

**SHIVALIK BEHROR**  
**MEDICAL/IIT-JEE PRE-FOUNDATION**  
**CLASS XII Appearing**  
**(LESSON IV<sup>th</sup>) (Chemical Kinetics)**

➤ **SUBJECT- CHEMISTRY (Varun Sir, Mob. 9784067297)**

- **Chemical Kinetics is the branch of chemistry that deals with rate of a reaction, the reaction mechanism and factor affecting the rate.**
- **The word *kinetics* is derived from the Greek word “Kinesis” meaning *movement*.**
- **Thermodynamics tells only about the *feasibility* of a reaction.**
- **Chemical kinetics tells about the *rate of reaction*.**
- **Classification of Reactions :-**

Three types on the basis of **time** of completion of reaction. *Slow, fast and moderate* Reaction.

**1. Slow Reaction :-** Which complete in *few days, months or years* at room temperature.  
Ex. Rusting of Iron, Formation of H<sub>2</sub>O by the reaction of H<sub>2</sub> and O<sub>2</sub> in absence of catalyst.

**2. Fast Reaction :-** These reactions completes *very fast in fractions of second*.  
Ex. neutralization Reactions, Ionic Reactions.

**3. Moderate Speed Reaction :-** These reactions complete in *few minutes or hours*, neither too fast nor too slow.

Ex. Combination of H<sub>2</sub> and O<sub>2</sub> in the of light, decomposition of diazomethane, decomposition of H<sub>2</sub>O<sub>2</sub> , catalytic hydrolysis of ester.

Hydrolysis of starch, inversion of cane sugar.

**Special Point :-** Moderate reactions are used to study in chemical kinetics.

- **Rate of Reaction :-** The rate of reaction is the change in the concentration of any one of the reactants or products per unit time.

$$\text{rate of reaction} = \frac{\text{concentration}}{\text{time}}$$

➤ **Average rate of a Reaction (  $r_{av}$  ):-**

$$r_{av} = \pm \frac{\Delta[C]}{\Delta t}$$

Rate of appearance of P =  $\frac{\text{increase in Concentration of P}}{\text{time taken}}$

$$r_{av} = + \frac{\Delta[P]}{\Delta t}$$

Rate of disappearance of R =  $\frac{\text{decrease in Concentration of R}}{\text{time taken}}$

$$r_{av} = - \frac{\Delta[R]}{\Delta t}$$

Where  $r_{av}$  = average rate of reaction

-ve sign = Concentration of Reactants is decreasing

+ve sign = Concentration of product is increasing

$\Delta[C]$  = Change in concentration

$\Delta[P]$  = Change in concentration of Product

$\Delta[R]$  = Change in concentration of Reactant

$\Delta t$  = Change in time

[ ] = molar concentration

➤ **Unit of Rate of Reaction :-**

$$\begin{aligned} \text{Rate of Reaction} &= \frac{\text{concentration}}{\text{time}} \\ &= \frac{\text{mol lit}^{-1}}{\text{sec}} \end{aligned}$$

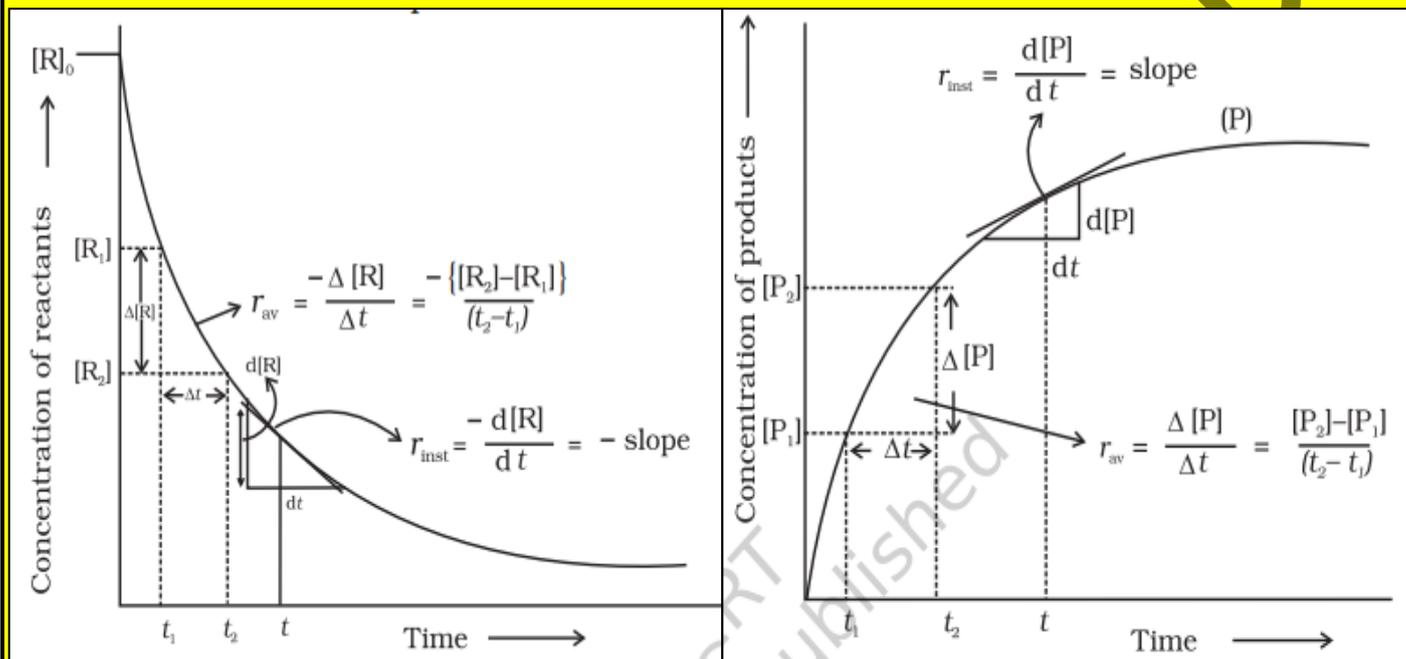
$$\text{Rate of Reaction} = \text{Mol lit}^{-1} \text{ sec}^{-1}$$

**Special Point :-** In gaseous reactions, when the concentration of gases is expressed in terms of their partial pressures, then the units of the rate equation will be **atm sec<sup>-1</sup>**.

- **Instantaneous rate** :- The rate at a particular moment of time that is instantaneous rate.

$$r_{\text{inst}} = \text{Limit } \Delta t \rightarrow 0 \pm \frac{\Delta[C]}{\Delta t} = \pm \frac{dc}{dt}$$

$$r_{\text{inst}} = - \frac{d[R]}{dt} = + \frac{d[P]}{dt}$$



*Instantaneous and average rate of a reaction*

- **Expressing the rate of reaction in terms of different Reactants and Products** :-

Ex. :-  $1 \quad 1 \quad 1 \quad \leftarrow$  Stoichiometric coefficient



$$r = - \frac{d(\text{PCl}_5)}{dt} = + \frac{d(\text{PCl}_3)}{dt} = + \frac{d(\text{Cl}_2)}{dt}$$

$$\text{Rate of disappearance of PCl}_5 = - \frac{d(\text{PCl}_5)}{dt}$$

$$\text{Rate of appearance of PCl}_3 = + \frac{d(\text{PCl}_3)}{dt}$$

$$\text{Rate of appearance of Cl}_2 = + \frac{d(\text{Cl}_2)}{dt}$$



$$r = - \frac{1}{\Delta t} \frac{\Delta[\text{Hg}]}{\Delta t} = - \frac{1}{\Delta t} \frac{\Delta[\text{Cl}_2]}{\Delta t} = + \frac{1}{\Delta t} \frac{\Delta[\text{HgCl}_2]}{\Delta t}$$

