Chemical Kinetics.

Chemical Kinetics - The branch of chemistry which deals with rate of reaction and factors affecting rate of reaction is called chemical kinetics.

*On the basis of speed of Reaction (Rate) Reaction are of three types:

Fast Reaction.	Moderate Rxn.	Slow Reaction.
• Very Very fast • Time : 10^{-16} sec • Eg: $HCl + NaOH \rightarrow NaCl + H_2O$	• It takes moderate time • Some min : Time. • Eg: curding of the Milk.	• Very Very Slow • Days or Month. • eg: Rusting of Iron.

$$\boxed{\text{Rate of Rxn} : \frac{\text{change in conc. of Reactant / Product}}{\text{change in time.}}}$$

$$r = \pm \frac{\Delta c}{\Delta t}$$

(+) = Refer. that this is conc. of product.

(−) = Refer. that this is conc. of Reactant.

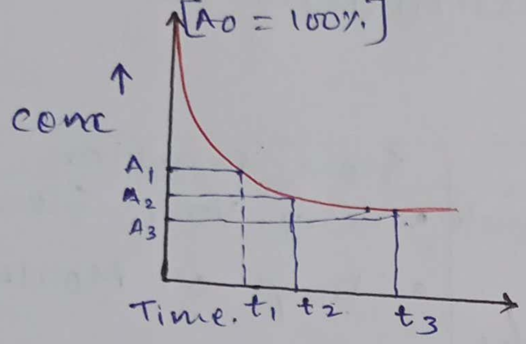
$$A \longrightarrow B$$

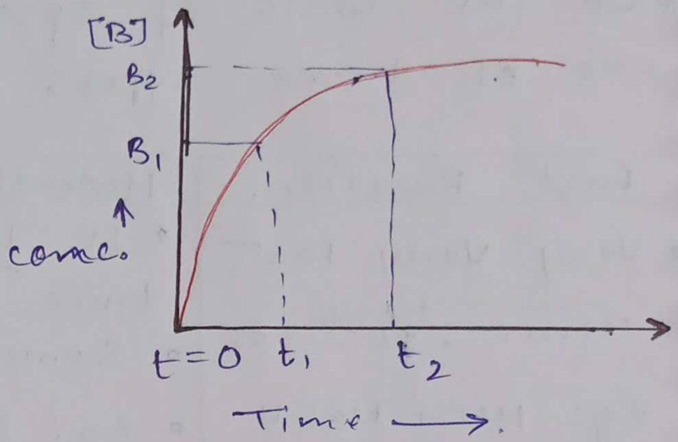
at $t = 0$ $A_0 = 100\%$ $B_0 = 0\%$

$t_1 = t_1$ $A_1 =$ $B_1 =$

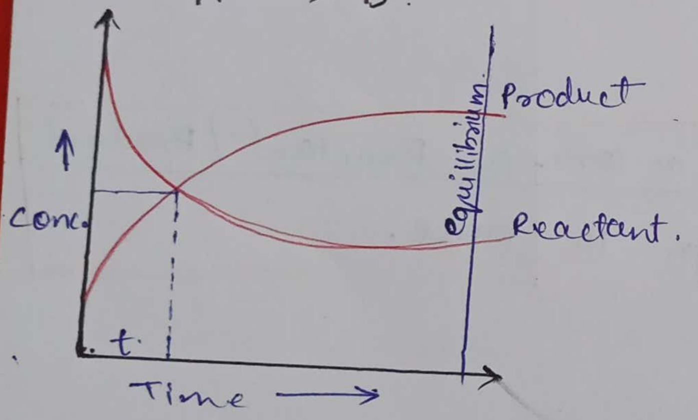
$t_2 = t_2$ $A_2 =$ $B_2 =$

$t_3 = t_3$ $A_3 =$ $B_3 =$

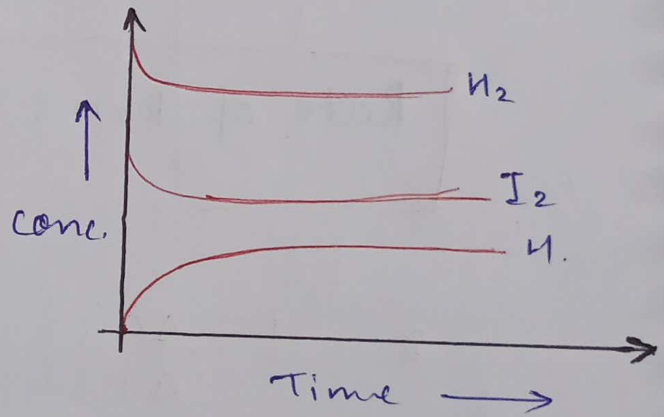




$$A \longrightarrow B.$$



$$H_2 + I_2 \longrightarrow 2HI$$



For Reactant

$$r = \frac{[A_2] - [A_1]}{t_2 - t_1}$$

$$r = -\frac{\Delta[A]}{\Delta t}$$

I am Reactant.

For Product

$$r = \frac{[B_2] - [B_1]}{t_2 - t_1}$$

$$r = +\frac{\Delta[B]}{\Delta t}$$

I am Product.

Rate of Reaction.

r

Average Rate of Rxn.

$r = \pm \frac{\Delta c}{\Delta t}$

Instantenous. Rate of Rxn.

$r = \pm \frac{dc}{dt}$

$A + B \longrightarrow C + D.$

$r = -\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{\Delta t}.$

$= +\frac{\Delta[C]}{\Delta t} = +\frac{\Delta[D]}{\Delta t}$

rate $= \frac{[\ ]}{\text{time}}$

Unit of rxn = mol $L^{-1} s^{-1}$

$A \longrightarrow B.$

Instantenous Rate of Rxn. $= -\frac{d[A]}{dt}$

$2A + 4B \longrightarrow 9C$

$r_{ins} = -\frac{1}{2}\frac{d[A]}{dt} = -\frac{1}{4}\frac{d[B]}{dt}$

$= +\frac{1}{9}\frac{d[C]}{dt}.$

$3A \longrightarrow 4C$

$r = -\frac{1}{3}\frac{\Delta[A]}{\Delta t} = +\frac{1}{4}\frac{\Delta[C]}{\Delta t}$

$aA + bB \longrightarrow cC + dD$

$r = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t}$

$= +\frac{1}{c}\frac{\Delta[C]}{\Delta t} = +\frac{1}{d}\frac{\Delta[D]}{\Delta t}.$

