Chemical Kinetics →

★ 1st Order Reaction → Vimp (Que)

Topics to be Covered →

① Rate of Reaction
② Factors affecting rate of reaction
③ Reaction mechanism by which, Reaction proceeds.

Types of Reaction →

Very fast Rx.	Moderate rx. / slow rx.	Very slow Rx.
$10^{-14} - 10^{-16}$ sec for completion	sec, min, hours for completion	days, months, years for completion
Ionic Rx. Acid-Base Rx. Neutralisation Rx. HCl+NaOH → NaCl +H_2O	$N_2 + 3H_2 \rightleftharpoons 3NH_3$ $H_2O_2 \rightleftharpoons H_2O$	Rusting of iron

Rate / Speed / Velocity of a Reaction

$$(R) \longrightarrow (P)$$

t=0	a	0	$Rate = \dfrac{a-x-a}{t_1-0} = \dfrac{-x}{t_1}$
t=t_1	a-x	x=	
t=t_2	0	a	$Rate = \dfrac{0-a-x}{t_2-t_1} = \dfrac{-a-x}{t_2-t_1}$

Rate of Rx. = Change in Conc. of Reactant/product / Change in time

Reactant → (-ve), product → (+ve)

$$\boxed{R = \dfrac{\Delta C}{\Delta t}}$$

$\boxed{\Delta C = C_f - C_i}$
$\boxed{\Delta t = t_f - t_i}$

Unit of Rate →
$R = \dfrac{\Delta C}{\Delta t} \curvearrowright \dfrac{mol}{lit}{\Large/}sec$

$\boxed{mol\ lit^{-1} sec^{-1}}$

Types of ROR →

avg. rate of rx.	instantaneous rate of rx.
interval of time	particular instant of time
$Rate = \dfrac{\Delta C}{\Delta t}$	$Rate = \dfrac{dC}{dt}$ → slope of graph

Average Rate

$$(R) \longrightarrow (P) \quad \begin{array}{l} A_1 > A_2 \\ B_2 > B_1 \\ t_2 > t_1 \end{array}$$

	R	P
t_1	A_1	B_1
t_2	A_2	B_2

avg rate $= \dfrac{\Delta C}{\Delta t} = \dfrac{A_2 - A_1}{t_2 - t_1}$ (-ve)

avg speed with reactant, already ek (-ve) sign lena hai So that, product (+) ho jaye

$$\boxed{R = -\left(\dfrac{A_2 - A_1}{t_2 - t_1}\right)}$$

avg rate with respect to product →

$$\boxed{R = +\left(\dfrac{B_2 - B_1}{t_2 - t_1}\right)}$$

Graphs →

Reactant	Product

Reactant conc. vs time (decreasing curve, A_1, A_2 at t_1, t_2)

avg rate $= \ominus \left(\dfrac{A_2 - A_1}{t_2 - t_1}\right)$

Product conc. vs time (increasing curve, B_2, B_1 at t_1, t_2)
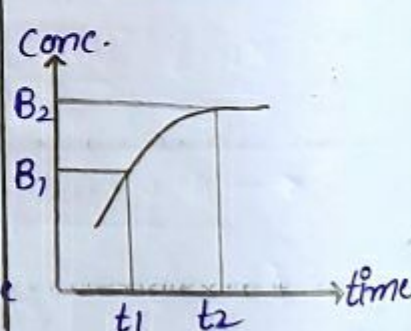
avg rate $= \oplus \left(\dfrac{B_2 - B_1}{t_2 - t_1}\right)$

Instantaneous Rate →

$R \longrightarrow P$
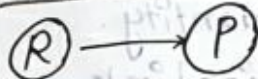
$$Rate = \frac{-dR}{dt}$$

$$Rate = \frac{+dP}{dt}$$

graph →

tangent slope

$slope = \tan\theta = \frac{dC}{dt}$

Que) Calculate avg rate b/w 0 to 5 sec. and 5-10 sec.
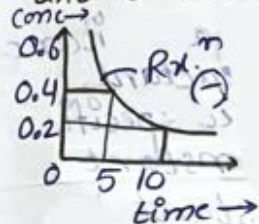
$avg \ rate = \frac{\Delta C}{\Delta t}$
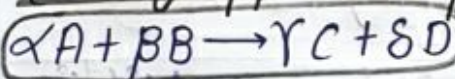
$R = \ominus \left(\frac{0.4 - 0.6}{5 - 0} \right)$

