UNIT 4 : CHEMICAL KINETICS

Chemical Kinetics:- It deals with the study of reaction rates and their mechanisms.

Rate of a chemical reaction: It is defined as the rate of change in concentration of either reactant or product per unit time.

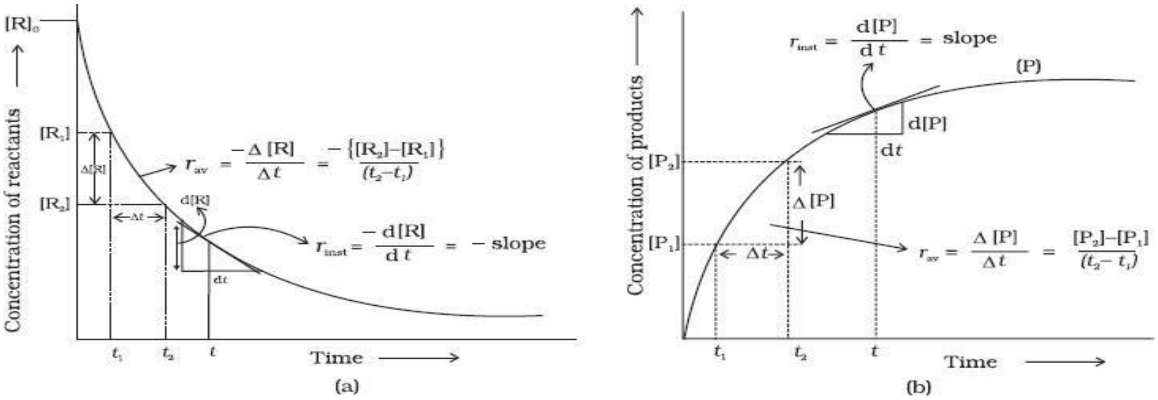
(a) **Average Rate of a reaction:** Average rate of reaction can be obtained by dividing the total change in concentration of reactant or product by the elapsed time.

Average rate = $\frac{-\Delta R}{\Delta T} = \frac{\Delta P}{\Delta T}$

(b) **Instantaneous rate of a reaction:** It is the rate of any one of the species involved in a reaction at particular instant of time.

Instantaneous rate= average rate as Δt approaches zero.

Instantaneous rate = $\frac{-d[R]}{dt} = \frac{d[P]}{dt}$



Factors affecting the rate of a reaction:-

1. Concentration of the reactants
2. Temperature of reactants
3. Presence of a catalyst

Effect of concentration: Rate of a reaction depends on concentration of reactants.

Rate law: Rate law is the expression in which reaction rate is given in terms of reactants with each term raised to some power ,which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

For a reaction: aA + bB → Product

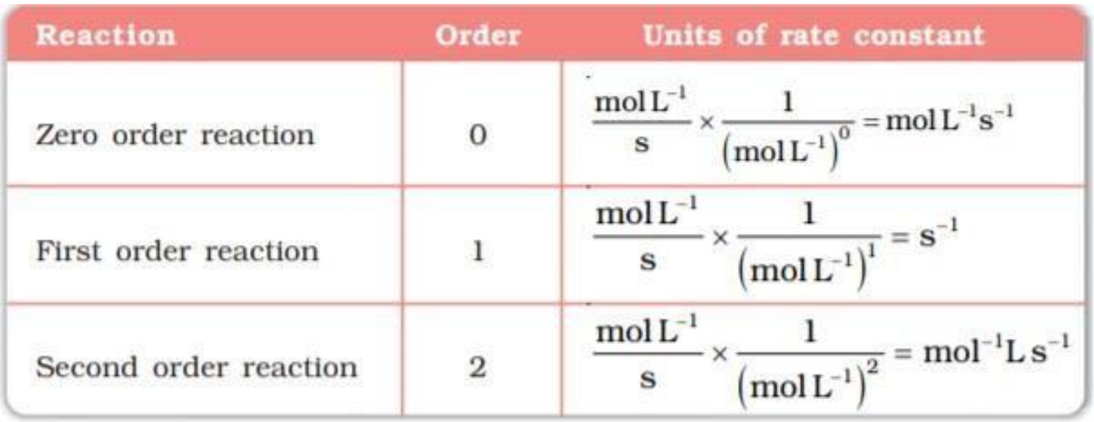
The rate law is written as: **Rate = k[A]^x[B]^y** where, x and y may or may not be equal to stoichiometric coefficients (a and b) of the reactants

Rate constant (K): It is equal to the rate of reaction when concentration of reactant(s) is unity.

Order of a reaction: It is defined as the sum of the powers of the concentration of the reactants terms in experimentally determined rate equation. It can have a value of zero, integral values as well as fractional values.

Units of rate constant:

Depending on the order of the reaction unit of rate constant changes It can be generally expressed as $mol^{(1-n)}\,L^{(n-1)}\,s^{-1}$,where n is the order of the reaction.



