30/3/18

# Chemical Kinetics

- It is branch of chemistry which deals with rate of chemical reaction and the factors affecting rate of chemical reaction like temp., conc., pressure catalyst, etc.

$$aA + bB \longrightarrow cC + dD$$

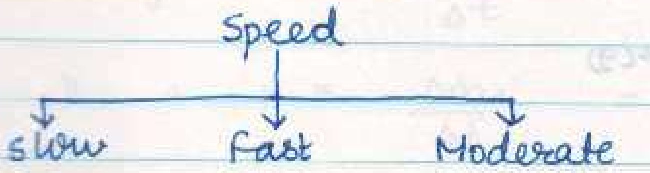
⇒ spontaneous / feasibility is predicted by Thermodynamics

⇒ extent of Rxn is predicted by chemical eq.

⇒ Rate of chemical Rxn is determined by Chemical kinetics.

## * Classification of chemical Rxn :-

Rxn can be classified on the basis of
a) Speed
b) Mechanism



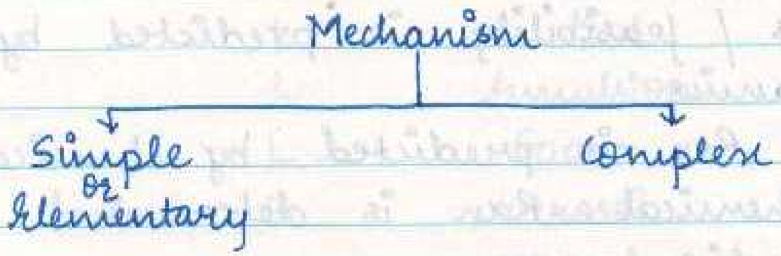
• Slow Rxn : These are the rxns which take place at a very low rate. For eg, rusting of iron.

• Fast Rxn : These are the rxns which occur instantaneously within a fraction of time. For eg, acid-base rxn.

$HCl + NaOH \xrightarrow{10^{-7}\,sec} NaCl + H_2O$

- **Moderate Rxn** : These are the rxns which are neither very slow nor instantaneous. For eg, decomposition of $H_2O_2$.

$$H_2O_{2\,(aq.)} \longrightarrow H_2O_{(l)} + \frac{1}{2} O_2 \uparrow_{(g)}$$



- **Elementary Rxn** : These are the reactions which get completed in single step.

- **Complex Rxn** : These are Rxns which take place in more than one step & each step of rxn will be an elementary rxn. For eg,

$$2NO_{(g)} + O_{2\,(g)} \longrightarrow 2NO_{2\,(g)}$$

**Step I** : $2NO_{(g)} \longrightarrow N_2O_{2\,(g)}$

**Step II** : $N_2O_{2\,(g)} + O_{2\,(g)} \longrightarrow 2NO_{2\,(g)}$

**Note** : - Just by seeing rxn, we cannot predict whether it is simple or complex rxn.
- We generally study moderate rxns.

- Rate of Rxn : change in amount of reactant or product per unit time.

- Rate of appearance of Product (ROA) :

Amount of product formed per unit time.

- Rate of Disappearance of reactant (ROD) :

Amount of reactant disappeared / reacted per unit time.

$$A_{(g)} \xrightarrow{1L} 2B_{(g)}$$

| | | |
|---|---|---|
| t=0 | 100 mol | – |
| t=1sec | 90 mol | 20 mol |

if V is constant,

ROD of A = $-\frac{\Delta n_A}{\Delta t} = -\frac{(n_{A_f} - n_{A_i})}{t_2 - t_1} = 10$ mol/sec

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

" " " = $-\frac{dP_A}{dt}$

RoA of B = $\frac{\Delta[B]}{\Delta t} = \frac{20-0}{1} = 20$ M/sec

if V is variable,

ROD of A = $-\frac{\Delta n_A}{\Delta t}$ ; $-\frac{\Delta m_A}{\Delta t}$

V → constant

$A \xrightarrow{1L} 2B$

100 –

90 20

$[A]_i = 10\,M$

$[A]_f = 9M$

V → Variable

$A \xrightarrow{10L} 2B$

100 – V → 10L.

90 20 V → 5L

$[A]_i = 10\,M$

$[A]_f = 18\,M$ ✗

<u>Note</u>: If volume is variable then ROA or ROD is expressed in terms of moles or mass but if volume is constant then it can also be expressed in terms of concentration or partial pressure.

eg,

$A_{(g)} \xrightarrow{1L} 2P_{(g)} + 3Q_{(g)}$

| | | | |
|---|---|---|---|
| t=0 | 100 | 0 | 0 |
| t=10s | 90 | 20 | 30 |

ROD of A = 1 mol/s = 1 M/s = $-\Delta[A]/\Delta t$

ROA of P = 2 M/s = $\Delta[P]/\Delta t$

ROA of Q = 3 M/s = $\Delta[Q]/\Delta t$

$$\text{Rate of Rxn} = -\frac{\Delta[A]}{\Delta t} = \frac{1}{2}\frac{\Delta[P]}{\Delta t} = \frac{1}{3}\frac{\Delta[Q]}{\Delta t} = 1\ M/s$$

In general,

$$RoR = \frac{-1\Delta[A]}{a\,\Delta t} = \frac{-1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

$A \xrightarrow{1L} 2B$

| | | |
|---|---|---|
| t=0 | 100 | 0 |
| t=10 | 90 | 20 |

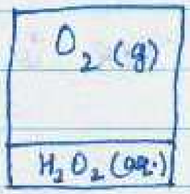
ROD of A = 1 M/s
ROA of B = 2 M/s
ROR = 1 M/s

$2A \xrightarrow{1L} 4B$

| | | |
|---|---|---|
| t=0 | 100 | |
| t=10 | 90 | 20 |

ROD of A = 1 M/s
ROA of B = 2 M/s
ROR = ½ M/s

- ROA or ROD are actual qty. and independent of stoichiom coeff. however ROR is theoritical qty. & it will depend on stoichiometric coeff.
 It means a rxn can have more than one ROR depending on its balancing. So whenever ROR is asked a balanced chemical rxn should be given. or ROR is defined only for balanced chemical eq^n.



$H_2O_2 (aq.) \longrightarrow H_2O (l) + \frac{1}{2} O_2 (g)$

$ROR = \cancel{-\frac{\Delta[H_2O_2]}{\Delta t} = \frac{2\Delta[O_2]}{\Delta t}}$ due to diff. volumes taken into consideration.

$$\boxed{ROR = \frac{-\Delta n_{H_2O_2}}{\Delta t} = \frac{2 n_{O_2}}{\Delta t}}$$

- **Units of ROR :→**

$mol\ s^{-1}$

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

$atm\ s^{-1}$ or $bar\ s^{-1}$

- **Conversion :→**

$$P_A V = n_A RT$$

$$P_A = \left(\frac{n_A}{V}\right) RT$$

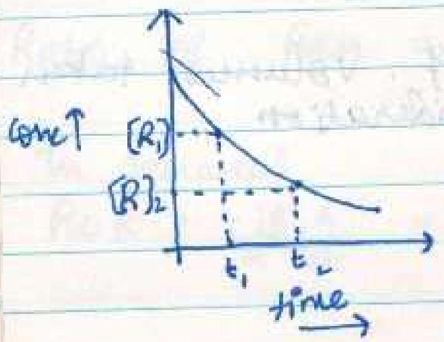
$$\Rightarrow \frac{1}{RT} \times \frac{\Delta P_A}{\Delta t} = \frac{\Delta [A]}{\Delta t}$$

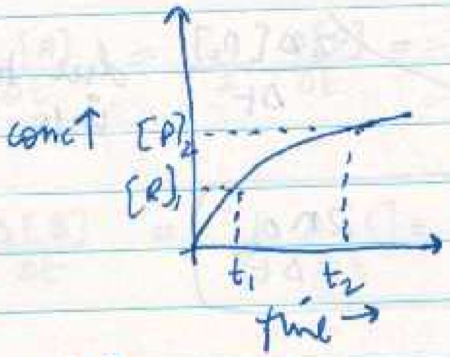
- **Types of Rate of Rxn :→**

i) Average ROR
ii) Instantaneous ROR

A] **Average Rate of Rxn :** If ROR is measured over a large interval of time.

$$R \longrightarrow P$$

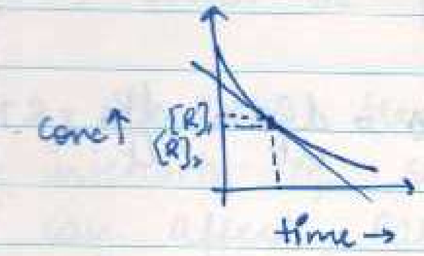


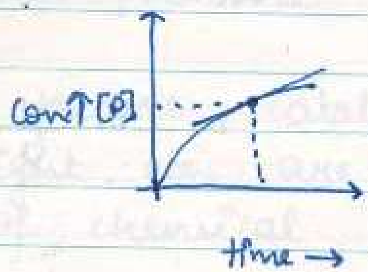


$$ROR = -\frac{\Delta [R]}{\Delta t} = \frac{\Delta [P]}{\Delta t}$$

B] **Instantaneous Rate of Rxn** : If rate of rxn is measured over a very short interval of time.

$$R \longrightarrow P$$





ROD of R = $\frac{-d[R]}{dt}$        ROA of P = $\frac{d[P]}{dt}$

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

Q. For the rxn

$$2A \longrightarrow 3B + 4C$$

The no. of moles of B increases by $6 \times 10^{-3}$ mol in 10 sec in 10 L vessel. Calculate a) ROA of B & C
b) ROD of A
c) ROR

→ ROA of B = $\frac{6 \times 10^{-3}}{100}$        ROD of A = $\frac{4 \times 10^{-3}}{100}$

C = $\frac{8 \times 10^{-3}}{100}$

ROR = $\frac{2 \times 10^{-3}}{100}$

Q. For the gaseous phase Rxn

$A(g) \longrightarrow$ Product, occuring at constant volume the correct relⁿ b/w $\frac{dC_A}{dt}$, $\frac{dn_A}{dt}$ & $\frac{dP_A}{dt}$

A. $\frac{dC_A}{dt} = \frac{dn_A}{dt} = \frac{dP_A}{dt}$

B. $\frac{1}{V}\frac{dn_A}{dt} = \frac{dC_A}{dt} = \frac{dP_A}{dt} \times RT$

⇒ C. $\frac{dC_A}{dt} = \frac{1}{RT}\frac{dP_A}{dt} = \frac{1}{V}\frac{dn_A}{dt}$

D. $\frac{1}{V}\frac{dP_A}{dt} = \frac{1}{V}\frac{dn_A}{dt} = \frac{dC_A}{dt}$

Q. The rate of disappearance of ammonia is 3.4g/L when it dissociates to form nitrogen and hydrog

i) The ROA of $N_2(g)$ will be

ii)

→ $2NH_3 \longrightarrow N_2 + 3H_2$

A] ROR $= \frac{1}{2} \times 3.4 = 1.7 =$ ROA of $N_2$.

Q. For Rxn,

$N_2O_5(g) \longrightarrow 2NO_2 + \frac{1}{2}O_2$ The variation of conc of $N_2O_5$ with time can be expressed by

conc↑ $[N_2O_5]_t = [N_2O_5]_0 e^{-kt}$ where $[N_2O_5]_0 = 1M$

& $k = 10^{-4}$ sec⁻¹ Determine

a) ROD of $N_2O_5$ at $10^4$ sec $\Rightarrow -k e^{-kt} = \frac{1}{e} \cdot 10^{-4}$

b) ROR during first $10^4$ sec $\Rightarrow \frac{1}{e} - 1/10^4$

c) variation of conc. of $NO_2$ with time.

$\frac{1}{e} - 1$ $\int 2k e^{-kt}$

## * Factors affecting Rate of Rxn :→

i) Nature of Rxn components
ii) Temperature
iii) Conc. or partial pressure

Besides these factors, catalyst, surface area, intensity of sunlight, etc. are other factor which can affect Rate of chemical rxn.

## * Rate law :→

$$aA + bB \longrightarrow cC + dD$$

Rate of Rxn $\propto a_A^{\alpha} \, a_B^{\beta}$

$$\boxed{\text{Rate of Rxn} = K\, a_A^{\alpha}\, a_B^{\beta}} \rightarrow \text{Rate law expression}$$

where,

$a_A, a_B$ → active masses of A & B resp.
$\alpha, \beta$ → experimentally determined factors
K → Rate constant / Velocity constant / specific Ra
Rate

- Case I : In case of liq. sol$^n$ active masses are replaced by conc.

$$\text{Rate} = K[A]^{\alpha}[B]^{\beta}$$

Case II : In case of gases active masses are replaced by either conc. or partial pressure

$$Rate = k P_A^{\alpha} P_B^{\beta}$$
$$Rate = k' [A]^{\alpha} [B]^{\beta}$$

- Case III : In case of pure liquid, pure solid and excess solvent active masses remain constant or replace by unity.

eg, $A_{(s)} + B_{(aq.)} \longrightarrow C_{(g)}$

$$Rate = k a_A^{\alpha} a_B^{\beta}$$
$$= k' a_B^{\beta} = k' [B]^{\beta}$$

* Order of Rxn :→

a/ sum of powers of molar conc. or partial pressure of rxn components in experimentally determined rate law expression.

$$aA + bB \longrightarrow cC + dD$$

$$\boxed{Rate = k [A]^m \cdot [B]^n} \rightarrow \text{Rate law expression}$$

where,

$m$ → order w.r.t. A

$n$ → order w.r.t. B

$m+n$ → order of Rxn

## Some imp. points regarding order of Rxn :→

- It is determined experimentally.
- Order of Rxn can be +ve, -ve, zero or fraction
- Order as well as mechanism of rxn may get changed on changing reaction conditions like pressure or temp.

eg, $NO_2(g) + CO(g) \longrightarrow NaOH + CO_2(g)$

$Rate = K[NO_2][CO]$ Above 500°C

$= K[NO_2]^2$ Below 500°C

eg, $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

$Rate = K$

order → 0

Rate constant → K

eg. $(H_2O_2(aq.) \longrightarrow H_2O(l) + \frac{1}{2}O_2(g)$

$Rate = K[H_2O_2]$

Order = → 1

Rate constant → K

eg, $2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$

$$Rate = \frac{K_1[NH_3]}{1+K_2[NH_3]}$$

order → N. D.

