

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.

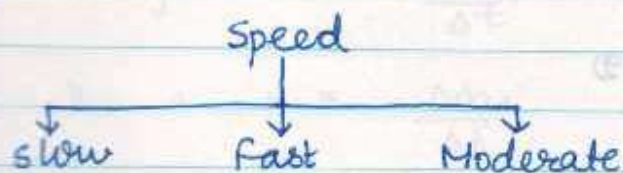


- ⇒ spontaneous / feasibility is predicted by Thermodynamics
- ⇒ extent of rxn is predicted by chemical eq.
- ⇒ Rate of chemical rxn is determined by Chemical kinetics.

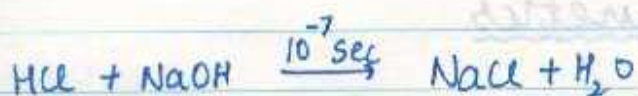
* Classification of Chemical Rxn :-

Rxn can be classified on the basis of

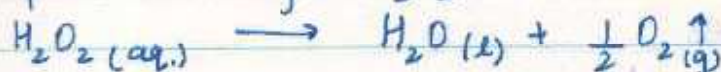
- a) Speed
- b) Mechanism



- 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.



- Moderate Rdn : These are the rans which are neither very slow nor instantaneous. For eg, decomposition of H_2O_2 .

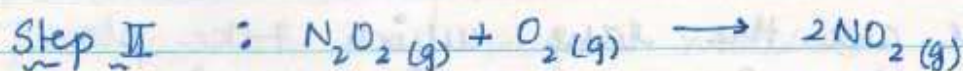
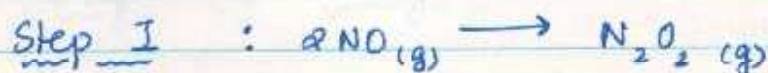
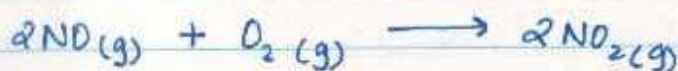


Mechanism

Simple
Elementary

Complex

- Elementary Rdn : These are the reactions which get completed in single step.
- Complex Rdn : These are Rans which take place in more than one step & each step of rdn will be an elementary rdn. For eg,



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

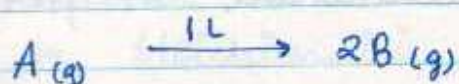
• Rate of Rxn: change in amount of reactant or product per unit time.

• 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.



$t=0$	100 mol	-
$t=1\text{sec}$	90 mol	20 mol

if v is constant,

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

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

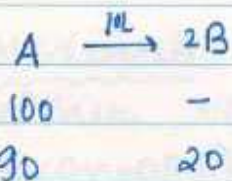
$$\text{" " " } = -\frac{dA}{dt}$$

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

if v is variable,

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

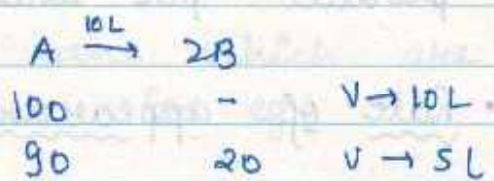
V → constant



$$[A]_i = 10M$$

$$[A]_f = 9M$$

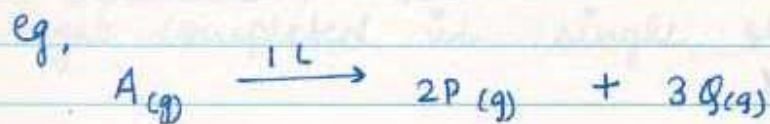
V → Variable



$$[A]_i = 10M$$

$$[A]_f = 18M$$

Note: 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.



$$t=0 \quad 100 \quad 0 \quad 0$$

$$t=10s \quad 90 \quad 20 \quad 30$$

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

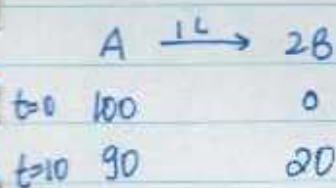
$$\text{ROA of P} = 2M/s = \Delta[P]/\Delta t$$

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

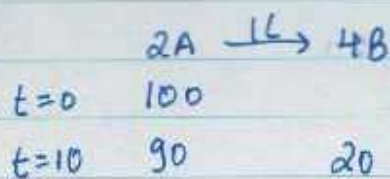
$$\text{Rate of Rxn} = -\frac{\Delta[A]}{\Delta t} = \frac{1}{2} \frac{\Delta[P]}{\Delta t} = \frac{1}{3} \frac{\Delta[Q]}{\Delta t} = 1M/s$$

In general,

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



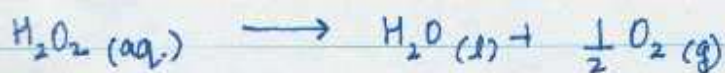
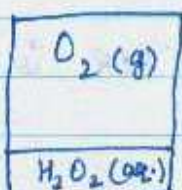
$$\begin{aligned} \text{ROD of A} &= 1 \text{ M/s} \\ \text{ROA of B} &= 2 \text{ M/s} \\ \text{ROR} &= 1 \text{ M/s} \end{aligned}$$



$$\begin{aligned} \text{ROD of A} &= 1 \text{ M/s} \\ \text{ROA of B} &= 2 \text{ M/s} \\ \text{ROR} &= \frac{1}{2} \text{ M/s} \end{aligned}$$

• ROA or ROD are actual qty. and independent of stoichiometric coeff. however ROR is theoretical 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 eqⁿ.



$$\text{ROR} = - \frac{\Delta [H_2O_2]}{\Delta t} = \frac{2 \Delta [O_2]}{\Delta t}$$

due to diff. volumes taken into consideration ..

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

• Units of ROR :-

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

$$\text{Ms}^{-1} \text{ or } \text{mol L}^{-1} \text{s}^{-1}$$

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

• Conversion :-

$$P_A V = n_A R T$$

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

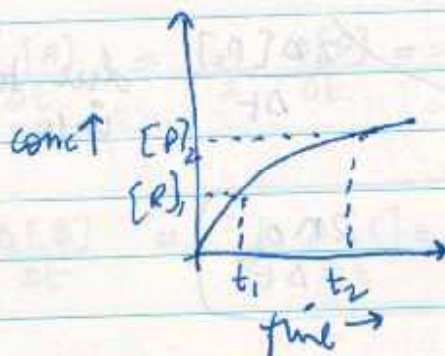
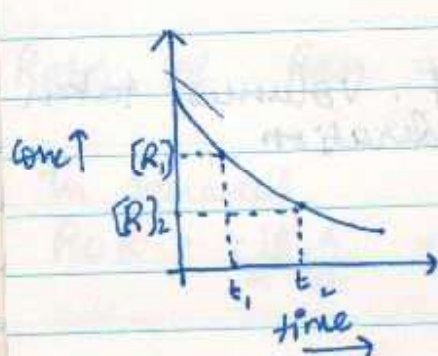
$$\Rightarrow \frac{1}{RT} \times \frac{\Delta P_A}{\Delta t} = \frac{\Delta [A]}{\Delta t}$$

• Types of Rate of Reaction :-

i) Average ROR

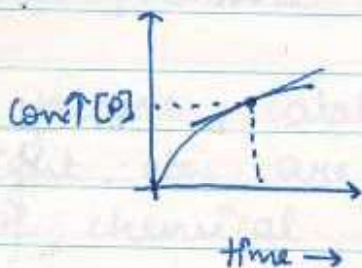
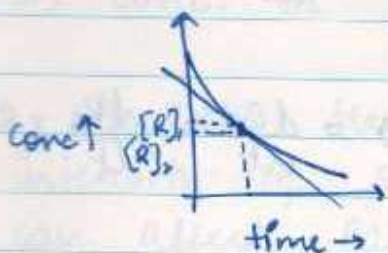
ii) Instantaneous ROR

A) Average Rate of Reaction : If ROR is measured over a large interval of time.



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

8) Instantaneous Rate of Rxn: If rate of rxn is measured over a very short interval of time.



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

$$\text{ROA of } P = \frac{d[P]}{dt}$$

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

Q. For the rxn



The no. of moles of B increases by 6×10^{-3} mol in 10 sec in 10L vessel. Calculate

- ROA of B & C
- ROD of A
- ROR

$$\rightarrow \text{ROA of B} = \frac{6 \times 10^{-3}}{100}$$

$$\text{ROD of A} = \frac{4 \times 10^{-3}}{100}$$

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

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

Q. For the gaseous phase Rxn

$A(g) \rightarrow \text{Product}$, occurring at constant volume
 The correct relⁿ b/w $\frac{d[A]}{dt}$, $\frac{dn_A}{dt}$ & $\frac{dP_A}{dt}$

A. $\frac{d[A]}{dt} = \frac{dn_A}{dt} = \frac{dP_A}{dt}$

B. $\frac{1}{V} \frac{dn_A}{dt} = \frac{d[A]}{dt} = \frac{dP_A}{dt} \times RT$

C. $\frac{d[A]}{dt} = \frac{1}{RT} \frac{dP_A}{dt} = \frac{1}{V} \frac{dn_A}{dt}$

D. $\frac{1}{V} \frac{dP_A}{dt} = \frac{1}{V} \frac{dn_A}{dt} = \frac{d[A]}{dt}$

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

The ROA of $N_2(g)$ will be



ROA = $\frac{1}{2} \times 3.4 = 1.7 = \text{ROA of } N_2$.

Q. For Rxn

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

$[N_2O_5]_t = [N_2O_5]_0 e^{-kt}$ where $[N_2O_5]_0 = 1M$
 & $k = 10^{-4} \text{ sec}^{-1}$ Determine

- ROD of N_2O_5 at $10^4 \text{ sec} \Rightarrow -k e^{-kt} = \frac{1}{e} \cdot 10^{-4}$
 - ROA during first $10^4 \text{ sec} \Rightarrow \frac{1}{e} \cdot 10^{-4}$
 - Variation of conc. of NO_2 with time.
- $\frac{1}{e} \cdot 10^{-4} \int 2x e^{-kt}$

* Factors affecting Rate of R_{an} :->

- i) Nature of R_{an} 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 :->



$$\text{Rate of R}_{an} \propto a_A^\alpha a_B^\beta$$

$$\boxed{\text{Rate of R}_{an} = k a_A^\alpha a_B^\beta} \rightarrow \text{Rate law expression}$$

where,

$a_A, a_B \rightarrow$ active masses of A & B resp.

$\alpha, \beta \rightarrow$ experimentally determined factors

$k \rightarrow$ Rate constant / velocity constant / specific R_{ate}

• Case I : In case of liq. solⁿ active masses are replaced by conc.

