

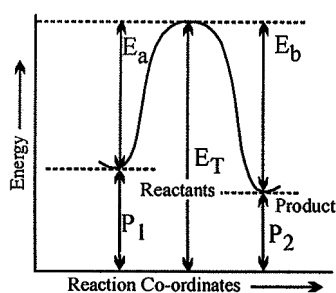
CHEMICAL KINETICS

❖ REACTION ENERGY DIAGRAM :

• Threshold energy :

For a reaction to take place the reacting molecules must collide together, but only those collisions, in which colliding molecules possess certain minimum energy is called threshold energy (E_T) or the total minimum energy that reacting species must possess in order to undergo effective collision to form product molecules is called threshold energy.

- **Activation energy :** It is extra energy which must be possessed by reactant molecules so that collision between reactant molecules is effective and leads to formation of product molecules.



E_T = Threshold energy

E_a = Activation energy of forward reaction

E_b = activation energy of backward reaction

P_1 = Potential energy of reactants

P_2 = Potential energy of products

- **Activated complex :** It is formed between reacting molecules which is highly unstable and readily changes into product.

❖ INFLUENCE OF TEMPERATURE ON REACTION RATES :

• Temperature coefficient :

The temperature coefficient of a chemical reaction is defined as the ratio of the reaction rates at two temperatures differing by 10°C . Its value usually lies between 2 & 3.

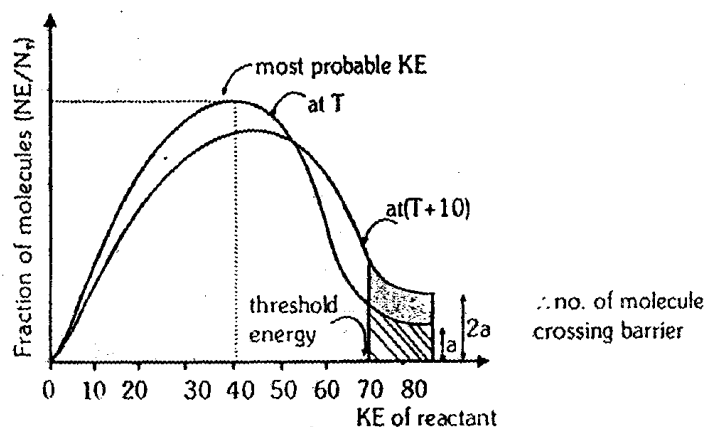
$$\text{temperature coefficient} = \frac{k_{t+10}}{k_t}$$

Temperature coefficient (μ) : It is defined as ratio of rate constant of a reaction at two different temperatures which will differ by 10°C .

$$\mu = \frac{K_{T+10}}{K_T} = 2 \text{ to } 3 ; \quad \frac{r_2}{r_1} = \frac{K_2}{K_1} = \mu^{\Delta T/10}$$

If temperature of reaction is not specified then consider 25°C .

If μ is not given consider it as minimum 2.



- **Arrhenius Equation :**

A quantitative relationship was proposed by Arrhenius

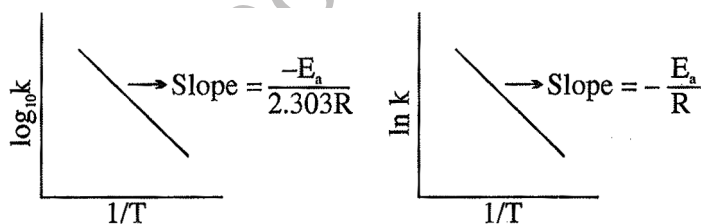
$$k = A \cdot e^{-E_a/RT}$$

where,

k = rate constant ; A = frequency factor (or pre – exponential factor)
 R = gas constant ; T = Temperature (kelvin) ; E_a = Activation energy).