Q. $2SO_2 + O_2 \longrightarrow 2SO_3.$

$r = -\frac{1}{2}\frac{\Delta[SO_2]}{\Delta t} = -\frac{\Delta[O_2]}{\Delta t}$

$= +\frac{1}{2}\frac{d}{dt}[SO_3].$

Q. $2NO + O_2 \longrightarrow 2NO_2.$

$r = -\frac{1}{2}\frac{\Delta[NO]}{\Delta t} = -\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NO_2]}{\Delta t}.$

Q. $N_2 + 3H_2 \longrightarrow 2NH_3$

$r = -\frac{\Delta[N_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta H_2}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}.$

RATE OF REACTION

$2A \longrightarrow 3B$

$3H_2 + N_2 \longrightarrow 2NH_3$

$$r = -\frac{1}{2}\frac{d[A]}{dt} = +\frac{1}{3}\frac{d[B]}{dt}$$

$$r = -\frac{1}{3}\frac{d[H_2]}{dt} = -\frac{d[N_2]}{dt} = \frac{1}{2}\frac{d(NH_3)}{dt}.$$

$A \longrightarrow B$

$-\frac{d[\ ]}{dt}$: Rate of Appearance ⟶ (Product)

$+\frac{d[\ ]}{dt}$: Rate of Disappearance (Reactant)

Eg: $A + B \longrightarrow C + D.$

rate of app. of C $= +\frac{d[C]}{dt}$.

rate of disapp. of

Q. $2N_2 + 6H_2 \longrightarrow 4NH_3$ • ROA of NH_3

• ROD of N_2 • ROD of H_2 • ROR ?

Sol: $$r = -\frac{1}{2}\frac{d[N_2]}{dt} = +\frac{1}{4}\frac{d[NH_3]}{dt} = -\frac{1}{6}\frac{d[H_2]}{dt}$$

• ROD of $N_2 = 2r$

$5 \times 10^{-2} = 2r.$

$r = \frac{5}{2} \times 10^{-2}$

• ROD of $H_2 = 6r$

$= \overset{3}{\cancel{6}} \times \frac{5}{\cancel{2}} \times 10^{-2}$

$= 15 \times 10^{-2}$

- ROA of $NH_3 = 4r$

$\frac{5}{\cancel{2}} \times 10^{-2} \times \cancel{4}\,2$

$= 10 \times 10^{-2}$.

Q. $2A + 4B \longrightarrow 6C$ • ROR ? • ROA of C $= 3\times10^{-3}$

- ROD of B ? • ROD of A ?

Sol: • ROA of C $= 6r$

$6r = 3 \times 10^{-3}$

$r = 0.5 \times 10^{-3}$

- ROD of A $= 2r$

$= \cancel{2} \times 0.5 \times 10^{-3}$

$= 10^{-3}$

- ROD of B $= 4r$

$= 4 \times 0.5 \times 10^{-3}$

$= 2 \times 10^{-3}$

- ROR $= 0.5 \times 10^{-3}$

Q. For the reaction $N_2 + 3H_2 \longrightarrow 2NH_3$, if rate of appearance (ROA) of $NH_3 = 2\times10^{-4}$ mol l^{-1} s^{-1}. Then calculate rate of disappearance (ROD) of N_2 & H_2 and also calcula rate of the reaction?

Sol: $N_2 + 3H_2 \longrightarrow 2NH_3$

Rate of app. of $NH_3 = 2r$

$\cancel{2}r = \cancel{2}\times10^{-4}$

$r = 10^{-4}$

- ROD of $N_2 = 1r$

$= 10^{-4}$

- ROD of $H_2 = 3r$

$= 3\times10^{-4}$

- ROR $= r$

$= 10^{-4}$

Q. If the reaction $2NO_2 \longrightarrow 2NO + O_2$ the rate of formation of NO is 6 g min^{-1}, calculate rate of disapp. of NO_2 in g min^{-1}.

Sol: ROF (formation) of NO = $2r$

ROD of NO_2 = $2r$.

$(Mw)\ NO = \dfrac{\frac{6g}{min}}{30} = \dfrac{0.2\ mol}{min.}$

$= \dfrac{0.2\ mol}{min} \times Mw = \dfrac{0.2 \times 46}{min}$

$= 9.2\ g\ min^{-1}$

Q. A gaseous hypothetical chemical eq. $2A \rightleftharpoons B + C$ is carried out in a closed vessel. The concentration of B is found to increases by 5×10^{-3} mol L^{-1} in 10 sec. The rate of appearance of B is.

Sol: $\dfrac{\text{Concentration}}{\text{Time}} = \dfrac{5 \times 10^{-3}}{10} = 5 \times 10^{-4}\ mol\ L^{-1} sec^{-1}$

RATE LAW: The experimental expression of the ROR in the terms of conc. of reactant.

$A \longrightarrow B$

$r \propto [A]$

$r = K[A]$

Rate const.

$2A \longrightarrow 3B$

$r = K[A]^2$

Eg: ① $N_2 + 3H_2 \longrightarrow 2NH_3$

$r = K[H_2]^3[N_2]$

② $2SO_2 + O_2 \longrightarrow 2SO_3$

$r = K[O_2][SO_2]^2$

③ $PCl_5 \longrightarrow PCl_3 + Cl_2$

$r = K[PCl_5]$

ORDER OF REACTION: The sum of power of conc. of reactant in rate law expression is known as order of Rxn.

- Order of Reaction maybe (positive) +ve, −ve, Zero or fraction.
- It is an experimental value.

$r = K[A]^x$ [: Sum of power of conc. of Rate law]

$r = K[A]^x[B]^y$

order $= x + y$

$r = K[A]^{1/2}[B]^3$

order $= \frac{1}{2} + 3$

$= 7/2.$

Eg: $r = K[A]^{-1}[B]$

Order $= 0.$

A : Product

$r \propto [A]$

$\text{ROR} \leftarrow r = K[A]^1$

Reactant

conc

order.

Rate const.

UNIT OF K

① Zero Order Rxn.

$r = K[A]^0$

$r = K$

$\boxed{K = mol\ L^{-1}\ s^{-1}}$

② First Order Rxn.