Rate of disappearance of Hg =  $-\frac{\Delta[\text{Hg}]}{\Delta t}$

Rate of disappearance of  $\text{Cl}_2 = -\frac{\Delta[\text{Cl}_2]}{\Delta t}$

Rate of appearance of  $\text{HgCl}_2 = +\frac{\Delta[\text{HgCl}_2]}{\Delta t}$



$$r = - \frac{2}{\Delta t} \frac{\Delta[\text{HI}]}{\Delta t} = + \frac{1}{\Delta t} \frac{\Delta[\text{H}_2]}{\Delta t} = + \frac{1}{\Delta t} \frac{\Delta[\text{I}_2]}{\Delta t}$$
 ← Stoichiometric coefficient

Rate of disappearance of HI =  $-\frac{\Delta[\text{HI}]}{\Delta t}$

Rate of appearance of  $\text{H}_2 = +\frac{\Delta[\text{H}_2]}{\Delta t}$

Rate of appearance of  $\text{I}_2 = +\frac{\Delta[\text{I}_2]}{\Delta t}$



$$r = - \frac{1}{5} \frac{\Delta[\text{Br}^-]}{\Delta t} = - \frac{1}{\Delta t} \frac{\Delta[\text{BrO}_3^-]}{\Delta t} = - \frac{1}{6} \frac{\Delta[\text{BrO}_3^-]}{\Delta t} = + \frac{1}{3} \frac{\Delta[\text{Br}_2]}{\Delta t} = + \frac{1}{3} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

**Ques :-** For the reaction  $\text{R} \rightarrow \text{P}$  the concentration of a reactant changes from 0.03M to 0.02M in 25 minutes. Calculate the *average rate* of reaction using units of time both in minutes and seconds.

Ans :-  $0.03\text{M} \rightarrow 0.02\text{M}$   
 $(\text{R}_1) \quad (\text{R}_2)$   
 $t_1 = 0 \quad t_2 = 25 \text{ Min.}$

$$\text{Average Rate} = - \frac{\Delta[\text{R}]}{\Delta t} = - \frac{[(\text{R}_2) - (\text{R}_1)]}{t_2 - t_1}$$

$$\begin{aligned}
 \text{Average Rate} &= \frac{-[(.02) - (.03)]}{25 - 0} \\
 &= \frac{-[-.01]}{25} = + \frac{.01}{25} \\
 &= \frac{1}{25 \times 100} = \frac{.04}{100} = \frac{4}{104} = 4 \times 10^{-4} \text{ mol lit}^{-1} \text{ min}^{-1} \\
 &= \frac{.01}{25 \times 60 \text{ sec}} = \frac{4}{10^4 \times 60} = \frac{2}{30 \times 10^4} \\
 &= \frac{2}{3 \times 10^5} = \frac{.666}{10^4} = .666 \times 10^{-5} \\
 &= 6.66 \times 10^{-6} \text{ mol lit}^{-1} \text{ sec}^{-1}
 \end{aligned}$$

**Ques :-** In a reaction  $2A \rightarrow \text{products}$ , the concentration of A decreases from  $0.5 \text{ mol l}^{-1}$  to  $0.4 \text{ mol l}^{-1}$  in 10 minutes. Calculate the rate during this interval.

**Ans :-**  $2A \rightarrow \text{Product}$

$0.5 \text{ mol l}^{-1} \rightarrow 0.4 \text{ mol l}^{-1}$

$(A_1) \quad (A_2)$

$t_1 = 0 \quad t_2 = 10 \text{ min}$

$$\begin{aligned}
 \text{Average rate} &= - \frac{1}{2} \frac{\Delta[A]}{\Delta t} = \frac{-1}{2} \frac{[A_2 - A_1]}{t_2 - t_1} \\
 &= \frac{-1}{2} \times \frac{(4 - .5)}{10 - 0} = \frac{-1}{2} \times \frac{-1}{10} \\
 &= \frac{.1}{20} = 5 \times 10^{-3} \text{ mol lit}^{-1} \text{ min}^{-1}
 \end{aligned}$$

**Ques :-** The decomposition of  $\text{N}_2\text{O}_5$  in  $\text{CCl}_4$  at 318 K has been studied by monitoring the concentration of  $\text{N}_2\text{O}_5$  in the solution. Initially the concentration of  $\text{N}_2\text{O}_5$  is  $2.33 \text{ mol l}^{-1}$  and after 184 min. It is reduced to  $2.08 \text{ mol l}^{-1}$ .

The reaction takes place according to the equation :-



Calculate the average rate of this reaction in terms of hours, minutes and seconds.

What is the rate of Production of  $\text{NO}_2$  during this period ?

**Ans :-**  $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$

$(\text{N}_2\text{O}_5)_1 \rightarrow (\text{N}_2\text{O}_5)_2$

$t_1 = 0 \quad t_2 = 184 \text{ min}$

$2.33 \text{ mol L}^{-1} \quad 2.08 \text{ mol L}^{-1}$

$$\begin{aligned}
 \text{Average Rate} &= -\frac{1}{2} \frac{\Delta(\text{N}_2\text{O}_5)}{\Delta t} \\
 &= \frac{-1}{2} \frac{[(\text{N}_2\text{O}_5)_2 - (\text{N}_2\text{O}_5)_1]}{t_2 - t_1} \\
 &= \frac{-1}{2} \frac{(2.08 - 2.33)}{184 - 0} \\
 &= \frac{-1}{2} \times \frac{-.25}{184} = \frac{.25}{368} \\
 &= .000679 \text{ mol l}^{-1} \text{ min}^{-1}
 \end{aligned}$$

$$\text{Average Rate (in Min.)} = 6.79 \times 10^{-4} \text{ mol l}^{-1} \text{ min}^{-1}$$

$$= 0.000679 \times 60 = .04076$$

$$\text{Average Rate (in Hour)} = 4.076 \times 10^{-2} \text{ mol l}^{-1} \text{ hour}^{-1}$$

$$= \frac{0.000679}{60} = \frac{679}{6 \times 10^7} = 113.16 \times 10^{-7}$$

$$\text{Average Rate (in Sec.)} = 1.1316 \times 10^{-5} \text{ mol l}^{-1} \text{ sec}^{-1}$$

$$r = \frac{-1}{2} \frac{\Delta(\text{N}_2\text{O}_5)}{\Delta t} = +\frac{1}{4} \frac{\Delta(\text{NO}_2)}{\Delta t} = +\frac{\Delta(\text{O}_2)}{\Delta t}$$

$$r = \frac{1}{4} \frac{\Delta(\text{NO}_2)}{\Delta t}$$

$$\begin{aligned}
 \frac{\Delta(\text{NO}_2)}{\Delta t} &= 4 \times r = 4 \times 6.79 \times 10^{-4} \\
 &= 27.16 \times 10^{-4} \\
 &= 2.72 \times 10^{-5} \text{ mol l}^{-1} \text{ min}^{-1}
 \end{aligned}$$

- **Law of mass action (Guldberg & Wage) :-** The rate of a chemical reaction is proportional to the product of the active masses of the reacting substances.



$$r \propto (A)^a (B)^b$$

$$r = K(A)^a (B)^b$$

active masses = molar concentration

(A) = Active mass of A

(B) = Active mass of B

K = rate constant (or velocity constant)

r = rate of reaction

**मुख्य बिन्दु :- Power equal to it's stoichiometric coefficient in LMA reaction**

When (A) = (B) = 1 molar

rate (r) = K

*Rate of reaction at Unit concentration of reactants is called rate constant or specific rate reaction.*

➤ **Rate law or rate equation or rate expression :-** The representation of rate

Of reaction in term of concentration of the reactants is known as rate law.



a, b → Stoichiometric coefficient

Rate expression :- rate  $\propto (A)^x (B)^y$

Where exponents  $x$  and  $y$  may or may not be equal to the Stoichiometric coefficient (a & b) of the reactants.

$$\text{Rate} = K (A)^x (B)^y$$

$$\frac{-d(R)}{dt} = K (A)^x (B)^y \dots\dots\dots (1)$$

Eq. 1 is known as **differential rate equation, Rate law or rate expression.**

➤ **Order of Reaction :-** *The sum of powers of the concentration of the reactants in the rate law expression is called the order of the reaction.*



rate law  $r = K (A)^x (B)^y$

Order with respect to reactant A =  $x$

Order with respect to reactant B =  $y$

Total order of Reaction =  $x + y$

❖ The order of reaction may be defined as the number of molecules whose concentrations determine the rate of the chemical reaction at a given temp.