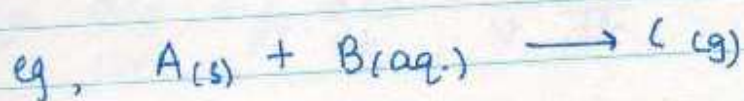
$$\text{Rate} = k [A]^\alpha [B]^\beta$$

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

$$\text{Rate} = k P_A^\alpha P_B^\beta$$

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

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



$$\text{Rate} = k a_A^\alpha a_B^\beta$$

$$= k' a_B^\beta = k' [B]^\beta$$

* Order of Rxn \Rightarrow

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



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

where,

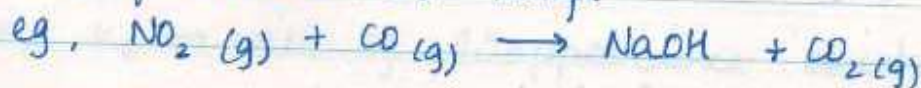
$m \rightarrow$ order w.r.t. A

$n \rightarrow$ order w.r.t. B

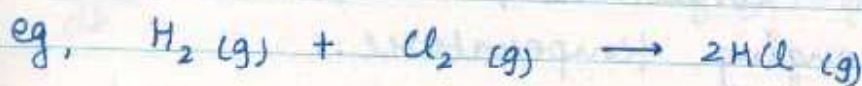
$m+n \rightarrow$ order of Rxn

Some imp. points regarding order of R_{an} :->

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



$$\begin{aligned} \text{Rate} &= k [\text{NO}_2][\text{CO}] && \text{Above } 500^\circ\text{C} \\ &= k [\text{NO}_2]^2 && \text{Below } 500^\circ\text{C} \end{aligned}$$



$$\text{Rate} = k$$

$$\text{order} \rightarrow 0$$

$$\text{Rate constant} \rightarrow k$$



$$\text{Rate} = k [\text{H}_2\text{O}_2]$$

$$\text{order} = \rightarrow 1$$

$$\text{Rate constant} \rightarrow k$$

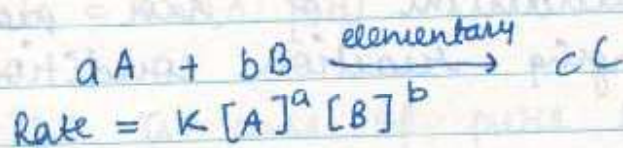


$$\text{Rate} = \frac{k_1 [\text{NH}_3]}{1 + k_2 [\text{NH}_3]}$$

$$\text{order} \rightarrow \text{N. D.}$$

$$\text{Rate constant} \rightarrow \text{N. D.}$$

- 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

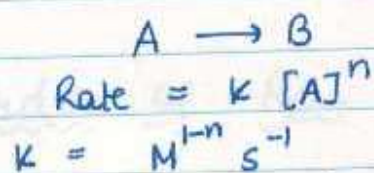


{ converse is not true }

* 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' :->



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' :->



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

$k_r \rightarrow$ rate constant of Rxn

$$-\frac{d[A]}{dt} = a k_r [A]^\alpha [B]^\beta = k_A [A]^\alpha [B]^\beta$$

$$-\frac{d[B]}{dt} = b k_r [A]^\alpha [B]^\beta = k_B [A]^\alpha [B]^\beta$$

where,

$k_A, k_B \rightarrow$ rate of disappearance const. w.r.t. A & B

$$\frac{d[C]}{dt} = c k_r [A]^\alpha [B]^\beta = k_C [A]^\alpha [B]^\beta$$

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

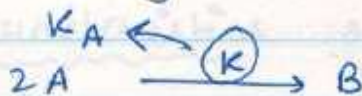
where,

$k_C, k_D \rightarrow$ 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

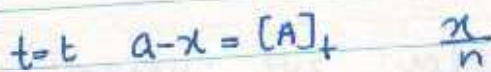
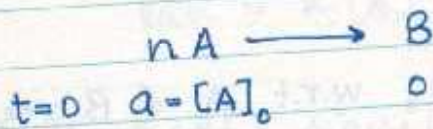


- Units of k helps in determination of order of reaction in numerical problems.

* Analysis of Various Orders of Reactions \Rightarrow

(Using Integrated Rate Law expressions)

1. Zero Order \Rightarrow



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

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

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

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

$$\Rightarrow x = k_A t$$

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

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

R

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

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

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

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

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

• Completion time (t_{comp}): →

$$[A]_t = 0$$

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

• Relⁿ b/w $t_{1/2}$ & t_{comp} :→

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

• Characteristics of zero order rxn :→

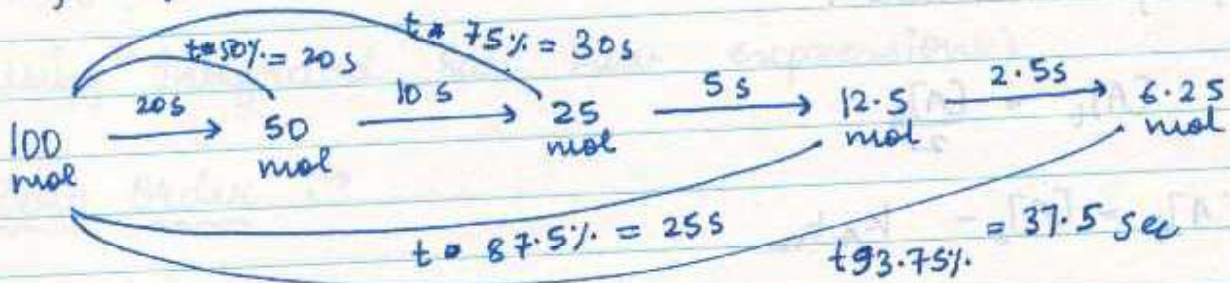
i] Units of $k \rightarrow \text{Ms}^{-1}$

ii] Conc. of reactant decreases linearly with time

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

$$y = c + m x$$

iii) Half life depends on initial conc. of reactant



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

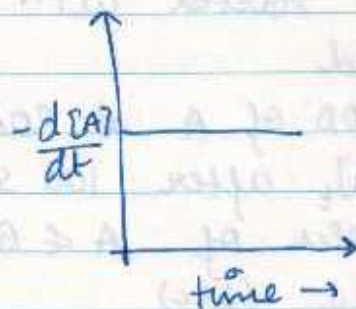
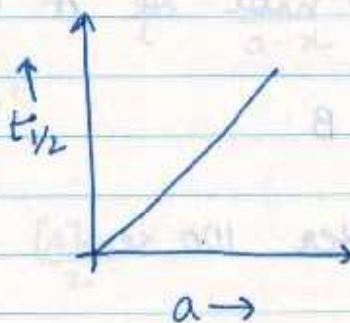
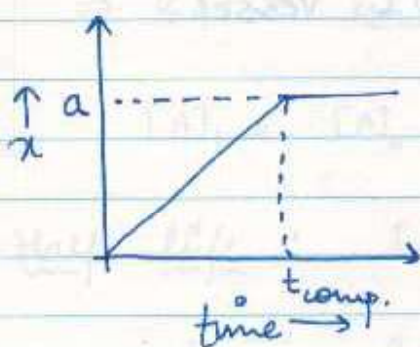
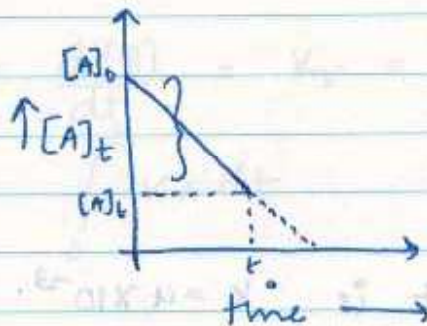
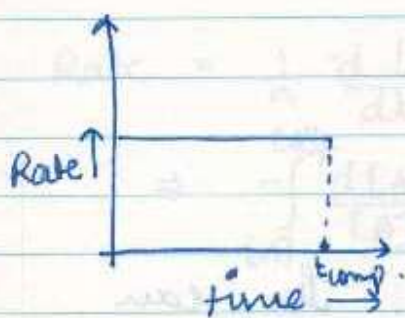
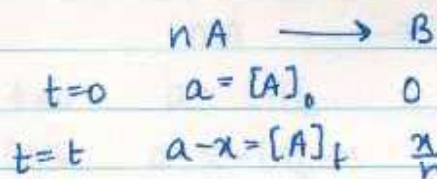
t_{comp} is also proportional to initial conc.

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	} Rate Constant
$[A]_t$	$[A]_0$	$[A]_0 - k_A t$	$[A]_0 - 2k_A t$	$[A]_0 - 3k_A t$	
		$-k_A t$	$-k_A t$	$-k_A t$	

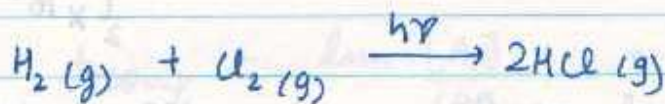
vi) Zero order rxn must be complex

• Graphical Form :-



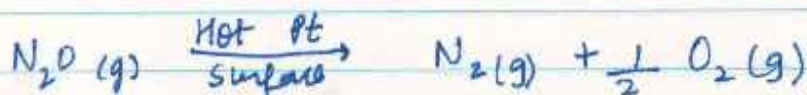
• Examples of zero order :-

i) Photochemical Rxn

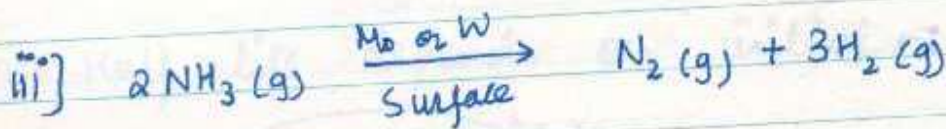


$$\text{Rate} = k$$

ii] Surface catalysed Rxn



$$\text{Rate} = k$$



Rate = k

H.W.

DPP # 9

Sheet : 10-17

Q. For the rxn
 $\text{A} \rightarrow 2\text{B}$

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

Find

- ROD of A & ROA of B
- $[\text{A}]_t$ after 100 sec
- Moles of A & B after 100 sec
- $t_{1/2}$ (sec)
- $t_{\text{completion}}$
- time at which conc. of A becomes equal to B
- conc. of A & B after 10 min from start of rxn

$\rightarrow \text{Rate} = 4 \times 10^{-3} \times 2^0 = 4 \times 10^{-3} \text{ M s}^{-1}$

a) $8 \times 10^{-3} \text{ M}, 16 \times 10^{-3} \text{ M}$

b) 1.6 M

c) 16 mol of A & 8 mol of B

d) $1/4 \times 10^3 \text{ sec}$

e) $1/2 \times 10^3 \text{ sec}$

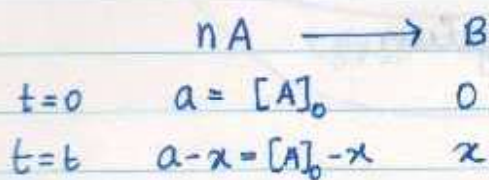
f) 1000 sec

g) $\text{A} = 0, \text{B} = 4 \text{ M}$

$2 - 4 \times 10^{-3} \times 100 = 1.6 \text{ M}$
 $1/2 \times 10^3 \text{ sec}$

$135 = 2 - 4 \times 10^{-3} \times t$
 $0.65 \times 10^3 = 4t$
 $t = 162.5 \text{ sec}$

2. First Order Reaction \Rightarrow



$$\text{Rate} = \frac{1}{n} \frac{d[A]}{dt} = \frac{d[B]}{dt} = k_r = k_A [A]_t$$
$$\Rightarrow \int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = \int_0^t k_A dt$$