$r = K[A]^1$

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

$\frac{mol\ L^{-1}\ s^{-1}}{mol\ L^{-1}} = K$

$\boxed{K = s^{-1}}$

③ Second Order Rxn.

$$r = K[A]^2$$

$$\frac{r}{[A]^2} = \frac{mol\,L^{-1}s^{-1}}{(mol\,L^{-1})^2} = \boxed{s^{-1}\,mol^{-1}\,L^{-1} = K.}$$

④ Third Order Rxn.

$$r = K[A]^3$$

$$\frac{r}{[A]^3} = K = \frac{mol\,L^{-1}\,s^{-1}}{(mol\,L^{-1})^3} = \boxed{mol^{-2}\,L^{2}\,s^{-1} = K.}$$

⑤ n^{th} order Rxn.

$$r = K[A]^n$$

$$\frac{r}{[A]^n} = k = \frac{mol\,L^{-1}\,s^{-1}}{(mol\,L^{-1})^n} = (mol\,L^{-1})^{1-n}\,s^{-1} = K.$$

$$\boxed{K = mol^{1-n}\,L^{n-1}\,s^{-1}}$$

Q. For a reaction rate law equation is $r = K(C)^{5/2}$. Then unit of rate const. will be:

Sol:

$$r = K[C]^{5/2}.$$

$$n = \frac{5}{2}$$

for n^{th} order.

$$K = mol^{1-n}\,L^{n-1}\,s^{-1}$$

$$= mol^{1-5/2}\,L^{5/2-1}\,s^{-1}$$

$$K = mol^{-3/2}\,L^{3/2}\,s^{-1}$$

Q. For a reaction the initial rate is given as: $R_0 = K[A]_0^2$ $[B]_0$ by what factor, the initial rate of reaction will increase if initial conc. of A is 1.5 times & B is triple?

1.) 4.5   2.) 2.25   3.) 6.75   4.) NOT.

Sol:
$$R_0 = K[A]_0^2[B]_0$$
$$A_1 = 1.5\ A_0$$
$$B_1 = 3\ B_0$$
$$\frac{R_0}{R_1} = \frac{\cancel{K}[A]_0^2[B]_0}{\cancel{K}[1.5\ A_0]^2[3B_0]} = \frac{1}{2.25\times 3}.$$
$$R_1 = 2.25\times 3 = 6.75\ R_0.$$
$$R_1 = 6.75\ R_0.$$

DPP-3

1. $A_2 + B_2 \longrightarrow 2AB$; ROR $= K[A_2]^a[B_2]^b$

A_2	B_2	ROR (Ms^{-1})
0.2	0.2	0.04
0.1	0.4	0.04
0.2	0.4	0.08.

$0.04 = K[.2]^a\ [.2]^b$ —— ①

$0.04 = K[.1]^a\ [.4]^b$ —— ②

$0.08 = K[.2]^a\ [.4]^b$. —— ③

order of Rxn with respect to A_2 and B_2 are respectively:

Sol: $r = K[A_2]^a[B_2]^b$ - real eq.

$$3\div 1 = \frac{\cancel{0.08}^{2}}{\cancel{0.04}} = \frac{\cancel{K}}{\cancel{K}}\left(\frac{.2}{.2}\right)^a\left(\frac{\cancel{.4}}{.2}\right)^b$$
$$= 2 = 1 \times (1)^a \times (2)^b$$
$$2 = 2^b = \boxed{b=1}$$

$$3\div 2 = \frac{0.08^{2}}{0.04} = \frac{K}{K}\left(\frac{.2}{.1}\right)^a\left(\frac{\cancel{.4}}{\cancel{.4}}\right)^b$$
$$2 = 2^a$$
$$\boxed{a=1}$$

2. for $A_{(g)} + B_{(g)} \longrightarrow C_{(g)}$: rate $= K[A]^{1/2}[B]^2$, if initial conc. of A and B are increaded by factor of 4 and 2 respectively, then the initial rate is changed by the factor:-

Sol:

$$r_1 = K[A]^{1/2}[B]^2$$

$$A \longrightarrow 4A$$

$$B \longrightarrow 2B$$

$$r_2 = K[4A]^{1/2}[2B]^2$$

$$r_2 = K\,2[A]^{1/2}\,4[B]^2$$

$$\frac{r_2}{r_1} = \frac{\cancel{K}\,2\,\cancel{[A]^{1/2}}\,4\,\cancel{[B]^2}}{\cancel{K}\,\cancel{[A]^{1/2}}\,\cancel{[B]^2}}$$

$$\boxed{r_2 = 8\,r_1}$$

Ans = 8.

3.

$$r = K[A]^x[B]^y$$

eq ① $4 = K[1]^x[2]^y$

eq ② $4 = K[2]^x[2]^y$

eq ③ $16 = K[2]^x[4]^y$

eq 2 ÷ 1

$$\frac{\cancel{4}}{\cancel{4}} = \frac{\cancel{K}}{\cancel{K}}\left(\frac{2}{1}\right)^x\left(\frac{\cancel{2}}{\cancel{2}}\right)^y$$

$$1 = 2^x$$

$$2^0 = (2)^x = \boxed{x = 0}$$

eq 3 ÷ eq 2

$$\frac{\cancel{16}^{\,4}}{\cancel{4}} = \frac{\cancel{K}}{\cancel{K}}\left(\frac{\cancel{2}}{\cancel{2}}\right)^x\left(\frac{\cancel{4}^{\,2}}{\cancel{2}}\right)^y$$

$$4 = (2)^y$$

$$(2)^2 = (2)^y$$

$$\boxed{y = 2}$$

MOLECULARITY :-

The No. of the Molecules/ Atoms / Ions of Reactant in any elemantry Reaction is called Molecularity of the Reaction.

- Molecularity is a theoretical Quantity.
- Molecularity can be ~~on~~ +ve integer only & can't be zero, -ve or fraction.
- In elementary Rxn molecularity is equal to its order (molecularity = Order).
- In complex Rxn molecularity of each steps are different & total molecularity are meaningless.
- Max. value of molecularity = 3 (Bcz chances of effective collusion of more than 3 molecules are rare.)

MECHANISM OF RXN :-

1) **Simple** Rxn, Elimentary Rxn. (One single step)

$$A \longrightarrow B$$

$r = K[A]$

order = 1

Molecularity = 1.

2) Complex Rxn, Multiple step Rxn.

$$A \longrightarrow B$$

$A \longrightarrow C$ (fast step)

$C \longrightarrow D + X$ (slow) ⟶ RDS - Rate of determination

$D + X \longrightarrow B$ (fast)

Eg: 1 $2NO_2Cl \longrightarrow 2NO_2 + Cl_2$.