**Ques :- Calculate the Overall order of a reaction which has the rate expression.**

(a)  $\text{Rate} = K(A)^{\frac{1}{2}} (B)^{\frac{3}{2}}$

(b)  $\text{Rate} = K(A)^{\frac{3}{2}} (B)^{-1}$

**Ans :-** (a)  $\text{Rate} = K(A)^{\frac{1}{2}} (B)^{\frac{3}{2}}$

**Order with respect to reactant A =  $\frac{1}{2}$**

**Order with respect to reactant B =  $\frac{3}{2}$**

$$\begin{aligned} \text{Total order of Reaction} &= \frac{1}{2} + \frac{3}{2} \\ &= \frac{1+3}{2} = \frac{4}{2} = 2 \text{ (i.e. second order)} \end{aligned}$$

(b)  $\text{Rate} = K(A)^{\frac{3}{2}} (B)^{-1}$

**Order with respect to reactant A =  $\frac{3}{2}$**

**Order with respect to reactant B = -1**

$$\begin{aligned} \text{Total order of Reaction} &= \frac{3}{2} + (-1) \\ &= \frac{3}{2} - 1 = \frac{3-2}{2} = \frac{1}{2} \text{ (i.e. Half order)} \end{aligned}$$

**Ques:- For a reaction  $A + B \rightarrow \text{Product}$ , the rate law is given by**

$r = K (A)^{\frac{1}{2}} (B)^2$  **What is the order of reaction ?**

**Ans :-**  $r = K (A)^{\frac{1}{2}} (B)^2$

Order with respect to reactant A =  $\frac{1}{2}$

Order with respect to reactant B = 2

$$\text{Total order of Reaction} = \frac{1}{2} + 2 = \frac{1+4}{2} = \frac{5}{2} = 2.5$$

➤ **Unit of rate constant or specific reaction rate for reactions of different orders :-**

In general, for a reaction of  $n^{\text{th}}$  power of concentration of reactant, then it is known as  $n^{\text{th}}$  order reaction.

$$\text{rate} \propto (\text{Concentration})^n$$

$$\frac{dx}{dt} = K (\text{Concentration})^n$$

$$\frac{\text{Concentration}}{\text{time}} = K (\text{Concentration})^n$$

$$K = \frac{(\text{Concentration})^1}{\text{time} \times (\text{Concentration})^n}$$

$$K = (\text{Concentration})^{1-n} \text{ time}^{-1}$$

$$K = (\text{mol lit}^{-1})^{1-n} \text{ sec}^{-1}$$

Order of reaction

Unit of K

$n = 0$  (Zero order)

$$(\text{mol lit}^{-1})^{1-0} \text{ sec}^{-1} = \text{mol lit}^{-1} \text{ sec}^{-1}$$

$n = 1$  (First order)

$$(\text{mol lit}^{-1})^{1-1} \text{ sec}^{-1} = (\text{mol lit}^{-1})^0 \text{ sec}^{-1} = \text{sec}^{-1}$$

$n = 2$  (Second order)

$$(\text{mol lit}^{-1})^{1-2} \text{ sec}^{-1} = (\text{mol lit}^{-1})^{-1} \text{ sec}^{-1} = \text{mol}^{-1} \text{ lit}^{+1} \text{ sec}^{-1}$$

$n = 3$  (Third order)

$$(\text{mol lit}^{-1})^{1-3} \text{ sec}^{-1} = (\text{mol lit}^{-1})^{-2} \text{ sec}^{-1} = \text{mol}^{-2} \text{ lit}^{+2} \text{ sec}^{-1}$$

**Ques :- Identify the reaction order from each of the following rate constant.**

(i)  $k = 2.3 \times 10^{-5} \text{ Lmol}^{-1} \text{ sec}^{-1}$

(ii)  $k = 3 \times 10^{-4} \text{ sec}^{-1}$

**Ans:-** (i) Second order

(ii) First order

**Ques :- The conversion of the molecules  $x$  to  $y$  follows second order kinetics. If the concentration  $x$  is increased to three times, how will it affect the rate of formation of  $y$  ?**

**Ans :-**  $x \rightarrow y$   $n = 2$  (Second order)

$$\text{Rate} \propto (x)^2$$

$$\text{Rate} = K (x)^2$$

If concentration of  $x$  is increased three times.

$$\text{now } x = 3x$$

$$\text{Rate} = K (3x)^2 = 9Kx^2$$

$$\text{Rate} = 9 \times K (x)^2$$

Rate of reaction will become 9 times, Hence the rate of formation of  $y$  will increase 9 times.

➤ **Molecularity of reaction :-** The number of reacting species (atoms, ions or molecules) taking part in an *elementary reaction (simple reaction)* which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.



Molecularity = 1



Molecularity = 2



Molecularity = 3

- ❖ Molecularity is defined only for elementary (one step) reactions.
- ❖ There is no meaning of Molecularity for complex (reactions occurring in more than one step) reactions.

➤ **Molecularity of Complex Reactions :-** Many reactions occur in two or more steps. Each Step is an elementary reaction. The rate of various elementary reactions generally differ from one another.

- ❖ The overall rate of the reaction is controlled by the slowest step in a reaction called the overall rate of the reaction is controlled by the slowest step in a reaction called the rate determining step.

➤ **Distinction between molecularity and order of a Reaction :-**

Order of a reaction	Molecularity of a reaction
1. It is the sum of powers raised on concentration terms in the rate expression.	1. It is the number of molecules of reactants taking part in elementary step of a reaction.
2. Order of a reaction is an experimental value, derived from rate expression.	2. It is a theoretical concept.
3. Order of a reaction can be zero, fractional or integer.	3. Molecularity can neither be zero nor fractional.
4. Order of a reaction may have negative value.	4. Molecularity can never be negative.
5. It is assigned for overall reaction.	5. It is assigned for each elementary step of mechanism.
6. It depends upon pressure, temperature and concentration (for pseudo order)	6. It is independent of pressure and temperature.

**Pseudo order Reactions :-** When one of the reactant is present in excess, the rate of reaction does not depend upon the concentration of that reactant these type of reactions known as *Pseudo Order Reaction*.

**Example of Pseudo unimolecular reactions:-**

1. Acidic hydrolysis of ester



$$\text{rate} = K (\text{CH}_3\text{COOC}_2\text{H}_5) \quad \text{order} = 1$$

2. Inversion of Sugar



glucose      Fructose

$$\text{rate} = K(\text{C}_{12}\text{H}_{22}\text{O}_{11}) \quad \text{order} = 1$$

**Differential Rate equations :-**

Ex.  $aA + bB \rightarrow \text{product}$

$$\text{rate} = \frac{dx}{dt} = K(A)^\alpha (B)^\beta$$

**Ques :- A reaction is first order in A and Second order in B.**

1. Write differential rate equation.
2. How is the rate affected on increasing the concentration of B three times ?
3. How is the rate affected when concentration of both A and B is doubled ?