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

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

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 :

$$t_{\text{comp}} = \ln \frac{[A]_0}{[A]_t = 0} = \infty$$

- 1st order rxn will never get completed in finite time

for numerical purpose :-

a) If % of reactant reacted is given

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

$$k_A t_{20\%} = \ln \frac{100}{80}$$

$$k_A t_{40\%} = \ln \frac{100}{60}$$

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

b) If fraction of reactant reacted is given

$$k t_{1/3} = \ln \frac{1}{1-1/3}$$

$$k t_{1/7} = \ln \frac{1}{1-1/7}$$

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

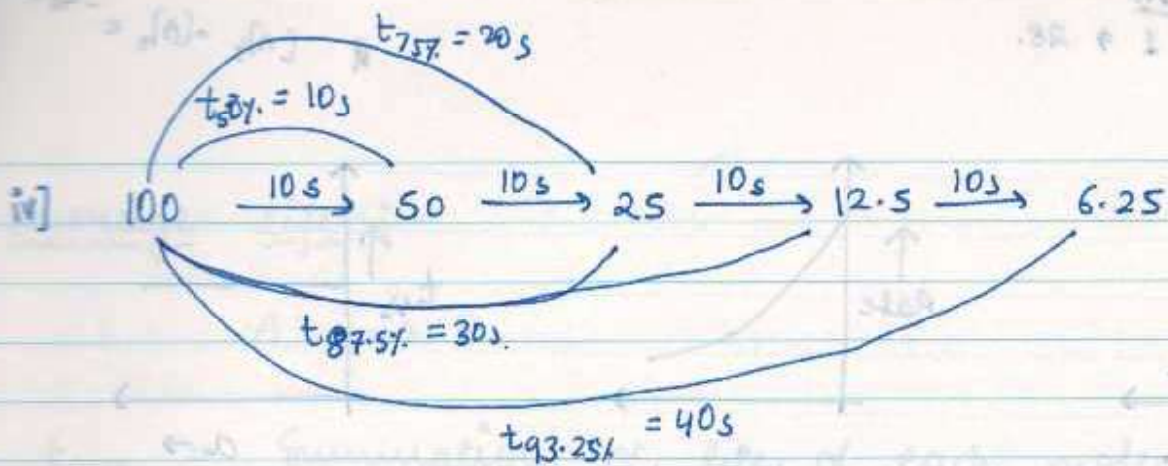
• Characteristics of 1st order reaction :

i] Units of $k \rightarrow s^{-1}$

ii] Conc. of reactant \downarrow exponentially with time

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

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



v) $t_{\text{completion}} = \infty$.

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^{-kAt} it means in equal interval of time, equal % of reactant reacts.

time (t)	0	t	2t
$[A]_t$	$[A]_0$	$[A]_0 e^{-kAt}$	$[A]_0 e^{-2kAt}$
		$\underbrace{e^{-kAt}}$	$\underbrace{e^{-kAt}}$

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

Graphical Analysis

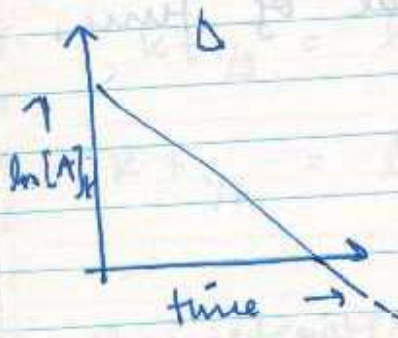
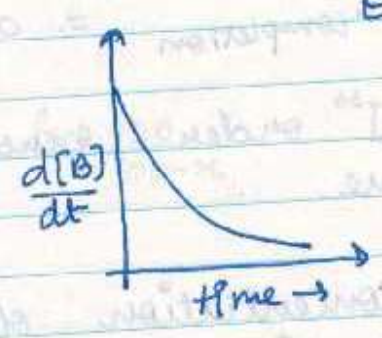
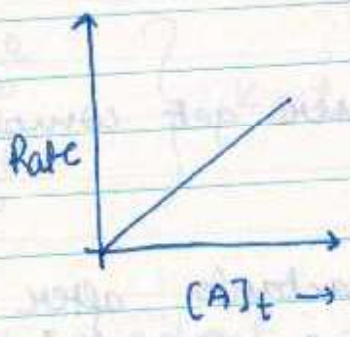
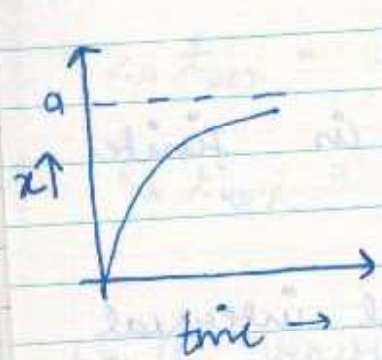
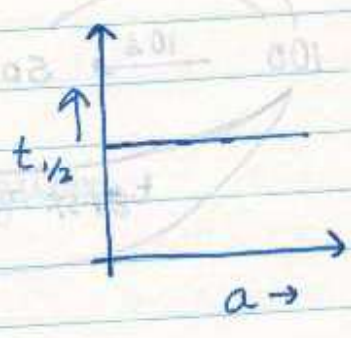
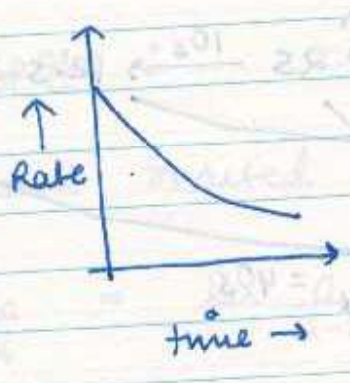
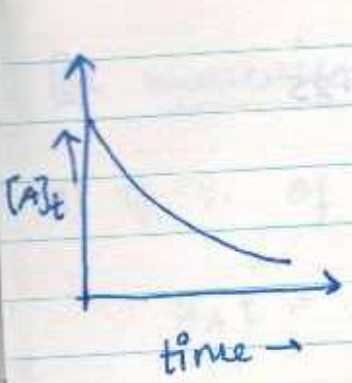


$t=0$ $a = [A]_0$

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

H.W.
Ex 1 ⇒ 28.

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



Units of $k_d = \frac{1}{\text{time}}$

low of reaction is proportional to time



• Average life :



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

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

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

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

$$\text{tang} = \int_0^{\infty} \frac{k_A [A]_t dt}{[A]_0} = \int_0^{\infty} \frac{k_A [A]_0 t e^{-k_A t} dt}{[A]_0}$$

$$(\text{tang})_I = \frac{1}{k_A}$$

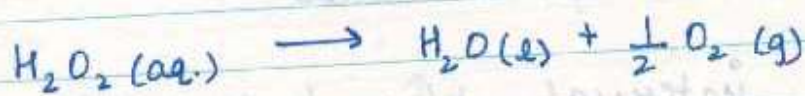
for zero order,

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

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

Examples of First Order Reaction:

- 1] All radioactive disintegration follows first order kinetics.
- 2] Decomposition of H_2O_2



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

Q. For 1st order reaction P.T.

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

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

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

$$\rightarrow \frac{1}{k_A} \times \ln \frac{100}{25} \text{--- (1)} \quad \left| \quad \frac{1}{k_A} \ln \frac{100}{50} \text{--- (2)}\right.$$

from (1) & (2)

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

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

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

Q. For a 1st order rxn ROR at $t_1 = 10 \text{ min}$ is $2 \times 10^{-3} \text{ MS}^{-1}$
 & at $t_2 = 20 \text{ min}$ is $4 \times 10^{-3} \text{ MS}^{-1}$ find k .

$$\begin{aligned} \rightarrow \text{ROR} &= k_A [A]_t \\ &= k_A [A]_0 e^{-k_A t} \\ \frac{1}{2} &= \frac{e^{-k_A \cdot 100}}{e^{-k_A \cdot 200}} \end{aligned}$$

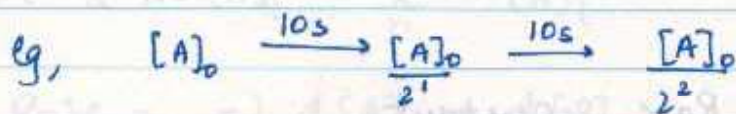
$$\Rightarrow k_A \times 600 = -\frac{\ln 2}{600} = 4.20 \text{ s}^{-1}$$

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

for numerical purpose

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

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



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

where n = no. of half lives

$$\frac{[A]_t}{[A]_0} = \frac{1}{2^n}$$

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

• 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	→	C
t=0	1000M	1M	0
t=t ₁	999.5M	0.5M	0.5M
t=t ₂	999.25M	0.25M	0.75M

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

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

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

where,

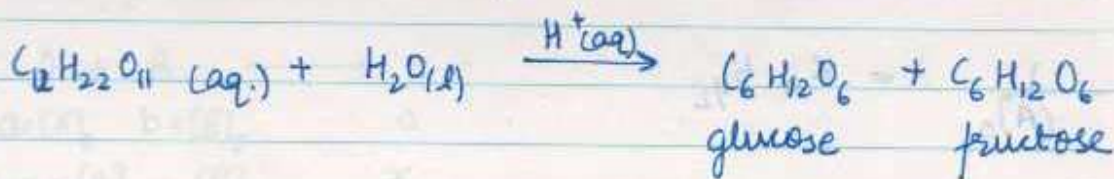
$$k' = k[A] = \text{Pseudo Rate constant}$$

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

$$\rightarrow k' = k[A]$$

↳ Rate constant for rxn.

eg, inversion of cane sugar is pseudo I order rxn



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

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

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

↓
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



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

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

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

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

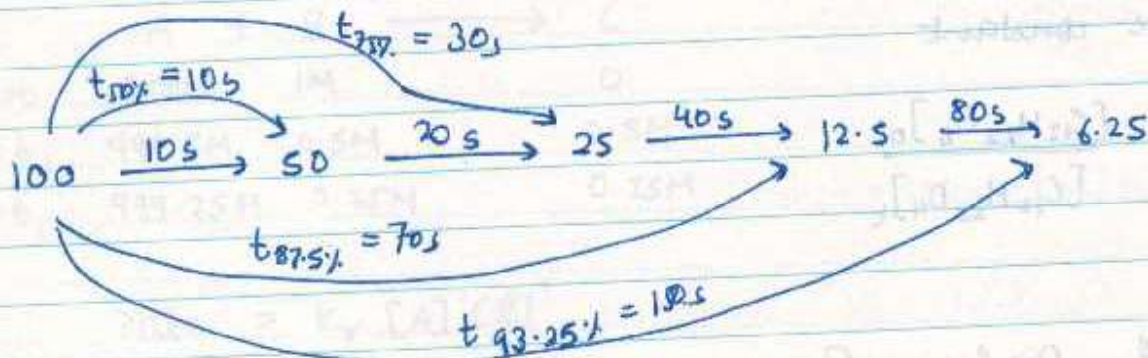
$$\Rightarrow \left[\frac{1}{[A]_t} - \frac{1}{[A]_0} \right] = k_A t$$

Half life :

