

## Chapter = 4

# CHEMICAL KINETICS

### ⇒ Rate of Reaction

$$\text{Rate of Reactant} = -\frac{d[R]}{dt} = \frac{R_2 - R_1}{t_2 - t_1} = \frac{-\Delta R}{\Delta t}$$

$$\text{Rate of product} = \frac{d[P]}{dt} = \frac{P_2 - P_1}{t_2 - t_1} = \frac{+\Delta P}{\Delta t}$$

$$\text{Rate of Reaction} = -\frac{d[R]}{dt} = \frac{+d[P]}{dt}$$

$$\text{unit} - \frac{\text{Concentration}}{\text{Time}} = \frac{\text{Mol}}{\text{L} \cdot \text{Sec.}}$$

### ⇒ Avg. Rate Reaction

$\Delta t = \text{large.}$

$$\text{Average rate} = \frac{-\Delta[R]}{\Delta t} + \frac{\Delta[P]}{\Delta t} = \frac{\Delta C}{\Delta t}$$

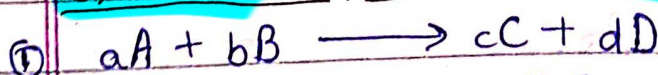
concentration  
s

### ⇒ Inst. Rate Reaction

$dt = \text{very small}$

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

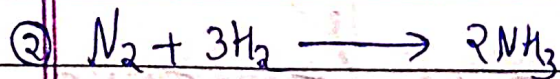
### General expression of rate of Rxn



$$r_{\text{avg.}} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

$r$

$$r_{\text{inst.}} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$



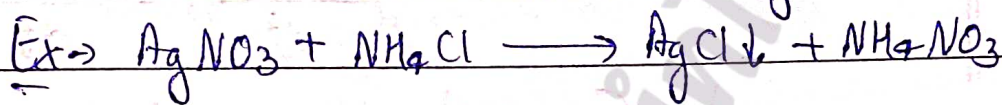
$$r_{\text{avg.}} = \frac{-\Delta[\text{N}_2]}{\Delta t} = \frac{-1}{3} \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NH}_3]}{\Delta t}$$

$$r_{\text{inst.}} = \frac{-d[\text{N}_2]}{dt} = \frac{-1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

## ⇒ Types of Reaction

### ① fast Reaction:

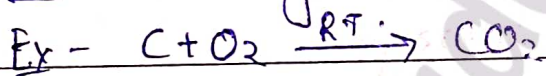
$\Delta t = \text{small}$ , Rate = large



### ② Slow Reaction:

$\Delta t = \text{large}$ , Rate = small

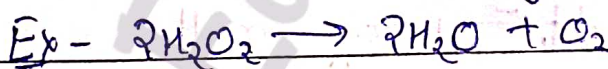
Ex - Rusting of Iron



### ③ Moderate Reaction:

$\Delta t = \text{not too large or not too small}$

Rate = Can be identify accurately:



## factors affecting of rate of Reaction

① Concentration of Reactant

② Large Surface Area

③ Temperature increases

④ Pressure of Catalyst

⑤ Pressure of light

⇒ Rate law: It states that the rate of Rxn is directly proportional to product of Concentration reactant.

Consider a general equation:



$$\text{Rate} \propto [A]^a [B]^b$$

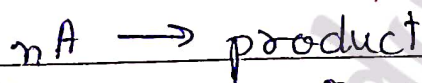
$$\text{Rate} = k[A]^a [B]^b$$

where,  $k$  = Rate constant

$$\text{if } [A] = [B] = 1 \text{ Mol/L}$$

$$\text{then, } \boxed{\text{Rate} = k}$$

## Unit of rate Constant



$$\text{Rate} = k[A]^n$$

$$k = \frac{\text{Rate}}{[A]^n} = \text{Rate} \times \frac{1}{[A]^n}$$

$$= \frac{(\text{Conc./L})}{\text{time}} \times \frac{1}{(\text{Conc})^n}$$

$$= (\text{Conc.})^{1-n} \times \text{time}^{-1}$$

$$\boxed{k = \left(\frac{\text{mol}}{\text{L}}\right)^{1-n} \text{ time}^{-1}}$$

$$\text{if } n=0, k = \text{mol/L} \cdot \text{sec}$$

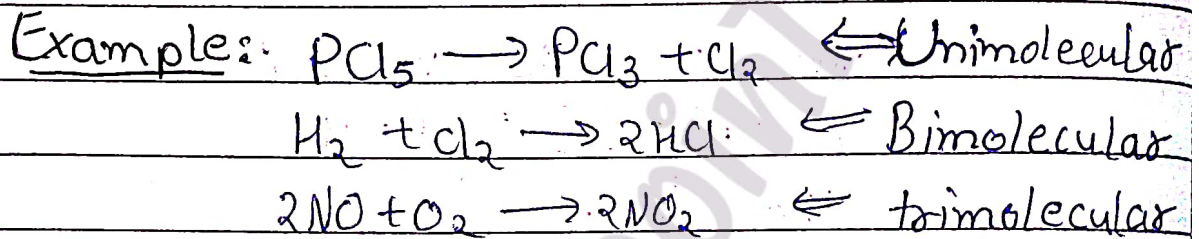
↑ zero order

$$n=1, k = \text{Sec}^{-1}$$

↑ first order

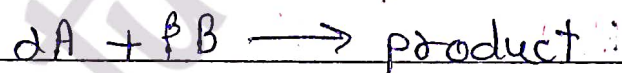
imp.  
⇒ **Molecularity**: The total no. of Reacting Species which taking part in a balanced chemical equation is known as molecularity.

- It independent on temp. & pressure.
- It can not be negative, zero or fractional.
- It define only elementary reaction.



## ⇒ **Order of Reaction**

It is the sum of power of concentration of reactant in rate law expression.

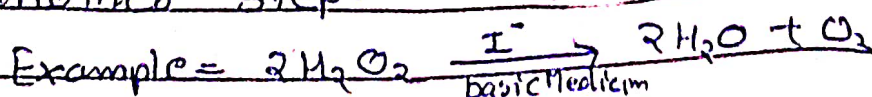


$$\text{order of Rm} = a + b$$

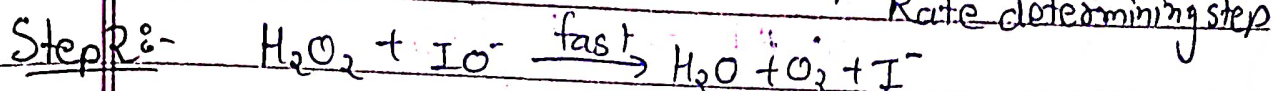
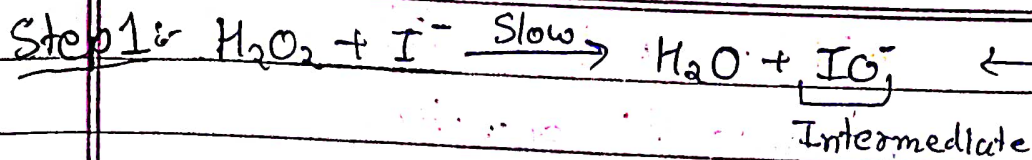
- It depends on temp. & pressure
- It can be zero or fractional or whole no.
- It define both elementary as well as complex reaction.

## → **Complex reaction**

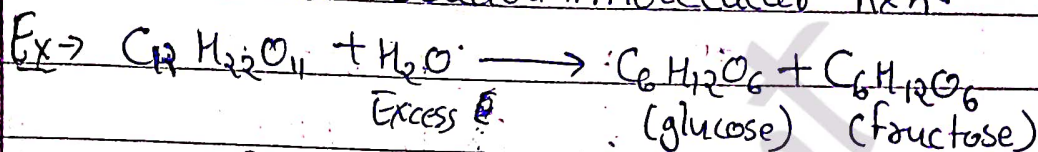
Reaction intermediate: Those species which produce in one-step but consume in another step.



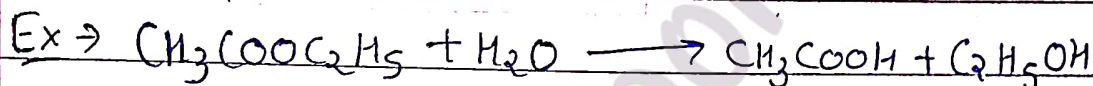
$$\text{Rate} = -\frac{1}{2} \frac{d[H_2O_2]}{dt} = k[H_2O_2]^2 [I^-]$$



⇒ **Pseudounimolecular Reaction**: Those reaction whose order is 1 but molecularity is 2 is known as Pseudounimolecular Rxn.