Rate constant → N. D

H.W.
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Ex. 1 : 1-9

- It is not necessary that rate constant as well as order of rxn is defined for every rxn.
- In case of elementary rxn, coeff. of reactants becomes equal to its order

$$aA + bB \xrightarrow{\text{elementary}} cC$$ {converse is not true}

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

* Physical significance of 'K'

- Larger the value of 'K' faster will be the rxn. Under given catalytic conditions, 'K' can be changed only by changing temperature.

- Units of 'K' :→

$$A \longrightarrow B$$

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

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

Units of 'K' will depend on order of rxn.

if $n=0 \Rightarrow$ zero order $\Rightarrow K \rightarrow M\,s^{-1}$

if $n=1 \Rightarrow$ first order $\Rightarrow K \rightarrow s^{-1}$

if $n=2 \Rightarrow$ second order $\Rightarrow K \rightarrow M^{-1}s^{-1}$

- Various types of 'K' :→

$$aA + bB \longrightarrow cC + dD$$

$$\text{ROR} = \frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt} = K_r[A]^\alpha[B]^\beta$$

$K_r \rightarrow$ rate constant of Rxn

$$-\frac{d[A]}{dt} = aK_r[A]^\alpha[B]^\beta = K_A[A]^\alpha[B]^\beta$$

$$-\frac{d[B]}{dt} = bK_r[A]^\alpha[B]^\beta = K_B[A]^\alpha[B]^\beta$$

where,
$K_A, K_B \rightarrow$ rate of disappearance consts w.r.t A & B re

$$\frac{d[C]}{dt} = cK_r[A]^\alpha[B]^\beta = K_c[A]^\alpha[B]^\beta$$

$$\frac{d[D]}{dt} = dK_r[A]^\alpha[B]^\beta = K_D[A]^\alpha[B]^\beta$$

where,
$K_c, K_D \rightarrow$ rate of app. const

$$\Rightarrow \boxed{K_r = \frac{K_A}{a} = \frac{K_B}{b} = \frac{K_c}{c} = \frac{K_D}{d}}$$

** Note :

- If nothing is mentioned than we will take it as

$$2A \xrightarrow{K_A \leftarrow \textcircled{K}} B$$

- Units of K helps in determination of order of reaction in numerical problems.

## * Analysis of Various Orders of Rxns :→

(Using Integrated Rate Law expressions)

### 1. Zero Order :→

$$nA \longrightarrow B$$

$t=0 \quad a=[A]_0 \qquad 0$

$t=t \quad a-x=[A]_t \qquad \frac{x}{n}$

$$ROR = \frac{-d[A]}{n\,dt} = \frac{d[B]}{dt} = k_r$$

$$\Rightarrow \frac{-d[A]}{dt} = nk_r = k_A$$

$$\Rightarrow -\int_{[A]_0}^{[A]_t} d[A] = \int_0^t k_A\,dt$$

$$\Rightarrow ([A]_t - [A]_0) = k_A t$$

$$\Rightarrow x = k_A t$$

$$\Rightarrow [A]_t = [A]_0 - k_A t$$

$$P_{A_t} = P_{A_0} - k'_A t$$

R

- **Half life** ($t_{1/2}$) :→ It is the time taken to reac
half of reactant.

$$[A]_t = \frac{[A]_0}{2}$$

$$[A]_t = [A]_0 - K_A t_{1/2}$$

$$\Rightarrow \boxed{t_{1/2} = \frac{[A]_0}{2K_A}} \qquad t_{1/2} \propto [A]_0$$

- **Completion time** ($t_{comp}$) :→

$$[A]_t = 0$$

$$\Rightarrow \boxed{t_{comp} = \frac{[A]_0}{K_A}}$$

- Relⁿ b/w $t_{1/2}$ & $t_{comp}$ :→

$$\boxed{t_{comp} = 2\, t_{1/2}}$$

- **Characteristics of zero order Rxn** :→

i] Units of K → $Ms^{-1}$

ii] Conc. of reactant decreases linearly with tim

$$[A]_t = [A]_0 - K_A t$$

$$y = c + m x$$

iii) Half life depends on initial conc. of reactant

$$\begin{tikzcd}
100\ \text{mol} \arrow[r, "20s"] \arrow[r, bend left, "t_{50\%} = 20s"] \arrow[rr, bend left=50, "t_{75\%} = 30s"] \arrow[rrr, bend right=40, "t_{87.5\%} = 25s"'] \arrow[rrrr, bend right=50, "t_{93.75\%} = 37.5\ sec"'] & 50\ \text{mol} \arrow[r, "10\ s"] & 25\ \text{mol} \arrow[r, "5\ s"] & 12.5\ \text{mol} \arrow[r, "2.5s"] & 6.25\ \text{mol}
\end{tikzcd}$$

iv) $t_{comp} = \frac{[A]_0}{K_A}$ { it gets completed in finite time }

$t_{comp.}$ is also proportional to initial conc.

v) Conc. of reactant in zero order rxn, after equal interval of time constitute an AP with C.D. $(-K_A t)$.

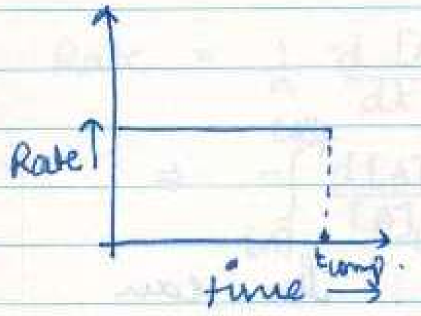
| time (t) | 0 | t | 2t | 3t |
|---|---|---|---|---|
| $[A]_t$ | $[A]_0$ | $[A]_0 - K_A t$ | $[A]_0 - 2K_A t$ | $[A]_0 - 3K_A t$ |

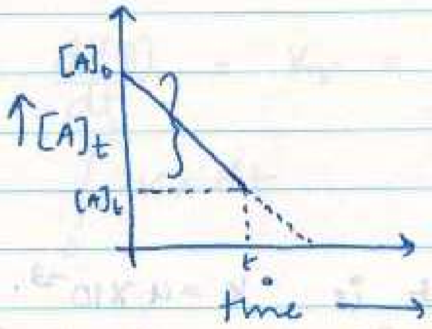
$\underbrace{[A]_0 \quad [A]_0 - K_A t}_{-K_A t}$, $\underbrace{[A]_0 - K_A t \quad [A]_0 - 2K_A t}_{-K_A t}$, $\underbrace{[A]_0 - 2K_A t \quad [A]_0 - 3K_A t}_{-K_A t}$ } Rate Constant

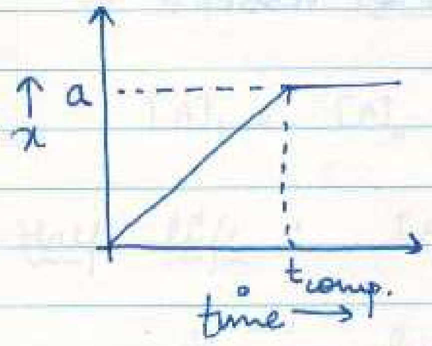
*vi) Zero order rxn must be complex

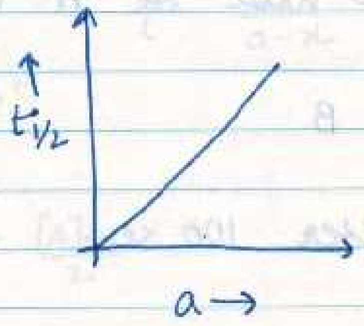
- Graphical Form :→

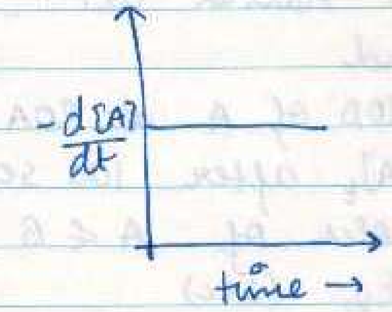
$$\begin{array}{lll} & nA \longrightarrow & B \\ t=0 & a=[A]_0 & 0 \\ t=t & a-x=[A]_t & \frac{x}{n} \end{array}$$











- Examples of zero order :→

i) Photochemical Rxn

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

Rate = K

ii] Surface catalysed Rxn

$$N_2O(g) \xrightarrow[\text{surface}]{\text{Hot Pt}} N_2(g) + \frac{1}{2}O_2(g)$$

Rate = K

iii] $2NH_3(g) \xrightarrow[\text{Surface}]{\text{Mo or W}} N_2(g) + 3H_2(g)$

Rate = k

**H.W.**

DPP # 9

Sheet : 10 - 17

Q. For the rxn

$A \longrightarrow 2B$

The rate constant is $k = 4\times10^{-3}\ M\,s^{-1}$. The rxn is started with 20 mol of A in 10 L vessel.

Find

a) ROD of A & ROA of B

b) $[A]_t$ after 100 sec

c) Moles of A & B after 100 sec

d) $t_{1/2}$ (sec)

e) $t_{\text{completion}}$

f) time at which conc. of A becomes equal to B from start of Rxn

g) Conc. of A & B after 10 min

→ Rate = $4\times10^{-3}\times2 = 8\times10^{-3}$

a) $8\times10^{-3}$, $[illegible]\times10^{-3}$

b) 1.6 M

c) 16 mol of A & 8 mol of B

d) $1/4\times10^{3}$ sec

e) $1/2\times10^{3}$ sec

f) ~~[illegible]~~ sec

g) A = 0, B = 4 M

$2 - 4\times10^{-3}\times100$

$\frac{1}{2}\times10^{3}$ sec

$1.35 = 2 - 4\times10^{-3}\times t$

$\frac{0.65\times10^{3}}{4}$

## 2. First Order Reaction :→

$$nA \longrightarrow B$$

$t=0 \quad a = [A]_0 \quad 0$

$t=t \quad a-x = [A]_0 - x \quad x$

$$\text{Rate} = \frac{1}{n}\frac{-d[A]}{dt} = \frac{d[B]}{dt} = k_r = k_A [A]_t$$

$$\Rightarrow -\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]_t} = \int_0^t k_A \, dt$$

$$\Rightarrow k_A t = \ln\frac{[A]_0}{[A]_t} = \ln\frac{a}{a-x}$$

$$[A]_t = [A]_0 \, e^{-k_A t}$$

Half life : $[A]_t = \frac{[A]_0}{2}$

$$t_{1/2} = \frac{\ln 2}{k_A}$$

- Half life will be independent of initial conc.

Completion time :

$$t_{comp} = \ln\frac{[A_0]}{[A_t]=0} = \infty$$

- Ist order Rxn will never get completed in finite time

For numerical purpose :

a) If % of reactant reacted is given

$$k_A t = \ln \frac{[A]_0}{[A]_t} = \ln \frac{a}{a-x}$$

$$\left.\begin{aligned} k_A t_{20\%} &= \ln \frac{100}{80} \\ k_A t_{40\%} &= \ln \frac{100}{60} \end{aligned}\right\} k_A t_{x\%} = \ln \frac{100}{100-x}$$

b) If fraction of reactant reacted is given

$$\left.\begin{aligned} k t_{1/3} &= \ln \frac{1}{1-1/3} \\ k t_{1/7} &= \ln \frac{1}{1-1/7} \end{aligned}\right\} k t_{1/n} = \ln \frac{1}{1-1/n}$$

- Characteristics of I$^{st}$ order Rxn :

i] Units of k → $s^{-1}$

ii] conc. of ~~rxn~~ reactant ↓ exponentially with time

$$[A]_t = [A]_0 e^{-k_A t}$$

iii] $t_{1/2} = \frac{\ln 2}{k_A}$

$$\begin{tikzcd}[column sep=large]
\text{iv]}\ 100 \arrow[r, "10s"] \arrow[r, bend left=50, no head, "t_{50\%} = 10s"] \arrow[rr, bend left=70, no head, "t_{75\%} = 20s"] \arrow[rr, bend right=40, no head] \arrow[rrr, bend right=40, no head, "t_{87.5\%} = 30s"'] \arrow[rrrr, bend right=60, no head, "t_{93.25\%} = 40s"'] & 50 \arrow[r, "10s"] & 25 \arrow[r, "10s"] & 12.5 \arrow[r, "10s"] & 6.25
\end{tikzcd}$$

v] $t_{completion} = \infty.$

$I^{st}$ order rxns never get completed in finite time.

vi] Concentration of reactants after equal interval of time constitute a G.P. with common ratio $e^{-K_A t}$ it means in equal interval of time, equal % of reactant reacts.

| time (t) | 0 | t | 2t |
|---|---|---|---|
| $[A]_t$ | $[A]_0$ | $[A]_0 e^{-K_A t}$ | $[A]_0 e^{-2K_A t}$ |

$$\underbrace{[A]_0 \quad [A]_0 e^{-K_A t}}_{e^{-K_A t}} \qquad \underbrace{[A]_0 e^{-K_A t} \quad [A]_0 e^{-2K_A t}}_{e^{-K_A t}}$$

vii] Average life $(t_{avg}) = \frac{1}{K_A} = \frac{t_{1/2}}{\ln 2} = 1.44\, t_{1/2}$

- Graphical Analysis

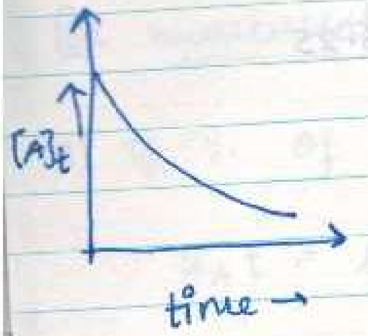
$$A \longrightarrow B$$

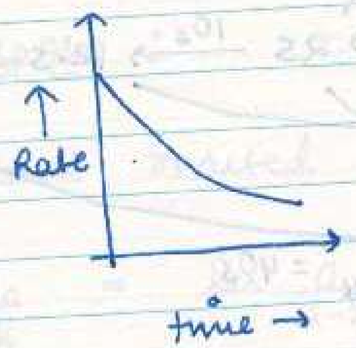
$t = 0 \quad a = [A]_0$

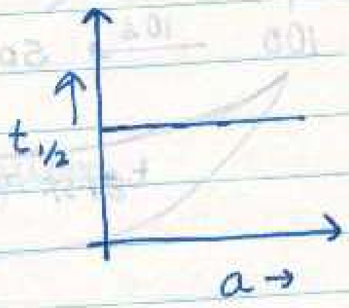
$t = t \quad a - x = [A]_t \quad x$

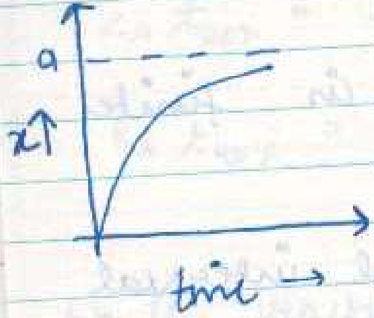
**H.W.**
Ex 1 ⇒ 28.