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

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

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

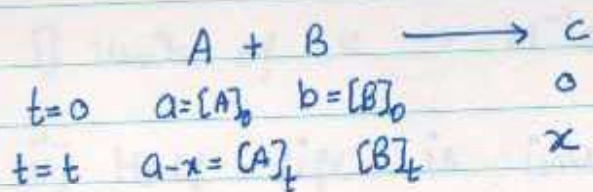


Completion time :

$$[A]_t = 0$$

$$t_{comp} = \text{infinite}$$

Case II : If more than one reactants are present



$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = k_2 [A]_t [B]_t$$

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

$$\Rightarrow -\frac{d(a-x)}{dt} = k_2 (a-x)(b-x)$$

$$\Rightarrow \int_0^x \frac{dx}{(a-x)(b-x)} = \int_0^t k_2 dt$$

$$\Rightarrow \frac{1}{a-b} \int_0^x \frac{(a-x) - (b-x)}{(a-x)(b-x)} = \int_0^t k_2 dt$$

$$\Rightarrow \frac{1}{a-b} \left\{ \int_0^x \frac{dx}{(b-x)} - \int_0^x \frac{dx}{(a-x)} \right\} = k_2 t$$

$$\Rightarrow \frac{1}{a-b} \left\{ -\ln(b-x) + \ln(a-x) \right\}_0^x = k_2 t$$

$$\Rightarrow \frac{1}{a-b} \left\{ \ln \frac{a-x}{b-x} - \ln \frac{a}{b} \right\} = k_2 t$$

$$\Rightarrow \frac{1}{a-b} \left[\ln \frac{(a-x)b}{(b-x)a} \right] = k_2 t$$

i) if $a \gg b$

$$k_{\gamma} t = \frac{1}{a-b^0} \ln \frac{(a-x^0)b}{(b-x)a}$$

$$\Rightarrow a k_{\gamma} t = \ln \frac{b}{b-x}$$

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

ii) if $a = b$

$$k_{\gamma} t = \frac{1}{a-b} \ln \frac{(a-x)b}{(b-x)a}$$

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

So,

$$k_{\gamma} t = \frac{1}{[A]_t} - \frac{1}{[A]_0}$$

Ex:2: 1-22 ; Ex:1: 73, 75, 76

R.B: 1

* Characteristics of Second Order :

i] Units of $k \rightarrow M^{-1}s^{-1}$

ii] Half life is inversely proportional to

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

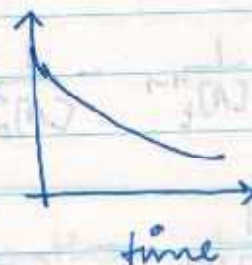
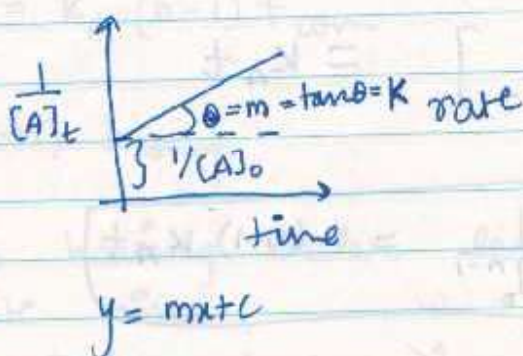
iii] $t_{comp.} = \text{infinite}$

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

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

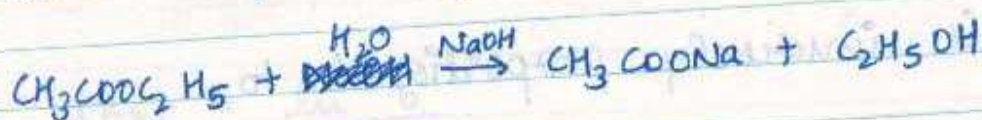
$$[A]_t = \frac{1}{\frac{1}{[A]_0} + kt}$$

* Graphical analysis :



Examples :

a) Base catalysed hydrolysis of Ester



$$\text{Rate} = k [\text{CH}_3\text{COOC}_2\text{H}_5] [\text{NaOH}]$$

4. n^{th} Order :

($n \neq 1$)



$$\begin{array}{l} t=0 \quad a = [A]_0 \quad 0 \\ t=t \quad [A]_t \quad x/a \end{array}$$

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

$$-d[A] = k_n [A]_t^n dt$$

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

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

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

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 $n > 1$

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

$\therefore \infty$

Case II : for $n < 1$

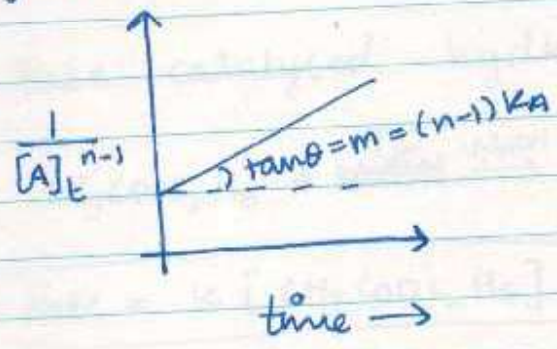
$$[A]_t^{1-n} - [A]_0^{1-n} = k_A (n-1) t_{comp.}$$

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

• Conclusion : Rxns having order less than 1 get completed in finite time.

For Rxns having order ≥ 1 , 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 order.



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

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

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

$k_A = \frac{[A]_0 - [A]_{t_2}}{t_2}$

if $k_{A_1} \approx k_{A_2}$
 \Rightarrow Reaction is of zero order

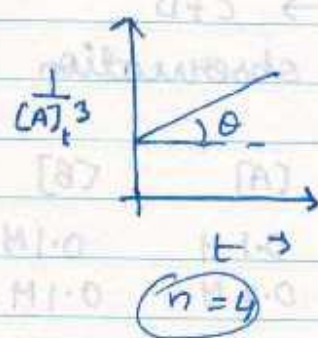
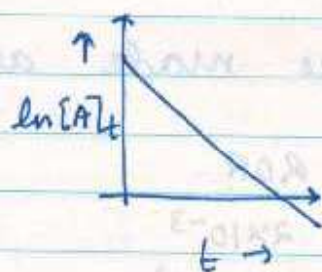
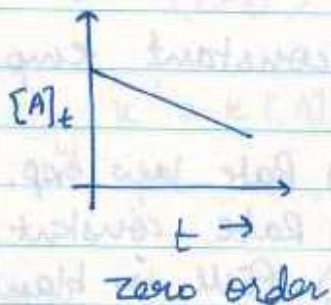
if $k_{A_1} \neq k_{A_2}$
 we assume order = 1

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

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

if $k_{A_1} \approx k_{A_2}$
 \Rightarrow Reaction is of first order.

2. Graphical Method :



3. Half life Method :

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

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

9. 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 $\frac{1}{10}^{\text{th}}$ of initial value. Find order of Rn.

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

4. Initial Rate law method :

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

Q. For the Rn



Following observations are made at constant Temp.

Exp. No.	[A]	[B]	ROR
1	0.1M	0.1M	2×10^{-3}
2	0.2M	0.1M	4×10^{-3}
3	0.2M	0.2M	4×10^{-3}
4	0.3M	0.2M	—
5	—	0.3M	8×10^{-3}

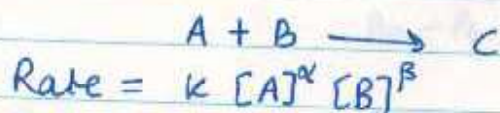
- Rate law exp.
- Rate constant
- Fill in blank

$$\begin{aligned} \rightarrow 2 \times 10^{-3} &= k \times [0.1]^a [0.1]^b \\ 4 \times 10^{-3} &= k \times [0.2]^a [0.1]^b \\ 4 \times 10^{-3} &= k \times [0.2]^a [0.2]^b \end{aligned}$$

$$\begin{aligned} a &= 1 \\ b &= 0 \\ k &= 2 \times 10^{-3} \end{aligned}$$

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 run & order of rxn w.r.t. other reactant is calculated.



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

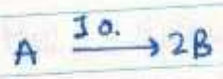
* Determination of Rate constant (k) using different parameters:
(for 1 order)



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

1] In terms of pressure \Rightarrow

Q. find (k) for



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

time (t)	0	t	∞
P_{total}	P_0	P_t	P_{∞}

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

Q. for 1 order rxn
 $A \rightarrow B + 2C$ find k

time (t)	t	∞
$P_B + P_C$	P_t	P_{∞}

$P_A + P_B = P_t$
 $0 + P_B = P_{\infty}$
 $3x = P_t$
 $P_0 + 2P_0 = P_{\infty}$
 $P_0 = P_{\infty}/3$

$$k_A t = \ln \frac{a}{a-x} = \frac{1}{t} \ln \frac{P_{\infty}}{P_{\infty} - P_t}$$

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

Q. Find k for,



(t)	0	t	∞
(P_T)	P_0	P_t	P_∞

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

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

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

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



time (s)	0	20	∞	find $t_{1/2}$
P_{total}	50	80	90	

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

M-I

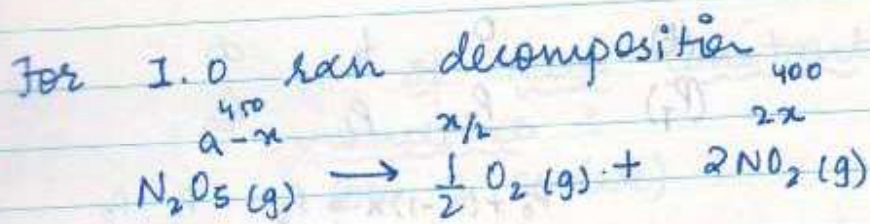
$$= \frac{\ln 2}{10}$$

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

M-II

$$x \propto 30 \quad a \propto 40 \quad k_A t = \ln \frac{a}{a-x} = \ln \frac{40}{10}$$

11



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 reaction $P_{O_2} = 100$ torr. Calculate $t_{1/2}$ [$\ln 3 = 1.1$, $\ln 2 = 0.7$]

$$\rightarrow k_A \times = \ln \frac{900}{200} = 2 \ln 3 - \ln 2 = 2.2 - 0.7 = \frac{1.5}{4}$$

$$k = \frac{1}{4} \times \ln \frac{650}{400}$$

$$t_{1/2} = \frac{0.7 \times 4}{1.5} = \frac{28}{15} = 1.87 \approx 2$$

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

Q. For a reaction $A(g) \rightarrow nB(g)$ the rate constant is $6.93 \times 10^{-4} s^{-1}$. The reaction 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 3 M. Then calculate 'n'.

3.25

$$\rightarrow \frac{n x}{V'} = \frac{3}{3.25}$$

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

$$4 - 4x = 1$$

$$x = 3/4$$

$$6.93 \times 10^{-4} \times 2 \times 10^3 = \ln 4$$

$$1.386 = \ln 4$$

14

Q. The rxn
 $2A + B \rightarrow C + D$ follows $-\frac{d[B]}{dt} = k[A][B]^2$

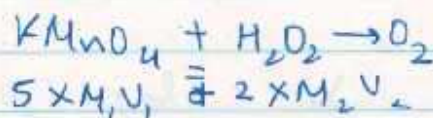
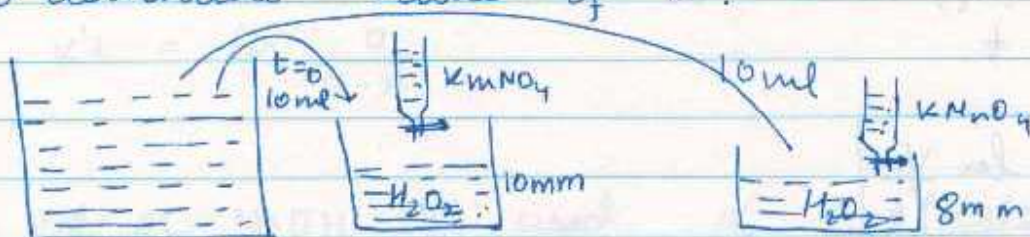
Find (nty)

S. No.	$[A]_0 \times 10^{-4} M$	$[B]_0 \times 10^{-4} M$	$t_{1/2}$ (sec)	$t_{1/2} \propto \frac{1}{[B]_0}$
1	500	2	10	
2	500	4	x	= $\frac{10}{2} = 5$
3	2	250	8	
4	4	500	y	= $\frac{10}{4} = 2.5$

$\propto \left(\frac{1}{[B]_0}\right)^2$

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

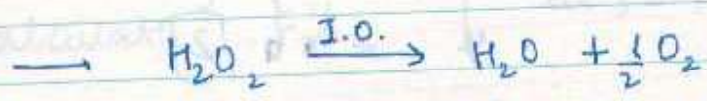
In this method a solⁿ of H_2O_2 is prepared and equal amount of sample or aliquot is taken from H_2O_2 solⁿ & after certain interval of time, it is titrated against standard solⁿ of $KMnO_4$ to determine value of 'k'.