Rate =  $k [C_6H_{12}O_{11}]$

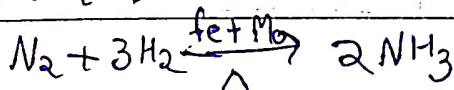
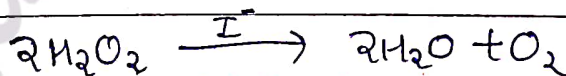
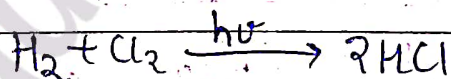


Rate =  $k [CH_3COOC_2H_5]$

⇒ **Zero order Reaction**: The rate of Rxn is directly proportional to zero order of concentration of reactant species.

Rate =  $k [A]^0$ , Rate = k

Examples:



# **Integrated or differential expression for zero order reaction**



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

$-\frac{d[R]}{dt} = -k \quad \text{--- (1)}$

$$d[R] = -k dt \quad \text{--- (2)}$$

Integrate this equation

$$\int_{R_0}^R d[R] = -k \int_0^t dt$$

$$[R]_R - [R]_{R_0} = -k [t]_0^t$$

$$[R] - [R_0] = -kt$$

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

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

$$k = \frac{[R]_0 - [R]}{t} \quad \text{--- (3)}$$

### # Half life time for zero order reaction

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

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

$$t_{1/2} = \frac{[R]_0}{2k} \quad \leftarrow \text{Half life}$$

$$t = \frac{[R]_0}{k} \quad \leftarrow \text{life time}$$

### ⇒ Graphical representation for zero order reaction

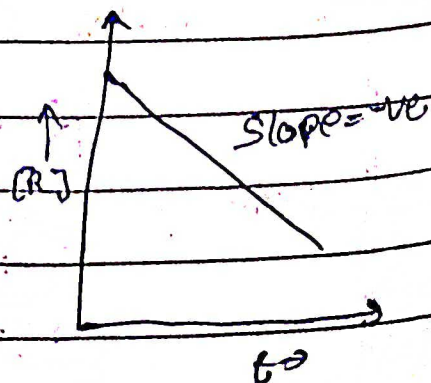
① [R] vs t :-

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

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

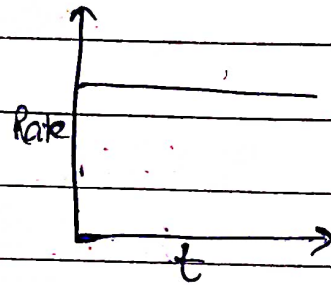
$$[R] = -kt + [R]_0$$

slope = -ve.



## ② Rate vs t

$$\frac{dc}{dt} = k = \text{constant}$$

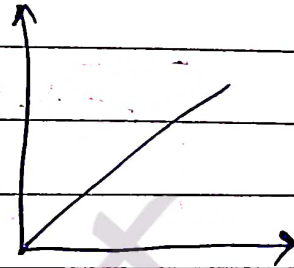


## ③ $t_{1/2}$ vs $R_0$

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

$$t_{1/2} = \frac{[R]_0}{2} \cdot \frac{1}{k} + 0$$

Slope  $\rightarrow +ve.$



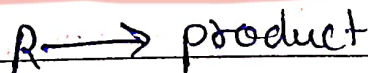
$\Rightarrow$  first order Reaction: - The rate of reaction is directly proportional to first power of concentration of Reactant.