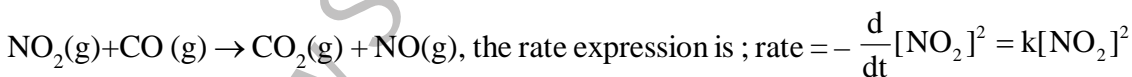
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Graphical representations are :



- ❖ **MECHANISM OF REACTIONS :**

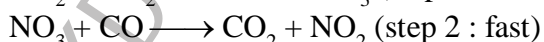
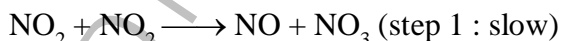
The path way by which reactants are converted into the products is called the reaction mechanism. It should be clear that experimentally determined rate expression cannot be predicted from the stoichiometry of the reaction. For example, for the reaction ;



i.e. the expression is independent of CO (g) concentration.

The reason is that the reaction occurs by a series of elementary steps.

The mechanism proposed for the above reaction is a two step one.

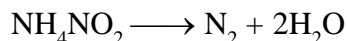


The sum of the two gives the stoichiometry & the slow step decided the rate expression.

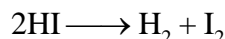
- ❖ **MOLECULARITY :**

The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide

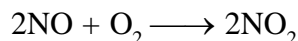
simultaneously in order to bring about a chemical reaction is called molecularity of a reaction. The reaction can be unimolecular when one reacting species is involved, for example, decomposition of ammonium nitrite.



Bimolecular reactions involve collision between two species, for example dissociation of hydrogen iodide.



Trimolecular or termolecular reactions involve simultaneous collision between three reacting species for example,



Molecularity of a reaction is :

- (i) Always a whole number (not zero) and never a fraction.
- (ii) The probability that more than three molecules can be collide and react simultaneously is very small. Hence, the molecularity greater than three is not observed.

❖ ORDER OF REACTION :

It is defined as the sum of the exponents (powers) of the molar concentrations of the reaction components in the experimentally determined rate equations.

If rate $\propto [\text{A}]^p [\text{B}]^q [\text{C}]^r$

$$\text{Rate} = k [\text{A}]^p [\text{B}]^q [\text{C}]^r$$

Order of reaction = $p + q + r$

The order w.r.t. A, B & C are p, q & r respectively.

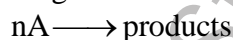
For a "Reaction of n^{th} order", the order of the reaction is n and the rate equation (or Rate law) is rate $\propto [\text{A}]^n = k[\text{A}]^n$.

The order of a reaction is obtained from the experimentally determined rate law and may be zero, an integer or a fraction or even negative.

- Thus, from the above discussion we can conclude the following :
 - (a) Order of a reaction is an experimental quantity. It can be zero and even a fraction but molecularity cannot be zero or a non integer.
 - (b) Order is defined to elementary as well as complex reactions whereas molecularity is defined only for elementary reactions. For complex reaction molecularity has no meaning.
 - (c) For an elementary reaction order and molecularity are same.

❖ ZERO ORDER REACTIONS : In these rate of reaction do not depend on concentration of reactants.

Consider of general reaction.



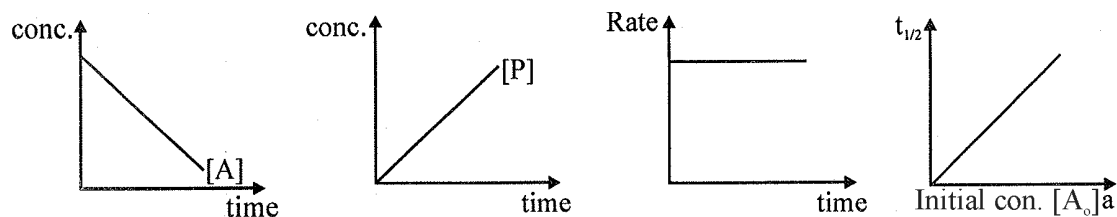
Rate = $k [\text{A}]^0$ Differential rate equation (DRE).