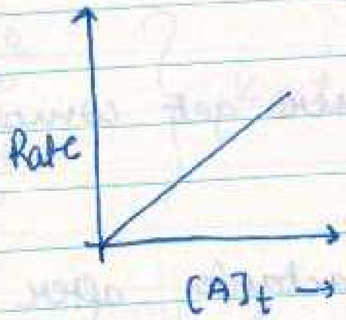
& $[A]_t = [A]_0 e^{-K_a t}$

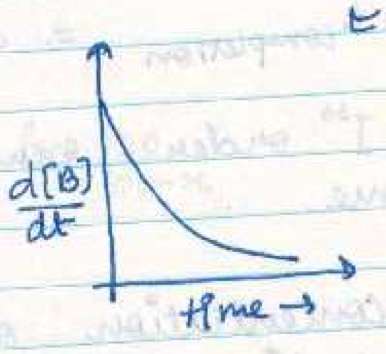


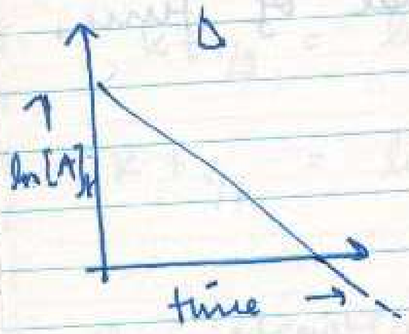












- **Average life :**

$$A \longrightarrow B$$

$$t_{avg.} = \frac{\text{Summation of life of each molecule}}{\text{Total no. of molecules}}$$

If we take time interval b/w t to t + dt

$$-\frac{d[A]}{dt} = k_A [A]_t$$

$$-d[A] = k_A [A]_t \, dt$$

$$t_{avg} = \int_0^\infty \frac{k_A [A]_t \, dt}{[A]_0} = \int_0^\infty \frac{k_A [A]_0 \, t e^{-k_A t} dt}{[A]_0}$$

$$(t_{avg})_I = \frac{1}{k_A}$$

For zero order,

$$-\frac{d[A]}{dt} = k_r = k_A$$

$$t_{avg} = \int_0^t \frac{k_A t dt}{[A]_0} = \frac{k_A t^2}{2[A]_0}$$

## Examples of First Order Rxn :

1] All radioactive disintegration follows first order kinetics.

2] Decomposition of $H_2O_2$

$$H_2O_2\,(aq.) \longrightarrow H_2O\,(l) + \frac{1}{2}O_2\,(g)$$

$$\text{Rate} = k[H_2O_2]$$

Q. For I order Rxn P.T.

i) $T_{75\%} = 2t_{50\%}$

ii) $t_{87.5\%} = 3t_{50\%}$

iii) $t_{99.9\%} = 10t_{50\%}$

$$\rightarrow \frac{1}{K_A} \times \ln\frac{100}{25} \quad -① \quad \Bigg| \quad \frac{1}{K_A} \ln\frac{100}{50} \quad -②$$

from ① & ②

$t_{75} = 2t_{50}$

$$t_{87.5\%} = \frac{1}{K_A}\ln 8 = 3t_{50\%}$$

$$t_{99.9\%} = \frac{1}{K_A}\ln\frac{100}{0.1} = 10\,t_{50\%}$$

Q. for a I order Rxn ror at $t_1 = 10$ min is $2 \times 10^{-3}$ MS
& at $t_2 = 20$ min is $4 \times 10^{-3}$ $MS^{-1}$ find K.

→ $ROR = K_A [A]_t$

$= K_A [A]_0 e^{-K_A t}$

$\frac{1}{2} = \frac{e^{-K_A 600}}{e^{-K_A 1200}}$

$\Rightarrow K_A \times 600 = -\frac{\ln 2}{600} =$ [illegible] $s^{-1}$

$\frac{2 \ln 2}{600} = \frac{1.4}{600}$

for numerical purpose

$\frac{[A]_t}{[A]_0}$ = Fraction of reactant left

$1 - \frac{[A]_t}{[A]_0}$ = " " " reacted.

eg, $[A]_0 \xrightarrow{10s} \frac{[A]_0}{2^1} \xrightarrow{10s} \frac{[A]_0}{2^2}$

$[A]_t = \frac{[A]^0}{2^n}$

where n = no. of half lives

$\frac{[A]_t}{[A_0]} = \frac{1}{2^n}$.

Q.
→ $1 - \frac{1}{2^6} = 63/64 \times 100$

- **Pseudo order Rxn :**

If more than one reactants are present & one of them is in large excess then during rxn conc. of reactant which is present in excess qty. almost becomes constant. In such a case its conc. is merged with k & order w.r.t. other reactant (lesser) is called pseudo order.

$$A + B \longrightarrow C$$

| | A | B | C |
|---|---|---|---|
| $t=0$ | 1000M | 1M | 0 |
| $t=t_1$ | 999.5M | 0.5M | 0.5M |
| $t=t_2$ | 999.25M | 0.25M | 0.75M |

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

$$\frac{r_1}{r_2} = \frac{\cancel{k} \times 1000 \times 1}{\cancel{k} \times 999.5 \times 0.5} = \frac{2}{1}$$

$$\therefore \text{rate} = k'[B]$$

where,
$k' = k[A]$ = Pseudo Rate constant

- $k't = \ln \frac{[B]_0}{[B]_t}$

$k' = k[A]$
↳ Rate constant for rxn.

eg. inversion of cane sugar is pseudo I order rxn

$$C_{12}H_{22}O_{11}\,(aq.) + H_2O\,(l) \xrightarrow{H^+(aq)} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$\text{rate} = k[H_2O][H^+][C_{12}H_{22}O_{11}]$$

$$\text{rate} = k'[C_{12}H_{22}O_{11}]$$

$$k' = k[H_2O][H^+]$$

↓

Pseudo rate constant

$$k't = \ln \frac{[C_{12}H_{22}O_{11}]_0}{[C_{12}H_{22}O_{11}]_t}$$

3. Second Order Rxn :

case I : only one reactant is present

$$nA \longrightarrow B$$

$t=0$ $a = [A]_0$ $0$

$t=t$ $a-x = [A]_t$ $\frac{x}{n} = [B]_t$

$$\text{Rate} = \frac{-1}{n}\frac{d[A]}{dt} = \frac{d[B]}{dt} = k_2[A]_t^2$$

$$\int_{[A]_0}^{[A]_t} \frac{-d[A]}{[A]^2} = k_A \int_0^t dt$$

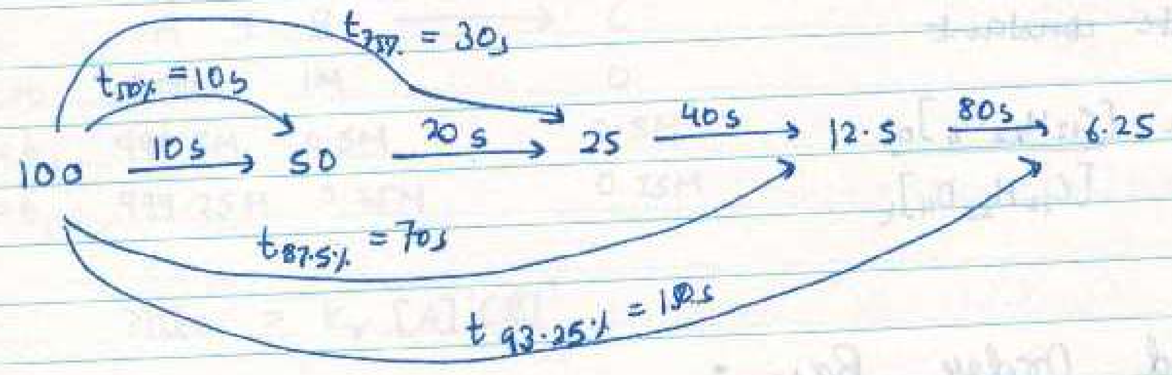
$$\Rightarrow \left[\frac{1}{[A]_t} - \frac{1}{[A]_0}\right] = k_A t$$

## Half life :

$$\frac{1}{[A]_0} - \frac{1}{[A]_0} = k_A t_{1/2}$$

$$\Rightarrow t_{1/2} = \frac{1}{k_A [A]_0}$$

$$\Rightarrow t_{1/2} \propto \frac{1}{[A]_0}$$



## Completion time :

$[A]_t = 0$

$t_{comp}$ = infinite

Case II : If more than one reactants are present

$$\begin{array}{llll} & A + & B \longrightarrow & C \\ t=0 & a=[A]_0 & b=[B]_0 & 0 \\ t=t & a-x=[A]_t & [B]_t & x \end{array}$$

$$\text{Rate} = \frac{-d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = K_r [A]_t^1 [B]_t^1$$

$$\frac{-d[A]}{dt} = K_r [A]_t [B]_t$$

$$\Rightarrow \frac{-d(a-x)}{dt} = K_r (a-x)(b-x)$$

$$\Rightarrow \int_0^x \frac{dx}{(a-x)(b-x)} = \int_0^t K_r dt$$

$$\Rightarrow \frac{1}{a-b} \int_0^x \frac{(a-x)-(b-x)}{(a-x)(b-x)} = \int_0^t K_r dt$$

$$\Rightarrow \frac{1}{a-b} \left\{ \int_0^x \frac{dx}{(b-x)} - \int_0^x \frac{dx}{(a-x)} \right\} = K_r t$$

$$\Rightarrow \frac{1}{a-b} \left\{ -\ln(b-x) + \ln(a-x) \right\}_0^x = K_r t$$

$$\Rightarrow \frac{1}{a-b} \left\{ \ln \frac{a-x}{b-x} - \ln \frac{a}{b} \right\} = K_r t$$

$$\Rightarrow \frac{1}{a-b} \left[ \ln \frac{(a-x)b}{(b-x)a} \right] = K_r t$$

i) if a >> b

$$k_r t = \frac{1}{a-\cancel{b}^{0}} \ln \frac{(a-\cancel{x}^{0})b}{(b-x)\,a}$$

$$\Rightarrow \quad a k_r t = \ln \frac{b}{b-x}$$

$$\Rightarrow \quad k' t = \ln \frac{[B]_0}{[B]_t} \quad \Rightarrow \boxed{t = \frac{1}{k'} \ln \frac{[B]_0}{[B]_t}}$$

ii) if a = b

$$k_r t = \frac{1}{a-b} \ln \frac{(a-x)b}{(b-x)\,a} \searrow \times$$

$$\Rightarrow \quad [A]_t = [B]_t$$

So,

$$k_r t = \frac{1}{[A]_t} - \frac{1}{[A]_0}.$$

<u>Ex:2</u>: 1-22 ; <u>Ex:1</u> : 73, 75, 76

<u>R.B</u> : 1

## * Characteristics of Second Order :

i] Units of K ⟶ $M^{-1}s^{-1}$

ii] Half life is inversely proportional to

$$t_{1/2} = \frac{1}{K_A[A]_0}$$

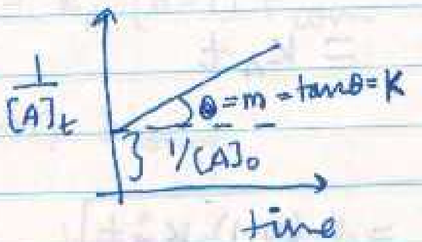
iii] $t_{comp.}$ = infinite

iv] Conc. of A after equal intervals of time constitute H.P.