Step - I

$NO_2Cl \longrightarrow NO_2 + Cl$ (slow)

Step - II

$NO_2Cl + Cl \longrightarrow NO_2 + Cl$ (fast)

$$r = K[NO_2Cl]$$

Eg: 2 $2NO + 2H_2 \longrightarrow N_2 + 2H_2O$

Step - I

$2NO \underset{K_b}{\overset{K_f}{\rightleftharpoons}} N_2O_2$ (fast)

Step - II

$N_2O_2 + H_2 \longrightarrow N_2O + H_2O$ (slow)

Step - III

$N_2O + H_2 \longrightarrow N_2 + H_2O$ (fast)

$$r = K[N_2O_2][H_2]$$

$$r_f = r_b$$

$$K_f[NO]^2 = K_b[N_2O_2]$$

$$r = K \times \frac{K_f}{K_b}[NO]^2[H_2]$$

$$r = K'[NO]^2[H_2]$$

order = 3

PSEUDO UNI MOLECULARITY RXN :-

A Rxn in which the value of order of Rxn is 1 but molecularity is more than one are known as Pseudo Uni Molecularity Rxn.

eg : 1 Invertion of Sugar.

$$\underset{1 mol}{C_{12}H_{22}O_{11}(s)} + \underset{(1l = 55.5 mol)}{\overset{(excess)}{H_2O}} \xrightarrow{H^+} \underset{(glucose)}{C_6H_{12}O_6} + \underset{(fructose)}{C_6H_{12}O_6}.$$

$$r = K[C_{12}H_{22}O_{11}]$$

* Order - 1
* Molecularity - 2

eg : 2 Hydration of Ether.

$$CH_3-COOC_2H_5 + \underset{(excess)}{H_2O} \longrightarrow CH_3-COOH + C_2H_5OH.$$

INTEGRATED RATE EQUATION :-

1) For Zero order Rxn.

Unit of $K = mol\,L^{-1}s^{-1}$

eg : 1 $H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl$

eg : 2 $2NH_3(g) \xrightarrow[\Delta]{Pt} 3H_2 + N_2$.

eg : 3 Rxn between Acetone & Br_2

eg : 4 Decomposition of HI on gold surface

eg : 5 Adsorption of gas at metal surface.

$A \longrightarrow \text{Product}$

$r = \frac{-d[A]}{dt}$ —— (i)

$r = K[A]^{0}$ —— (ii)

$-\frac{d[A]}{dt} = K\cancel{[A]}^{\overset{\cancel{0}}{}\to 1}$

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

$\int d[A] = \int -K\,dt$

$A = -Kt + C$

at $t = 0$

$A_0 = C$

$A = -Kt + A_0$.

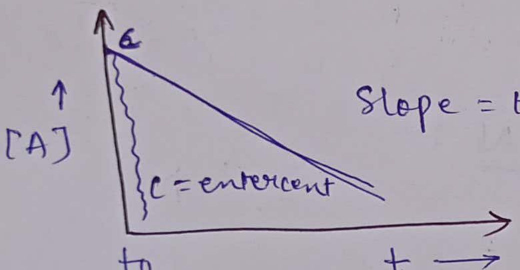
$Kt = A_0 - A$

$k = \frac{A_0 - A}{t}$

Graph — ①.

$A = -kt + A_0$

A VS T



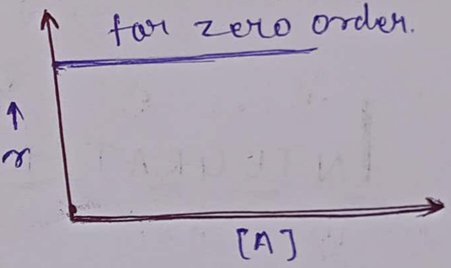
$\text{Slope} = \tan\theta = \frac{P}{B} = -K$

Graph — ②

$r = K[A]^{0} = 1$

$r = K$

r vs A.



HALF REACTION

$A^{0} \longrightarrow \frac{A^{0}}{2}$.

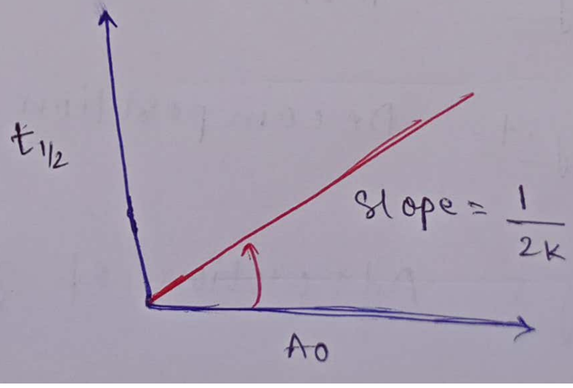
$t = t_{1/2}$

$K = \frac{A_0 - A}{t}$

$k = \frac{A_0 - \frac{A_0}{2}}{t_{1/2}}$.

$t_{1/2} = \frac{A_0\left[1 - \frac{1}{2}\right]}{K}$.

$t_{1/2} = \frac{A_0}{2k}$



2) First Order Rxn.

Unit of $k = s^{-1}$

Ex: 1 $2N_2O_5 \longrightarrow 4NO_2 + O_2$

Ex: 2 $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

Ex: 3 $CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$

Ex: 4 $2H_2O_2 \longrightarrow 2H_2O_2 + O_2$.

Ex: 5 All radio activity decay.

$A \longrightarrow$ product

$$r = \frac{-d[A]}{dt} \quad — ①.$$

$$r = k[A]^{-1} \quad — ②$$

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

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

$$\frac{1}{x} dx = \ln x$$

$$\ln[A] = -kt + c$$

at $t = 0$, $c = \ln[A_0]$

$$\ln[A] = -kt + \ln[A_0]$$

$$kt = \ln[A_0] - \ln[A].$$

$$\log \frac{x}{y} = \log x - \log y.$$

$$kt = \ln \frac{[A_0]}{[A]}$$

$$k = \frac{1}{t} \ln \frac{[A_0]}{[A]}$$

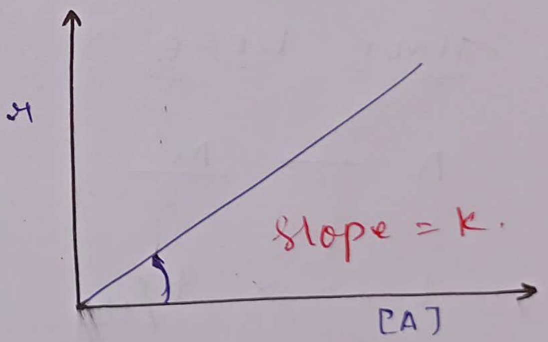
$\ln \longrightarrow \log_{10} \times 2.303$.