$= \frac{0.2 \times 1}{5 \cdot 25} = \frac{1}{25}$ ①

② → $R = \ominus \left(\frac{0.4 - 0.2}{10 - 5} \right)$

$= \frac{0.2}{5} = \frac{1}{25}$ ②

$mol \ L^{-1} s^{-1}$

Rate of appearance / dissapearance

$\alpha A + \beta B \longrightarrow \gamma C + \delta D$ stoichiometry not needed

Rate of dissapearance $= - \frac{\Delta C}{\Delta t}$
(Reactant)

$$(ROD)_A = -\frac{\Delta A}{\Delta t} = \frac{-dA}{dt}$$ Coeff. se Koi matlab nahi
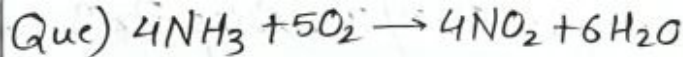
$$(ROD)_B = -\frac{\Delta B}{\Delta t} = \frac{-dB}{dt}$$

Rate of appearance (products) $\oplus \frac{\Delta C}{\Delta t}$

$$(ROA)_c = \frac{\Delta C}{\Delta t} = \frac{dC}{dt}$$
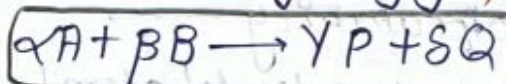
$$(ROA)_D = \frac{\Delta D}{\Delta t} = \frac{dD}{dt}$$

Que) $4NH_3 + 5O_2 \longrightarrow 4NO_2 + 6H_2O$

R.O.A. of NO?

Sol.ⁿ → $ROA = \frac{\Delta C}{\Delta t} = \oplus \frac{\Delta [NO]}{\Delta t}$

ROD of NH_3?

$$ROD = \ominus \frac{\Delta [NH_3]}{\Delta t} \quad or \quad -\frac{d[NH_3]}{dt}$$

Rate of Reaction →

Stoichiometry aayega...   Rx.ⁿ must be balance

$$\boxed{\alpha A + \beta B \longrightarrow \gamma P + \delta Q}$$

$$ROR = -\frac{1}{\alpha}\frac{\Delta A}{\Delta t} = -\frac{1}{\beta}\frac{\Delta B}{\Delta t} = +\frac{1}{\gamma}\frac{\Delta P}{\Delta t} = +\frac{1}{\delta}\frac{\Delta Q}{\Delta t}$$

Que) Write the Rate of Rx.ⁿ
$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$

Solⁿ
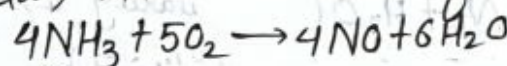
$$ROR = -\frac{1}{4}\frac{\Delta NH_3}{\Delta t} = -\frac{1}{5}\frac{\Delta O_2}{\Delta t} = \frac{1}{4}\frac{\Delta NO}{\Delta t} = \frac{1}{6}\frac{\Delta H_2O}{\Delta t}$$

Que) If rx.ⁿ $2NO_2 \longrightarrow 2NO + O_2$, rate of formation of NO is 6 m/s. Calculate rate of dissapearance of NO_2.