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^1$$



$$\text{Rate} = k[\text{NH}_4\text{NO}_2]$$

## Integrated expression for first order Reaction



$$\text{Rate} = -\frac{d[R]}{dt} = k[R]$$

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

Integrate this equation.

$$\int_{R_0}^R \frac{d[R]}{[R]} = -k \int_0^t dt$$

$$\ln [R]_R - \ln [R]_{R_0} = -kt$$

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

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

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

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

Half life time for first order

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

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

$$t_{1/2} = \frac{2.303 \log 2}{k} = t_{1/2} = \frac{2.303 \times 0.3010}{k}$$

$$t_{1/2} = \frac{0.6932}{k}$$

Qus- The rate constant for a first order reaction is  $60 \text{ sec}^{-1}$ . How much time will it take to reduce the initial concentration of the reactant to its  $1/16^{\text{th}}$  value.

$$\text{Sol}^n \quad t = \frac{2.303}{k} \log \frac{[R]_0}{[R]} = \frac{2.303}{k} \log \frac{[R]_0}{[R]_0/16}$$

$$t = \frac{2.303}{k} \log 16$$

$$t = \frac{2.303}{60} \times 4 \log 2 = \frac{2.303}{60} \times 4 \times 0.30 = 4.62 \times 10^{-2} \text{ sec}$$



Ques- A first order reaction takes 40 min. for 30% decomposition. Calculate  $t_{1/2}$ .

Sol<sup>n</sup>

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$
$$= \frac{2.303}{40} \log \frac{100}{70}$$
$$= \frac{2.303}{40} \times 0.154$$

$$t_{1/2} = \frac{0.6932 \times 40}{2.303 \times 0.1548} = 77.78 \text{ min}$$

Ques- A first order reaction takes 40 min for 75% completion. Calculate  $t_{1/2}$ ?

Ans

$$\frac{t_{75\%}}{t_{50\%}} = \frac{t_{75}}{t_{1/2}} = \frac{\frac{2.303}{k} \times \log \frac{100}{25}}{\frac{2.303}{k} \times \log \frac{100}{50}}$$
$$= \frac{2 \log 2}{\log 2} = 2$$

$$\frac{40}{t_{1/2}} = 2$$

$$t_{1/2} = 20 \text{ min}$$

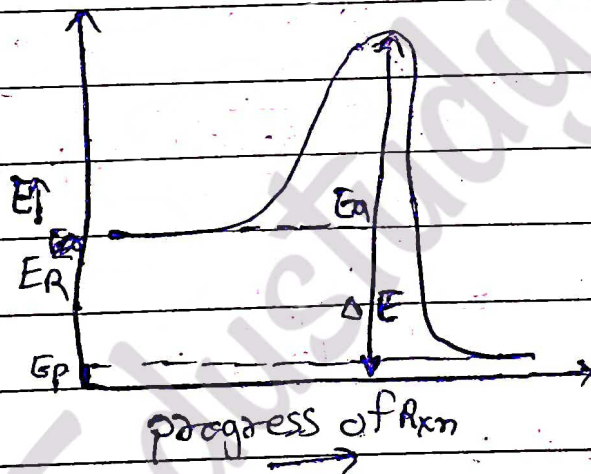
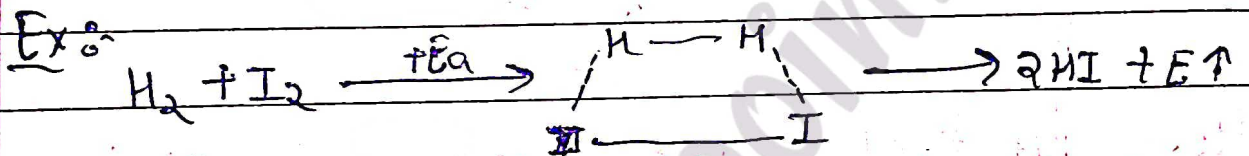
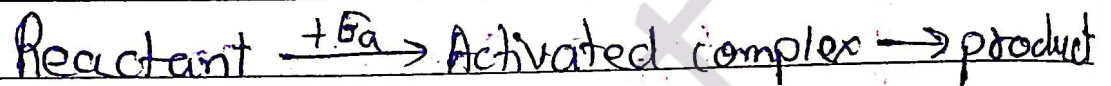
⇒ Activation energy (AE): The amount of energy required to form activative complex is known as Activation energy.

$$AE = TE - \text{Average } kE$$

∴ TE = min energy present in molecule

$\Rightarrow$  Threshold Energy (TE) :- The minimum energy of reactive molecule in order to undergo effective collision which leads to the formation of product is known as Threshold Energy