On integration $[\text{A}]_0 - [\text{A}]_t = kt$. Integrated Rate Equation (IRE)

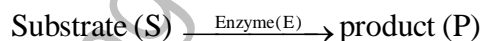
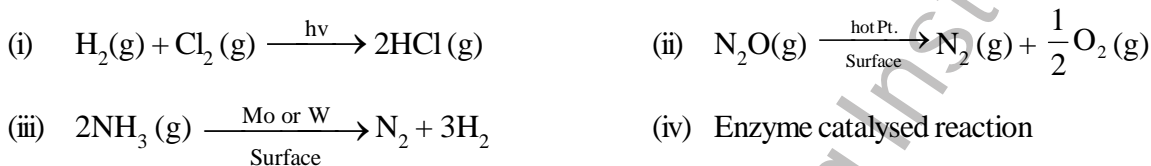
Characteristics of zero order reactions :

- (i) Concentration of reactant decrease linearly with time.
- (ii) Units of k are $\text{mol l}^{-1}\text{time}^{-1}$.
- (iii) Time required for the completion of reaction is $\frac{[\text{A}]_0}{k}$

- (iv) $t_{1/2} = \frac{[A]_0}{2k}$
 (v) Zero order reaction must be complex reaction
 (vi) Graph related with zero order reactions



• **Examples :**



❖ **FIRST ORDER REACTIONS :** Rate of reaction directly depends on power one of concentration term. Consider of general reaction

at time $t = 0$ concentration of A = a or $[A]_0$
 at time $t = t$ concentration of A = (a-x) or $[A]_t$ $t = t$ (a-x) x
 Rate of reaction,

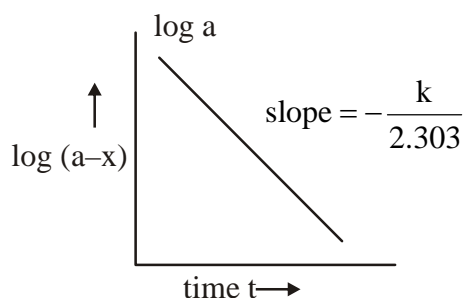
$$-\frac{d[A]}{dt} = k[A] \text{ or } \frac{dx}{dt} = k(a-x) \quad \text{DRE}$$

Exponential form of 1st order equation is $[A]_t = [A]_0 e^{-kt}$

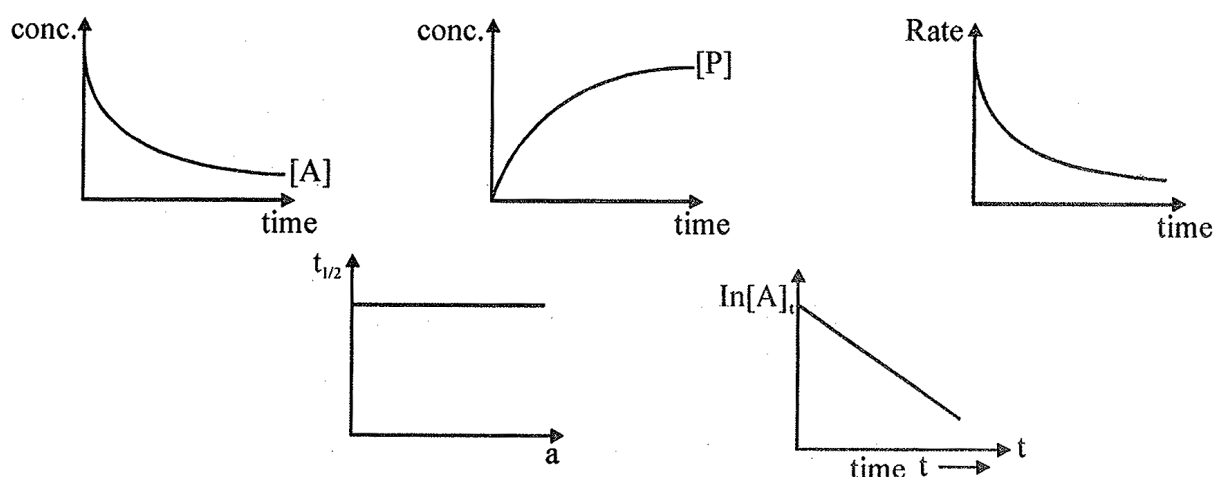
or $k = \frac{2.303}{t} \log \frac{a}{a-x} \quad \text{IRE}$