Solⁿ

$\frac{d[NO]}{dt} = 6 m/s$

$$ROR = -\frac{1}{2}\frac{d[NO_2]}{dt} = \frac{1}{2}\frac{d[NO]}{dt} = \frac{d[O_2]}{dt}$$

$$= -\frac{d[NO_2]}{dt} = \frac{d[NO]}{dt}$$

$$ROD = 6 m/s$$

Types of Reaction (Mechanism)

① **Elementary Reaction / Simple Rx.ⁿ / Single step Rx.ⁿ** →
Completes in single step.
Don't need mechanism
Exponents in rate law = stoichiometric coeff. of Rx.ⁿ

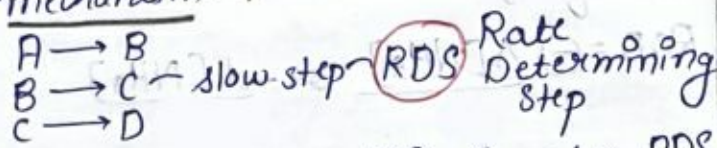$aA + bB \longrightarrow cC + dD$

$$\boxed{R = K[A]^a [B]^b} \quad \boxed{order = n = a+b}$$

$a+b \rightarrow$ can't be negative, zero, fraction

② Complex Rx.ⁿ / Multistep Rx.ⁿ →

Rx.ⁿ completes in multisteps.
Mechanism is must

main Rx.ⁿ $A \longrightarrow D$

mechanism →

$A \longrightarrow B$
$B \longrightarrow C$ — slow step (RDS) Rate Determining Step
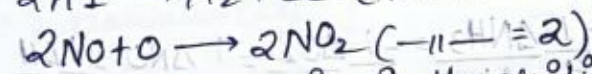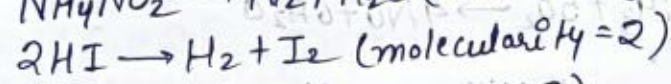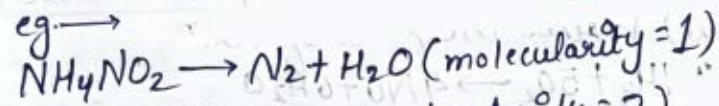$C \longrightarrow D$

Rate of complex rx.ⁿ is given by RDS

$$Rate = K[B']^1$$

Molecularity →

Total number of molecule/ atom/ ion participating in an elementary rx.ⁿ is called molecularity

eg. →

$NH_4NO_2 \longrightarrow N_2 + H_2O$ (molecularity = 1)

$2HI \longrightarrow H_2 + I_2$ (molecularity = 2)

$2NO + O \longrightarrow 2NO_2$ (—"— = 2)

→ molecularity is theoritical concept

→ only integer, can't be 0, -ve, fraction.

Elementary Rx.ⁿ
↓
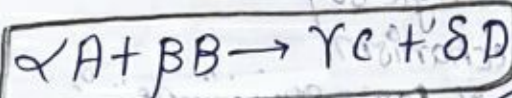Molecularity = stoichiometry = Order.

Complex Rx.ⁿ
↓
molecularity is seen for each step.

Rx.ⁿ todo, mechanism me aur har step ka likho.

Complex Rx.ⁿ → Overall molecularity is meaningless.

Max value of molecularity is ③.

← Rate Law →

$$\alpha A + \beta B \longrightarrow \gamma C + \delta D$$

$$Rate \propto [A]^x [B]^y \qquad \begin{pmatrix} x = \alpha \\ y = \beta \end{pmatrix} \text{or} \begin{matrix} x \neq \alpha \\ y \neq \beta \end{matrix}$$

x = Order w.r.t A
y = Order w.r.t B   elementary Rx.ⁿ

$x + y = n$ → overall order of Rx.ⁿ

Order →

→ experimental quantity
→ Zero / -ve / fraction / integer

Elementary Rx.ⁿ
↳ Order = Stoichiometric Coeff

Rate Constant (K) →

proportionality constant / rate const. / Velocity cons. / Specific rate const.

$$R \propto [A]^x [B]^y$$

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

If, $[A] = [B] = 1$, → ROR at unit conc. of reactant,
Then, $Rate = K$ is called specific Rate constant

Unit of Rate Constant K

$$R \propto [A]^x [B]^y \qquad \boxed{x + y = n} \text{ Order}$$

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

$$K = \frac{Rate}{[A]^x[B]^y} = \frac{Rate}{conc} = \frac{(mol/litre) \, time}{(mol/litre^{-1})^n}$$

$$\boxed{K = (mol/litre)^{1-n} \, time^{-1}}$$

Unit for Zero Order → mol lit⁻¹ time⁻¹
$$K = (mol/litre)^1 \, time^{-1}$$

Unit for 1st Order →
$$K = (time^{-1})$$

Unit for 2nd Order →
$$K = (mol/litre)^{-1} \, time^{-1}$$
or $mol^{-1} \, litre \, time^{-1}$

factors affecting K →

$K \longrightarrow$ Temp (dependent)

Independent of Conc.

