Chemical kinetics

- Rate of Reaction, factors affecting rate of reaction and mechanism of reaction]

- Rate of Reaction = $\dfrac{-(\text{decrease in conc}^n \text{ of Reactant})}{\text{time interval}}$

  always +ve $= \dfrac{(\text{increase in conc of product})}{\text{time interval}}$

  Unit of Rate of Reaction $= \dfrac{M}{\text{time}} = Mol\,L^{-1}\,time$

  In Gaseous state, conc = Pressure

  Unit = atm time^{-1}, mm time^{-1}

- Types of Rate of Reaction:

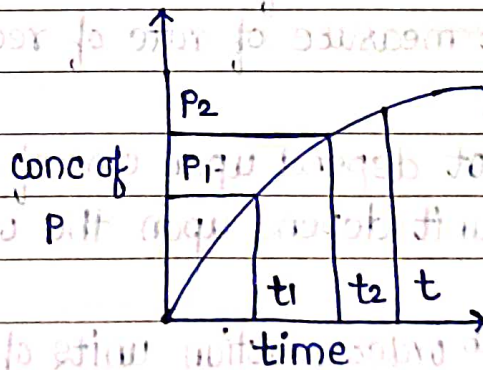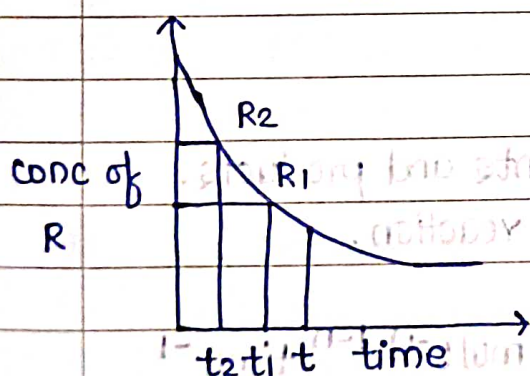| Instantaneous rate (rinst)	Average rate (rav)
① time interval — very small	① time interval = Big
$r_{inst} = \dfrac{-d[R]}{dt} = \dfrac{+d[P]}{dt}$	$r_{avg} = \dfrac{-\Delta[R]}{\Delta t} = \dfrac{+\Delta[P]}{\Delta t}$

$r_{avg} = \dfrac{-\Delta[R]}{\Delta t} = \dfrac{[R_1]-[R_2]}{t_1-t_2}$ $r_{avg} = \dfrac{+\Delta[P]}{\Delta t} = \dfrac{[P_2]-[P_1]}{t_2-t_1}$

$r_{inst} = -$ slope of tangent $r_{inst} = +$ slope of tangent

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- For a general reaction $aA + bB \longrightarrow cC + dD$

  Rate of Reaction $= -\dfrac{1}{a}\dfrac{d[A]}{dt} = -\dfrac{1}{b}\dfrac{d[B]}{dt} = +\dfrac{1}{c}\dfrac{d[C]}{dt} = +\dfrac{1}{d}\dfrac{d[D]}{dt}$

① $-\dfrac{d[A]}{dt}$ = rate of dissappearance or decomposition or consumption of A.

② $-\dfrac{d[B]}{dt}$ = (increase in conc of product) = $\dfrac{\text{time interval}}{}$

③ $+\dfrac{d[C]}{dt}$ = rate of appearance or production or formation of C

④ $+\dfrac{d[D]}{dt}$ =

- Rate law : For a general Reaction $aA + bB \longrightarrow P$

  rate $\propto [A]^x [B]^y$ — x and y are determined

  rate $= k[A]^x [B]^y$ experimentally and they

       may or may not be equal

  rate $= k$ when $[A] = 1$ to a and b.

  $[B] = 2$ — k is called rate constant

- characteristics of k :

① It is measure of rate of reaction

② $k \propto T$,

③ Do not depend upon conc of reactants and products.

④ Its unit depend upon the order of reaction.