• **Characteristics of First Order Reaction :**

- (i) Unit of rate constant is time^{-1} .
 (ii) $t_{1/2} = \frac{0.693}{k}$ (Half-life)
 (iii) $\log(a-x)$ v/s t is a straight line with slope $-\frac{k}{2.303}$

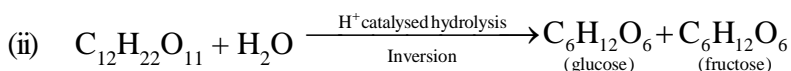


(iv) Graph related with first order reactions.



• **Examples :**

(i) Radioactive disintegration is a first order reaction

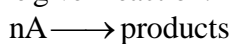


(iii) Mineral acid catalyzed hydrolysis of esters. (it is pseudo unimolecular reaction)

(iv) Decomposition of H_2O_2 in aqueous solution.

❖ **SECOND ORDER REACTIONS :** Rate of reaction directly depends on power two of concentration term.

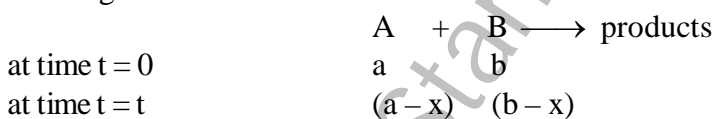
• For the given reaction.



Differential rate equation
$$\frac{dx}{dt} = k(a-x)^2$$

Integrated rate equation
$$kt = \frac{1}{a-x} - \frac{1}{a} \text{ or } k = \frac{1}{t} \left[\frac{1}{c_t} - \frac{1}{c_0} \right]$$

• For the given reaction



differential rate equation
$$\frac{dx}{dt} = k(a-x)(b-x)$$

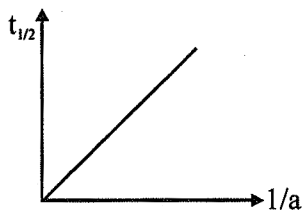
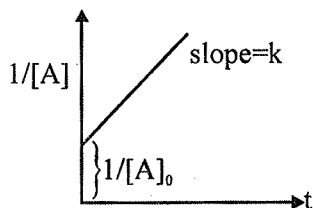
Integrated rate equation
$$k = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)} \quad k = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)} \quad a > b \text{ If } a =$$

$$b, \text{ then } kt = \frac{1}{(a-x)} - \frac{1}{a}$$

• **Characteristics of Second Order Reaction :**

(i) Unit of rate constant $\text{L mol}^{-1} \text{time}^{-1}$.

(ii) $t_{1/2} \propto a^{-1}$ (In general $t_{1/2} \propto a^{(1-n)}$; $n =$ order of reaction).



Examples :

(i) Saponification (hydrolysis of esters catalysed with alkali).
 $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \longrightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$

(ii) Hydrogenation of ethane $\text{C}_2\text{H}_4 + \text{H}_2 \xrightarrow{100^\circ\text{C}} \text{C}_2\text{H}_6$.

(iii) $2\text{O}_3 \longrightarrow 3\text{O}_2$.

• n^{th} Order Reaction :

Consider the reaction

$n\text{A} \longrightarrow \text{Product}$

$$\text{rate of rea}^n \quad \boxed{\frac{dx}{dt} = k[\text{A}]^n = k(a-x)^n} \quad \text{DRE}$$

$$kt = \boxed{kt = \frac{1}{n-1} \left\{ \frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right\}} \quad \text{IRE} \quad [n \neq 1, n = \text{order}]$$

$$\boxed{t_{1/2} \frac{1}{k(n-1)} \cdot \left[\frac{2^{n-1} - 1}{a^{n-1}} \right]}$$