Que: $2NH_3 \rightarrow N_2 + 3H_2$, If

$$\frac{-d(NH_3)}{dt} = K_1[NH_3], \quad \frac{d[N_2]}{dt} = K_2(NH_3)$$
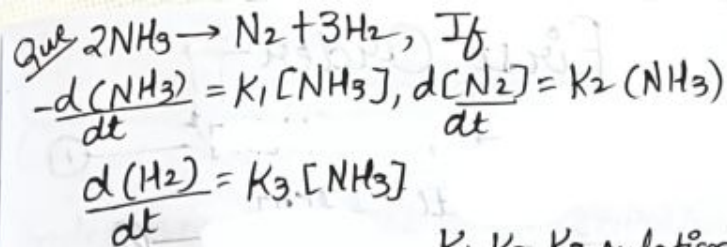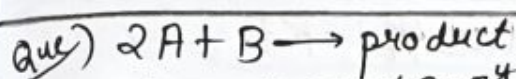
$$\frac{d(H_2)}{dt} = K_3[NH_3]$$

K_1, K_2, K_3 relation?

Sol^n $ROR = \frac{-1}{2}\frac{[NH_3]}{dt} = +\frac{d[N_2]}{dt} = \frac{1}{3}\cdot\frac{d[H_2]}{dt}$

$$\frac{K_1[NH_3]}{2} = K_2[NH_3] = \frac{1}{3}K_3[NH_3]$$

$$\frac{K_1}{2} = K_2 = \frac{K_3}{3}$$

$$\boxed{3K_1 = 0.6K_2 = 2K_3} \quad \text{(X by 6)}$$

Que) $2A + B \rightarrow$ product
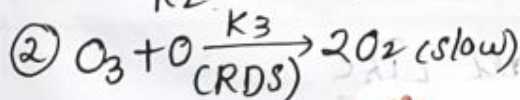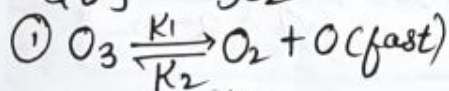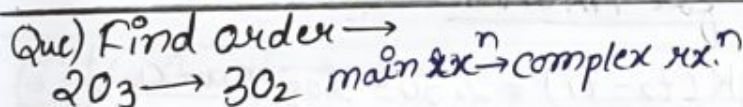
Rate law $= K[A]^x[B]^y$

→ if conc. of A is doubled, ROR becomes double, cal. X.

→ $R \propto [A]^x \quad \boxed{x=1}$

$2^1 \propto 2^x$

→ Conc of B → double, then ROR becomes half, Calculate Y.

Sol^n → $R \propto [B]^y$

$\frac{1}{2} \propto [2]^y \quad \boxed{y=-1}$

$2^{-1} \propto 2^y$

Que) Find order →

$2O_3 \rightarrow 3O_2$ main rx^n → complex rx^n

① $O_3 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} O_2 + O$ (fast)

② $O_3 + O \xrightarrow[\text{(RDS)}]{K_3} 2O_2$ (slow)

Rate $= K_3[O_3]'[O]'$

$K_{eq} = \frac{[O_2][O]}{[O_3]}$

$[O] = \frac{[O_3]K_{eq}}{[O_2]}$

(O intermediate)