$$K = \frac{2.303}{t} \log_{10} \frac{[A_0]}{[A]}$$

Graph - ①

r vs A

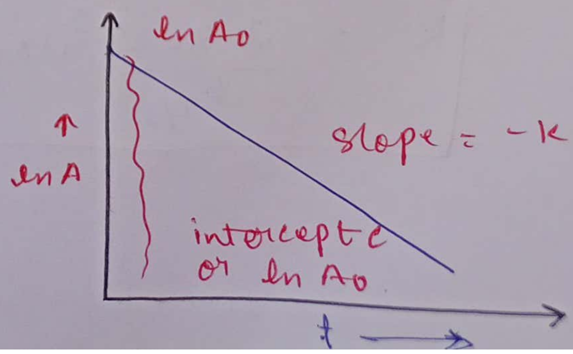
$r = k[A]^1$



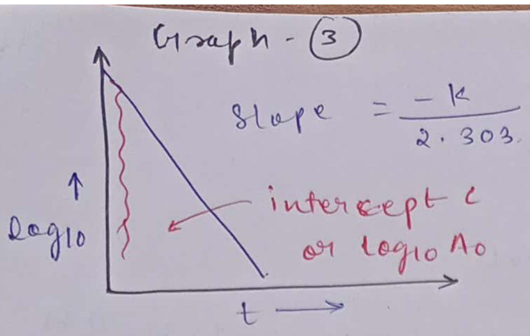
Graph - ②

A & t

$\ln A = -kt + \ln A_0$



Graph - ③



$\ln[A] = -kt + \ln[A_0]$

$$\frac{2.303 \log_{10} A = -kt + 2.303 \log_{10} A_0}{2.303}$$

$$\log_{10} A = \frac{-kt}{2.303} + \log_{10} A_0$$

$\ln A = -kt + \ln[A_0]$

$\ln A - \ln[A_0] = -kt$

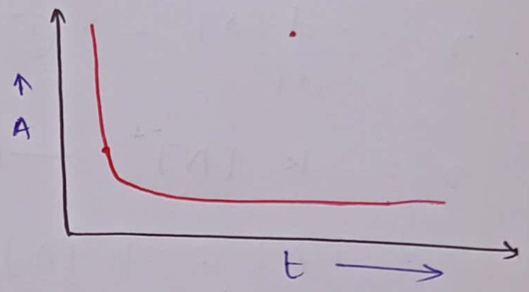
$\frac{\ln A}{\ln A_0} = -kt$

$\frac{A}{A_0} = e^{-kt}$

$$\boxed{A = A_0 e^{-kt}}$$

$\frac{1}{\ln} x = e^{x}$

Graph - ④



HALF LIFE

$A \longrightarrow \frac{A_0}{2}$

$t \longrightarrow t_{1/2}$

$t_{1/2} = \frac{0.693}{k}$

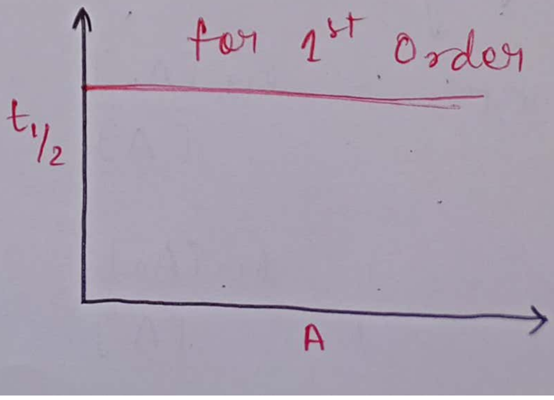
$$\boxed{t_{avg} = \frac{1}{t_{1/2}}}$$

$k = \frac{2.303}{t_{1/2}} \log_{10} \frac{A_0}{\frac{A_0}{2}}$

$$\boxed{k = \frac{2.303}{t_{1/2}} \log_{10} 2}$$

Graph - ⑤

$t_{1/2}$ Vs A.



For Reaction

$$A_{(g)} \longrightarrow B_{(g)} + C_{(g)}$$

at $t = 0$ $\quad P_i \quad 0 \quad 0$

at $t = t$ $\quad P_i - x \quad x \quad x$

Total press :- $P_i - x + x + x$

$$P_f = P_i + x$$

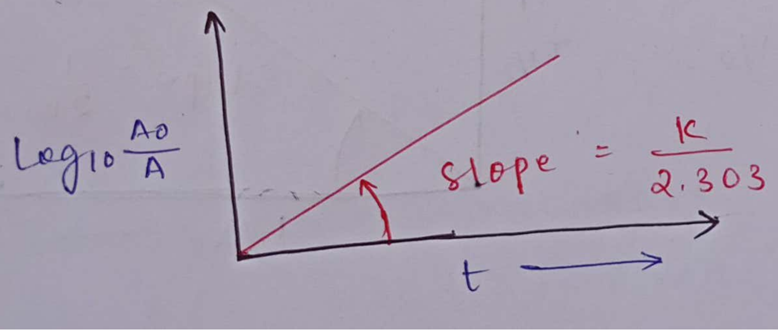
$$\boxed{x = P_f - P_i}$$

$$K = \frac{2.303}{t} \text{long}_{10} \frac{P_i}{P_A}.$$

$$k = \frac{2.303}{t} \frac{P_i}{P_i - x}. = K = \frac{2.303}{t} \log_{10} \frac{P_i}{P_i - (P_f - P_i)}$$

$$\boxed{K = \frac{2.303}{t} \log_{10} \frac{P_i}{2P_i - P_f}}$$

25 ★ Graph :- $\log_{10} A_0/A$ VS t



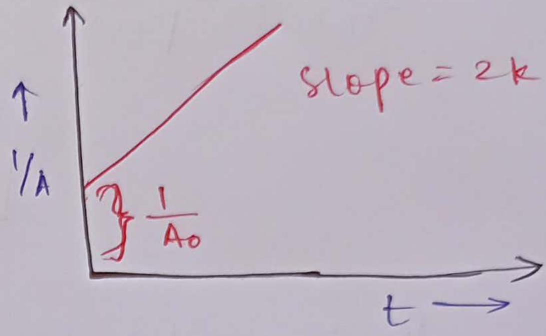
3) For Second Order Reaction.