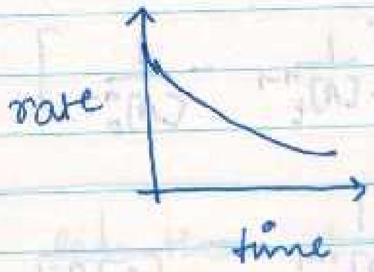
$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$$

$$[A]_t = \frac{1}{\frac{1}{[A]_0} + kt}$$

## * Graphical analysis :



y = mx+c



Examples :

a] Base catalysed hydrolysis of Ester

$CH_3COOC_2H_5 + \overset{H_2O}{\cancel{xxxx}} \xrightarrow{NaOH} CH_3COONa + C_2H_5OH$

$$\boxed{Rate = k[CH_3COOC_2H_5][NaOH]}$$

4. $n^{th}$ Order :
$(n \neq 1)$

$$aA \longrightarrow B$$

$t=0 \quad a = [A]_0 \qquad 0$

$t=t \quad [A]_t \qquad x/a$

$-2 \cdot \frac{1}{x^3}$

$\frac{1}{x^2} \qquad \frac{1}{x^2}$

$\frac{1}{x}$

$$Rate = -\frac{1}{a}\frac{d[A]}{dt} = \frac{d[B]}{dt} = k_r[A]_t^n$$

$$-\frac{d[A]}{dt} = k_A[A]_t^n$$

$$\Rightarrow -\int \frac{d[A]}{[A]_t^n} = \int k_A\, dt$$

$$\Rightarrow \frac{1}{n-1}\left[\frac{1}{[A]_t^{n-1}} - \frac{1}{[A]_0^{n-1}}\right] = k_A t$$

$$\Rightarrow \boxed{\frac{1}{[A]_t^{n-1}} - \frac{1}{[A]_0^{n-1}} = (n-1)k_A t}$$

## Half life ($t_{1/2}$) :

$$\frac{2^{n-1}}{[A]_0^{n-1}} - \frac{1}{[A]_0^{n-1}} = (n-1) K_A t_{1/2}$$

$$\Rightarrow t_{1/2} = \frac{2^{n-1}-1}{(n-1)K_A [A]_0^{n-1}}$$

*
$$\boxed{t_{1/2} \propto [A]_0^{1-n} \propto a^{1-n} \propto P_A^{1-n}}$$

## Completion time ($t_{comp.}$) :

Case I : for $n>1$

$$\frac{1}{\underset{\nwarrow 0}{[A]_t^{n-1}}} - \frac{1}{[A]_0^{n-1}} = K_A (n-1) t_{comp.}$$

$\therefore \infty.$

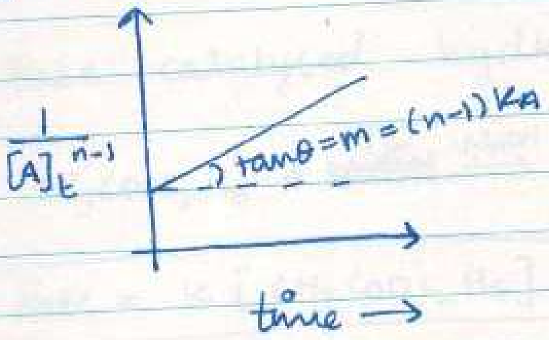
Case II : for $n<1$

$$[A]_t^{1-n} - [A]_0^{1-n} = K_A (n-1) t_{com.}$$

$$\Rightarrow [A]_0^{1-n} = K_A (1-n) t_{comp.}$$

- Conclusion : Rxns having order less than 1 get completed in finite time.
For Rxns having order 1 or >1, rxn will never get completed in finite time.

Graph :



### * Experimental determination of Order :

**1. Integrated rate law method or hit & trial method:**

In this method conc. of reactant is given at different instants of time and we assume that rxn to be of particular order and then determine rate constant for that order using integrated rate law eqn. If rate cons. comes out to be same then rxn is of same order as we have assumed otherwise we will check it for another other.

$$A \longrightarrow B$$

| eg | | | | |
|---|---|---|---|---|
| time (t) | 0 | $t_1$ | $t_2$ | $t_3$ |
| $[A]_t$ | $[A]_0$ | $[A]_{t_1}$ | $[A]_{t_2}$ | $[A]_{t_3}$ |

we assume order is zero

$$[A]_t = [A]_0 - K_A t$$

$$K_{A_1} = \frac{[A]_0 - [A]_{t_1}}{t_1}$$

$$K_{A_2} = [A]_0 - [A]_{t_2}$$

if $K_{A_1} \approx K_{A_2}$

⇒ Rxn is of zero order

if $K_{A_1} \neq K_{A_2}$

we assume order = 1

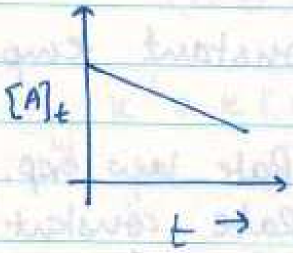
$$K_{A_1} t_1 = \ln \frac{[A]_0}{[A]_{t_1}}$$

$$K_{A_2} t_2 = \ln \frac{[A]_0}{[A]_{t_2}}$$

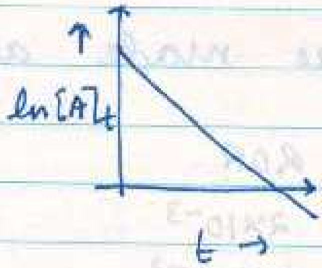
if $K_{A_1} \approx K_{A_2}$

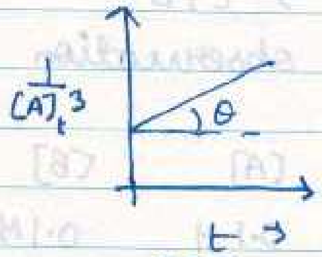
⇒ Rxn is of first order.

## 2. Graphical Method :



zero order





$\boxed{n=4}$

## 3. Half life Method :

$$t_{1/2} \propto a^{1-n} \propto p^{1-n}$$

$$\frac{(t_{1/2})_{I}}{(t_{1/2})_{II}} = \left(\frac{a_{I}}{a_{II}}\right)^{1-n} = \left(\frac{P_{A_{I}}}{P_{A_{II}}}\right)^{1-n}$$

Q. When HI is taken at a pressure of 1 atm, its half life is 135 min & when partial pressure of HI is 0.1 atm. The half life comes down to $1/10^{th}$ of initial value. Find order of Rxn.

$$\rightarrow \quad 10 = \left(\frac{1}{0.1}\right)^{1-n} \Rightarrow n = 0$$

## 4. Initial Rate Law method :

This method is used to determine order of Rxn where more than one reactants are present.

Q. For the Rxn

$$A + B \longrightarrow C + D$$

Following observation are made at constant temp.

| Exp. No. | [A] | [B] | ROR |
|---|---|---|---|
| 1 | 0.1 M | 0.1 M | $2\times10^{-3}$ |
| 2 | 0.2 M | 0.1 M | $4\times10^{-3}$ |
| 3 | 0.2 M | 0.2 M | $4\times10^{-3}$ |
| 4 | 0.3 M | 0.2 M | — |
| 5 | — | 0.3 M | $8\times10^{-3}$ |

a) Rate law exp.
b) Rate constant
c) Fill in blank

$$\rightarrow \quad 2\times10^{-3} = K \times [0.1]^a \; [0.1]^b$$

$$4\times10^{-3} = K \times [0.2]^a \; [0.1]^b$$

$$4\times10^{-3} = K \times [0.2]^a \; [0.2]^b$$

$a = 1$
$b = 0$
$K = 20\times10^{-3}$

## 5. Isolation Method :

In this method, when more than one reactants are present then one of the reactant is taken in large excess as a result its conc. remains almost constant during rxn & order of rxn w.r.t. other reactant is calculated.

$$A + B \longrightarrow C$$

$$\text{Rate} = k\,[A]^{\alpha}\,[B]^{\beta}$$

if $[A] \gg [B]$

$$\text{Rate} = k'\,[B]^{\beta}$$

$$\frac{r_1}{r_2} = \left(\frac{[B_1]}{[B_2]}\right)^{\beta}$$

$$k' = k\,[A]^{\alpha}$$

$||^{ly}$ for 'α'.

**H.W**

DPP # 9,10

Ex. 1 : 29-36

R.B. : 1, 2, 8, 13-15, 16, 20,

Ex. 2 : 48, 49, 52, 53

## * Determination of Rate constant (K) using different parameters :
(for I order)

$$A \longrightarrow B$$

$$K_A t = \ln \frac{[A]_0}{[A]_T} = \ln \frac{P_{A_0}}{P_{A_T}} = \ln \frac{n_{A_0}}{n_{A_t}}$$

### i] In terms of pressure :→

Q. find (K) for

$$A \xrightarrow{I\,o.} 2B$$

$P_0$

$P_0 - x$ $\quad$ $2x$

$P_0 + x = P_t \Rightarrow x = P_t - P_0$

| time (t) | 0 | t | ∞ |
|---|---|---|---|
| $P_{Total}$ | $P_0$ | $P_t$ | $P_\infty$ |

$$K_A t = \ln \frac{P_0}{2P_0 - P_t} \Rightarrow \boxed{K_A = \frac{1}{t}\left[\ln P_0 - \ln(2P_0 - P_t)\right]}$$

Q. for 1 order rxn

$A \longrightarrow B + 2C$ find K

| time (t) | t | ∞ |
|---|---|---|
| $P_B + P_{\cancel{B}C}$ | $P_t$ | $P_\infty$ |

$P_A + P_B = P_t$

$0 + P_B = P_\infty$

$3x = P_t$

$P_0 + 2P_0 = P_\infty$

$P_0 = P_\infty/3$

→ ~~$K_A t = \ln \frac{a}{a-x}$~~ ~~$= \frac{1}{t} \ln P_t - P_\infty$~~

$$K = \frac{1}{t} \ln \frac{P_\infty/3}{P_\infty - P_t} = \frac{1}{t}\left(\ln P_\infty - \ln(P_\infty - P_t)\right)$$

Q. find k for,

| $(t)$ | $0$ | $t$ | $\infty$ |
|---|---|---|---|
| $(P_T)$ | $P_0$ | $P_t$ | $P_\infty$ |

$A \longrightarrow nB$

$P_0 + (n-1)x = P_t$ $\quad \frac{P_t - P_0}{(n-1)}$

→ $k_A t = \ln \frac{P_0}{P_0 - \left[\frac{P_t - P_0}{(n-1)}\right]}$

$= \ln \frac{P_\infty - P_0}{P_\infty - P_t}$

Q. Progress of decomposition of $NH_4NO_2$ (aq) is obs. by total pressure

$NH_4NO_2\,(aq) \xrightarrow{I.O.} N_2\,(g) + 2H_2O\,(l)$

| time (s) | 0 | 20 | ∞ |
|---|---|---|---|
| $P_{total}$ | 50 | 80 | 90 |

find $\boxed{t_{1/2}}$

→ $k_A = \frac{1}{20} \times \ln \frac{80}{50} \quad 4$

M-I

$= \frac{\ln 2}{10}$

$t_{1/2} = 10\ s$

M-II

$x \propto 30$

$a \propto 40$

$k_A t = \ln \frac{a}{a-x} = \ln \frac{40}{10}$

. For I.0 rxn decomposition

$$\underset{N_2O_5\,(g)}{\overset{\overset{450}{a-x}}{}} \longrightarrow \underset{\frac{1}{2}O_2\,(g)}{\overset{x/2}{}} + \underset{2NO_2\,(g)}{\overset{\overset{400}{2x}}{}}$$

Initially the total pressure is found to be 650 torr & after a very long time total pressure is found to be 1550 torr. If after 4 min from start of Rxn $P_{O_2} = 100$ torr calculate $t_{1/2}$ [ $\ln 3 = 1{\cdot}1$, $\ln 2 = 0{\cdot}7$ ]

$\longrightarrow$ $K_A \cancel{t} = \ln \frac{9\cancel{00}}{2\cancel{00}} = 2\ln 3 - \ln 2$ $\quad k = \frac{1}{4} \times \ln \frac{\overset{13}{\cancel{650}}}{\underset{9}{\cancel{400}}}$

$= 2{\cdot}2 - 0{\cdot}7 = \frac{1{\cdot}5}{4}$

$t_{1/2} = \frac{0{\cdot}7 \times 4}{1{\cdot}5} \quad \frac{28}{15} = \boxed{7}$

$\boxed{7}$

— x —

- If $P_t$ is given at initial ~~at~~ and after long time then we can check it for presence of inert gas.

Q. For a Rxn $\underset{A(g)}{\overset{1-x}{}} \longrightarrow \underset{nB(g)}{\overset{nx}{}}$ the rate constant is $6{\cdot}93 \times 10^{-4}\ s^{-1}$. The rxn is performed at constant pressure & temp. of 24.63 & 300 K. Starting with 1 mol of pure A. If conc. of B after 2000 sec is $\frac{3}{3{\cdot}25}$ M. then calculate 'n'.