$\Rightarrow$  Activated Complex :-

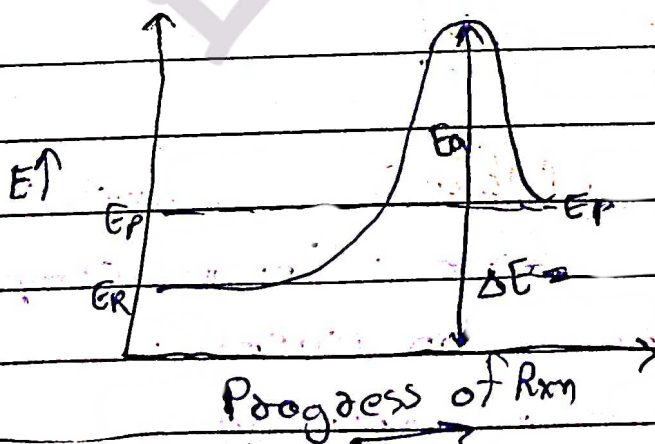


$E_a \rightarrow$  Activation energy

$\Delta E = E_p - E_r = -ve.$

exothermic Rxn

$E_f < E_b$



$\Delta E = E_p - E_r = +ve$

Endothermic Rxn

$E_f > E_b$

collision frequency

⇒ **Collision Theory** :-  $k = P Z_{AB} e^{-E_a/RT}$  → fraction of collision

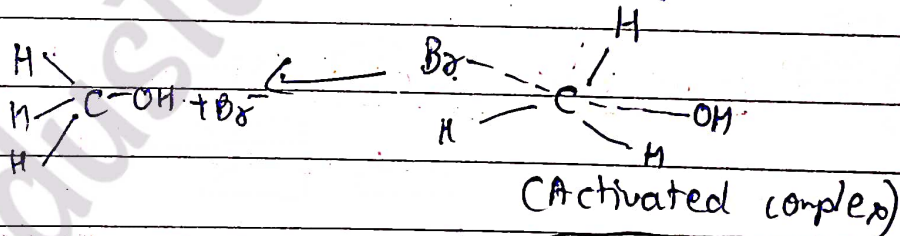
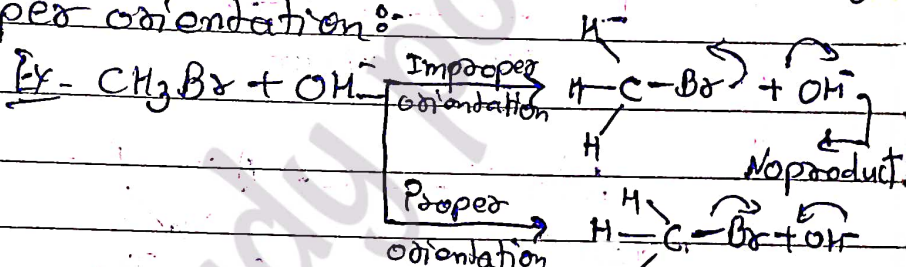
↓  
Probability factor

① Collision frequency :- The total No. of collision take place per unite vol. per unit time

② Effective collision :- it depends upon two factors

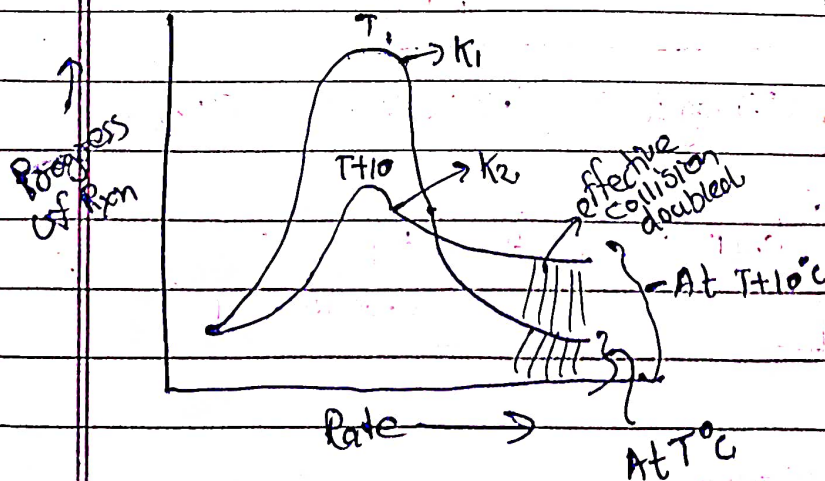
1) energy barrier :- Molecule has must have greater energy than the Activation energy