Q. 8. For decomposition of H_2O_2

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

Find $t_{1/2}$.



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

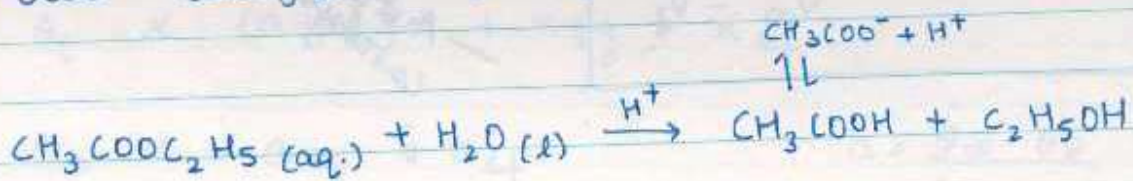
$$k_A t = \ln \frac{a}{a-x}$$

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

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

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

iii] Acid catalysed hydrolysis of ester :-



$t=0$	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_∞

$$\rightarrow \text{Rate} = k [\text{H}^+][\text{H}_2\text{O}][\text{CH}_3\text{COOC}_2\text{H}_5]$$

$$\Rightarrow \text{Rate} = k' [\text{CH}_3\text{COOC}_2\text{H}_5]$$

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

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

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

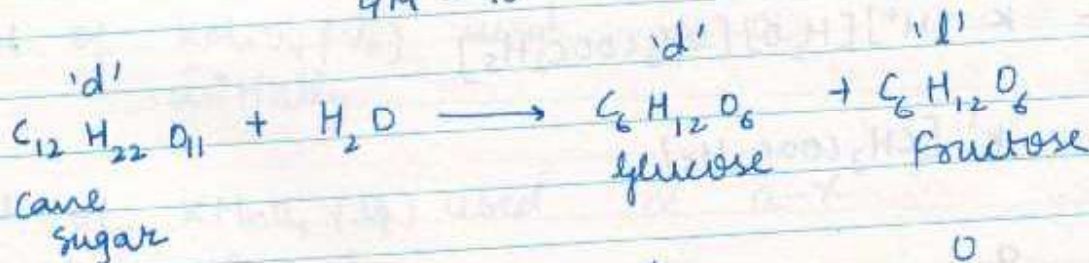
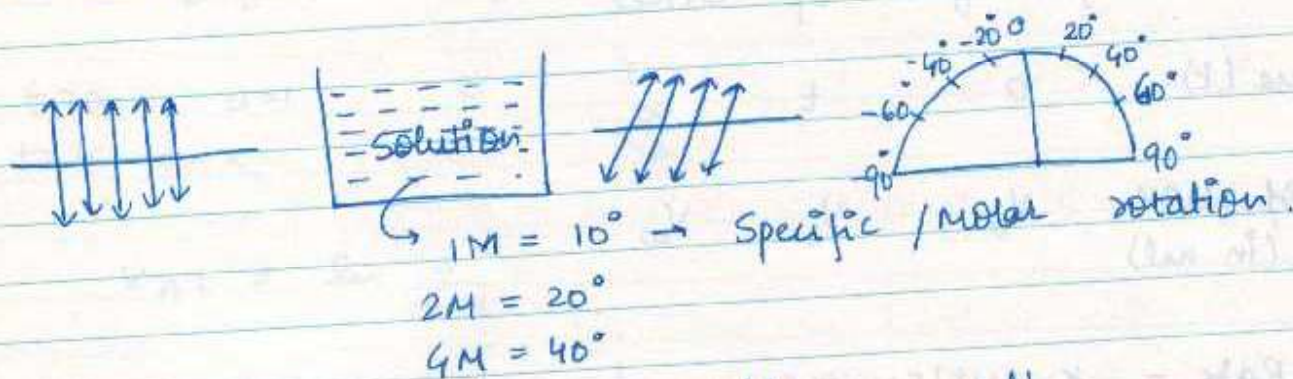
Vol. of NaOH (V_∞) used after long time $\propto C + a$

$$\Rightarrow k't = \ln \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$$

— Auto catalysis.

iv) Inversion of cane sugar \Rightarrow

• Specific Rotation : angle of rotation per unit concentration.



$t=0$ a
 $t=t$ $a-x$
 $t=\infty$ 0

0 x 0
 x a x
 a a a

$k_s, k_g, k_f \rightarrow$ specific rotation of cane sugar, glucose & fructose.

time (t) 0 t ∞

angle of rot. θ_0 θ_t θ_2

$$\theta_0 \propto a \times r_s$$

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

$$\theta_0 \propto a r_g + a r_f$$

$$a = \frac{\theta_0 - \theta_0}{r_g - r_f - r_s}$$

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

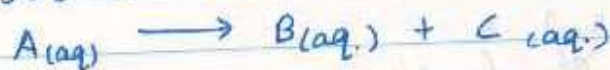
$$= \ln \frac{\theta_0 - \theta_t}{\theta_0 - \theta_0}$$

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

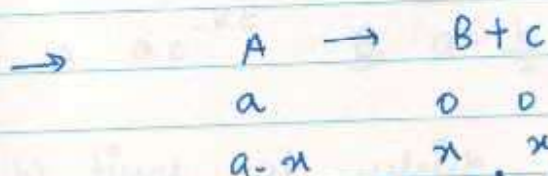
Note :

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

Q. For a rxn



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 racemic mixture will be formed.

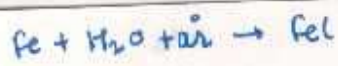


$$k_A 10 = \ln \frac{a}{a-x}$$

$$k_A 20 = \ln \frac{a}{a-x-y}$$

$$\begin{aligned} (a-x) \times 20^\circ + 0 \times 30^\circ - x \times 40^\circ &= 33^\circ & \frac{1}{2} &= \frac{\ln(a-(x+y))}{\ln(a-x)} \\ (a-x-y) \times 20^\circ + y \times 30^\circ + x \times 30^\circ - (x+y) \times 40^\circ &= 18^\circ \end{aligned}$$

32 min



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

Z_{∞}

v) Thickness of Oxide layer formation :

If oxide formation follows 1st order kinetics

time $t \rightarrow \infty$

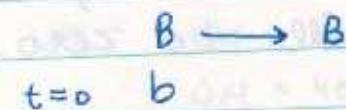
Find k .

Thickness of layer $Z_t \rightarrow Z_{\infty}$

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

vi) Bacteria growth :

If bacteria growth follows 1st order kinetics



$t=0$ b

$t=t$

$b+x$

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

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

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

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

$$\rightarrow kt = \ln 2$$

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

Q. For a Rdn



Kinetics is determined by analysis of partial pressure of gases at different instants. Calculate $a+b+c$.

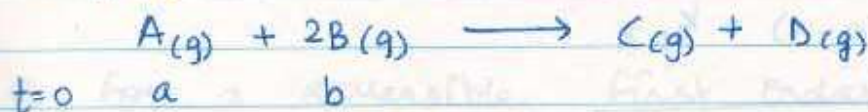
P (mm of Hg)	t=0	t=30 min	t=60 min
P_A	20	10	a = 5
P_B	10000	NA	NA
P_C	0	NA	15
P_D	0	b	NA

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

→ $k_p = k' P_A$ (8) $k \times t = \ln \frac{20}{10} \Rightarrow k = \frac{\ln 2}{30}$

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

Q. Consider the following rxn occurring at constant volume



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

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

A. $a e^{-kt}$ B. $a - \frac{b}{2} (1 - e^{-2kt})$ C. $a - kt$ D. $a - b(1 - e^{-t})$

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

A. $\frac{a}{2k}$ B. $\frac{a}{k}$ C. $\frac{1}{2k} \ln \frac{b}{b-a}$ D. $\frac{\ln 2}{k}$

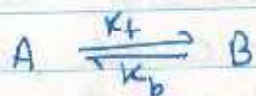
c) For what cond. $(t_{1/2})_A = (t_{1/2})_B$

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 r.a.n.

* Reversible elementary Rdn:

i) First order opposed by first order:



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

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

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

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

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

At equilibrium,

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

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

$$\Rightarrow \frac{dx}{dt} = (k_f + k_b)(x_e - x)$$

$$\Rightarrow \int_0^x \frac{dx}{x_e - x} = \int_0^t (k_f + k_b) dt$$

$$\Rightarrow -[\ln(x_e - x)]_0^x = (k_f + k_b)t$$

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

where,

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

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

$$\rightarrow (k_f + k_b)t = \ln 2$$

$$\Rightarrow t = \frac{\ln 2}{(k_f + k_b)}$$

Q. For a reversible first order rxn



$$k_1 = 10^{-2} s^{-1}$$

$$\& [B]_{eq} = 4$$

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

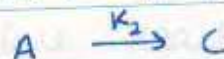
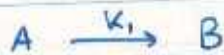
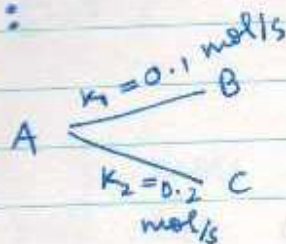
what will be the conc. of B after 30 sec.

$$\rightarrow 0.01 \times 10^{-2} = [B]_{eq} (k_f + k_b) \left| \begin{array}{l} \frac{10^{-4}}{[B]_{eq}} \times \frac{100 \times 10^{-4}}{30} = \ln \frac{[B]_{eq}}{[B]_{eq} - x} \\ \frac{0.15}{4} \end{array} \right.$$

$$\begin{aligned} \frac{1}{4} \quad \frac{3}{4} \\ [A]_{eq} \\ \frac{x_e}{a-x_e} = 4 \\ x_e = 0.04 \times a \\ x_e = 0.04 \times 0.01 \\ x_e = 4 \times 10^{-4} \\ \frac{4}{4-500x} \end{aligned}$$

First order parallel or side rxn:

I:



Imp:

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = k_1 [A]$$

$$-\frac{d[A]}{dt} = \frac{d[C]}{dt} = k_2 [A]$$

$$-\frac{d[A]}{dt} = \left(\frac{d[A]}{dt} \right)_I + \left(\frac{d[A]}{dt} \right)_II$$