$3n/4$

$24{\cdot}63 \times V = k \times 24{\cdot}63$

$\longrightarrow$ $\frac{nx}{V'} = \frac{3}{3{\cdot}25}$

$4 = \frac{a}{a-x}$

$6{\cdot}93 \times 10^{-4} \times 2 \times 10^{3} = \ln$

$1{\cdot}386 = \ln 4$

$4 - 4x = 1$

$x = 3/4$

$\boxed{4}$

Q The rxn

$2A + B \longrightarrow C + D$ follows $-\frac{d[B]}{dt} = k[A][B]^2$

Find $(x+y)$

$\underline{\underline{7}}$

| S. No. | $[A]_0 \times 10^{-4}$ M | $[B]_0 \times 10^{-4}$ M | $t_{1/2}$ (sec) |
|---|---|---|---|
| 1 | 500 | 2 | 10 |
| 2 | 500 | 4 | $x$ |
| 3 | 2 | 250 | 8 |
| 4 | 4 | 500 | $y$ |

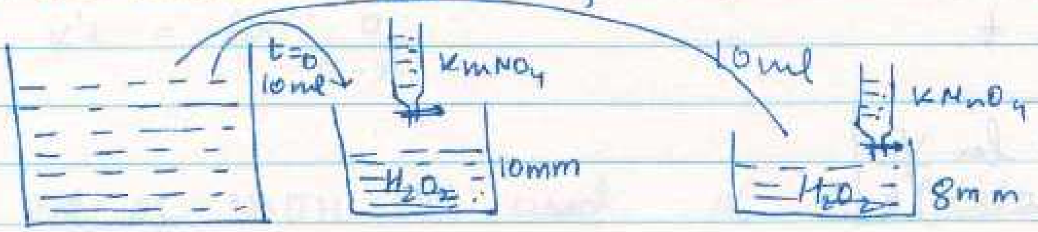
$t_{1/2} \propto \frac{1}{[B]_0}$

$x = \boxed{5}$

$y = \boxed{2}$

## ii] In terms of decomposition of $H_2O_2$ (aq.) :

In this method a sol$^n$ of $H_2O_2$ is prepared and equal amount of sample or aliquot is taken from $H_2O_2$ sol$^n$ & after certain interval of time, it is titrated against standard sol$^n$ of KMnO to determine value of 'k'.



$KMnO_4 + H_2O_2 \rightarrow O_2$

$5 \times M_1V_1 = 2 \times M_2V_2$

Q. For decomposition of $H_2O_2$

| time (t) | 0 | t | ∞ |
|---|---|---|---|
| Vol. of $KMnO_4$ used (in ml) | $V_0$ | $V_t$ | $V_\infty$ |

Find $t_{1/2}$.

→ $H_2O_2 \xrightarrow{I.O.} H_2O + \frac{1}{2}O_2$

| | | | |
|---|---|---|---|
| $t=0$ | $a=1$ | 0 | 0 |
| $t=t$ | $a-x$ | $x$ | $x/2$ |

$$k_A t = \ln \frac{a}{a-x}$$

- Vol of $KMnO_4$ ($V_0$) used initially $\propto a$

- Vol. of $KMnO_4$ ($V_t$) used after time t $\propto a-x$

$$\therefore \boxed{k_A t = \ln \frac{V_0}{V_t}}$$

## iii] Acid catalysed hydrolysis of Ester :→

$$CH_3COOC_2H_5\,(aq.) + H_2O\,(l) \xrightarrow{H^+} \overset{\overset{CH_3COO^- + H^+}{\Updownarrow}}{CH_3COOH} + C_2H_5OH$$

| | $CH_3COOC_2H_5$ | $CH_3COOH$ | $C_2H_5OH$ |
|---|---|---|---|
| $t=0$ | $a$ | $0$ | $0$ |
| $t=t$ | $a-x$ | $x$ | $x$ |
| $t=\infty$ | $0$ | $a$ | $a$ |

Q. For hydrolysis of ester

| time (t) | 0 | t | ∞ |
|---|---|---|---|
| Vol. of NaOH used (in ml) | $V_0$ | $V_t$ | $V_\infty$ |

$\rightarrow$ Rate $= k\,[H^+][H_2O][CH_3COOC_2H_5]$

$\Rightarrow$ Rate $= k'\,[CH_3COOC_2H_5]$

$$k't = \ln \frac{a}{a-x}$$

Vol. of NaOH ($V_0$) used initially $\propto c$ (catalyst)

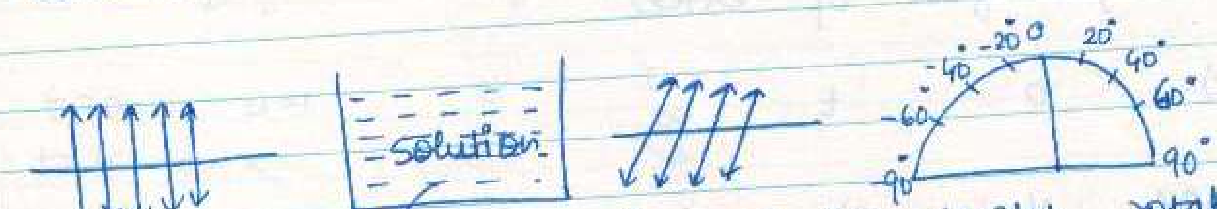
Vol. of NaOH ($V_t$) used after time t $\propto c + x$

Vol. of NaOH ($V_\infty$) used after long time $\propto c + a$

$$\Rightarrow \boxed{k't = \ln\frac{V_\infty - V_0}{V_\infty - V_t}}$$ — Auto catalysis.

## iv] Inversion of cane sugar :→

- Specific Rotation : angle of rotation per unit concentration.



1M = 10° → Specific / Molar rotation.
2M = 20°
4M = 40°

$$\underset{\text{cane sugar}}{\overset{'d'}{C_{12}H_{22}O_{11}}} + H_2O \longrightarrow \underset{\text{glucose}}{\overset{'d'}{C_6H_{12}O_6}} + \underset{\text{Fructose}}{\overset{'l'}{C_6H_{12}O_6}}$$

|  | cane sugar | glucose | Fructose |
|---|---|---|---|
| t=0 | aM | 0 | 0 |
| t=t | a−x | x | x |
| t=∞ | 0 | a | a |

- $r_s, r_g, r_f$ → specific rotation of cane sugar, glucose & fructos.

| time (t) | 0 | t | ∞ |
|---|---|---|---|
| angle of rot. | $\theta_0$ | $\theta_t$ | $\theta_\infty$ |

$\theta_0 \propto a \times r_s$

$\theta_t \propto (a-x) r_s + x r_g \mp x r_f$

$\theta_\infty \propto a r_g \mp a r_f$

$a = \dfrac{\theta_\infty - \theta_0}{r_g - r_f - r_s}$

$k_A t = \ln \dfrac{a}{a-x}$

$x = \dfrac{\theta_t - \theta_0}{r_g - r_f - r_s}$

$$= \boxed{\ln \dfrac{\theta_\infty - \theta_0}{\theta_\infty - \theta_t}}$$

**Note :**

- Resemic mixture is optically inactive, it means angle of rotation will be zero.

Q. For a rxn

$A_{(aq)} \longrightarrow B_{(aq.)} + C_{(aq.)}$

Starting with only $A_{(aq)}$, optical rotation after 10 min & 20 min is obs. to be 33° & 18° when initial optical rotation was 48°. If specific optical rotation for A, B & C are 20°, 30° & −40°. Calculate the time (in min) when a recemic mixture will be formed.

$\boxed{32\ \text{mi}}$

$\rightarrow$

| $A$ | $\longrightarrow$ | $B$ | $+$ | $C$ |
|---|---|---|---|---|
| $a$ | | $0$ | | $0$ |
| $a-x$ | | $x$ | | $x$ |

$K_A\, 10 = \ln a/_{a-x}$

$K_A\, 20 = \ln a/_{a-x-y}$

$(a-x)\times 20^\circ + \overset{x\times 10^\circ}{\cancel{0}}\ \cancel{x\times 30^\circ - x\times 40^\circ} = 33^\circ$

$(a-x-y)\times 20^\circ + y\times 30^\circ + x\times 30^\circ - (x+y)\times 40^\circ = 18^\circ$

$-(x+y)\times 10^\circ$

$\dfrac{1}{2} = \dfrac{\ln (a-(x+}{\ln (a-x)}$

$Fe + H_2O + air \rightarrow Fel$

$x_A t = \ln \frac{a}{a-x}$

$\underline{Z_\infty}$

## v] Thickness of Oxide layer formation :

If oxide formation follows $1^{st}$ order kinetics

| | | |
|---|---|---|
| time | $t$ | $\infty$ |
| Thickness of layer | $Z_t$ | $Z_\infty$ |

Find k.

$$kt = \ln \frac{Z_\infty}{Z_\infty - Z_t}$$

## vi] Bacteria growth :

If bacteria growth follows $1^{st}$ order kinetics

$$B \longrightarrow B$$

$t=0$ $\quad b$

$t=t$ $\quad\quad b+x$

$$\frac{dB}{dt} = kB \Rightarrow \int_b^{b+x} \frac{dB}{B} = \int_0^t k\,dt$$

$$= \ln B\Big|_b^{b+x} = kt$$

$$= \ln \frac{b+x}{b} = kt$$

Q. After how much time no. of bacteria will become double of its initial value.

$\rightarrow \quad kt = \ln 2$

$\Rightarrow t = \frac{\ln 2}{k}$

Q. For a Rxn
$$A + B \longrightarrow C + \frac{1}{5} D$$
kinetics is determined by analysis of partial pressure of gases at different instants. Calculate a+b+c.

| P (mm of Hg) | t = 0 | t = 30 min | t = 60 min |
|---|---|---|---|
| $P_A$ | 20 | 10 | a = 5 |
| $P_B$ | 10000 | NA | NA |
| $P_C$ | 0 | NA | 15 |
| $P_D$ | 0 | b | NA |

Order of Rxn with respect to A = C = 1, a = 5, b = 2

$\longrightarrow$ $K_r = K' P_A$ ⑧ $K \times t = \ln \frac{20}{10}$ $\Rightarrow K = \frac{\ln 2}{30}$

$$\frac{\ln 2}{\cancel{30}} \times \overset{2}{\cancel{60}} = \ln \frac{20}{a}$$

Q. Consider the following Rxn occuring at constant volume
$$A_{(g)} + 2B_{(g)} \longrightarrow C_{(g)} + D_{(g)}$$
t=0 a b

Rate = K[B]

a) conc. of 'A' at time t is given as

A. $ae^{-kt}$ <u>B.</u> $a - \frac{b}{2}(1-e^{-2kt})$ C. $a - kt$ D. $a-b(1-e^{-1}$

b) time at which conc. of A reduces to half

A. $\frac{a}{2K}$ B. $\frac{a}{K}$ <u>C.</u> $\frac{1}{2K} \ln \frac{b}{b-a}$ D. $\frac{\ln 2}{K}$

c) For what cond. $(t_{1/2})_A = (t_{1/2})_B$

A. $\frac{a}{b} = \frac{1}{2}$  B. $\frac{a}{b} = 1$  C. None

**Note** : If more than one reactants are present then half life of l.r. will be half life of rxn.

* Reversible Elementary Rxn :

i] First order opposed by first order :

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

$$K_{eq} = \frac{k_f}{k_b} = \frac{[B]_{eq}}{[A]_{eq}} = \frac{x_e}{a - x_e}$$

| | A | B |
|---|---|---|
| $t = 0$ | $a$ | $0$ |
| $t = t$ | $a - x$ | $x$ |
| $t = t_{eq}$ | $a - x_e$ | $x_e$ |

$$-\frac{d[A]}{dt} = k_f [A]^1 - k_b [B]^1$$

$$\Rightarrow -\frac{d(a-x)}{dt} = k_f (a-x) - k_b x$$

$$\boxed{\frac{dx}{dt} = a k_f - x(k_f + k_b)}$$

At equilibrium,

$$-\frac{d[A]}{dt} = 0 = k_f (a - x_e) - k_b x_e$$

$$a k_f = x_e (k_f + k_b)$$

$$\Rightarrow \frac{dx}{dt} = (K_f + K_b)(x_e - x)$$

$$\Rightarrow \int_0^x \frac{dx}{x_e - x} = \int_0^t (K_f + K_b)\,dt$$

$$\Rightarrow -\left[\ln(x_e - x)\right]_0^x = (K_f + K_b)t$$

$$\Rightarrow \boxed{(K_f + K_b)t = \ln \frac{x_e}{x_e - x}}$$

where,

$x_e \rightarrow$ conc. of B at eq.

Q. Calculate time at which conc. of B becomes half of its value at equilibrium.

$\rightarrow \quad (K_f + K_b)\,t = \ln 2$

$$\Rightarrow t = \frac{\ln 2}{(K_f + K_b)}$$

Q. For a reversible first order Rxn

$$\underset{a-x_e}{A} \underset{K_2}{\overset{K_1}{\rightleftharpoons}} \underset{x_e}{B} \qquad K_1 = 10^{-2}\,s^{-1} \quad \& \quad \frac{[B]_{eq}}{[A]_{eq}} = 4$$

$1/4 \quad 3/4$

If $[A]_0 = 0.01\ M\,L^{-1}$ & $[B]_0 = 0$

what will be the conc. of B after 30 sec.

$\frac{x_e}{a - x_e} = 4$

$5x_e = 0.04 \times$

$x_e = \frac{0.04}{5}$

$4/500$

$\rightarrow \quad 0.01 \times 10^{-2} = [B]_{eq}(K_f + K_b) \;\Big|\; \frac{10^{-4}}{[B]_{eq}} \times 30 = \ln \frac{[B]_{eq}}{[B]_{eq} - x}$

$\frac{1500 \times 10^{-4}}{4} =$

$\frac{0.15}{4}$

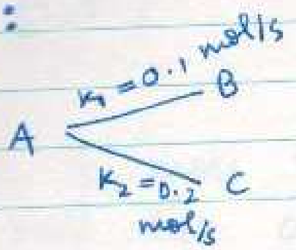
$4/500$

$\frac{4}{4 - 500x}$

Sheet
DPP #11
Redox.