**Ans :-**

(i)  $A + B \rightarrow \text{Product}$

$$r \propto (A)^1 (B)^2$$

$$r = K (A)^1 (B)^2$$

$$\frac{dx}{dt} = K(A)^1 (B)^2$$

(ii) If B is tripled

$$r = K (A)^1 (3B)^2$$

$$r = K (A)^1 (9B)^2$$

$$r = 9 k (A)^1 (B)^2$$

rate of reaction 9 times.

(iii) In both (A) & (B) are doubled

$$r = K (2A)^1 (2B)^2$$

$$r = K \times 2(A)^1 \times 4(B)^2$$

$$r = 8 k(A)^1 (B)^2$$

rate of reaction 8 times.

➤ **Zero Order Reaction** :- If rate of reaction depend on *Zero power* of concentration of Reactant, then it is known as zero order reaction.



$$-\frac{d[R]}{dt} \propto [R]^0$$

$$-\frac{d[R]}{dt} \propto [R]^0$$

$$-\frac{d[R]}{dt} = k [R]^0$$

$$\therefore [R]^0 = 1$$

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

$$-d[R] = k dt$$

$$d[R] = -k dt$$

Integrating both sides

$$\int d [R] = -K \int dt$$

$$[R] = -kt + c \dots\dots\dots(1)$$

C = constant of integration

When  $t = 0$   $[R] = [R]_0$

$[R]_0$  = initial concentration of reactant

Put the value of  $[R]_0$  in equation [1]

$$[R]_0 = -k \times 0 + c$$

$$[R]_0 = C$$

Substituting the value of C in the equation [1]

$$[R] = -kt + [R]_0$$

$$Kt = [R]_0 - [R]$$

$$K = \frac{[R]_0 - [R]}{t} \dots\dots\dots (2)$$

Equation (2) is **integrated rate equation** of zero order reaction.

➤ **Half life period** :- The half life of a reaction is the time in which the concentration of a reactant is *reduced to one half of its initial concentration*. it is represented as  $t_{1/2}$ .  
for zero order reaction

$$t = t_{1/2} \quad [R] = \frac{1}{2}[R]_0$$

$$K = \frac{[R]_0 - [R]}{t}$$

$$K = \frac{[R]_0 - \frac{[R]_0}{2}}{t_{1/2}}$$

$$K = \frac{[R]_0}{2 \times t_{1/2}}$$

$$t_{1/2} = \frac{[R]_0}{2k}$$

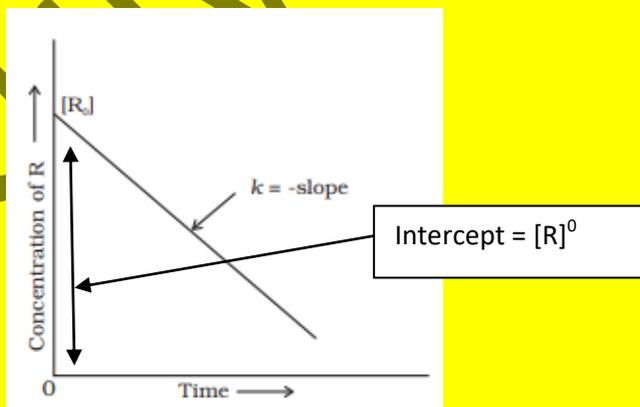
$t_{1/2}$  for a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

$$t_{1/2} \propto [R]_0 \quad t_{1/2} \propto \frac{1}{k}$$

Variation in the concentration vs time plot for a zero order reaction :-

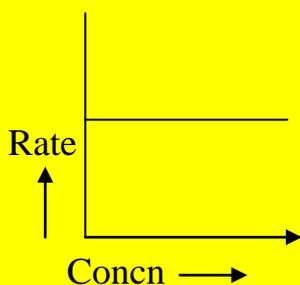
$$[R] = -kt + [R]_0$$

$$y = -mx + c$$



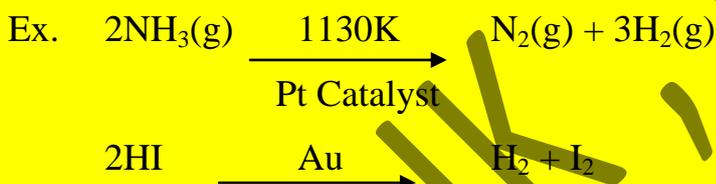
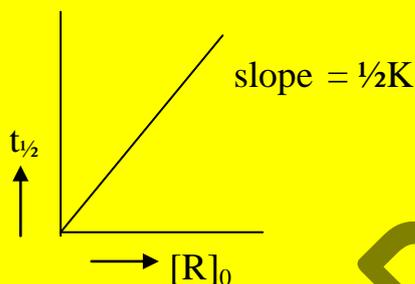
Graph between rate of reaction and concentration :-

$$r = k(R)^0$$



Graph between half life period & initial concentration :-

$$t_{1/2} = \frac{[R]_0}{2k} \quad y = mx$$



➤ **First Order Reaction :-** If rate of reaction depend on **First power** of concentration of Reactant, then it is known as first order Reaction.



$$-\frac{d[\text{R}]}{dt} \propto [\text{R}]^1$$

$$-\frac{d[\text{R}]}{dt} = K [\text{R}]^1$$

$$-\frac{d[\text{R}]}{[\text{R}]^1} = kdt$$

$$\frac{1}{(\text{R})} d[\text{R}] = -kdt$$

Integrating both side

$$\int \frac{1}{[\text{R}]} d[\text{R}] = -K \int dt$$

$$\ln [\text{R}] = -kt + c \quad \dots\dots\dots(1)$$

C = Constant of integration

$$t = 0 \quad [R] = [R]_0$$

$[R]_0$  = Initial Concentration of Reactant

Put these value in above equation (1)

$$\ln [R]_0 = -k \times 0 + c$$

$$C = \ln [R]_0$$

Substituting the value of C in the equation (1)

$$\ln [R] = -kt + \ln [R]_0$$

$$Kt = \ln[R]_0 - \ln[R]$$

$$Kt = \ln \frac{[R]_0}{[R]}$$

$$K = \frac{2.303}{t} \log \frac{[R]_0}{[R]} \dots\dots\dots (2)$$

Equation (2) is integrated rate equation of first order reaction.

**Half life Period :-**

For first order reaction

$$t = t_{1/2} \quad [R] = \frac{1}{2}[R]_0$$

$$K = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$K = \frac{2.303}{t_{1/2}} \log \frac{2 \times [R]_0}{[R]}$$

$$K = \frac{2.303}{t_{1/2}} \log 2$$

$$t_{1/2} = \frac{2.303 \times .3010}{k}$$

$$t_{1/2} = \frac{.693}{k}$$

for first order reaction  $t_{1/2}$  is independent of  $(R)_0$ .

➤ **Graph :-** A plot between  $\ln(R)$  and  $t$  for a first order reaction.