$$2A \longrightarrow \text{Product}$$

$$r = -\frac{1}{2}\frac{d[A]}{dA} \longleftarrow ①$$

$$r = k[A]^2 \text{ —— } ②$$

$$-\frac{1}{2}\frac{d[A]}{dt} = k[A]^2$$



$$\int \frac{d[A]}{A^2} = -2kt$$

$$\left[-\frac{1}{A}\right]_{A_0}^{A} = -2kt$$

$$-\frac{1}{A} + \frac{1}{A_0} = -2kt$$

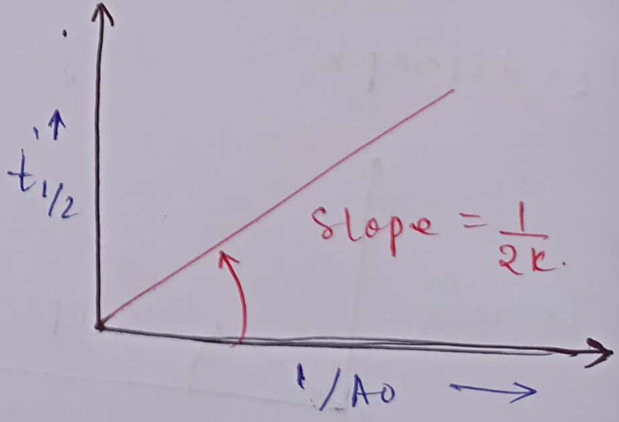
$$\boxed{\frac{1}{2t}\left(\frac{1}{A} - \frac{1}{A_0}\right) = k.}$$

HALF LIFE

$$A = \frac{A_0}{2} \qquad t = t_{1/2}$$

$$\frac{1}{2k}\left[\frac{2}{A_0} - \frac{1}{A_0}\right] = t_{1/2}$$

$$\boxed{\frac{1}{2kA_0} = t_{1/2}.}$$



DPP - 07

Trick.

* Only for 1st Order Rxn.

% of conc. 100% $\longrightarrow$ 50% $\longrightarrow$ 25% $\longrightarrow$ 12.5% $\longrightarrow$ 6.25%

Rest conc. 100% $\longrightarrow$ 50% $\longrightarrow$ 75% $\longrightarrow$ 87.5% $\longrightarrow$ 93.75%

Conc of Rxn. $A \longrightarrow \frac{A}{2} \longrightarrow \frac{A}{4} \longrightarrow \frac{A}{8} \longrightarrow \frac{A}{16}$.

Rest conc. of Rxn $0 \longrightarrow \frac{A}{2} \longrightarrow \frac{3A}{4} \longrightarrow \frac{7A}{4} \longrightarrow \frac{15A}{16}$.

→ FACTOR AFFECTING RATE OF RXN.

1. Concentration $r \propto [A]^n$
   - $\rightarrow$ zero order
   - $\rightarrow$ 1st order $\propto [A]$
   - $\rightarrow$ 2nd order $\propto [A]^2$
2. Nature of Reactant
3. Pressure (only for gas)
4. Radiation (light) $h\nu$ $CH_4 + Cl_2 \xrightarrow{h\nu}$?
5. Temperature.
6. catalyst

* EFFECT OF TEMPERATURE.

"When we increase temperature by 10°C rate of Rxn also increase by 2 times"

$$\frac{r_{new}}{r_{old}} = \mu = 2 \frac{T_2 - T_1}{T_0}$$

ror ratio.

a) 50°C ⟶ 90°C Rate of Reaction. How much times?

Sol. $2 \frac{90-50}{10} = 2^4 = 16$ times

ARRHENISUS EQUATIONS.

$$\boxed{K = Ae^{-\frac{Ea}{RT}}}$$

K → rate constant

Ea ⟶ Activation energy (J / kJ)

R ⟶ Universal gas const. (J) 8.314

T ⟶ Temp (in K)

A ⟷ Arrhenisus factor per exponent factor (frequency factor)

- $K = Ae^{-\frac{Ea}{RT}}$

Taking both sides.

$$\ln k = \ln\left(Ae^{-\frac{Ea}{RT}}\right)$$

$$(\log x.y = \log x + \log y)$$

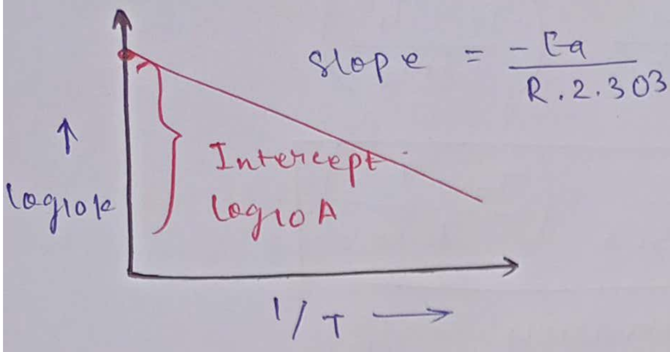
$$\ln k = \ln A + \ln e^{-\frac{Ea}{RT}}$$

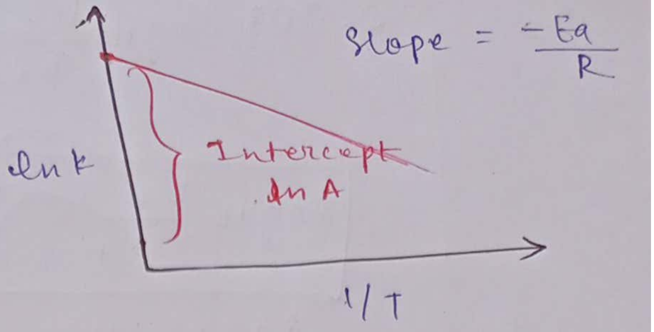
$$\ln k = \ln A - \frac{Ea}{RT} \overset{\to 1}{\ln e}$$

$$\ln k = \ln A - \frac{Ea}{RT}$$

$$2.303 \log_{10} k = \ln k$$

$$\boxed{\log_{10} K = \log_{10} A - \frac{Ea}{2.303\,RT}}$$





→ for two different Temperature

for T_1 Temp

$$k_1 = A . e^{-\frac{Ea}{RT_1}} \text{ ——— } ①$$

for T_2 Temp.

$$k_2 = Ae^{-\frac{Ea}{RT_2}} \text{ ——— } ②$$

equating ① & ②

$$\frac{k_2}{k_1} = \frac{Ae^{-\frac{Ea}{RT_2}}}{Ae^{-\frac{Ea}{RT_1}}}$$

Taking ln both sides.