## irst order parallel or side rxn :

I :



$A \xrightarrow{K_1} B$

$A \xrightarrow{K_2} C$

hyp.

$$-\frac{d[A]}{dt}_{\text{rxn I}} = \frac{d[B]}{dt} = K_1[A]$$

$$-\frac{d[A]}{dt}_{\text{rxn II}} = \frac{d[C]}{dt} = K_2[A]$$

$$-\frac{d[A]}{dt} = \left(\frac{-d[A]}{dt}\right)_{I} + \left(\frac{-d[A]}{dt}\right)_{II}$$

$$-\frac{d[A]}{dt} = (K_1 + K_2)[A]$$

$$\Rightarrow \quad -\int \frac{d[A]}{[A]} = \int (K_1 + K_2)\,dt$$

$$\Rightarrow \quad [A]_t = [A]_0\, e^{-(K_1+K_2)t}$$

For $[B]_t$ ,

$$\frac{d[B]}{dt} = K_1 [A]_0\, e^{-(K_1+K_2 t)}$$

$$\Rightarrow \quad [B]_t = -\frac{K_1[A]_0}{K_1+K_2}\left[e^{-(K_1+K_2)t} - 1\right]$$

Similarly

$$[C]_t = \frac{K_2[A]_0}{K_1+K_2}\left(1 - e^{-(K_1+K_2)t}\right)$$

$$\frac{[B]_t}{[C]_t} = \frac{K_1}{K_2}$$

$$\% \text{ B in product} = \frac{K_1}{K_1+K_2} \times 100$$

$$\% \text{ C in product} = \frac{K_2}{K_1+K_2} \times 100$$

- Case II :

$$-\frac{d[A]}{dt} = (K_1+K_2+K_3)[A]$$

$$\Rightarrow \quad [A]_t = [A]_0\, e^{-(K_1+K_2+K_3)t}$$

also,

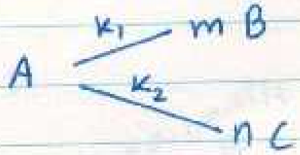
$$[B]_t = \frac{-K_1[A]_0}{K_1+K_2+K_3}\left(e^{-(K_1+K_2+K_3)t} - 1\right)$$

$$[C]_t = \frac{-K_2[A]_0}{K_1+K_2+K_3}\left(e^{-(K_1+K_2+K_3)t} - 1\right)$$

$$[D]_t = \frac{-K_3[A]_0}{K_1+K_2+K_3}\left(e^{-(K_1+K_2+K_3)t} - 1\right)$$

$$\therefore [B]_t : [C]_t : [D]_t = K_1 : K_2 : K_3$$

- Case III :



$$A \xrightarrow{k_1} mB$$
$$A \xrightarrow{k_2} nC$$

$$-\frac{d[A]}{dt}_{\textcircled{\scriptsize I}} = \frac{1}{m}\frac{d[B]}{dt} = k_1[A]$$

$$-\frac{d[A]}{dt}_{\textcircled{\scriptsize II}} = \frac{1}{n}\frac{d[C]}{dt} = k_2[A]$$

$$\Rightarrow -\frac{d[A]}{dt} = (k_1+k_2)[A]$$

$$\Rightarrow [A]_t = [A]_0\, e^{-(k_1+k_2)t}$$

For $[B]_t$,

$$\frac{1}{m}\frac{d[B]}{dt} = k_1[A]_0\, e^{-(k_1+k_2)t}$$

$$\Rightarrow [B]_t = \frac{m k_1 [A]_0}{(k_1+k_2)}\left(1 - e^{-(k_1+k_2)t}\right)$$

$||^{ly}$,

$$[C]_t = \frac{n k_2 [A]_0}{(k_1+k_2)}\left(1 - e^{-(k_1+k_2)t}\right)$$

$$\frac{[B]_t}{[C]_t} = \frac{m k_1}{n k_2}$$

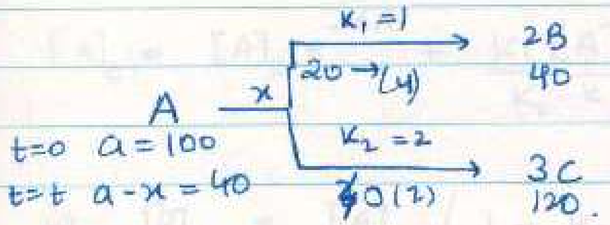
- Case IV :

$$\nu_1 A \xrightarrow{K_1} mB$$

$$\nu_2 A \xrightarrow{K_2} nC$$

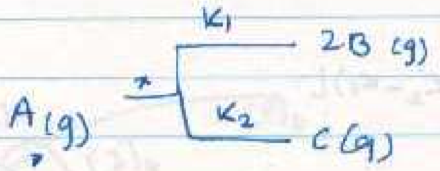
$$\frac{-d[A]}{dt} = (\nu_1 K_1 + \nu_2 K_2)[A]$$

For numerical Purpose,



$$\frac{y}{2} = \frac{K_1}{K_2}$$

Q. For following I order gaseous rxn.



$$\frac{K_1}{K_2} = \frac{y}{(x-y)}$$

$$K_1 x = (K_1 + K_2) y$$

The initial pressure in a container of cap. VL 1 atm. Pressure at t = 10s is 1.4 atm & after infinite time it becomes 1.5 atm. Find $K_1$ & $K_2$

$$\frac{3x}{2} - x$$

$$\rightarrow \quad 1 - x + \frac{2K_1 x}{K_1 + K_2} + \frac{K_2 x}{K_1 + K_2} = 1.4$$

$$0 + \frac{2K_1}{K_1 + K_2} + \frac{K_2}{K_1 + K_2} = 1.5$$

$$\frac{K_1}{K_1 + K_2} = 0.5$$

## * Consecutive or sequential Rxn :

$$A \longrightarrow P$$

Step I $\quad A \xrightarrow{k_1} I$

Step II $\quad I \xrightarrow{k_2} P$

$$A_1 \xrightarrow{k_1} I \xrightarrow{k_2} P$$

|  | $A_1$ | $I$ | $P$ |
|---|---|---|---|
| $t=0$ | $a$ | $0$ | $0$ |
| $t=t$ | $a-x$ | $x-y$ | $y$ |

- $[A]_t = [A]_0 \, e^{-k_1 t}$

- $\frac{d[I]}{dt} = k_1[A]_t - k_2[I]_t$

$$e^{k_2 t}\frac{d[I]}{dt} + e^{k_2 t} k_2 [I]_t = k_1 [A]_0 \, e^{(k_2-k_1)t}$$

$$\Rightarrow \quad \frac{d}{dt}\left([I]_t \, e^{k_2 t}\right) = k_1 [A]_0 \, e^{(k_2-k_1)t}$$

$$\int d\left([I]_t \, e^{k_2 t}\right) = k_1 [A]_0 \int e^{(k_2-k_1)} dt$$

$$\Rightarrow \quad [I]_t \, e^{k_2 t} = \frac{k_1[A]_0}{(k_2-k_1)} \, e^{(k_2-k_1)t} + c$$

At $t=0 \quad [I]_t = 0$

$$0 = \left(\frac{k_1[A]_0}{k_2-k_1}\right) + c$$

$$\Rightarrow \quad [I]_t e^{k_2 t} = \frac{k_1[A]_0}{k_2-k_1}\left(e^{(k_2-k_1)t}-1\right)$$

$$[I]_t = \frac{k_1[A]_0}{k_2-k_1}\left(e^{-k_1 t}-e^{-k_2 t}\right)$$

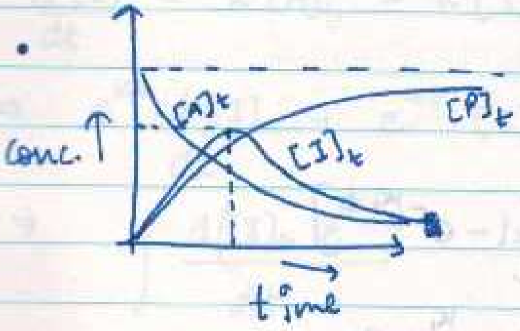
For $[P]_t$;

$$a = (a-x)+(x-y)+y$$

$$[A]_0 = [A]_t + [I]_t + [P]_t$$

$$[A]_0 = [A]_0 e^{-k_1 t} + \frac{k_1[A]_0}{k_2-k_1}\left(e^{-k_1 t}-e^{-k_2 t}\right) + [P]_t$$

$$\Rightarrow \quad [P]_t = [A]_0\left(1 - \frac{k_2}{k_2-k_1}e^{-k_1 t} + \frac{k_1}{k_2-k}e^{-k_2 t}\right)$$



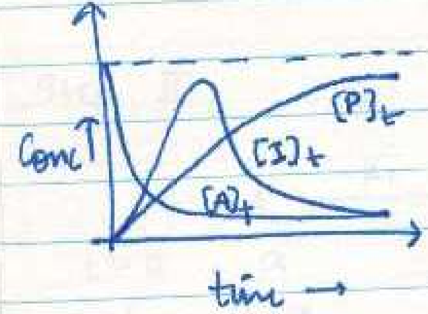
q. Calculate the time at which [I] is max.

$$\rightarrow \quad \frac{d[I]_t}{dt} = \frac{k_1[A]_0}{k_2-k_1}\left(-k_1 e^{-k_1 t} + k_2 e^{-k_2 t}\right).$$

$$\Rightarrow t = \frac{\ln\frac{k_2}{k_1}}{(k_2-k_1)}$$

Case I : if $K_1 >> K_2$

$$A \xrightarrow[fast]{K_1} I \xrightarrow[slow]{K_2} P$$



$$[P]_t = [A]_0 \left[ 1 - \frac{K_2}{K_2 - K_1} e^{-K_1 t} + \frac{K_1}{K_2 - K_1} e^{-K_2 t} \right]$$

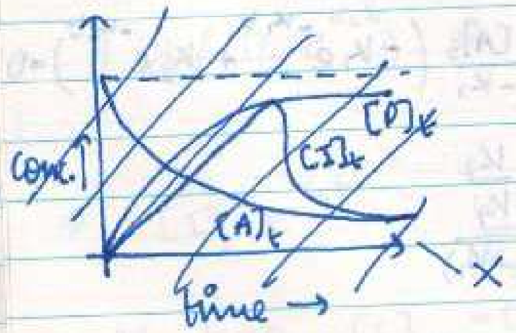
$$[P]_t = [A]_0 \left[ 1 - e^{-K_2 t} \right]$$

Imp $\Rightarrow A \xrightarrow{K_2} P$

• Conc. of product will depend on slowest step of rxn. From here comes the concept of Rate determining step (RDS). So slowest step will be R.D.S.

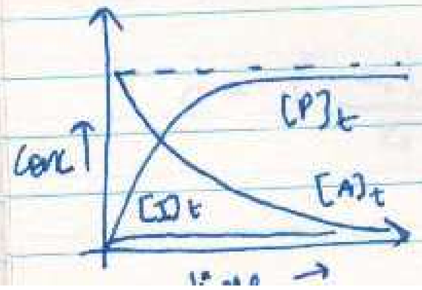
Case II : if $K_2 >> K_1$

$$A \xrightarrow[slow]{K_1} I \xrightarrow[fast]{K_2} P$$



$$[P]_t = [A]_0 \left[ 1 - e^{-K_1 t} \right]$$

Imp $\Rightarrow A \xrightarrow{K_1} P$



Steady state : It is the state at which rate of formation of intermediate becomes equal to rate of disappearance of intermediate or conc. of I becomes very very small.

For steady state ; $K_2 >> K_1$ :

$$\frac{d[I]}{dt} = 0 = K_1[A]_t - K_2[I]_t$$

$$\Rightarrow [I]_t = \frac{K_1}{K_2}[A]_t$$

$\downarrow$

at steady state.

Case III : if $K_1 = K_2 = K$

$$A \xrightarrow{K_1 = K} I \xrightarrow{K_2 = K} P$$

|  | A | I | P |
|---|---|---|---|
| $t=0$ | $a$ | $0$ | $0$ |
| $t=t$ | $a-x$ | $x-y$ | $y$ |

$$[A]_t = [A]_0 (e^{-Kt})$$

$$\frac{d[I]}{dt} = K[A]_t - K[I]_t = K\{[A]_t - [I]_t\}$$

$$\Rightarrow e^{Kt}\frac{d[I]}{dt} + e^{Kt}[I]_t K = K[A]_0$$

$$\Rightarrow \int \frac{d([I]_t e^{Kt})}{dt} = \int K[A]_0 \, dt$$

$$\Rightarrow K[A]_0 t = [I]_t e^{Kt} + C$$

At $t=0$, $[I]_t = 0$

$0 = 0 + C$

$$[I]_t = K[A]_0 t . e^{-Kt}$$

## * Arrhenius Equation :→

It is quantitative relationship proposed by Arrhenius b/w rate constant and temperature.

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

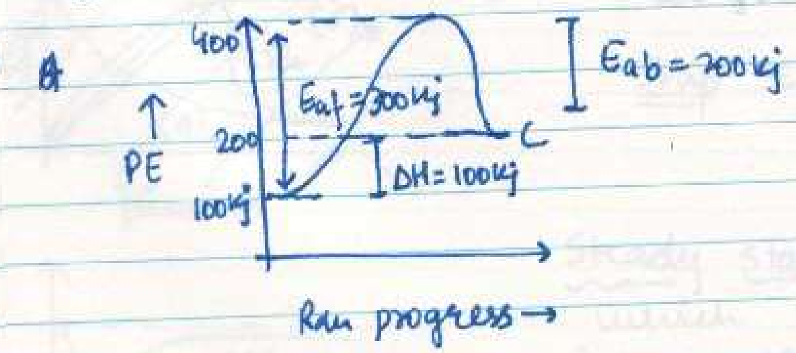
where,

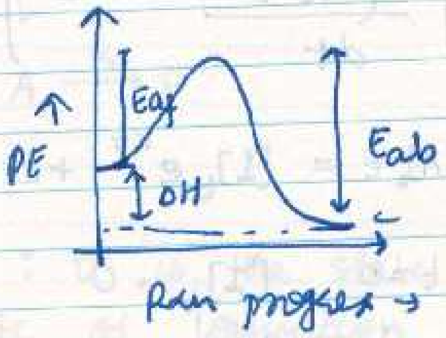
$K$ → Rate constant / Specific Rxn Rate / velocity constant
$R$ → gas constant
$T$ → Temperature (in kelvin)
$E_a$ → Activation Energy (in KJ/mol)
$A$ → Arrhenius constant / Pre-exponential factor / frequency factor.