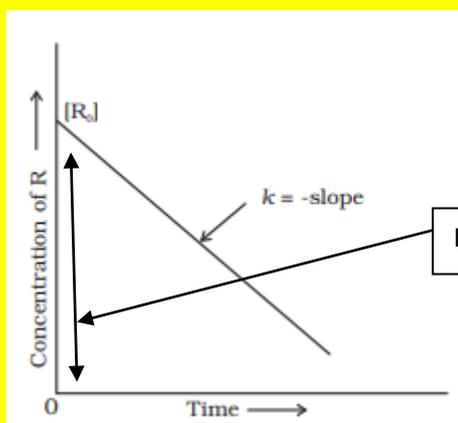
$$K = \frac{1}{t} \ln \frac{[R]_0}{[R]}$$

$$kt = \ln \frac{[R]_0}{[R]}$$

$$kt = \ln[R]_0 - \ln[R]$$

$$\ln[R] = -kt + \ln[R]_0$$

$$y = -mx + c$$



Slope = - K

Intercept =  $\ln [R]_0$

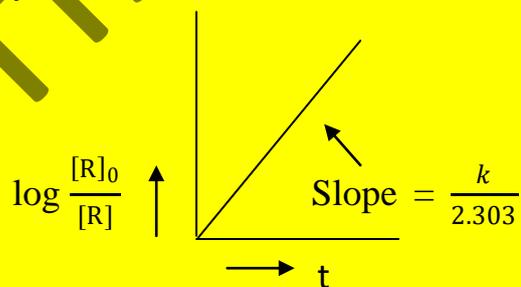
Plot a graph  $\log \frac{[R]_0}{[R]}$  and time :-

$$K = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$K = 2.303 \log \frac{[R]_0}{[R]}$$

$$\log \frac{[R]_0}{[R]} = \frac{kt}{2.303}$$

$$y = mx$$



Ex. Hydrogenation of Ethene

Natural and artificial radioactive decay.



Decomposition of  $\text{N}_2\text{O}_5$  and  $\text{N}_2\text{O}$

**Expression for the rate constant for reactions of first order from concentrations of the reactant at two different times :-**

$$K = \frac{1}{t} \ln \frac{[R]_0}{[R]}$$

$$kt = \ln[R]_0 - \ln[R]$$

$$\ln[R] = \ln[R]_0 - kt$$

At time  $t_1$  -

$$\ln[R]_1 = \ln[R]_0 - kt_1$$

At time  $t_2$

$$\ln[R]_2 = \ln[R]_0 - kt_2$$

Subtracting equation 2 from equation 1

$$\ln[R]_1 - \ln[R]_2 = [\ln[R]_0 - kt_1] - [\ln[R]_0 - kt_2]$$

$$\ln \frac{[R]_1}{[R]_2} = \ln[R]_0 - kt_1 - \ln[R]_0 + kt_2$$

$$\ln \frac{[R]_1}{[R]_2} = kt_2 - kt_1$$

$$\ln \frac{[R]_1}{[R]_2} = k(t_2 - t_1)$$

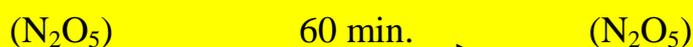
$$k = \frac{1}{t_2 - t_1} \ln \frac{[R]_1}{[R]_2}$$

$$k = \frac{2.303}{t_2 - t_1} \log \frac{[R]_1}{[R]_2}$$

**Ques :- The initial concentration of  $\text{N}_2\text{O}_5$  in the following first order reaction  $\text{N}_2\text{O}_5(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$  was  $1.24 \times 10^{-2} \text{ mol L}^{-1}$  at 318K. The concentration of  $\text{N}_2\text{O}_5$  after 60 minutes was  $0.20 \times 10^{-2} \text{ mol L}^{-1}$ . Calculate the rate constant of the reactant at 318K. ( $\log 6.2 = .7924$ )**

**Ans :-** To be given

Order = First



(R)<sub>1</sub> (R)<sub>2</sub>

$$1.24 \times 10^{-2} \text{ mol L}^{-1} \qquad 0.20 \times 10^{-2} \text{ mol L}^{-1}$$

$$t_1 = 0$$

$$t_2 = 60 \text{ min.}$$

K = ?

$$k = \frac{2.303}{t_2 - t_1} \log \frac{[R]_1}{[R]_2}$$

$$k = \frac{2.303}{(60-0)} \log \frac{1.24 \times 10^{-2}}{.20 \times 10^{-2}}$$

$$= \frac{2.303}{60} \log \frac{1.24}{.20} \qquad \log 6.2 = .7924$$

$$= \frac{2.303}{60} \log 6.2$$

$$= \frac{2.303}{60} \times .7924 = \frac{1.824}{60} = 0.0304 \text{ min}^{-1}$$

**Ques :-** A first order reaction is found to have a rate constant  $K = 5.5 \times 10^{-14} \text{ Sec}^{-1}$   
find the half life of the reaction.

**Ans :-** To be given

Order = First

$$K = 5.5 \times 10^{-14} \text{ S}^{-1}$$

$$t_{1/2} = ?$$

$$t_{1/2} = \frac{.693}{K}$$

$$t_{1/2} = \frac{.693}{5.5 \times 10^{-14}}$$

$$= \frac{.693 \times 10^{14}}{5.5}$$

$$= \frac{6.93 \times 10^{13}}{5.5}$$

$$= 1.26 \times 10^{13} \text{ sec.}$$

**Ques :- Show that in a first order reaction, time required for completion of 99.9% is 10 times of half life ( $t_{1/2}$ ) of the reaction.**

**Ans :-** Order = First

Suppose  $[R]_0 = 100$

$$[R] = 100 - 99.9 = 0.1$$

$$K = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$K = \frac{2.303}{t} \log \frac{100}{.1}$$

$$K = \frac{2.303}{t} \log 10^3 \quad (\because \log m^n = n \log m)$$

$$K = \frac{3 \times 2.303}{t} \log 10 \quad (\because \log 10 = 1)$$

$$K = \frac{3 \times 2.303}{t} \dots \dots \dots (1)$$

Half life period  $t_{1/2} = \frac{.693}{k}$

$$K = \frac{2.303 \times .3010}{t_{1/2}} \dots \dots \dots (2)$$

Put the value of K in equation (1)

$$\frac{2.303 \times .3010}{t_{1/2}} = \frac{3 \times 2.303}{t}$$

$$\frac{t}{t_{1/2}} = \frac{3}{.3010}$$

$$\frac{t}{t_{1/2}} = \frac{3000}{3010}$$

$$= \frac{t}{t_{1/2}} = 9.96$$

$$\frac{t}{t_{1/2}} = 10$$

$t = 10 \times t_{1/2}$

**Ques :- A first order reaction has a rate constant  $1.15 \times 10^{-3} \text{ sec}^{-1}$  . How long will 5 gm of this reactant take to reduce to 3gm.**

**Ans :-** To be given

Order = First

$$K = 1.15 \times 10^{-3} \text{ sec}^{-1}$$

$$[R]_0 = 5\text{g}$$

$$[R] = 3\text{g}$$

$$t = ?$$

$$K = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

$$t = \frac{2.303}{1.15 \times 10^{-3}} \log \frac{5}{3}$$

$$t = \frac{2.303 \times 1000}{1.15} \log 1.67$$

$$t = \frac{2.303}{1.15} \times .223$$

$$t = \frac{512.9}{1.15} = 446.01 \text{ sec}$$

**Ques :- Time required to decompose  $\text{SO}_2\text{Cl}_2$  to half of its initial amount is 60 minutes. If the decomposition is a first order reaction .calculate the rate constant of the reaction.**

**Ans :-** To be given

$$t_{1/2} = 60\text{min}$$

Order = First

$$K = ?$$

$$t_{1/2} = \frac{.693}{K}$$

$$k = \frac{.693}{\frac{t_1}{2}}$$

$$k = \frac{.693}{60}$$

$$k = 0.01155$$

$$k = 1.15 \times 10^{-2} \text{ min}^{-1}$$

➤ First Order reaction for numerical purpose :-

$$K = \frac{2.303}{t} \log \frac{a}{a-x}$$

$k$  = Rate constant

$a$  = initial concentration

$t$  = time

$x$  = product for some time

➤ Integrated rate equation of first order reaction in gaseous state :-

	$A_{(g)}$	$\longrightarrow$	$B_{(g)}$	$+$	$C_{(g)}$
Initial Pressure	$P_i$		0		0
After $t$ – time	$P_i - x$		$x$		$x$
Pressure					

$$\text{Total Pressure } (P_t) = (P_i - x) + x + x$$

$$P_t = P_i + x$$

$$\text{Initial Pressure } a = P_i$$

$$\text{Final Pressure } (a - x) = P_i - (P_t - P_i)$$

$$(a - x) = 2P_i - P_t$$

$$K = \frac{2.303}{t} \log \frac{P_i}{2P_i - P_t}$$

**Ques :-** The following data were obtained during the first order thermal decomposition of  $N_2O_5(g)$  at constant volume :-



S.R.	time(sec)	total pressure (atm)
1	0	0.5
2	100	0.512

Calculate the rate constant.