Rate $= K_3[O_3]\frac{K_{eq}[O_3]}{[O_2]}$

$= \frac{K'[O_3]^2}{[O_2]} \longrightarrow K'[O_3]^2[O_2]^{-1}$

$$\boxed{\text{Order} = 2 - 1 = 1}$$

Zero Order Reaction

$(A) \longrightarrow (B)$

Rate $= K[A]^0$ ——②

Differential rate eq^n →

Rate $= \frac{-d[A]}{dt}$ ——①

① = ②

$$\frac{-d[A]}{dt} = K[A]^0$$

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

$$\boxed{d[A] = -K\,dt}$$

Integral Rate Law → ① = ②

$$\frac{-d[A]}{dt} = K[A]^0$$

$-\frac{d[A]}{[A]^0} = K\,dt$

$$\overset{A_t}{\underset{A_0}{-\int}}d[A] = \int_0^t K\,dt$$

$$\boxed{A_0 - A_t = Kt}$$

Half life

$t_{50\%} \,/\, t_{1/2} \,/\, t_{50\%} \text{ remaining} \,/\, t_{half}$

$[A_t] = \frac{A_0}{2}$ when $t = \frac{t_1}{2}$

$A_0 - A_t = Kt \rightarrow 0$ order

$A_0 - \frac{A_0}{2} = K\,t_{1/2}$

$\frac{A_0}{2} = K\,t_{1/2}$

$$\boxed{t_{1/2} = \frac{A_0}{2K}} \qquad \boxed{t_{1/2} \propto A_0} \quad \text{initial concentration}$$

Time for Completion →

when $t = t_{100}$, $A_t = 0$

$A_0 - A_t = Kt$ — 0 order

$A_0 - 0 = K t_{100}$

$\boxed{2 \times t_{50\%} = t_{100\%}}$

$\boxed{t_{100} = \dfrac{A_0}{K}}$

$\boxed{2 \times t_{half} = t_{complete}}$

Zero Order Rx.ⁿ completes in two half life

Graph → Zero Order
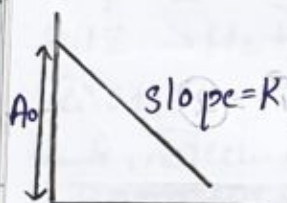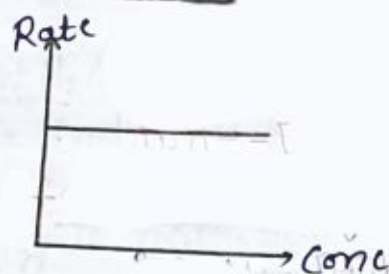
① A_t v/s t →