{ A & $E_a$ are considered as temperature independent.

[Although A & $E_a$ ~~are considered~~ as depends on temp. but on change in temp. their values change negligibly.]

Cas





Cor

$$A + B \longrightarrow C$$

$\Delta H = Ea_f - Ea_b = E_P - E_R$

if $\Delta H < 0 \Rightarrow$ Rxn is exothermic
$\Delta H > 0 \Rightarrow$ Rxn is endothermic

- <u>Activation Energy</u> : Minimum K.E. possessed by reactant molecules in order to get converted into product.

- <u>Threshold Energy</u> : It is min. P.E. possessed by activated complex in order to get converted to product.

* <u>Variation of K</u> :

- For complete elementary rxn (not elementary step) $E_A > 0$, but in case of complex rxn $E_A$ can be -ve or zero.

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

$\Rightarrow$ if $T \uparrow \Rightarrow K \uparrow \Rightarrow$ ROR will increase (in general)

$\Rightarrow$ if $E_a \uparrow \Rightarrow K \downarrow \Rightarrow$ ROR will decrease

$\Rightarrow$ At $T = 0K \Rightarrow K = 0$

$\Rightarrow$ At $T = \infty \Rightarrow K = A$

Q. On ↑ temp. rate of rxn will always change.

→ false. If $E_A = 0$, then $K = A$ & A is independent of temp.

* Variation of K with temperature:

$$K = Ae^{-E_a/RT}$$

Considering A & Ea to be temp. independent

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

At temp. $T_1$,

$$\ln K_{T_1} = \ln A - \frac{E_a}{RT_1} \quad — ①$$

At temp. $T_2$,

$$\ln K_{T_2} = \ln A - \frac{E_a}{RT_2} \quad — ②$$

② − ①

$$\ln \frac{K_{T_2}}{K_{T_1}} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Or

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

- if $E_a > 0$ ⇒ on ↑ temp., K will ↑

if $E_a < 0$ ⇒ on ↑ temp. K will ↓

**Case I :**

$A \xrightarrow{E_a=40} B$ $\qquad\qquad$ $A \xrightarrow{E_a=40} B$

$$\frac{K_{410K}}{K_{400K}} < \frac{K_{310K}}{K_{300K}}$$

From this data, it can be concluded that % change in value of 'K' will be more at low temp. as compared to at high temp. for same temp. rise

OR

Rate of rxn is more sensitive to temp. at low temperature.

**Case II :**

$A \xrightarrow{E_a=80} B$ $\qquad\qquad$ $A \xrightarrow{E_a=40} B$

$$\frac{K_{310K}}{K_{300K}} > \frac{K'_{310K}}{K'_{300K}}$$

% change will be more where ↑ activation energy is high.

* Temperature Coefficient ($\mu$) :

It is ratio of rate constant or rate of rxn at 2 temperatures differing by 10K.

$$\boxed{\mu = \frac{K_{(T+10)K}}{K_{TK}} = 2-3}$$

If temp. is not mentioned then it is taken as 298 K.

Case I : If temp. coeff. is independent of temp.

$$\underset{r}{200K} \longrightarrow \underset{2r}{210K} \longrightarrow \underset{2.2r}{220K}$$

(actually slightly less than 4r)

Q. For rxn A → B temp. coeff is 3 at 25°c. How many times ROR will increase if temp. is ↑ from 25°c to 75°c

→ $3^5 r$

## Case II :

If temp. coeff. depends on temp.

Q. The temp. coeff. ($\mu$) of rxn at 300K is "e". Assuming temp. coeff. to be dependent on temp. what would be the value of

$$\ln\frac{K_{620K}}{K_{300K}} = ?$$

$$\rightarrow \ln\frac{K_{310K}}{K_{300K}} = \frac{E_a}{R}\left(\frac{10}{310\cdot300}\right) = 1$$

$$\ln\frac{K_{620K}}{K_{300K}} = \frac{\cancel{310}\cdot\cancel{300}}{\cancel{10}} \times \frac{\overset{32}{\cancel{320}}}{\underset{2}{\cancel{620}}\cdot\cancel{300}} = \boxed{16}$$

Q. For 2 Parallel Rxn

$$A \xrightarrow{K_1 E_1} B$$

$$A \xrightarrow{K_2 E_2} C$$

Show that for disappearance of A net activation energy $(E_3) = \frac{K_1E_1 + K_2E_2}{K_1 + K_2}$

$$\rightarrow \quad K_1 = A_1 e^{-E_1/RT} \quad \& \quad K_2 = A_2 e^{-E_2/RT}$$

$$K_3 = K_1 + K_2 \Rightarrow A_3 e^{-E_3/RT} = A_1 e^{-E_1/RT} + A_2 e^{-E_2/RT}$$

$\frac{d}{dt}$ w.r.t. T

$$A_3 e^{-E_3/RT}\left(\frac{E_3}{\cancel{RT^2}}\right) = A_1 e^{-E_1/RT}\left(\frac{E_1}{RT^2}\right) + A_2 e^{-E_2/RT}\left(\frac{E_2}{\cancel{RT^2}}\right)$$

$$\boxed{K_3E_3 = K_1E_1 + K_2E_2}$$

Q. The desorption of gas molecules from the adsorbent obeys arrhenius eq. The average time upto which a $N_2$ molecule may remain adsorbed at Pt surface at 400 K is

Given $A = 1.25 \times 10^8\ s^{-1}$

$E_a = 16$ Kcal/mol

$e^{20} = 5 \times 10^8$.

$\rightarrow$ $T_{avg.} = \frac{1}{K_A}$.

$$K = 1.25\times10^8\ e^{-16\times10^3\times4.2/400\times8.21}$$

$$= 1.25\times10^8\ e^{-20} = \frac{1}{4} = \boxed{4s} = T_{avg}.$$

Ex 1: 50-53 ; 56-63, 64, 65-67

* Differential form of Arrhenius Equation:

$$\frac{d(\ln k)}{dT} = \frac{E_a}{RT^2}$$

Case I : if $E_a$ is independent of temp.

$$\int_{\ln K_1}^{\ln K_2} d(\ln k) = \frac{E_a}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

$$\Rightarrow \ln \frac{K_{T_2}}{K_{T_1}} = \frac{E_a}{R} \times \frac{(T_2 - T_1)}{T_1 T_2}$$

$$\int d(\ln k) = \frac{E_a}{R} \int \frac{dT}{T^2}$$

$$\Rightarrow \ln k = -\frac{E_a}{R} \times \frac{1}{T} + c$$

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

<u>Case</u> II : if $E_a = f(T)$

$E_a = aT^3$

$$\int_{\ln k_{T_1}}^{\ln k_{T_2}} d(\ln k) = \int_{T_1}^{T_2} \frac{E_a}{RT^2}\, dT$$

$$\Rightarrow \ln \frac{K_{T_2}}{K_{T_1}} = \frac{a}{2R}(T_2^2 - T_1^2).$$

Q. Find $E_a$ at 300 K if expression of rate constant as f:n of temp is given by

$$K = 30\, e^{-\frac{40}{T}} \cdot e^{\frac{300}{T^2}}$$

40×3

12000

1170

300

$$\rightarrow K = 30\, e^{\frac{300 - 40T}{T^2}}$$

$$-\frac{E_a}{RT} = \frac{--}{T^2}$$

$$E_a = -\frac{(300 - 40T)RT}{T} = \underline{\underline{38R}}$$

$$\ln k = \ln 30 - \frac{40}{T} + \frac{300}{T^2}$$

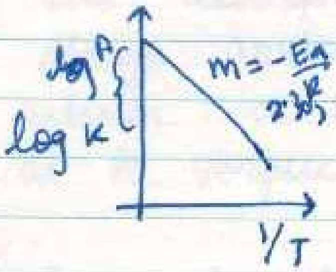
$$\Rightarrow \frac{d(\ln k)}{dT} = 0 + \frac{40}{T^2} - \frac{600}{T^3}$$

$$\Rightarrow E_a = R\left(40 - \frac{600}{T}\right)$$

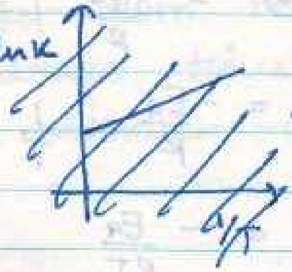
$$= 38R$$

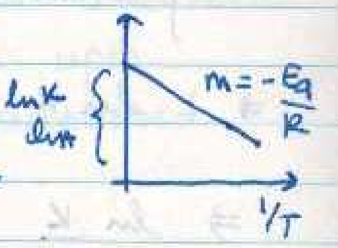
## * Graphical Representation

1. log k v/s 1/T

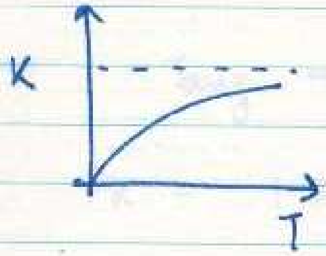


2. ln k v/s $\frac{1}{T}$





3. K v/s T



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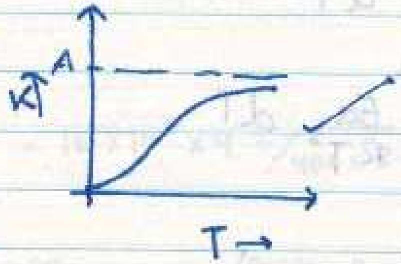


$K = A\,e^{-E_a/RT}$

## * Theories of Chemical Rxn :

### 1] Collision Theory :

- This theory was given by Arrhenius & Went Hof
- This theory is applicable mainly for bimolecular or gases rxn.

Acc$^n$ to it, a chemical rxn takes place due to collision b/w reactant molecules coz during collision old bonds are broken and new bonds are formed.

Under normal conditions, collision frequency $(Z_{11})$ is equal to $10^{30}$ collisions / s·L

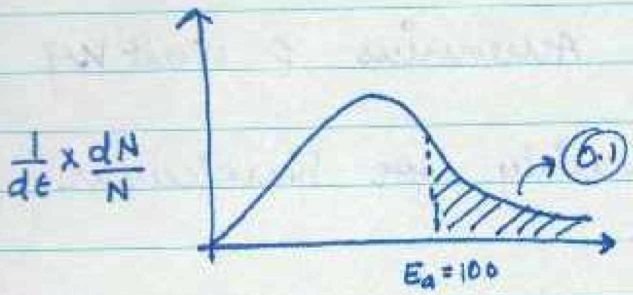
If all these collisions were effective then every rxn would have been completed within a fraction of time but this is not the case. It means all collisions are not effective.

• **Effective collision** :→ These are the collisions which cause product formation

In order to be effective collision, it should satisfy following two criteria :

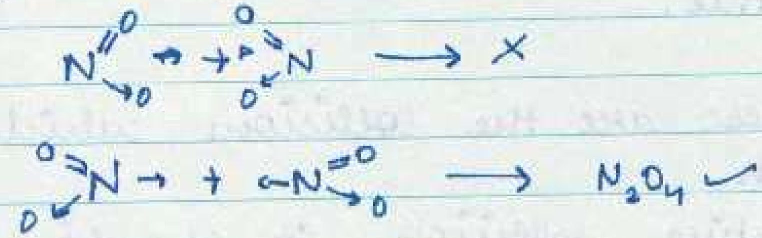
i) Energy barrier
ii) Orientation factor

- **Energy Barrier** : Colliding molecules must have sufficient K.E. so that it can cross Activation / Threshold barrier.



Fraction of molecules having sufficient KE $= e^{-Ea/RT}$

- **Orientation Factor** : All colliding molecules having sufficient KE should also have proper orientation in order to get converted into product.



- **Steric factor (P)** : It represents the fraction of molecules having proper orientation.

Considering all above factors, rate of chemical rxn can be given by

RDR = collision freq. × effective collision

= collision freq. × collision with sufficient energy × collision wi proper orie

$$= \left(\pi(r_A+r_B)^2 u_{avg}\, N_A^* N_B^*\right) \times e^{-Ea/RT} \times P$$

$$= \left(\pi(r_A+r_B)^2 u_{avg} \times N_0^2 \times P\right) e^{-Ea/RT} \times [A][B]$$

$$\text{Rate} = A \cdot e^{-Ea/RT}\,[A][B]$$

$$= k[A][B]$$

$$K = A \cdot e^{-Ea/RT}$$ &

$$A = \pi(r_A+r_B)^2 u_{avg} \times N_0^2 \times P$$

$$\boxed{A \propto u_{avg} \propto \sqrt{T}}$$

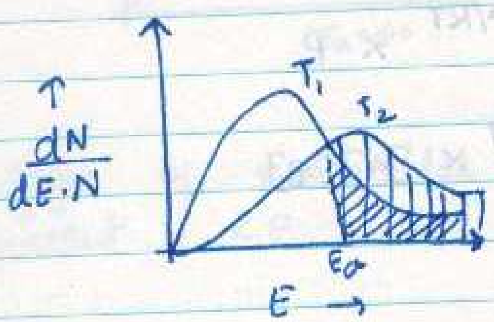
Actually 'A' depends on temp. but on small cha in temp., its value does not change significantl that is why it is considered as independent of temp.

DPP # 2

54 - 67
73 - 84

- why on 10°K rise in temperature ROR becomes double ?