- For n^{th} order reaction units of $k = (mol\,L^{-1})^{1-n} time^{-1}$

  $= (atm)^{1-n} time^{-1}$

- Order of Reaction :

  $x + y$ —— order of reaction

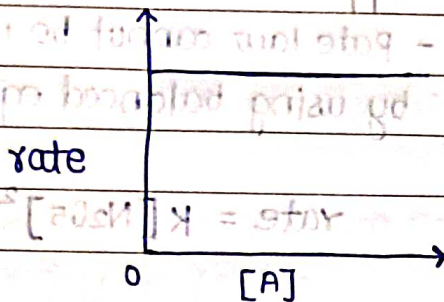 x —— order of reaction w.r.t A

  y —— order of reaction w.r.t B

① zero order Reaction

$\text{rate} = k[A]^0$

$\text{rate} = k$

rate of reaction is constant throughout
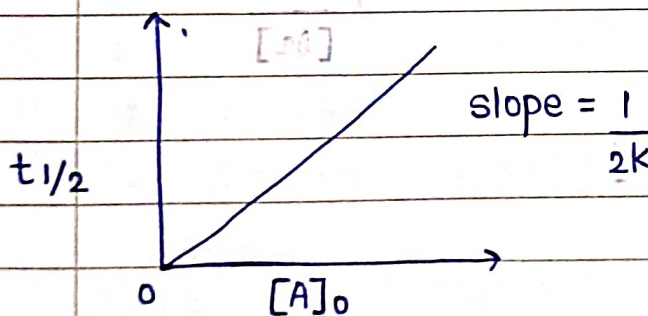
i·e· rate do not depend on the conc of reactant

rate

0   [A]

② First order Reaction

$\text{rate} = k[A]^1$

$\text{rate} \propto [A]$

rate

0   [A]

- Integrated rate eqn :

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

- $t_{1/2}$ or $50\% = \dfrac{[A]_0}{2k}$
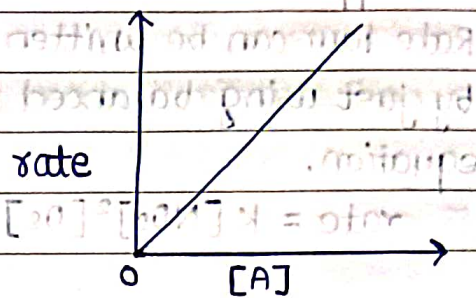
$\therefore t_{1/2} \propto [A]_0$

$t_{1/2}$

slope $= \dfrac{1}{2k}$
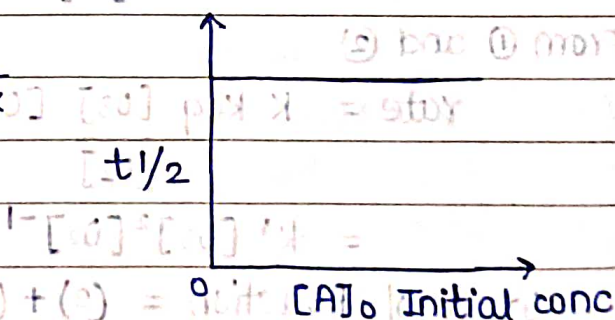
0    $[A]_0$

- $t_{100\%} = \dfrac{[A]_0}{k}$

– Integrated rate eqn :

$$k = \frac{2 \cdot 303}{t} \log \frac{[A]_0}{[A]t}$$

– $t_{1/2}$ or $50\% = \dfrac{0.693}{k}$ ←

$t_{1/2}$ is independent upon initial conc· of reactants
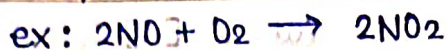

$t_{1/2}$

$[A]_0$ Initial conc

– $t_{100\%} = \infty$

- order of Reaction from the mechanism :

Two types of Reaction on the basis of number of steps·
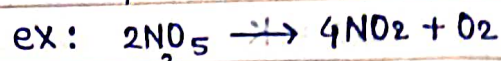
① Elementary Reaction

completes in single step

ex: $2NO + O_2 \longrightarrow 2NO_2$

② complex Reaction

completes in more than one step

ex: $2NO_5 \longrightarrow 4NO_2 + O_2$

- mechanism concept is not applicable.