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

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

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

For $[B]_t$,

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

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

Similarly

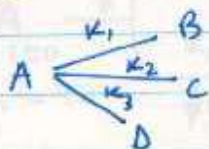
$$[C]_t = \frac{k_2 [A]_0}{k_1 + k_2} (1 - e^{-(k_1 + k_2)t})$$

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

$$\% \text{ B in product} = \frac{k_1}{k_1 + k_2} \times 100$$

$$\% \text{ C in product} = \frac{k_2}{k_1 + k_2} \times 100$$

• Case I :



$$-\frac{d[A]}{dt} = (k_1 + k_2 + k_3) [A]$$

$$\Rightarrow [A]_t = [A]_0 e^{-(k_1 + k_2 + k_3)t}$$

also,

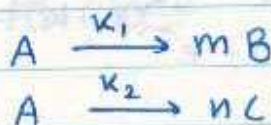
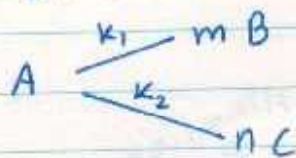
$$[B]_t = \frac{-k_1 [A]_0}{k_1 + k_2 + k_3} (e^{-(k_1 + k_2 + k_3)t} - 1)$$

$$[C]_t = \frac{-k_2 [A]_0}{k_1 + k_2 + k_3} (e^{-(k_1 + k_2 + k_3)t} - 1)$$

$$[D]_t = \frac{-k_3 [A]_0}{k_1 + k_2 + k_3} (e^{-(k_1 + k_2 + k_3)t} - 1)$$

$$\cong [B]_t : [C]_t : [D]_t = k_1 : k_2 : k_3$$

• Case III :



$$- \frac{d[A]}{dt} \text{ (I)} = \frac{1}{m} \frac{d[B]}{dt} = k_1 [A]$$

$$- \frac{d[A]}{dt} \text{ (II)} = \frac{1}{n} \frac{d[C]}{dt} = k_2 [A]$$

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

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

For $[B]_t$,

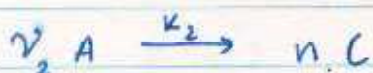
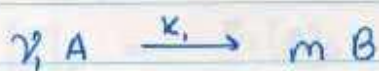
$$\frac{1}{m} \frac{d[B]}{dt} = k_1 [A]_0 e^{-(k_1 + k_2)t}$$

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

$$\text{||} \int \frac{d[C]}{dt} = \frac{n k_2 [A]_0}{(k_1 + k_2)} (1 - e^{-(k_1 + k_2)t})$$

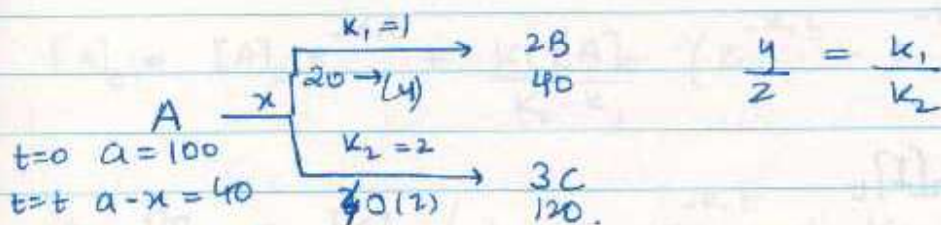
$$\frac{[B]_t}{[C]_t} = \frac{m k_1}{n k_2}$$

• Case IV :



$$-\frac{d[A]}{dt} = (v_1 k_1 + v_2 k_2) [A]$$

For numerical Purpose,



Q. For following I order gaseous rxn,



The initial pressure in a container of cap. VL is 1 atm. Pressure at $t=10s$ is 1.4 atm & after infinite time it becomes 1.5 atm. Find k_1 & k_2

$$\rightarrow 1-x + \frac{2k_1 x}{k_1+k_2} + \frac{k_2 x}{k_1+k_2} = 1.4$$

$$0 + \frac{2k_1}{k_1+k_2} + \frac{k_2}{k_1+k_2} = 1.5$$

$$\frac{k_1}{k_1+k_2} = 0.5$$

* consecutive or sequential Reaction :



Step I



Step II



$$t=0 \quad a \quad 0 \quad 0$$

$$t=t \quad a-x \quad x-y \quad y$$

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

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

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

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

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

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

$$\text{At } t=0 \quad [I]_t = 0$$

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

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

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

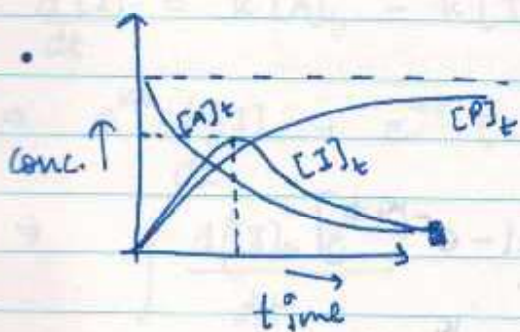
for $[P]_t$,

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

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

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

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

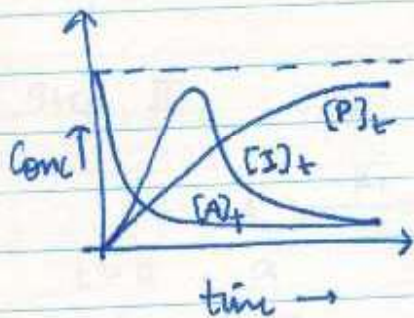
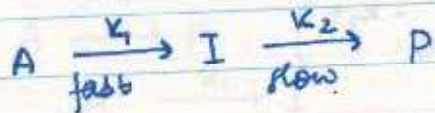


g. Calculate the time at which $[I]$ is max.

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

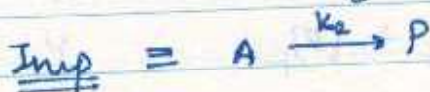
$$\Rightarrow t = \frac{\ln \frac{k_2}{k_1}}{(k_2 - k_1)}$$

Case I: if $k_1 \gg k_2$



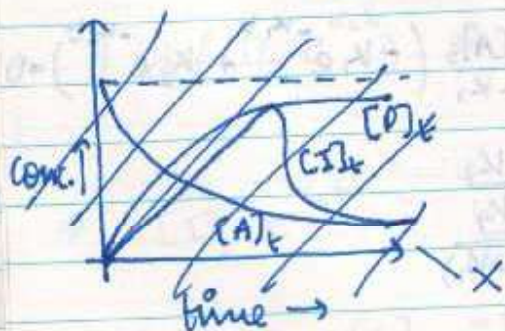
$$[P]_t = [A]_0 \left[1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right]$$

$$[P]_t = [A]_0 \left[1 - e^{-k_2 t} \right]$$

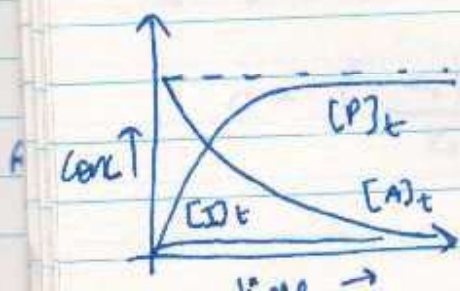


• Conc. of product will depend on slowest step of rxn. From here comes the concept of Rate determining step (RDS). So slowest step will be R.D.S.

Case II: if $k_2 \gg k_1$



$$[P]_t = [A]_0 \left[1 - e^{-k_1 t} \right]$$



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, $k_2 \gg k_1$

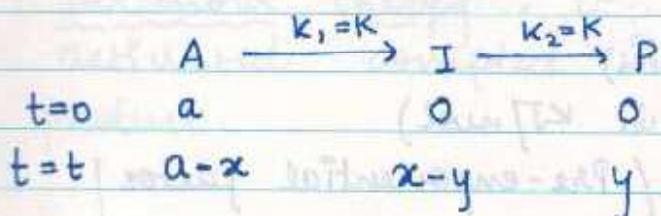
$$\frac{d[I]}{dt} = 0 = k_1 [A]_t - k_2 [I]_t$$

$$\Rightarrow [I]_t = \frac{k_1}{k_2} [A]_t$$

↓

at steady state.

Case III: if $k_1 = k_2 = k$



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

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

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

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

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

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 Rate / Velocity constant

R → Gas constant

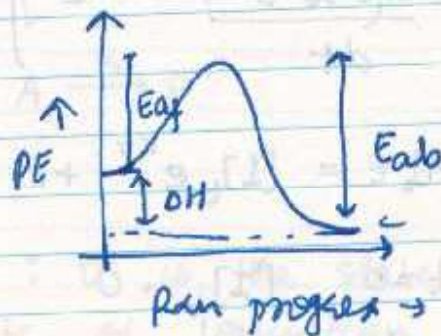
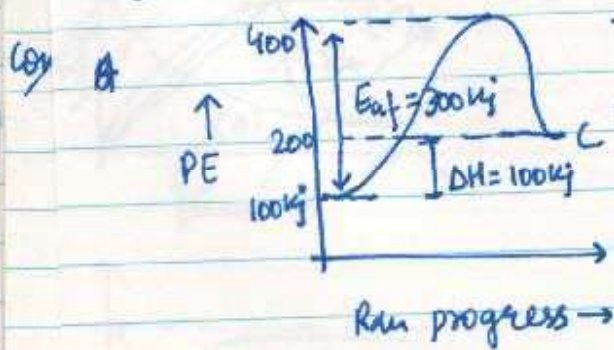
T → Temperature (in Kelvin)

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.]



Ex 2



$$\Delta H = E_{af} - E_{ar} = E_p - E_r$$

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

• Activation energy: Minimum K.E. possessed by reactant molecules in order to get converted into product.

• Threshold Energy: It is min. P.E. possessed by activated complex in order to get converted to product.

* Variation of k:

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

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

\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:

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

Considering A & E_a to be temp. independent

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

At temp. T_1 ,

$$\ln k_{T_1} = \ln A - \frac{E_a}{RT_1} \quad \text{--- (1)}$$

At temp. T_2 ,

$$\ln k_{T_2} = \ln A - \frac{E_a}{RT_2} \quad \text{--- (2)}$$

(II) - (I)

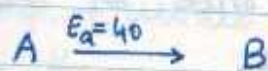
$$\ln \frac{k_{T_2}}{k_{T_1}} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

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

• if $E_a > 0 \Rightarrow$ on \uparrow temp., k will \uparrow

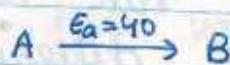
if $E_a < 0 \Rightarrow$ on \uparrow temp., k will \downarrow

Case I:



$$\frac{k_{410K}}{k_{400K}}$$

<



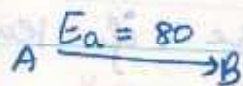
$$\frac{k_{310K}}{k_{300K}}$$

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

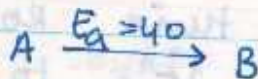
Rate of rxn is more sensitive to temp. at low temperature.

Case II:



$$\frac{k_{310K}}{k_{300K}}$$

>



$$\frac{k'_{310K}}{k'_{300K}}$$

% change will be more where activation energy is high.

* Temperature Coefficient (μ):

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

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

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

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

200K \longrightarrow 210K \longrightarrow 220K
2 \quad 2.2 \quad 2.2 (actually slightly less than 4x)

Q. For rxn $A \rightarrow B$ temp. coeff. is 3 at 25°C.
How many times ROR will increase if temp. is \uparrow from 25°C to 75°C

$\rightarrow 3^5$

Case II:

If temp. coeff. depends on temp.