$A_0 - A_t = Kt$

$A_t = A_0 - Kt$

$\boxed{y = C - mx}$

② Rate v/s Conc →

Rate $= K[A]^0$

$\boxed{Rate = K}$

Rate

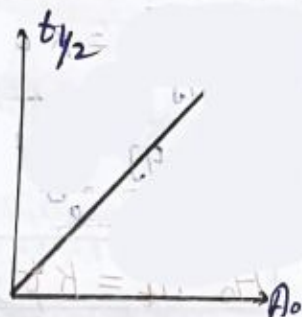A_0 slope = K

→ Conc

③ $t_{1/2}$ v/s A_0 →

$t_{1/2} = \dfrac{A_0}{2K}$

$\boxed{m = \dfrac{1}{2K}}$

$y = mx$

$t_{1/2}$

→ A_0

Zero Order

$t_{fraction}$

$\boxed{t_{frac.} = frac \times \dfrac{A_0}{K}}$

$\dfrac{50}{100} = t_{1/2} = \dfrac{1}{2} \times \dfrac{A_0}{K}$

$\dfrac{100}{100} = t_1 = \dfrac{A_0}{K}$

$\dfrac{75}{100} = t_{3/4} = \dfrac{3}{4} \times \dfrac{A_0}{K}$

$\dfrac{20}{100} = t_{1/5} = \dfrac{1}{5} \times \dfrac{A_0}{K}$

$\dfrac{25}{100} = t_{1/4} = \dfrac{1}{4} \times \dfrac{A_0}{K}$

First Order →

Rate law → Rate $= K[A]^2$ —①

$Rate = \dfrac{-d[A]}{dt}$ —②

① = ②

$K[A] = \dfrac{-d[A]}{dt}$

$\boxed{\dfrac{-d[A]}{A} = Kdt}$

Integral rate eqⁿ →

$\boxed{ln[A_0] - ln[A_t] = Kt}$

$\boxed{ln \dfrac{A_0}{A_t} = Kt}$

$\dfrac{A_0}{A_t} = e^{Kt}$

$\boxed{A_t = A_0 e^{-Kt}}$

$Kt = 2.303 \log \dfrac{A_0}{A_t}$

$\boxed{Kt = 2.303 \log \left(\dfrac{a}{a-x}\right)}$

for interval →

$\boxed{K(t_2 - t_1) = 2.303 \log \left(\dfrac{a - x_1}{a - x_2}\right)}$

Half Life

$A_t = \dfrac{A_0}{2}$ when $t = t_{1/2}$

$\boxed{ln \dfrac{A_0}{A_t} = Kt}$ 1ˢᵗ order

$ln \dfrac{A_0 \times 2}{A_0} = Kt_{1/2}$

$ln 2 = K \times t_{1/2}$

$t_{1/2} = \dfrac{\ln 2}{K} = \dfrac{0.693}{K}$

($t_{1/2}$ of first order reaction is independent of initial concentration)

Time for Completion → $t_{100\%}$

when $t = t_{100\%}$, $A_t = 0$

$Kt = \ln \dfrac{A_0}{A_t}$ $\boxed{t_{100\%} = \infty}$

1st order reaction never completes.

Short trick →

$\boxed{t_{3/4} = 2t_{1/2}}$ $\boxed{t_{75\%} = 2t_{50\%}}$

Que) ← **Graph** →

① $\ln A_t$ v/s t →   ② A_t v/s t →

$\ln A_0 - \ln A_t = Kt$ $A_t = A_0 e^{-Kt}$

$\ln A_t = \ln A_0 - Kt$ $y = C e^{-x}$

$y = c - mx$

$m = -K$

$\ln A_0$

③ $\log A_t$ v/s t →

$Kt = 2.303 \log \dfrac{A_0}{A_t}$

$Kt = 2.303 (\log A_0 - \log A_t)$

$\log A_t = \dfrac{-Kt}{2.303} + \log A_0$

$y = -mx + c$

slope $= \dfrac{-K}{2.303}$

$\log A_0$

Degree of Dissociation (α) →

$\alpha = \dfrac{\text{moles dissociated}}{\text{initial moles}}$

$\boxed{\alpha = \dfrac{x}{a}}$ $A_t = A_0 e^{-Kt}$ ——1st Order

$a - x = a e^{-Kt}$

$x = a(1 - e^{-Kt})$

$\dfrac{x}{a} = 1 - e^{-Kt}$

$\boxed{\alpha = 1 - e^{-Kt}}$

Que) $t_{1/2}$ of 1st Order reaction, 0.3 min, then ROR when conc. of reactant is 0.5 M.

Soln → $\boxed{Rate = K[A]^2}$

$\boxed{t_{1/2} = \dfrac{0.693}{K}}$ Rate $= 2.31 \times 0.5$

$0.3 = \dfrac{0.693}{K}$ $= 1.155\, M\, min^{-1}$

$\underline{K = 2.31\, min^{-1}}$

n^{th} Order →

$\boxed{Kt = \dfrac{1}{n-1}\left[\dfrac{1}{[A_t]^{n-1}} - \dfrac{1}{[A_0]^{n-1}}\right] \quad n \ne 1}$

$t_{1/2}$ of nth Order →

$\boxed{t_{1/2} \propto \dfrac{1}{[A_0]^{n-1}}}$ $\boxed{t_{1/2} \propto \dfrac{1}{a^{n-1}}}$

Zero Order →	First Order →
$\boxed{t_{1/2} \propto A_0}$	$\boxed{t_{1/2} \propto 1}$

Second Order →

$\boxed{n = 2}$

$\boxed{Kt = \left[\dfrac{1}{[A_t]} - \dfrac{1}{[A_0]}\right]}$

$t_{1/2}$ →

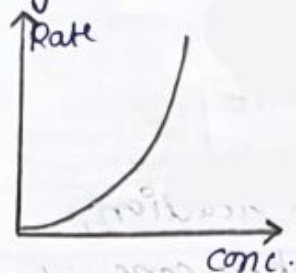$\boxed{t_{1/2} \propto \dfrac{1}{[A_0]}}$ $\boxed{t_{1/2} = \dfrac{1}{K[A_0]}}$

