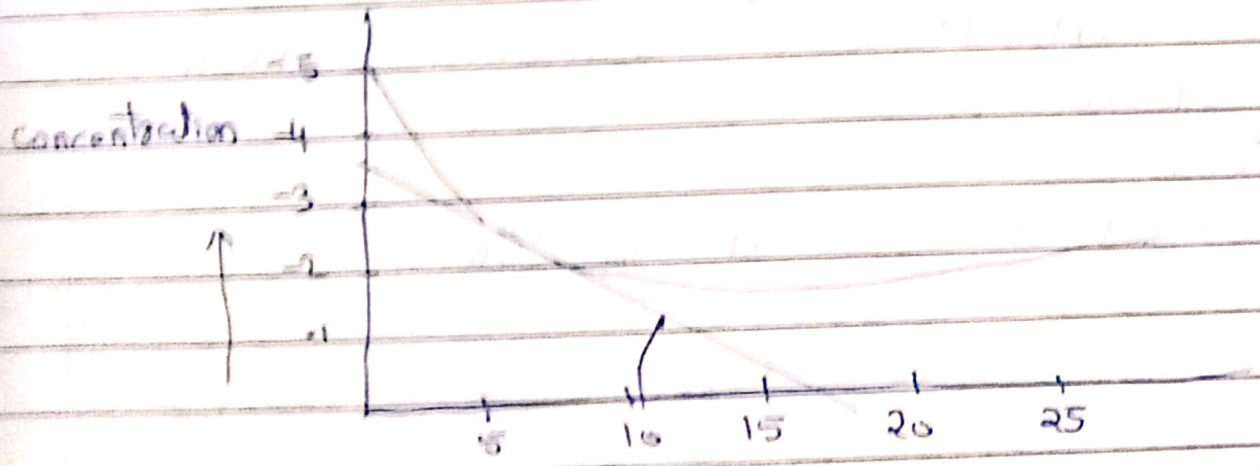
or

The rate of reaction is defined as the amount of product (in gm moles) formed in unit time under stated conditions.

The unit of time is generally taken in one second.

Unit of the rate of the reaction = mole litre^{-1} sec^{-1}

The rate of the reaction cannot be compared with the mechanical rate because it goes on changing at every instant. i.e. the rate of the reaction is determined at a particular instant. say we have to determine the rate of decomposition of H_2O_2 at the 10th minute. For this we take the help of calculus. We determine dx/dt where dx is the infinitesimal change in concentration during the infinitesimally small time dt. For this we plot a graph between time in minute and concentration. The nature of the curve is shown in the following figure:-



$$\frac{\Delta x}{\Delta t} = \frac{\cdot 37}{17 \times 60}$$

The rate of decomposition of H_2O_2 at the 10th minute.

$\frac{dx}{dt} = \frac{0.37}{11 \times 60}$ mole litre^{-1} sec^{-1}

Factors influencing the rate of the reaction:

(i) Concentration - The concentration of the reactant greater will be the rate of the reaction.

(ii) Temperature - Greater the temperature, greater will be the rate of the reaction. For every 10° rise in temperature the rate of the reaction is doubled and some times tripled also.

(iii) Nature of the reactants - Nature of the reactants also influence the rate of the reaction.

eg.

$NO + \frac{1}{2} O_2 \longrightarrow NO_2$ (Fast)

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ (Slow)

In case of NO one bond is broken per molecule and two bonds are formed in case of NO_2. But in case of CH_4 four bonds are broken per molecule and six bonds are formed (two in case of one molecule of CO_2 and four in case of two molecules of H_2O). Therefore the former reaction is fast and the latter reaction is slow. This example clearly show that the nature of the reactant also influence the rate of the reaction.

(iv) Surface area - Greater the surface area greater will be the rate of the reaction. A log of wood burns slowly than the same amount of wood in the form of sawed saw dust.

(v) Catalyst - Those substance which alter the rate of reaction but remain unchanged

in the overall reaction. The catalyst also influences the rate of reaction. eg $KClO_3$ when heated liberates O_2. The rate of liberation of O_2 is slow. When $KClO_3$ is mixed with MnO_2 and heated the rate of liberation of O_2 increases. Hence MnO_2 serves the purpose of positive catalyst.
Similarly H_2O_2 decomposes to give H_2O and O_2. The rate of decomposition is de retarded by the presence of phosphoric acid. Hence phosphoric acid is called negative catalyst.

(vi) Radiation. Radiation also influence the rate of the reaction. eg CH_4 does not react with chlorine in dark But in diffussed sunlight we get methyl chloride (CH_3Cl), methylene chloride, (CH_2Cl_2) chloroform ($CHCl_3$) and carbon chloride, (CCl_4).

RATE OF THE REACTION.

1) $A \longrightarrow$ Product

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

where K is the rate constant

$r \propto [A]$

$r = K[A]$

$$\boxed{r = K[A]}$$

This equation is called rate law equation.

2) $A + B \longrightarrow L + M$

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