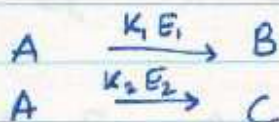
Q. The temp. coeff. (n) of k at 300K is "e".
Assuming temp. coeff. to be dependent on temp. what would be the value of

$$\ln \frac{k_{620\text{K}}}{k_{300\text{K}}} = ?$$

$$\rightarrow \ln \frac{k_{310\text{K}}}{k_{300\text{K}}} = \frac{E_a}{R} \left(\frac{10}{310 \cdot 300} \right) = 1$$

$$\ln \frac{k_{620\text{K}}}{k_{300\text{K}}} = \frac{310 \cdot 300}{10} \times \frac{32}{620 \cdot 300} = \boxed{16}$$

Q. For 2 parallel Rxn



Show that for disappearance of A net activation energy (E_3) = $\frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}$

$$\rightarrow k_1 = A_1 e^{-E_1/RT} \quad \& \quad k_2 = A_2 e^{-E_2/RT}$$

$$k_3 = k_1 + k_2 \Rightarrow A_3 e^{-E_3/RT} = A_1 e^{-E_1/RT} + A_2 e^{-E_2/RT}$$

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

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

$$K_3 E_3 = K_1 E_1 + K_2 E_2$$

g. 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

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

$$E_a = 16 \text{ kcal/mol}$$

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

$$\rightarrow \text{Lang.} = \frac{1}{k_A}$$

$$k = 1.25 \times 10^8 e^{-\frac{16 \times 10^3 \times 4.2}{400 \times 8.21}}$$

$$= 1.25 \times 10^8 e^{-20} = \frac{1}{4} = \boxed{4 \text{ s}} = \text{Lang.}$$

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.

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

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

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

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

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

Case 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 300K if expression of rate constant as f'n of temp is given by

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

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

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

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

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

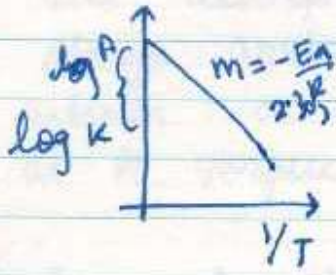
$$\Rightarrow \frac{d(\ln k)}{dT} = 0 + \frac{40}{T^2} - \frac{600}{T^3}$$

$$\Rightarrow E_a = R\left(40 - \frac{600}{T}\right) = 38R$$

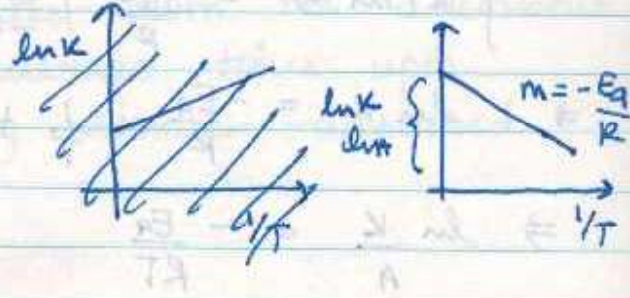
40x3
12000
11700
30R

* Graphical Representation

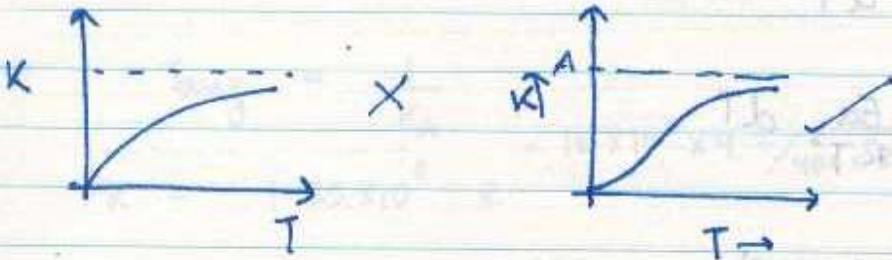
1. $\log k$ v/s $1/T$



2. $\ln k$ v/s $1/T$



3. k v/s T



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

* Theories of Chemical Reaction :

1] Collision Theory :

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

Accⁿ 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

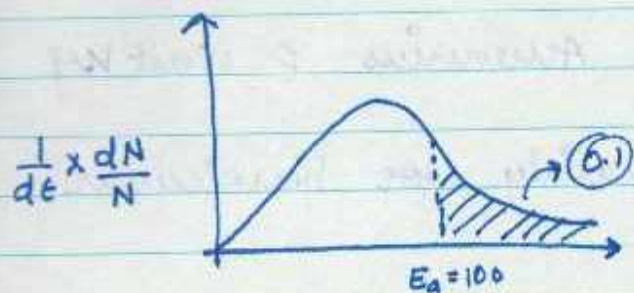
If all these collisions were effective then every rxn would have been completed within a fraction of time but this is not the case. It means all collisions are not effective.

• Effective collision \Rightarrow These are the collisions which cause product formation

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

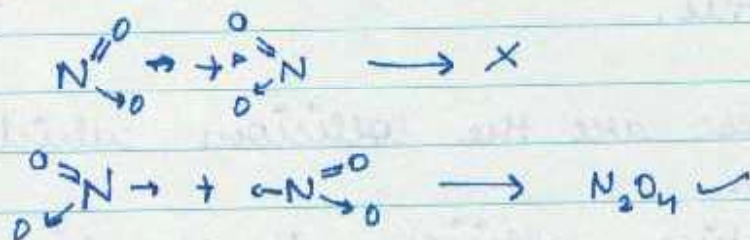
- i) Energy barrier
- ii) Orientation factor

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



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

- 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

$$\begin{aligned} \text{ROR} &= \text{collision freq.} \times \text{effective collision} \\ &= \text{collision freq.} \times \text{collision with sufficient energy} \times \text{collision with proper orientation} \end{aligned}$$

$$= \left(\pi (\sigma_A + \sigma_B)^2 u_{\text{avg}} N_A^* N_B^* \right) \times e^{-E_a/RT} \times P$$

$$= \left(\pi (\sigma_A + \sigma_B)^2 u_{\text{avg}} \times N_0^2 \times P \right) e^{-E_a/RT} \times [A][B]$$

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

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

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

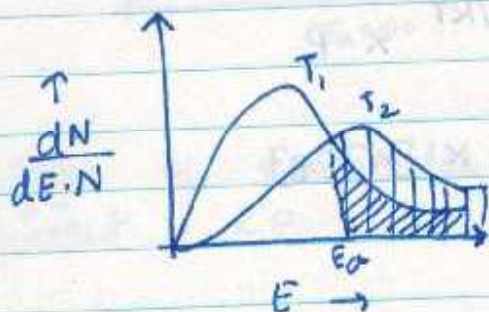
$$A = \pi (\sigma_A + \sigma_B)^2 u_{\text{avg}} \times N_0^2 \times P$$

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

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

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

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



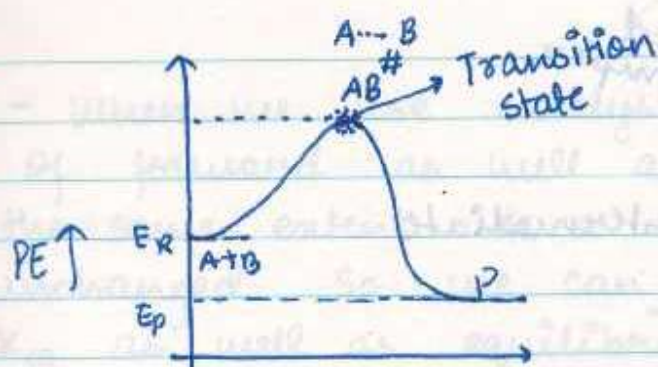
* Activated Complex Theory:

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

- It can be applied for gaseous reactants as well as for the rxns taking place in liquid solⁿ.
- Steric factor appears automatically in contrast to collision theory where 'P' has to be grafted.

- Reaction Profile :

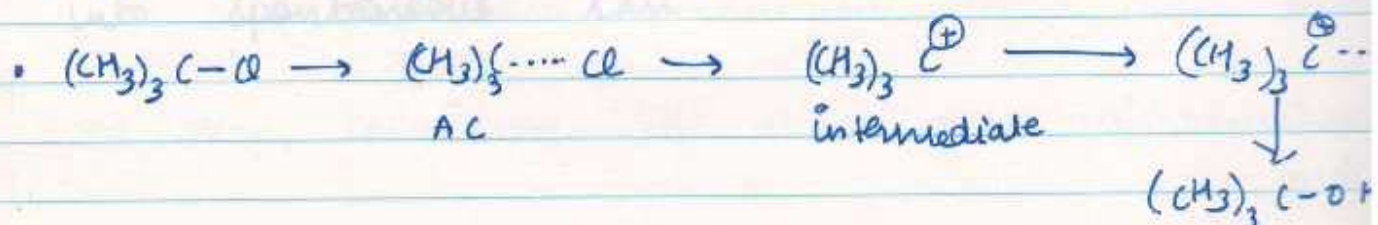
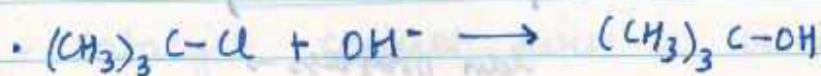


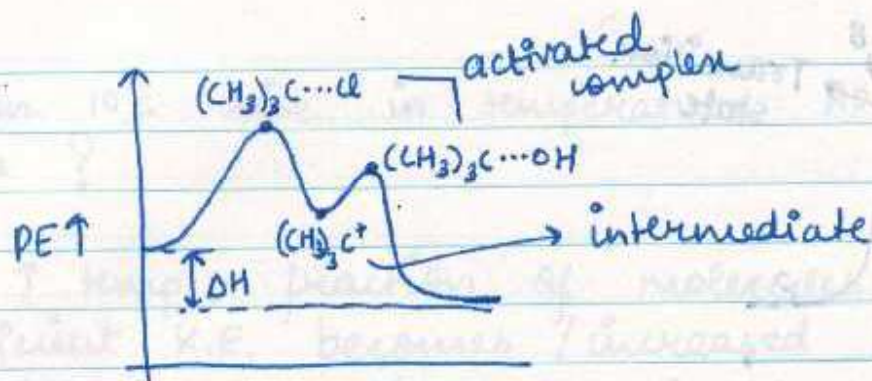


- Initially only react A & B are present.
- As rxn proceeds, A & B come into contact, distraught & begin to exchange atoms.
- As PE ↑ to a maxima, the cluster of atoms corresponds to the region near maxima are referred as activated complex. The confⁿ at actual peak of curve is called transition state.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

Note : AB[#] is not an intermediate compd in rxn but rather it is a structure that is in process of change in direcⁿ of product.