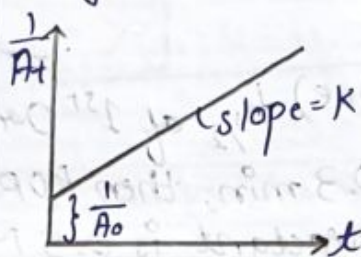## Graph

① Rate v/s Conc.

$$Rate = K(conc)^2$$
$$y = Kx^2$$

② $\frac{1}{A_t}$ v/s t

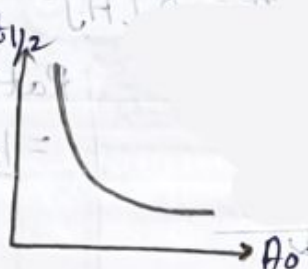$$Kt = \frac{1}{A_t} - \frac{1}{A_0}$$
$$y = mx + c$$

slope = K

③ $t_{1/2}$ v/s A_0 →

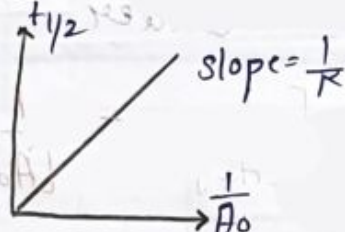$$t_{1/2} = \frac{1}{K A_0}$$
$$y = \frac{1}{Kx}$$
$$xy = K$$

④ $t_{1/2}$ v/s $\frac{1}{[A_0]}$

$$t_{1/2} = \frac{1}{K A_0}$$
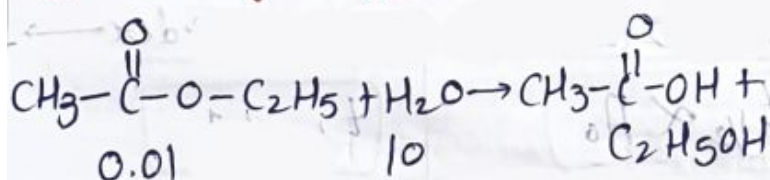$$y = \frac{1}{K} \cdot \frac{1}{A_0}$$
$$y = mx$$

slope = $\frac{1}{K}$

Pseudo 1st Order Rx.^{n} →

$Rx.^n$ → Order = 1 but molecularity = 2

eg- Hydrolysis of ester —

$$CH_3-\overset{O}{\overset{||}{C}}-O-C_2H_5 + H_2O \rightarrow CH_3-\overset{O}{\overset{||}{C}}-OH + C_2H_5OH$$
$$0.01 \qquad\qquad 10$$

$$R = K[CH_3-\overset{O}{\overset{||}{C}}-OC_2H_5][H_2O]_{const}$$

$$R = K'[CH_3-\overset{O}{\overset{||}{C}}-O-C_2H_5]$$

Order = 1
molecularity = 2

One reactant be in excess.

Collision Theory →

activation energy —
minimum energy required by reactant for converting into product

Threshold Energy —
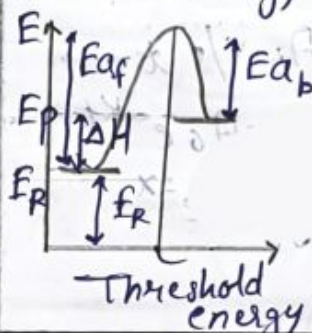min. energy possesed by reacting molecule for chemical rx.^{n} to occur

Energy diagram

Endothermic	Exothermic
$H_P - H_R > 0$	$H_P - H_R < 0$
$\Delta H > 0$	$\Delta H < 0$
$R + Heat \rightarrow P$	$R \rightarrow P + heat$
Stable → less energy	stable less energy