Solu :-	$2\text{N}_2\text{O}_5(\text{g})$	$2\text{N}_2\text{O}_4(\text{g})$	$+\text{O}_2(\text{g})$
Initial Pressure	$P_0$	0	0
Pressure after time t	$(P_0 - 2P)$	2P	P

Total Pressure after time t

$$P_t = (P_0 - 2P) + 2P + P$$

$$P_t = P_0 + P$$

$$P = P_t - P_0$$

Pressure of  $\text{N}_2\text{O}_5$  after time t  $(\text{N}_2\text{O}_5) = P_0 - 2P$

$$= P_0 - 2(P_t - P_0)$$

$$= P_0 - 2P_t + 2P_0$$

$$= 3P_0 - 2P_t$$

This  $(\text{N}_2\text{O}_5)_0 \propto P_0$        $(\text{N}_2\text{O}_5)_t \propto 3P_0 - 2P_t$

$$K = \frac{2.303}{t} \log \frac{[\text{R}]_0}{[\text{R}]}$$

$$K = \frac{2.303}{t} \log \frac{(\text{N}_2\text{O}_5)_0}{(\text{N}_2\text{O}_5)_t}$$

$$K = \frac{2.303}{t} \log \frac{P_0}{3P_0 - 2P_t}$$

$$P_0 = 0.5 \text{ atm}$$

$$P_t = 0.512 \text{ atm}$$

$$K = \frac{2.303}{100} \log \frac{0.5}{3 \times 0.5 - 2 \times 0.512}$$

$$K = \frac{2.303}{100} \log \frac{0.5}{1.5 - 1.024}$$

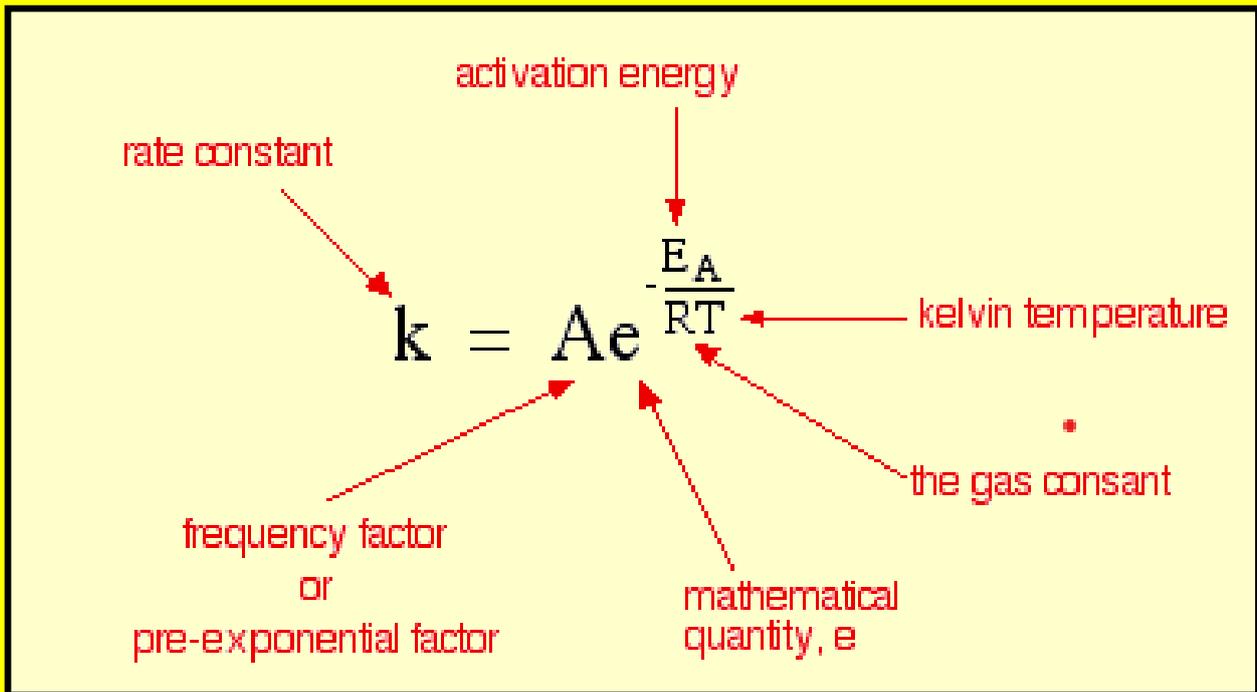
$$K = .02303 \log \frac{0.5}{.476}$$

$$K = .02303 \log 1.050$$

$$K = 0.02303 \times 0.0212$$

$$K = 0.000488 \quad K = 4.88 \times 10^{-4} \text{ sec}^{-1}$$

➤ Arrhenius equation :-



$A$  = Arrhenius factor or frequency factor or pre – exponential factor.

$K$  = rate constant                       $E_a$  = activation energy

$R$  = gas constant                       $T$  = temperature

➤ Relation between the  $\log K$  and  $\frac{1}{T}$  of arrhenius equation :-

According to Arrhenius equation :-

$$K = Ae^{-\frac{E_a}{RT}} \dots\dots\dots (1)$$

Taking natural logarithm of both sides of equation

$$\ln K = \ln \left( Ae^{-\frac{E_a}{RT}} \right)$$

$$\ln K = \ln A + \ln e^{-\frac{E_a}{RT}} \quad (\because \log mn = \log m + \log n)$$

$$\ln k = \ln A - \frac{E_a}{RT} \ln e \quad (\because \log m^n = n \log m)$$

$$\ln K = \ln A - \frac{E_a}{RT} \quad (\because \ln_e e = 1)$$

$$\frac{E_a}{RT} = \ln A - \ln K$$

$$\frac{E_a}{RT} = \ln \frac{A}{K}$$

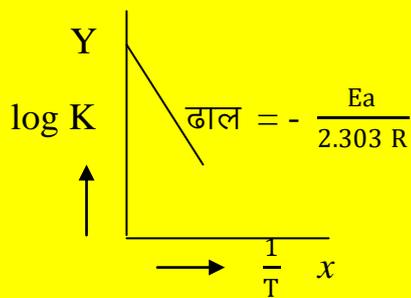
$$\frac{E_a}{RT} = 2.303 \log \frac{A}{K}$$

$$\frac{E_a}{2.303 RT} = \log \frac{A}{K}$$

$$\frac{E_a}{2.303 RT} = \log A - \log K$$

$$\log K = - \frac{E_a}{2.303 RT} + \log A$$

$$y = -mx + c$$



➤ Arrhenius equation for  $T_1$  &  $T_2$  temp. (temp. Difference) :-

Arrhenius equation  $K = Ae^{-\frac{E_a}{RT}}$  ..... (1)