- Rate law can be written by just using balanced equation.

$$rate = K[NO_2]^2[O_2]^1$$

- mechanism concept is applicable

- Rate law cannot be written by using balanced equation

$$rate = K[N_2O_5]^2$$

Q. The chemical reaction $2O_3 \longrightarrow 3O_2$ proceeds as

step I : $O_3 \rightleftharpoons O_2 + O$ (Fast)

step II : $O + O_3 \rightleftharpoons 2O_2$ (slow)
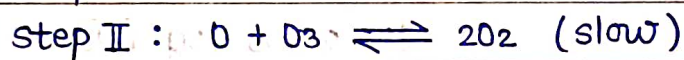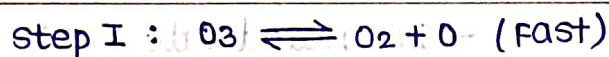
Find the order of the Reaction:

→ step II is RDS (slow)

$\therefore Rate = K[O]^1[O_3]^1$ ——— ①

O is intermediate

From step I : $Keq = \dfrac{[O_2][O]}{[O_3]}$ $[O] = Keq\dfrac{[O_3]}{[O_2]}$ ——— ②

From ① and ②

$$rate = \dfrac{K\,Keq\,[O_3]\,[O_3]}{[O_2]}$$

$$= k'[O_3]^2[O_2]^{-1}$$

$\therefore$ Order of Reaction $= (2) + (-1)$

$$= 1$$

• Methods to determine order of Reaction:

① Half life method:

For n^{th} order reaction:

$$t_{1/2} \propto (a_0)^{1-n}$$

① For zero order reaction $n=0$

$$t_{1/2} \propto a_0^{1-0}$$
$$t_{1/2} \propto a_0$$
$$t_{1/2} = \frac{[A]_0}{2K}$$

② For second order reaction $n=1$

$$t_{1/2} \propto (a_0)^{1-1}$$
$$\therefore t_{1/2} \propto (a_0)^0$$

$t_{1/2}$ is independent upon initial concenteration

$$t_{1/2} = 0.693/K$$

③ For second order reaction $n=2$

$$t_{1/2} \propto (a_0)^{1-2}$$
$$t_{1/2} \propto a_0^{-1}$$
$$t_{1/2} \propto \frac{1}{a_0}$$

- **Initial Rate method :**

Q. During the kinetic study of the Reaction $2A+B \longrightarrow C+D$ Following results were obtained.

Run	[A]	[B]	Initial Rate
I	0.1	0.1	6×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

Find the order of Reaction?.

$\therefore$ Rate law - Rate $= K[A]^1[B]^2$

Order of Reaction $= 1+2 = 3$

① w.rt A

I and II consider

On increasing conc A 4 times rate also increases 4 times

$\therefore$ rate $\propto [A]^1$

② w.rt B

II and III consider

On increasing conc B 2 times rate increased 4 times

$\therefore$ rate $\propto [B]^2$

- **Effect of Temperature on the rate of Reaction:**

Rate of Reaction $\propto T$

$$K \propto T$$

- Temperature coefficient (μ or n)

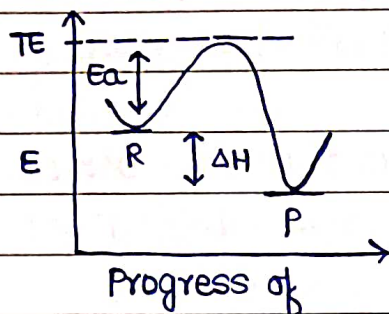$$\mu = \frac{K \text{ at } (T+10)^\circ}{K \text{ at } T^\circ}$$

$$K_2 = \mu^{(T_2-T_1)/10}$$

$$2 \leq \mu \leq 3$$

- Concept of Activation energy (E_a):