→ On ↑ temp., fraction of molecules having sufficient K.E. becomes / increased drastically. As a result rate becomes double or more than that.



## • * Activated complex Theory :

- ACT formerly known as transition state theory offers following advantage over C.T. :

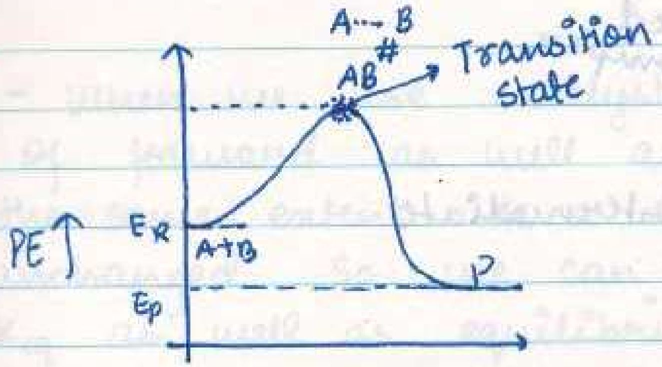
i) It can be applied for gaseous reactants as well as for the rxns taking place in liquid sol$^n$.

ii) Stearic factor appears automatically in contrast to collision theory where 'P' has to be grafted.

- Reaction Profile :

$$A + B \longrightarrow P$$

$$A + B \longrightarrow \underset{\text{Activated complex}}{AB^{\#}} \longrightarrow P$$

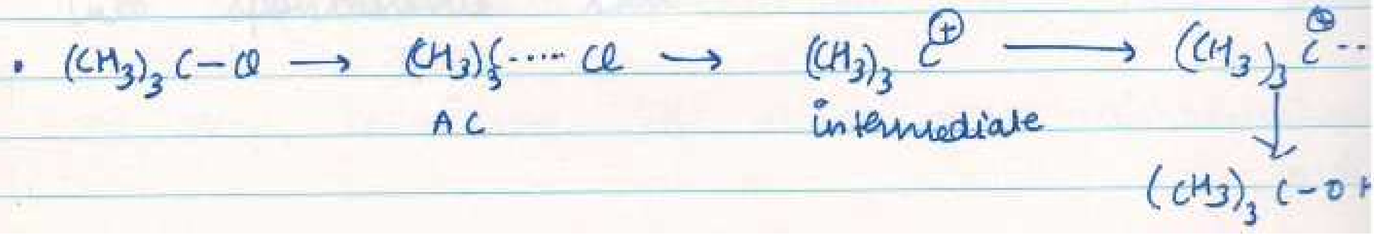


- Initially only r'ant A & B are present.
- As rxn proceeds, A & B come into contact, distraught & begin to exchange atoms.
- As PE ↑ to a maxima, the cluster of atoms corresponds to the region near maxima are referred as activated complex. The confn at actual peak of curve is called transition stat
- After maxima P.E. falls as atoms rearrange to form product.
- In fact All $AB^{\#}$ will not proceed to form produc Some of $AB^{\#}$ will decay back to reactants.

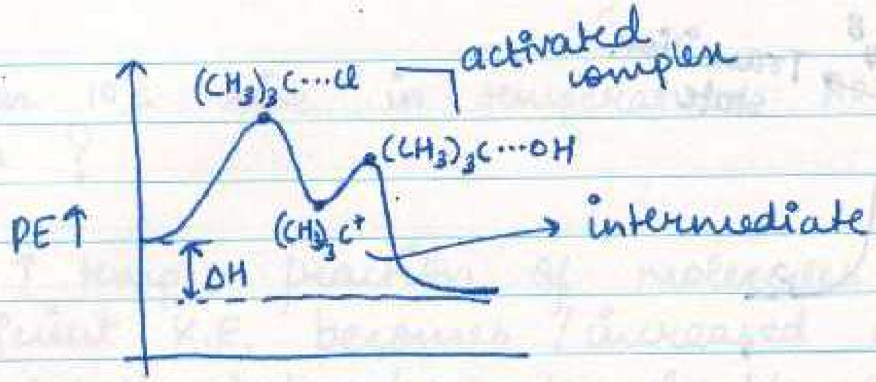
<u>Note</u> : $AB^{\#}$ is not an intermediate cmpd in rxn but rather it is a structure that is in process of change in direcn of product.

<u>SN₁</u>

- $(CH_3)_3C-Cl + OH^- \longrightarrow (CH_3)_3C-OH$



- $(CH_3)_3C-Cl \longrightarrow \underset{AC}{(CH_3)_3C\cdots Cl} \longrightarrow \underset{\text{intermediate}}{(CH_3)_3\overset{\oplus}{C}} \longrightarrow (CH_3)_3\overset{\oplus}{C}\cdots \rightarrow (CH_3)_3C-O$



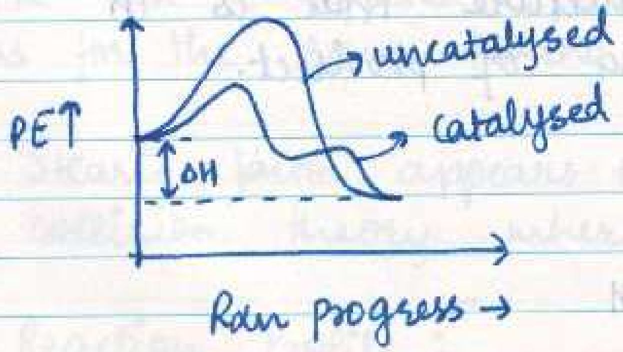
## * CATALYST :

- These are the substances which ↑ the rate of rxn without actually being consumed.

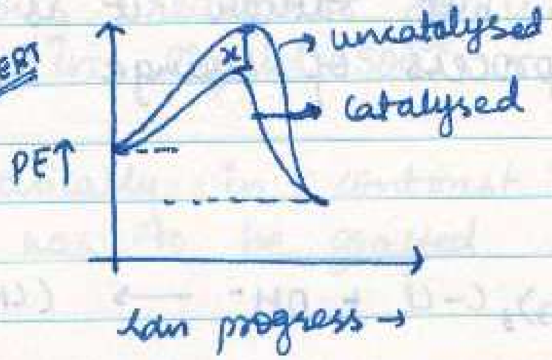
- Catalyst participates qualitatively not quantitatively.

- Catalyst increases the rate of chemical rxn by providing an alternative path with lower activation energy.

- Catalysed rxns are generally complex rxns



NCERT



- When we use catalyst it increases the rate of forward as well as backward rxn to the same extent. As a result, $K_{eq}$ remains unchanged. So we can say, it does not alter $K_{eq}$ as well as equilibrium concentrations or partial pressures of rxn components.

For uncatalysed,

$$K_{eq} = \frac{K_f}{K_b} = \frac{A_f e^{-Ea_f/RT}}{A_b e^{-Ea_b/RT}} = A e^{-(Ea_f - Ea_b)/RT}$$

For catalysed,

$$K_f' = A_f e^{-(Ea_f - x)/RT} = A_f e^{-Ea_f/RT} \cdot e^{x/RT}$$

$$K_b' = A_b e^{-(Ea_b - x)/RT} = A_b e^{-Ea_b/RT} \cdot e^{x/RT}$$

$$K_{eq} = \frac{K_f'}{K_b'} = A e^{-(Ea_f - Ea_b)/RT}.$$

- Catalyst does not alter value of ΔH or ΔG for rxn.

- Catalyst cannot turn a non-spontaneous rxn into spontaneous rxn.

## * MECHANISM OF RXN :

- It represents a path thru which the reactants get converted into products.

- During mechanism rxn is explained step wise.

- Rate determining step (RDS) : This is the slowest step of rxn. (If rxn takes place in more than one step).

- Molecularity : The no. of reacting species (atoms, ions, molecules) taking part in an elementary rxn which must collide simultaneously in order to bring about a chemical change.

Types:

a) Unimolecular Rxn :

$$NH_4NO_2\,(g) \xrightarrow{\Delta} N_2\,(g) + H_2O\,(l)$$

b) Bimolecular Rxn :

$$2HI\,(g) \longrightarrow H_2\,(g) + I_2\,(g)$$

c) Trimolecular Rxn :

$$2NO\,(g) + O_2\,(g) \longrightarrow 2NO_2\,(g)$$

- Some imp. points regarding molecularity :

* Molecularity can never be fractional, -ve or zero.

* Probability of simultaneous collision of three or more molecules is very low. As a result rxns with molecularity 4 or more are not observed.

* In case of elementary rxn, molecularity as well as order will be same.

* There is no meaning of molecularity for complex rxn, while order can be defined for complex rxn. However, molecularity can be defined for each step of a complex rxn coz each step will be an elementary rxn.

Q. An elementary rxn can't be of fractional order.

→ True.

Case I : If reactants directly get converted to product.

$$A + B \xrightarrow{K_1} P$$

Rate = $K_1 [A][B]$

eg : $NO_{(g)} + O_{3(g)} \xrightarrow{K_1} NO_{2(g)} + O_{2(g)}$

Rate = $K_1 [NO_2][O_3]$

**Case II** : If rxn takes place in more than one step & one of them is slow

$$A + B \longrightarrow P$$

Step I $\quad A + B \xrightarrow{K_1} I^*$ (slow)

Step II $\quad I^* \xrightarrow{K_2} P$ (fast)

$$\text{Rate} = K_1 [A][B]$$

eg. $2NO_2 + F_2 \longrightarrow 2NO_2F$

Step I $\quad NO_2 + F_2 \xrightarrow{K_1} NO_2F + F$ (slow)

Step II $\quad NO_2 + F \xrightarrow{K_3} NO_2F$ (fast)

$$\text{Rate} = K_1 [NO_2][F_2]$$

**Case III** : If rxn takes place in more than one step & one of them is slow, & one is reversible.

Step I $\quad A + B \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} I^*$ (fast)

Step II $\quad I^* \xrightarrow{K_2} P$ (slow)

$$\text{Rate} = K_2 [I^*]$$

$$= K_2 \times \frac{K_1}{K_{-1}} \times [A][B]$$

$ROR = K_{or}[A][B]$

$$K_{or} = \frac{k_1 k_2}{k_{-1}} = \frac{A_1 e^{-E_1/RT} \cdot A_2 e^{-E_2/RT}}{A_{-1} \cdot e^{-E_{-1}/RT}}$$

$$K_{or} = \frac{A_1 A_2}{A_{-1}} \times e^{-(E_1 + E_2 - E_{-1})/RT}$$

$$E_{overall} = E_1 + E_2 - E_{-1}$$

Activation Energy (overall) can be +ve, -ve or zero.

eg. $2NO_{(g)} + O_{2\,(g)} \longrightarrow 2NO_{2\,(g)}$

Step I $\quad 2NO_{(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$ [fast]

Step II $\quad N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$ (slow) $\qquad \frac{k_1}{k_{-1}} = \frac{[N_2O_2]}{[NO]^2}$

$$ROR = k_2 [N_2O_2][O_2]$$

$$= k_2 \cdot \frac{k_1}{k_{-1}} \cdot [NO]^2 [O_2]$$

- Case IV : If rxn takes place in more than one step & one of them is reversible & steps are moving with comparable.

$$A + B \longrightarrow P$$

Step I $\quad A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I^*$

Step II $\quad I^* \xrightarrow{k_2} P$

$$Rate = \frac{d[P]}{dt} = k_2 [I^*]$$

We can apply steady state on $[I^*]$

$$\frac{d[I]}{dt} = 0$$

$$Rate = \frac{k_1 k_2}{k_{-1} + k_2} [A][B]$$

if $k_1$ & $k_{-1} >> k_2$,

$$Rate = \frac{k_1 k_2}{k_{-1}} [A][B]$$

if $k_2 >> k_{-1}$,

$$Rate = k_1 [A][B]$$

* Photochemical Rxn:

$$H_{2(g)} + Cl_{2(g)} \xrightarrow[\text{sunlight}]{h\nu} 2HCl_{(g)}$$

Chain initiation,

$$Cl_{2(g)} \xrightarrow[I]{h\nu} 2\dot{Cl}_{(g)} \qquad Rate \propto I$$

$$\left.\begin{aligned} \dot{Cl} + H_2 &\rightarrow HCl + \dot{H} \\ \dot{H} + Cl_2 &\rightarrow HCl + \dot{Cl} \end{aligned}\right\} \text{chain propagation step}$$

$$\left.\begin{aligned} \dot{H} + \dot{H} &\longrightarrow H_2 \\ \dot{Cl} + \dot{Cl} &\longrightarrow Cl_2 \end{aligned}\right\} \text{chain terminating step}$$

- first step of photochemical rxn will be of zero order. It's rate will depend on intensity of light (I).
- Photochemical rxn will be complex.
- Photochemical rxn can have any order.

Q. $C_{12}H_{14} + h\nu \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_{12}H_{14}^{*} \Rightarrow k_1 I$ $\qquad \frac{k_1 - k_2[C_{12}H_1}{k_2}$

$C_{12}H_{14} + C_{12}^{*}H_{14} \xrightarrow{k_2} C_{24}H_{28}$ $\qquad k_1 - k_2[C_{12}H_{14}] - k_2[C_{12}^{*}H_{14}] = 0$

$\rightarrow$ Rate $= \frac{d[C_{24}H_{28}]}{dt} =$ [illegible] , ~~I~~ $\quad k_2 \; [C_{12}H_{14}] \cdot [k_1 - k_2[C_1$

Q. $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$

**Mech**

$N_2O_5(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2(g) + NO_3(g)$

$NO_2 + NO_3 \xrightarrow{k_2} NO + NO_2 + O_2$

$NO_3 + NO \longrightarrow 2NO_2$

P.T. $\frac{d[O_2]}{dt} = k[N_2O_5]$