Taking natural logarithm of both sides of equation.

$$\ln K = \ln A + \ln e^{-\frac{E_a}{RT}}$$

$$\ln K = \ln A - \frac{E_a}{RT} - \ln e$$

$$\ln K = \ln A - \frac{E_a}{RT} \text{ .....(2)}$$

$$\ln K_1 = \ln A - \frac{E_a}{RT_1} \text{ .....(3)}$$

$$\ln K_2 = \ln A - \frac{E_a}{RT_2} \text{ .....(4)}$$

equation (4) – equation (3)

$$\ln K_2 - \ln K_1 = \left( \ln A - \frac{E_a}{RT_2} \right) - \left( \ln A - \frac{E_a}{RT_1} \right)$$

$$\ln \frac{K_2}{K_1} = \ln A - \frac{E_a}{RT_2} - \ln A + \frac{E_a}{RT_1}$$

$$\ln \frac{K_2}{K_1} = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

$$2.303 \log \frac{K_2}{K_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303 R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

$R = 8.314 \text{ j mol}^{-1}$        $E_a = \text{activation energy}$

$K_1$  &  $K_2 = \text{rate constant}$     $T$  &  $T_2 = \text{temp.}$

**Ques :- The rate constants of a reaction at 500K and 700K are  $0.02 \text{ sec}^{-1}$  and  $0.07 \text{ sec}^{-1}$  respectively. Calculate the value of  $E_a$ .**

**Ans :-** To be given

$$T_1 = 500\text{K}$$

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303 R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

$$T_2 = 700\text{K}$$

$$\log \frac{0.07}{0.02} = \frac{E_a}{2.303 \times 8.314} \left( \frac{700 - 500}{700 \times 500} \right)$$

$$K_1 = 0.02 \text{ sec}^{-1}$$

$$\log 3.5 = \frac{E_a}{2.303 \times 8.314} \times \frac{200}{350000}$$

$$K_2 = 0.07 \text{ sec}^{-1}$$

$$.5441 = \frac{E_a}{2.303 \times 8.314} \times \frac{200}{350000}$$

$$E_a = ?$$

$$E_a = \frac{.5441 \times 2.303 \times 8.314 \times 350000}{200}$$

$$R = 8.14 \text{ j mol}^{-1}$$

$$E_a = \frac{5441 \times 2.303 \times 8.314 \times 35}{200}$$

$$E_a = 18231.4 \text{ J}$$

**Ques :- The rate of the chemical reaction doubles for an increase of 10k in absolute temp. from 298k, Calculate  $E_a$ .**

**Ans :-** To be given

$$K_1 = K \quad K_2 = 2K$$

$$T_1 = 298\text{K}$$

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303 R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

$$T_2 = 298 + 10 = 308\text{K}$$

$$\log \frac{2K}{K} = \frac{E_a}{2.303 \times 8.314} \left( \frac{308 - 298}{308 \times 298} \right)$$

$$K_1 = K$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \times \frac{10}{308 \times 298}$$

$$K_2 = 2K$$

$$.3010 = \frac{E_a}{2.303 \times 8.314} \times \frac{10}{300 \times 298}$$

$$R = 8.314 \text{ jk}^{-1} \text{ mol}^{-1}$$

$$E_a = ?$$

$$E_a = \frac{.3010 \times 2.303 \times 8.314 \times 308 \times 298}{10}$$

$$E_a = \frac{.693 \times 8.314 \times 308 \times 298}{10}$$

$$= \frac{5.7616 \times 91784}{10} = \frac{528822.69}{10}$$

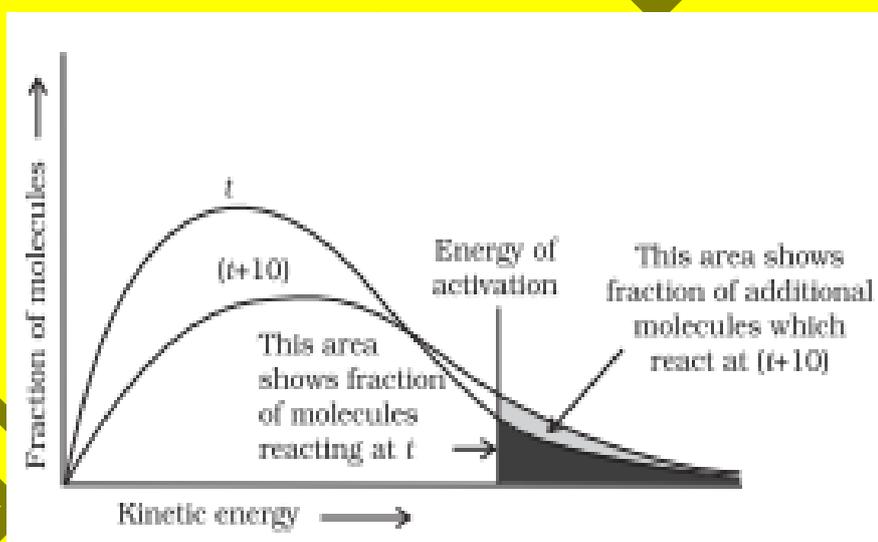
$$= 52882.26 \text{ Jmol}^{-1}$$

$$E_a = 52.9 \text{ kJmol}^{-1}$$

➤ **Temperature Coefficient :-**

for most of the reactions, the rate of reaction increase two or three times, with every  $10^{\circ}\text{C}$  rise in temp. This rate of increase factor is known as temperature coefficient.

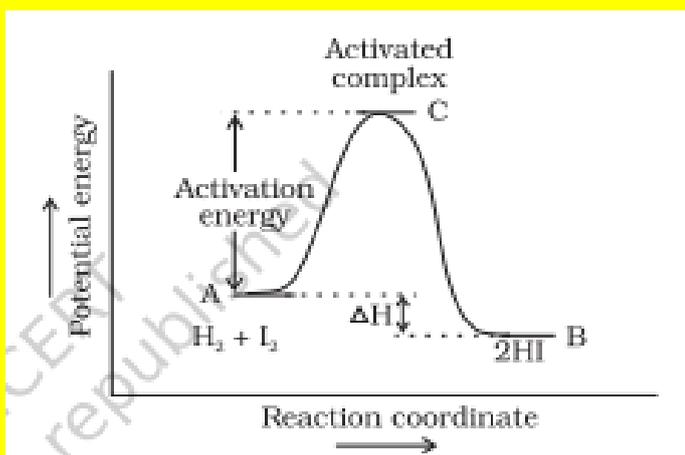
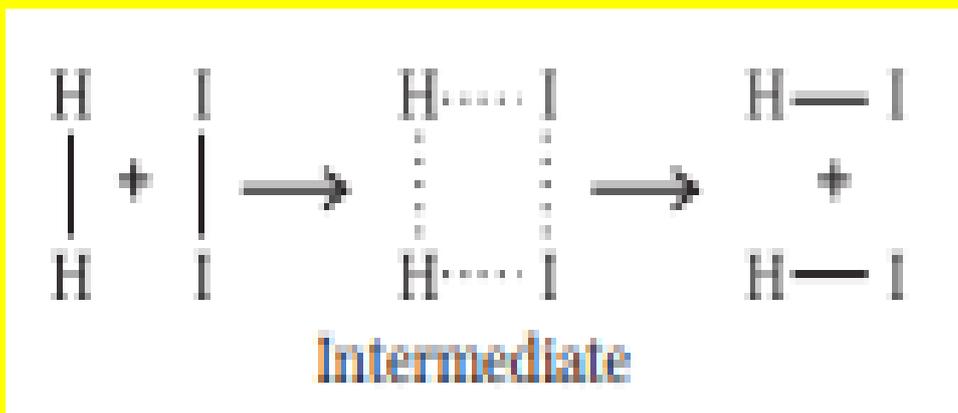
$$\text{Temperature Coefficient} = \frac{K_{T+10}}{K_T} = 2 \text{ to } 3$$