Progress of Reaction ΔH –ve (For exothermic reaction)	Progress of Reaction ΔH +ve (For endothermic Reaction)
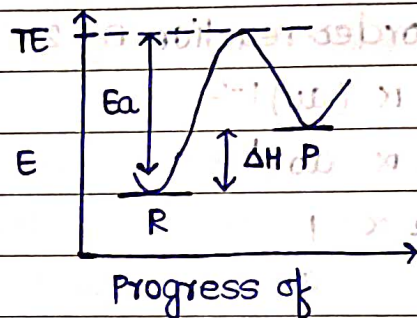
- $E_a = TE -$ energy passed by reactant.
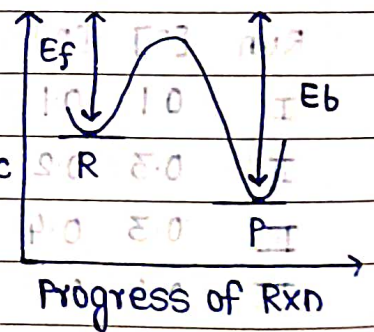- In exothermic $E_f < E_b$
- In endothermic $E_b < E_f$

Exothermic — Progress of Rxn

- Arrhenius Equation

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

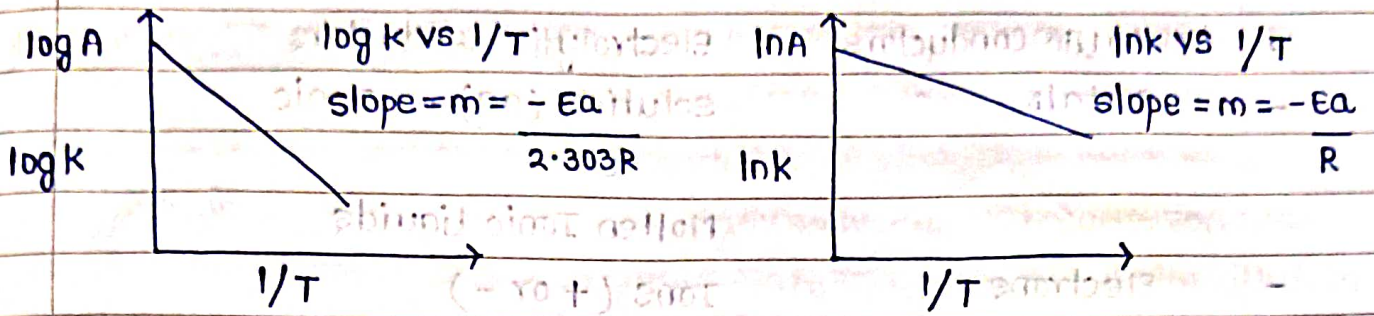$A \rightarrow$ pre exponential Factor or Frequency factor

Endothermic — Progress of Rxn

① $\ln K = \ln A - \dfrac{E_a}{RT}$

② $\log K = \log A - \dfrac{E_a}{2.303 RT}$

Rate of Reaction $\propto \dfrac{1}{E_a}$

log k vs 1/T   **ln k vs 1/T**

slope = m = $-\dfrac{Ea}{2\cdot303R}$ slope = m = $-\dfrac{Ea}{R}$

(graph: log A, log K vs 1/T)   (graph: lnA, lnk vs 1/T)
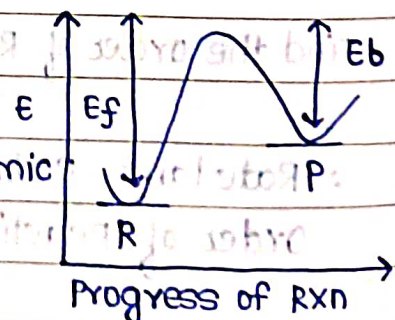
— $\log \dfrac{K_2}{K_1} = \dfrac{Ea}{2\cdot303R}\left(\dfrac{T_2 - T_1}{T_2 T_1}\right)$

— $Ea = J\,mol^{-1}$ $R = 8\cdot314 \ (25/3)$

$Ea = KJ\,mol^{-1}$ $R = 8\cdot314 \times 10^{-3}$

$Ea = cal\,mol^{-1}$ $R = 2$

$Ea = Kcal\,mol^{-1}$ $R = 2 \times 10^{-3}$

$Ea = ergs$ $R = 8\cdot314 \times 10^{7}$

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