$$\ln\frac{k_2}{k_1} = \ln\left(\frac{e^{-\frac{Ea}{RT_2}}}{e^{-\frac{Ea}{RT_1}}}\right)$$

$$\ln\frac{k_2}{k_1} = \ln e^{-\frac{Ea}{RT}} - \ln e^{-\frac{Ea}{RT}}$$

* $\ln x e = 1$

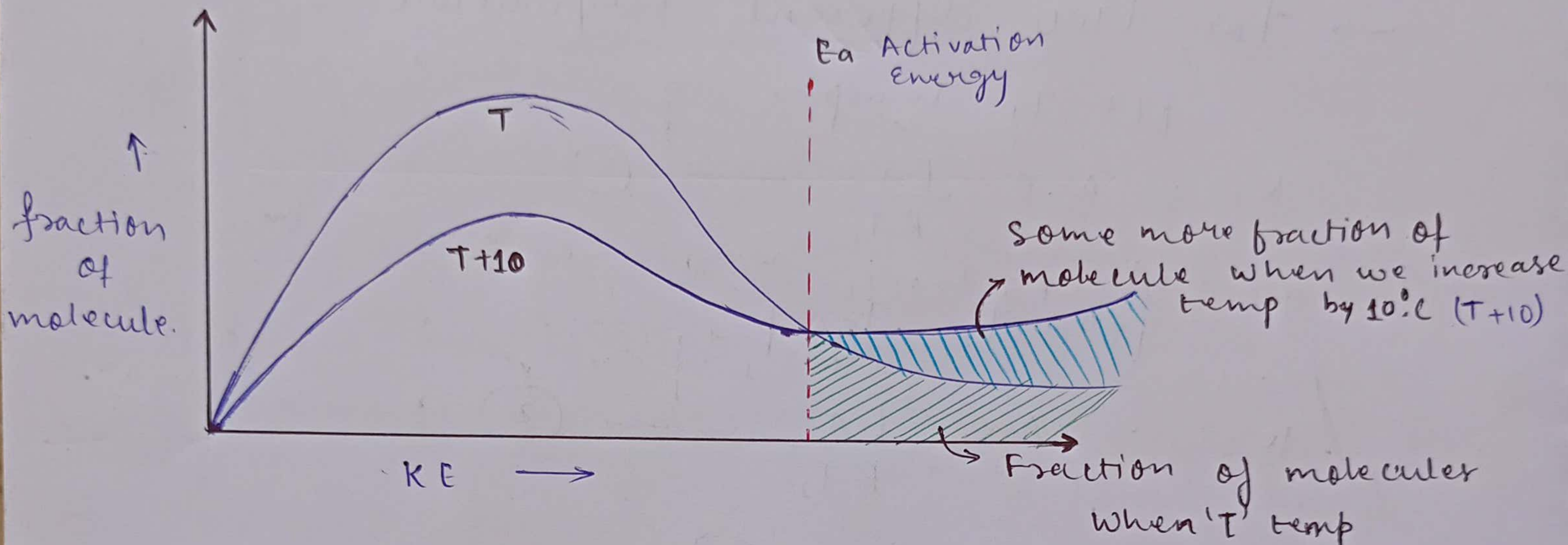
$$\ln\frac{k_2}{k_1} = \frac{-Ea}{RT_2} + \frac{Ea}{RT_1}$$

$$\ln\frac{k_2}{k_1} = \frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$2.303 \log_{10} \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\boxed{\log_{10} \frac{k_2}{k_1} = \frac{E_a}{R \times 2.303}\left(\frac{T_2 - T_1}{T_1 T_2}\right)}$$

Calculation of Activation Energy.



Maxwell & Boltzman Energy Distribution curve.

① Threshold Energy :- The minimum energy which must be processed by reacting molecules for a chemical reaction to occur.

② Activation Energy: The minimum extra amount of energy required by reactant molecule for converting into products.

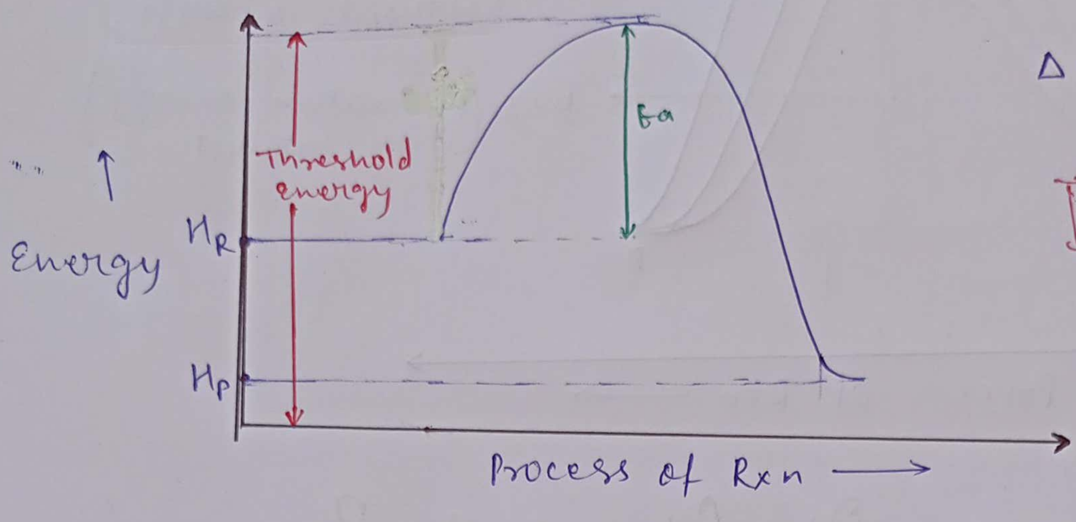
③ Factors Affecting Activation Energy
1) Nature of Reactant 2) Presence of Catalyst

Different Types Of Energies :-

ΔH

(Endothermic) +ve

−ve (Exothermic)