Endothermic: Threshold energy

Exothermic: Threshold energy

$\Delta H = E_P - E_R = E_{af} - Ea_b$	$\Delta H = E_P - E_R$
$TE = E_R + E_{af}$	$= E_{af} - Ea_b$
$= E_R + \Delta H + Ea_b$	
$= E_P + Ea_b$	$TE = E_P + \Delta H + E_{af}$
	$= E_P + Ea_b$

Catalyst and AE →

(-ve) Catalyst inhibitor ↑ses activation energy (Rx.^{n} slow)

(+ve) catalyst, ↓ses activation energy (Rx.^{n} fast)
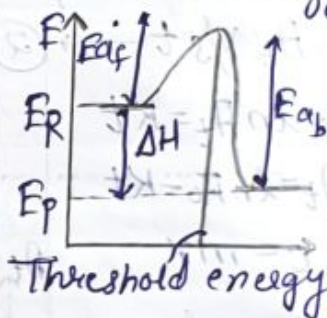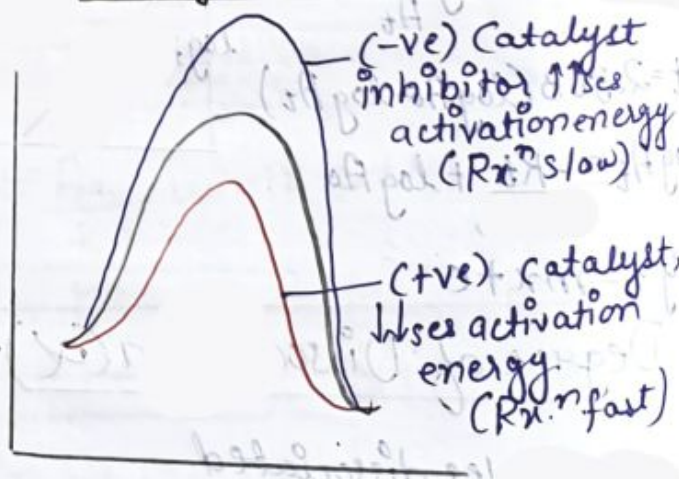
Arrhenius Eq^n.

$$K = A e^{\frac{-Ea}{RT}}$$

- Rate constant $\leftarrow K$
- Arrhenius const. $\leftarrow A$
- Activation energy $\rightarrow Ea$
- Temp(K) $\rightarrow$ Temp(K)
- gas const $\rightarrow$

$$\ln K = \ln A - \frac{Ea}{RT}$$
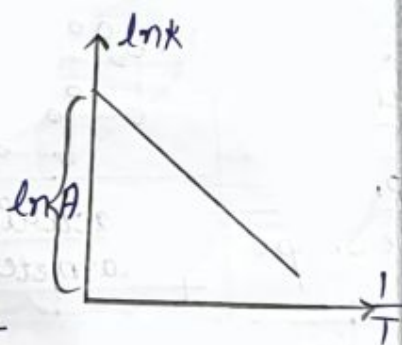
Graph $\rightarrow$

$\ln K$ v/s $\frac{1}{T} \rightarrow$

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

$$y = C - mx$$

$$m = \tan\theta = \frac{-Ea}{R}$$

Relation b/w K_1 and K_2 in Arrhenius

$$K_1 = A e^{\frac{-Ea}{RT_1}} \quad \text{—①}$$

$$K_2 = A e^{-Ea/RT_2} \quad \text{—②}$$

$$\left(\frac{2}{1}\right) \rightarrow$$

$$\frac{K_2}{K_1} = \frac{e^{-Ea/RT_2}}{e^{-Ea/RT_1}}$$

$$\boxed{\ln \frac{K_2}{K_1} = \frac{Ea}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]}$$

$$\boxed{\log \frac{K_2}{K_1} = \frac{Ea}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]}$$

Que) Cal value of pre-exponential factor and activation energy. (K cal) — $\log K = 6 - \frac{200}{T}$

Sol^n $\rightarrow$

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

$$\boxed{\log A = 6} \rightarrow \boxed{A = 10^6}$$

$$\frac{Ea}{2.303RT} = \frac{200}{T} = \underline{Ea = 9.2\,Kcal}$$