Reaction	Order	Units of rate constant
Zero order reaction	0	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^{0}} = \text{mol L}^{-1}\text{s}^{-1}$
First order reaction	1	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^{1}} = \text{s}^{-1}$
Second order reaction	2	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^{2}} = \text{mol}^{-1}\text{L s}^{-1}$

Examples of zero order reactions

The reaction of hydrogen with chlorine (Photochemical reaction)

$$H_2(g) + Cl_2(g) \overset{hv}{\rightarrow} 2HCl(g)$$

Decomposition of nitrous oxide in the presence of hot Platinum catalyst

$$2N_2O \overset{Pt(hot)}{\rightarrow} 2N_2 + O_2$$

Decomposition of gaseous ammonia on a hot platinum surface

$$2NH_3\,(g) \xrightarrow[\text{Pt catalyst}]{1130K} N_2\,(g) + 3H_2\,(g)$$

Examples of first order reaction

Hydrogenation of ethene is an example of first order reaction.

$$C_2H_4(g) + H_2\,(g) \rightarrow C_2H_6(g)$$

All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.

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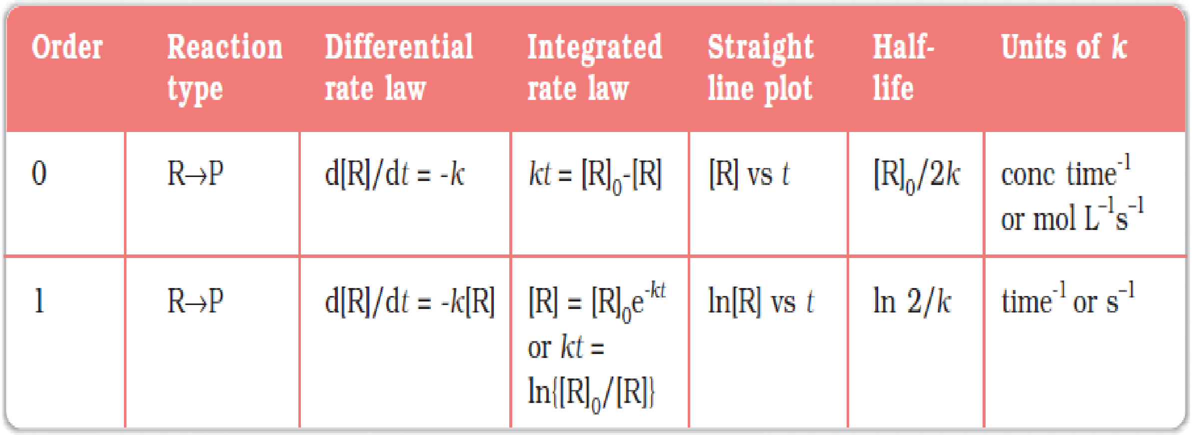
Molecularity of a reaction: It is the number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction. It can't be zero.

Difference between order and molecularity

Order	Molecularity
Experimental quantity	theoretical
It can be zero and even a fraction but	molecularity cannot be zero or a non integer
Order is applicable to elementary as well as complex reactions	molecularity is applicable only for elementary reactions.
For complex reaction, order is given by the slowest step	molecularity of the slowest step is same as the order of the overall reaction.



Order	Reaction type	Differential rate law	Integrated rate law	Straight line plot	Half-life	Units of k
0	$R \to P$	$d[R]/dt = -k$	$kt = [R]_0 - [R]$	$[R]$ vs t	$[R]_0/2k$	conc time^{-1} or mol $L^{-1}s^{-1}$
1	$R \to P$	$d[R]/dt = -k[R]$	$[R] = [R]_0 e^{-kt}$ or $kt = \ln\{[R]_0/[R]\}$	$\ln[R]$ vs t	$\ln 2/k$	time^{-1} or s^{-1}

Integrated rate equation:

For a typical first order gas phase reaction

$$A(g) \rightarrow B(g) + C(g)$$

The integrated rate expression will be

$$k = \left(\frac{2.303}{t}\right)\left(\log\frac{p_i}{p_A}\right)$$

$$= \frac{2.303}{t}\log\frac{p_i}{(2p_i - p_t)}$$

Pseudo First Order Reaction : In a chemical reaction between two substances when one reactant is present in large excess. The concentration of water does not get altered much during the course of the reaction and the reaction behaves as first order reaction. e.g.

$$\begin{array}{llllll} & CH_3COOC_2H_5 & + H_2O & \xrightarrow{H^+} & CH_3COOH & + \quad C_2H_5OH \\ t = 0 & 0.01 \text{ mol} & 10 \text{ mol} & & 0 \text{ mol} & 0 \text{ mol} \\ t & 0 \text{ mol} & 9.9 \text{ mol} & & 0.01 \text{ mol} & 0.01 \text{ mol} \end{array}$$

$$\text{Rate} = k' [CH_3COOC_2H_5] [H_2O]$$

The term $[H_2O]$ may be taken as constant, therefore the rate becomes

$$\text{Rate} = k [CH_3COOC_2H_5]$$

$$\text{where } k = k' [H_2O]$$

2. Temperature dependence of the rate of reaction: It has been found that for a chemical reaction with rise in temperature by 10°, the rate constant is nearly doubled. The temperature dependence on the rate of a chemical reaction can be accurately explained by Arrhenius equation