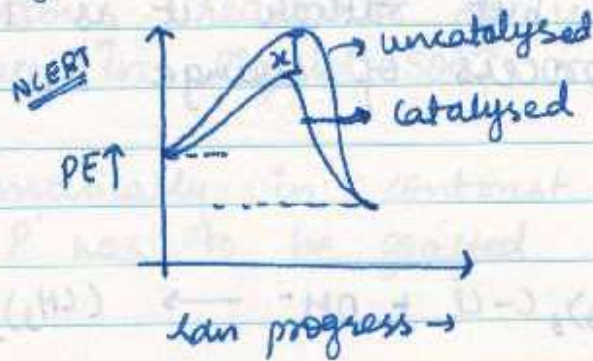
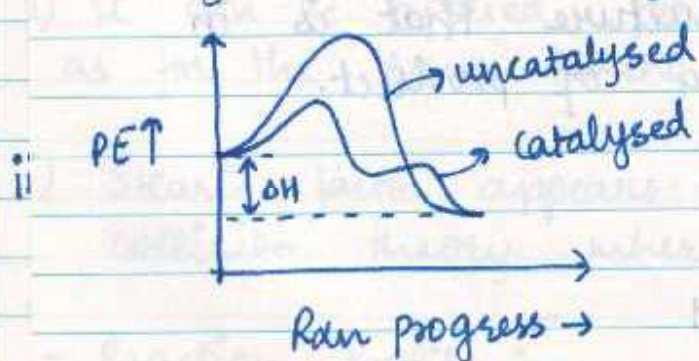
SN₁





* 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



- 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,

$$K_{eq} = \frac{k_f}{k_b} = \frac{A_f e^{-E_{af}/RT}}{A_b e^{-E_{ab}/RT}} = A e^{-(E_{af}-E_{ab})/RT}$$

For catalysed,

$$k_f' = A_f e^{-(E_{af}-x)/RT} = A_f e^{-E_{af}/RT} \cdot e^{x/RT}$$

$$k_b' = A_b e^{-(E_{ab}-x)/RT} = A_b e^{-E_{ab}/RT} \cdot e^{x/RT}$$

$$K_{eq} = \frac{k_f'}{k_b'} = A e^{-(E_{af}-E_{ab})/RT}$$

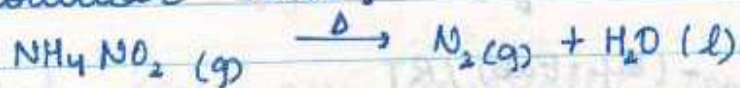
- Catalyst does not alter value of ΔH or ΔG for rxn.
- Catalyst cannot turn a non-spontaneous rxn into spontaneous rxn.

* MECHANISM OF RAN :

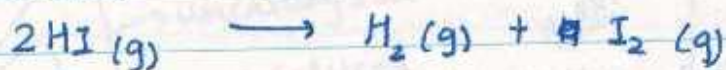
- It represents a path thru which the reactants get converted into products.
- During mechanism rdn is explained step wise.
- Rate determining step (RDS) : This is the slowest step of rdn. (If rdn takes place in more than one step).
- Molecularity : The no. of reacting species (atoms, ions, molecules) taking part in an elementary rdn which must collide simultaneously in order to bring about a chemical change.

Types:

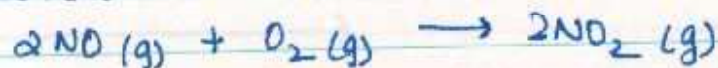
a) Unimolecular Rdn :



b) Bimolecular Rdn :



c) Trimolecular Rdn :



• 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.

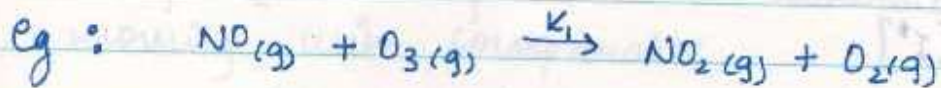
Q. An elementary rxn can't be of fractional order.

→ True.

Case I: If reactants directly get converted to product.

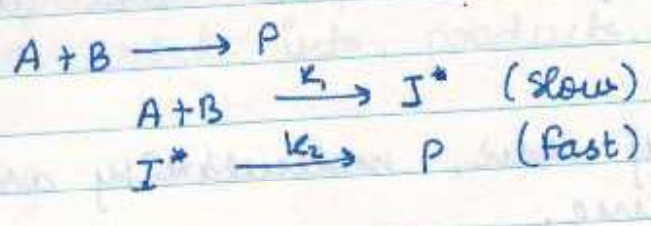


$$\text{Rate} = k_1 [A][B]$$

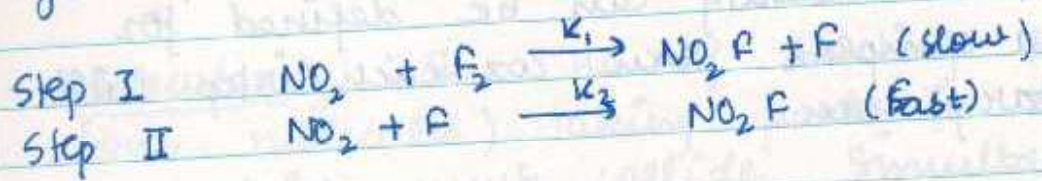
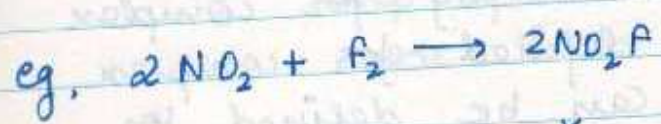


$$\text{Rate} = k_1 [\text{NO}][\text{O}_3]$$

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

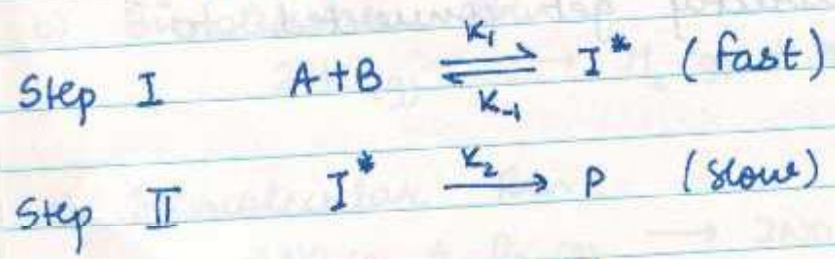


$$\text{Rate} = k_1 [A][B]$$



$$\text{Rate} = k_1 [NO_2][F_2]$$

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



$$\begin{aligned} \text{Rate} &= k_2 [I^*] \\ &= k_2 \times \frac{k_1}{k_{-1}} v [A][B] \end{aligned}$$

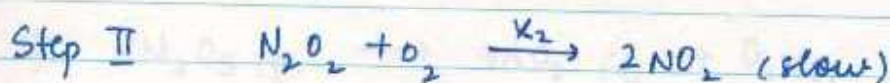
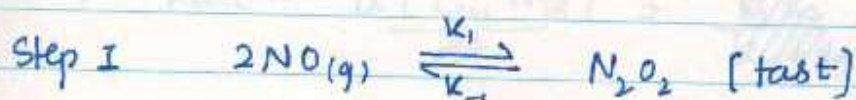
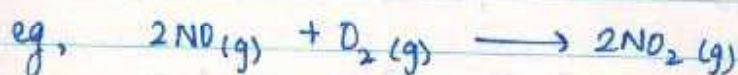
$$ROR = k_{or} [A][B]$$

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

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

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

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

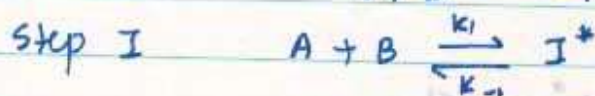


$$\frac{k_1}{k_{-1}} = \frac{[N_2O_2]}{[NO]^2}$$

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

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

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



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

We can apply steady state on $[\text{I}^*]$

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

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

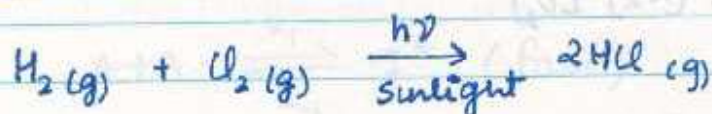
if $k_1, k_{-1} \gg k_2$,

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

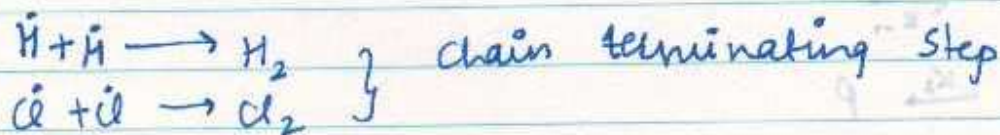
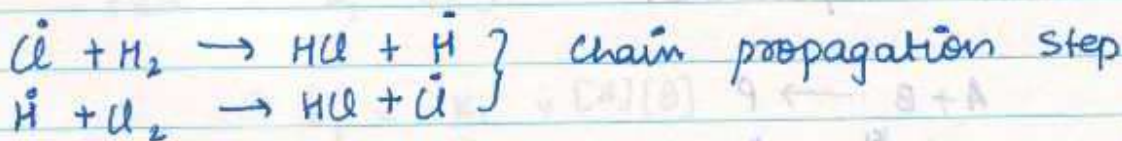
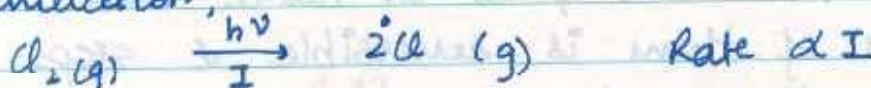
if $k_2 \gg k_{-1}$,

$$\text{Rate} = k_1 [\text{A}][\text{B}]$$

* Photochemical Rexn:



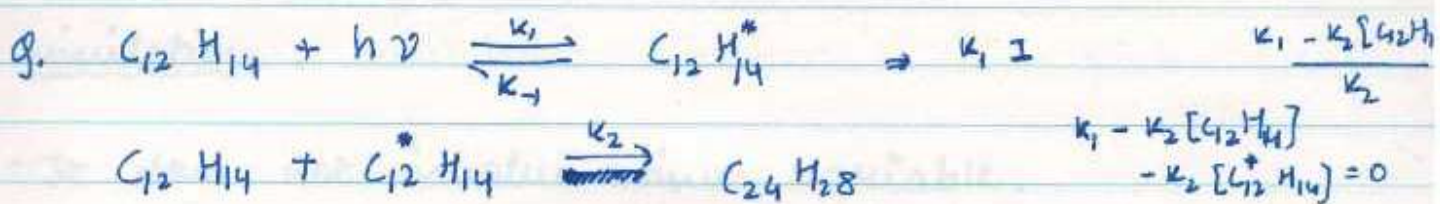
Chain initiation,



• first step of photochemical rxn will be of zero order. Its rate will depend on intensity of light (I).

• Photochemical rxn will be complex.

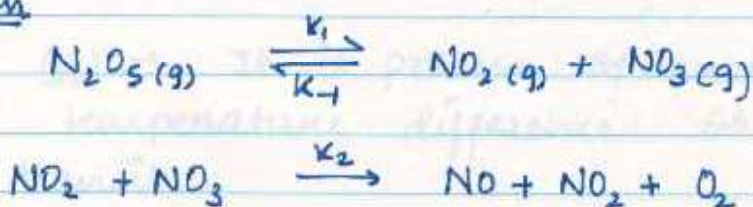
• Photochemical rxn can have any order.



$$\rightarrow \text{Rate} = \frac{d[C_{24}H_{28}]}{dt} = \frac{k_1 k_2}{k_1 + k_2} [C_{12}H_{14}] \cdot [k_1 - k_2 [C_{12}H_{14}]]$$



Mech



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