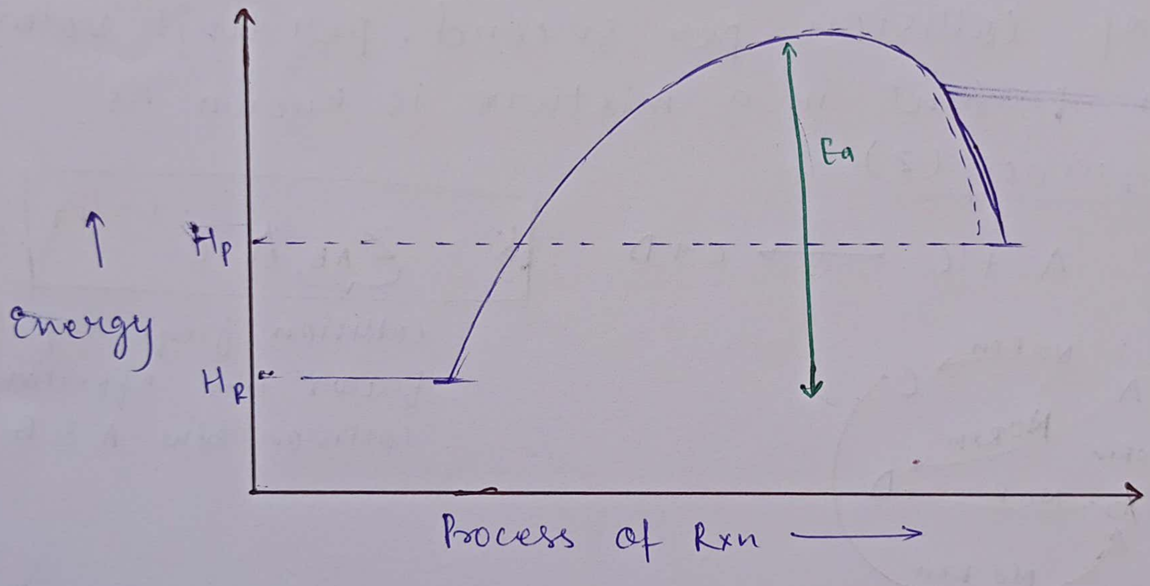


$\Delta H = H_P - H_R$

$= -ve$

(Exothermic)

$[H_P > E_a]$



$[E_a > H_P]$

$\Delta H = H_P - H_R$

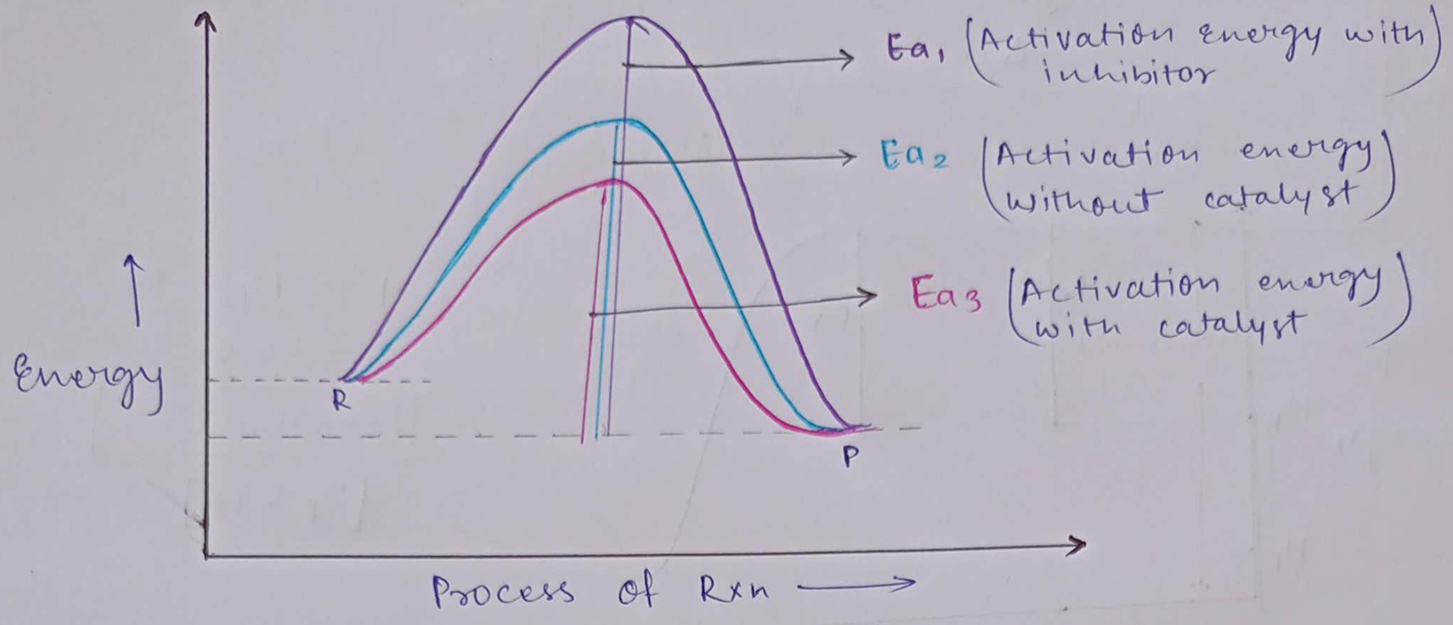
$= +ve.$

Endothermic.

• EFFECT OF CATALYST

Catalyst provides an alternate Path of Reaction mechanism for the rxn, in the presence of catalyst threshold energy decreases, activation Energy decrease and Rate of reaction increases.

In the presence of catalyst (−ve catalyst) (inhibitor), threshold energy increases, activation Energy increases and Rate of reaction decreases.



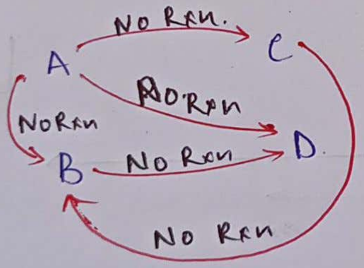
Collision Theory Of Chemical Rxn.

The no. of collision per second, per unit volume of the rxn present in a mixture is known as collision frequency (Z)

$$\boxed{K = \underbrace{Z_{AB}}_{} A e^{-Ea/RT}}$$

collision frequency factor of effective collision b/w A & B.

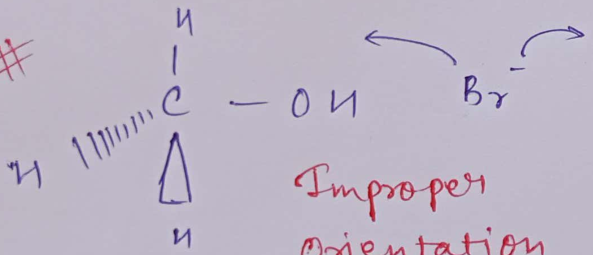
$\therefore A + C \longrightarrow C + D$



The proper orientation of reactant is very important for effective collision And form a molecule which is called PRODUCT but in improper orientation, makes them simply bounce back and no. products are formed. P is called probability or steric factor.

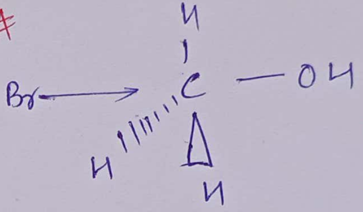
$$\boxed{K = P Z_{AB} A e^{-Ea/RT}}$$

#



Improper Orientation

#



Proper orientation.