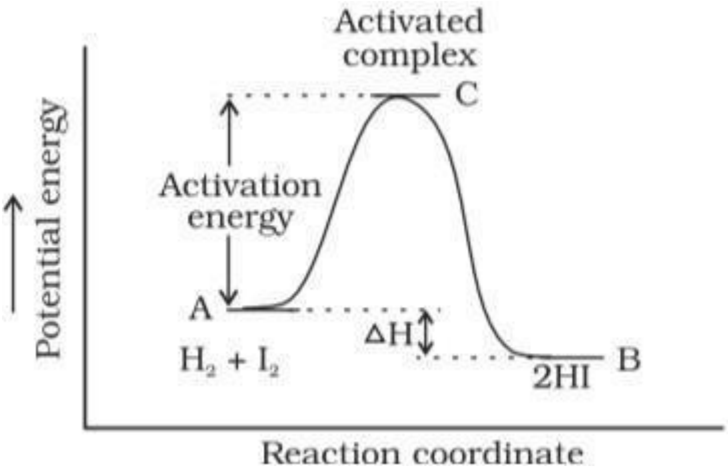
$$k = A\, e^{-Ea/RT}$$

Where k is rate constant for the reaction, A is pre-exponential factor or frequency factor, R is gas constant, T is temperature and E_a is activation energy of the reactant molecules.

According to Arhennius a reaction takes place only when reactant molecules collide to form an unstable intermediate called activated complex,which exists for a short time and then breaks up to form products.

It can be clearly explained using the example

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

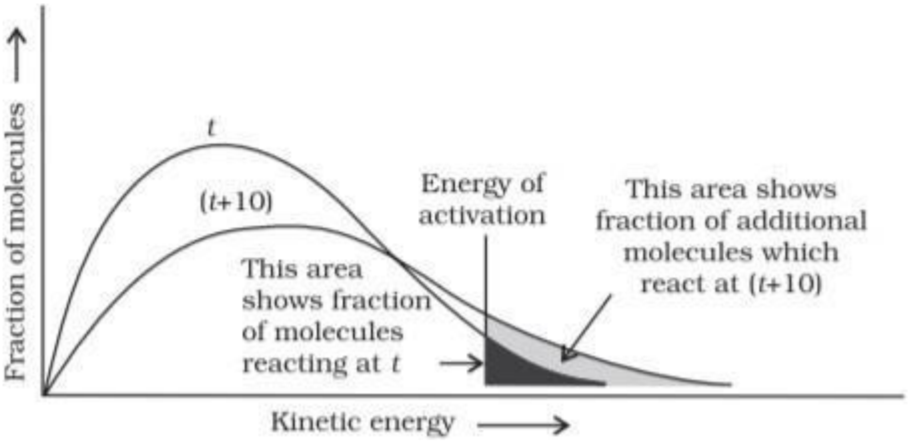


Activation energy:- It is the extra energy which must be possessed by reactant molecules so that collision between reactant molecules is effective and leads to formation of product molecules. Activation energy can be calculated if we know the rate constants K_1 and K_2 at temperatures T_1 and T_2 respectively, for the reaction.

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

Activation energy = threshold energy – energy normally possessed by molecules.

Distribution curve explaining temperature dependence of rate of reaction is given below

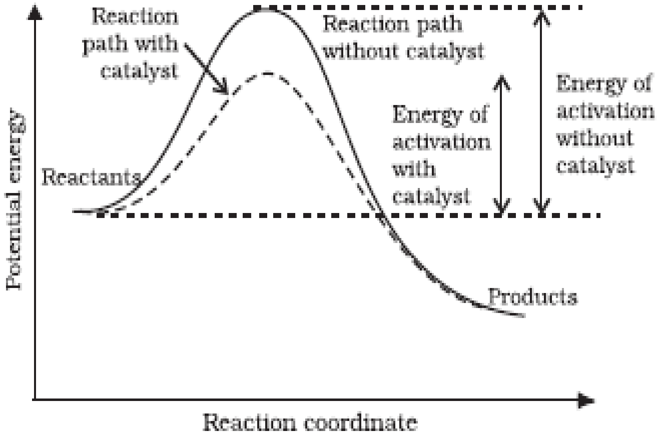


3.Effect of catalyst on rate of reaction:

A catalyst is a substance which increases the rate of a reaction without itself undergoing any permanent chemical change.

For example, MnO_2 catalyses the following reaction.

$$2KClO_3 \xrightarrow{MnO_2} 2\ KCl + 3O_2$$



catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier.

Collision theory of chemical reactions: According to this theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other
For a bimolecular elementary reaction A + B → Products

Rate of reaction can be expressed as Rate = $\mathbf{Z_{AB}\, e^{-Ea/RT}}$ where Z_{AB} represents the collision frequency of reactants, A and B and $\mathbf{e}^{-Ea/RT}$ represents the fraction of molecules with energies equal to or greater than E_a.