2) Proper orientation :-



⇒ **Temperature Coefficient** :-  $\frac{\text{Rate Constant at } T+10}{\text{Rate Constant at } T}$

Maxwell Boltzman graph



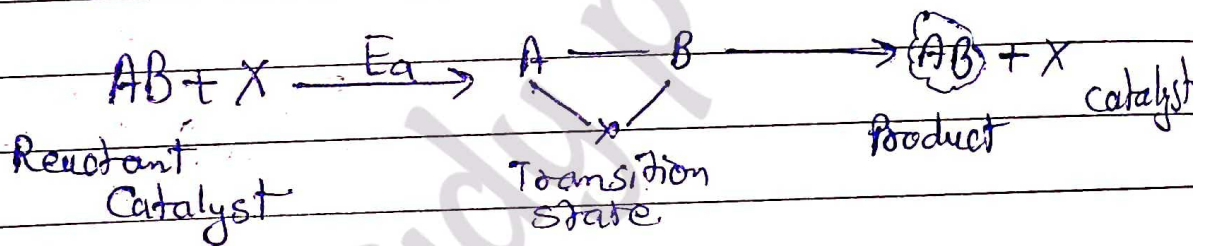
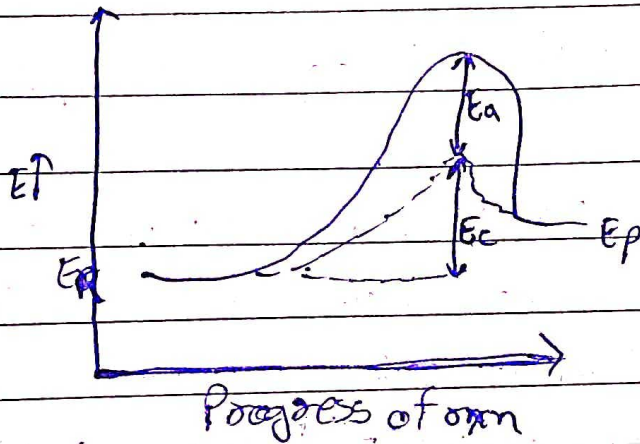
$T_1 = T = k_1$   
 $T_2 = T+10 = k_2$

$k_2 = 2k_1$

## ⇒ Catalyst :-

→ It change the Rate of Reaction at Constant temp.

→ Catalyst decrease the Activation energy of the molecule.



Imp:

⇒ Arrhenius equation :- Relation b/w Rate constant & Temp.

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

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

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

$$\because \ln e = 1$$

$$\boxed{\ln k = \ln A - \frac{E_a}{RT}}$$

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

$$\boxed{\log k = \log A - \frac{E_a}{2.303RT}} \quad \text{--- (1)}$$

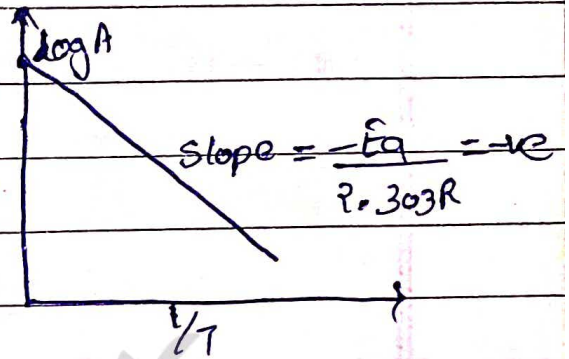
## log k vs 1/T

$$\log k = \frac{-E_a}{2.303R} \cdot \frac{1}{T} + \log A$$

y = mx + c.

$$\log k_1 = \log A - \frac{E_a}{2.303RT_1} \quad \text{--- (1)}$$

$$\log_{10} k_2 = \log A - \frac{E_a}{2.303RT_2} \quad \text{--- (2)}$$



$$\log k_2 - \log k_1 = \frac{-E_a}{2.303RT_2} - \left[ \frac{-E_a}{2.303RT_1} \right]$$

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

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

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