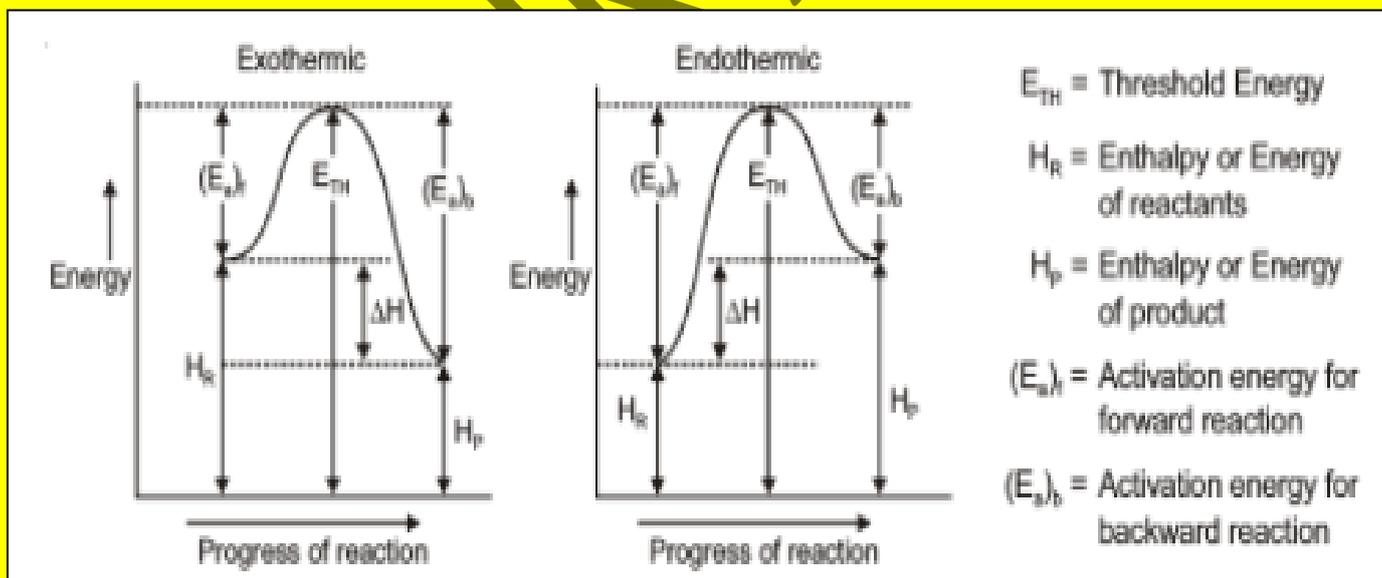
➤ **Activation Energy Concept :-**



This reaction can take place only when a molecule of hydrogen and a molecule of Iodine collide to form an intermediate. It exists for a very short time and then breaks up to form two molecules of hydrogen Iodide.



The energy required to form this intermediate, called activated complex (C) is known as activation energy. ( $E_a$ )



$(E_a)_f$  = Activation energy for forward reaction

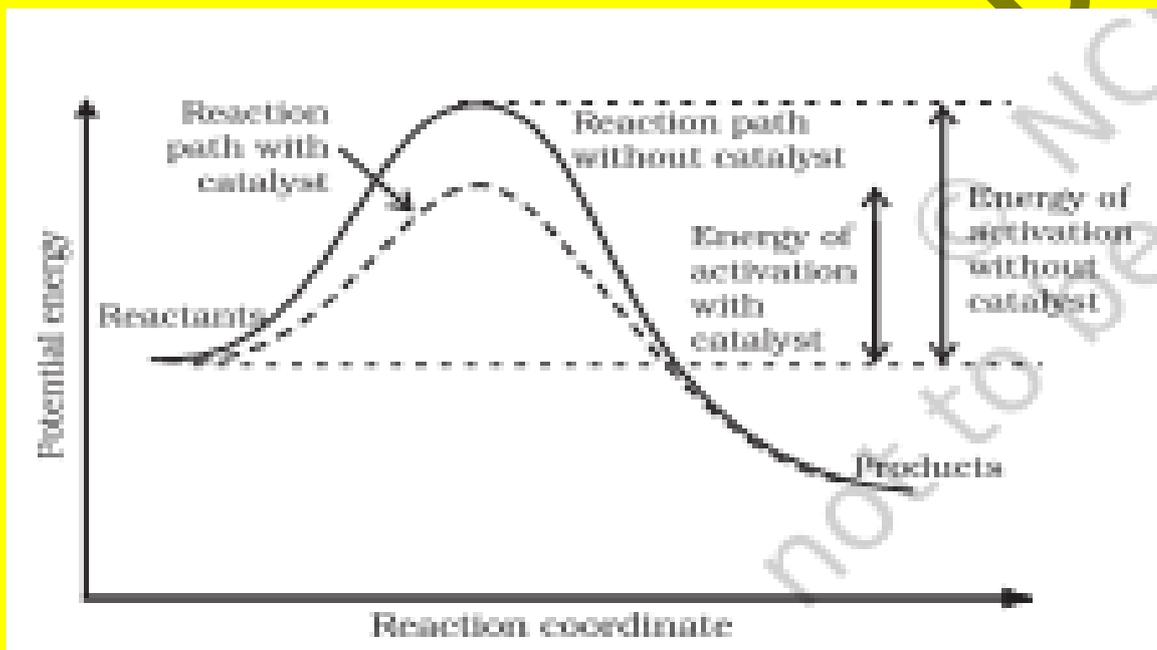
$(E_a)_b$  = activation energy for backward reaction

The minimum amount of energy which the colliding molecules must possess to make the chemical reaction to occur, is known **threshold energy**.

➤ **Effect of catalyst :-** A catalyst is a substance which increases the rate of a reaction without itself undergoing any permanent chemical change.



The word catalyst should not be used when the added substance reduces the rate of reaction. The substance is then called Inhibitor.



- ❖ Lower the value of activation energy faster will be the rate of a reaction.
- ❖ A catalyst does not change Gibbs energy ( $\Delta G$ ) of a reaction.
- ❖ It catalyses the spontaneous reactions but does not catalyse non spontaneous reactions.
- ❖ A catalyst does not change the equilibrium constant (equilibrium State) of a reaction.
- ❖ It helps in attaining the equilibrium faster.

➤ **Collision theory of chemical reaction :-** The number of collisions per second per unit volume of the reaction mixture is called **collision frequency (Z)**.

For a bimolecular elementary reaction



$\text{Rate} = Z_{ABE} \cdot e^{-\frac{E_a}{RT}}$

$Z_{AB}$  = Collision frequency of reactions A & B.

- ❖ All collisions do not lead to formation of products. The molecules which have sufficient energy and proper orientation collide to give product. Such collisions are called effective collisions.
- ❖ The proper orientation of reactant molecules lead to product formation where as improper orientation makes them simply bounce back and no products are formed.

To account for effective collisions, another factor “P” called the **probability or steric factor** is introduced. It takes into account the fact that in a collision, molecules must be properly oriented.

$$\text{Rate} = PZ_{AB}e^{-\frac{E_a}{RT}}$$

Thus, in collision theory activation energy and proper orientation of the Molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.



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