

Chemical Kinetics

It is the branch of chemistry which deals with the study of rate of reacⁿ & factors affecting rate of reacⁿ.

$$r = \frac{\Delta C}{\Delta t}$$

Type of reacⁿ

1. Very fast reacⁿ or instantaneous reacⁿ :

$\Delta t \rightarrow$ very small

$r \rightarrow$ very high

eg : ionic reacⁿ $\rightarrow 10^{-14}$ s to 10^{-16} s

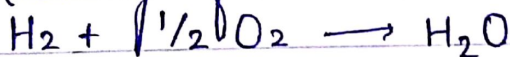


2. Very slow reacⁿ :

$\Delta t \rightarrow$ very large

$r \rightarrow$ very small

eg: Rusting of Iron

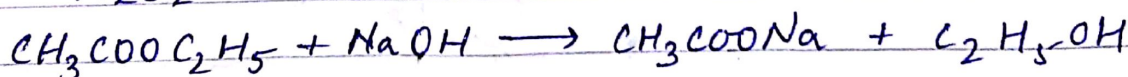


3. Moderate reacⁿ :

$\Delta t \rightarrow$ neither too small nor too large

$r \rightarrow$ intermediate value

eg $\text{H}_2\text{O}_2 \rightarrow \text{H}_2 + \text{O}_2$

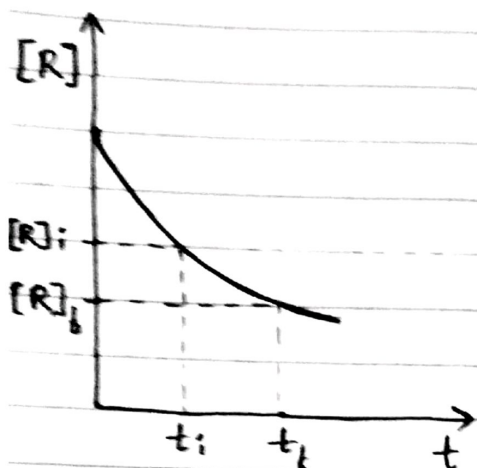
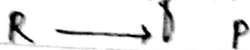


Rate of Reaction: It is defined as the change in concⁿ of reactant or product per unit time.

******, It is always +ve.

Average rate

It is change in concⁿ of reactant / product in an interval of time.

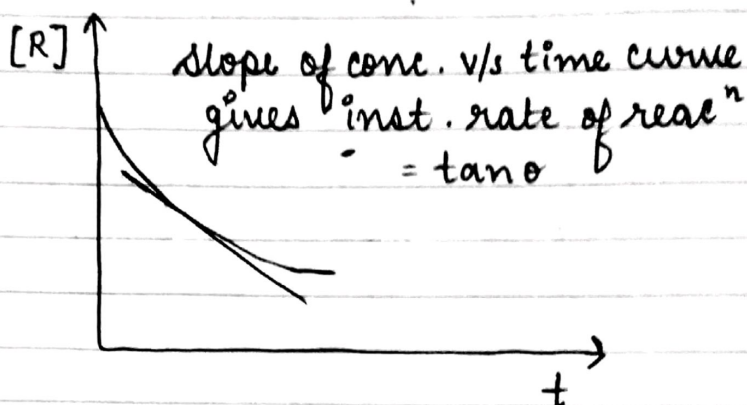


$$r = -\frac{\Delta[R]}{\Delta t} = -\frac{([R]_f - [R]_i)}{t_f - t_i}$$

-ve sign shows that conc. of R ↓ing

Instantaneous rate

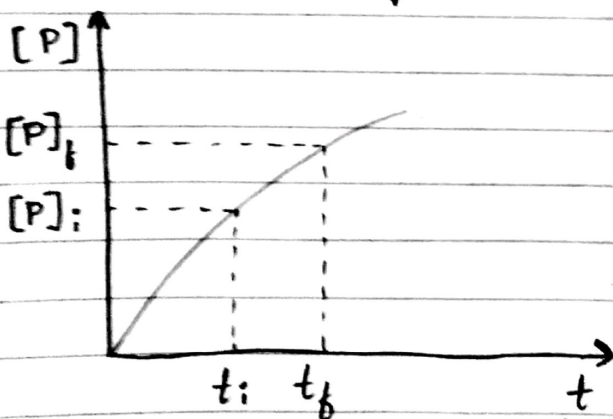
It is change in conc. of reactant / product at an instant.



$$r_{inst} = -\left(\frac{\Delta[R]}{\Delta t}\right)_{\lim_{t \rightarrow 0}} = (r_{avg})_{\lim_{t \rightarrow 0}}$$

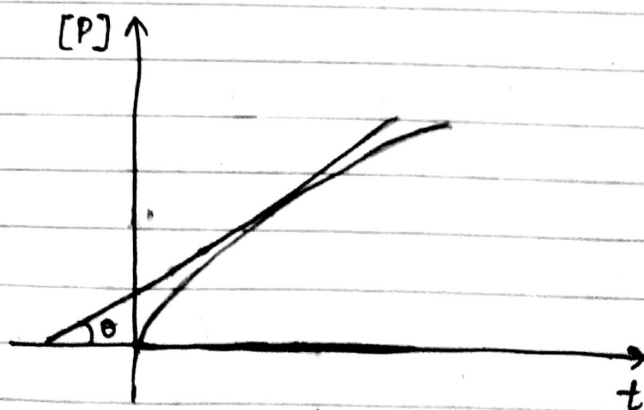
$$r_{inst} = -\left(\frac{[R]_f - [R]_i}{t_f - t_i}\right)_{\lim_{t \rightarrow 0}}$$

$$r_{inst} = -\frac{d[R]}{dt}$$



$$r = +\frac{\Delta[P]}{\Delta t} = +\frac{([P]_f - [P]_i)}{t_f - t_i}$$

+ve sign shows that concⁿ of Product ↑ing



$$r_{inst} = (r_{avg})_{\lim_{t \rightarrow 0}}$$

$$r_{inst} = \left(\frac{[P]_f - [P]_i}{t_f - t_i}\right)_{\lim_{t \rightarrow 0}}$$

$$r_{inst} = \frac{d[P]}{dt} = \tan \theta$$

Rate in terms of stoichiometric coefficient :-
 $m_1 A + m_2 B \rightarrow n_1 C + n_2 D$ [Balanced reaction]
rate of disappearance of A = $-\frac{d[A]}{dt}$

rate of disappearance of B = $-\frac{d[B]}{dt}$

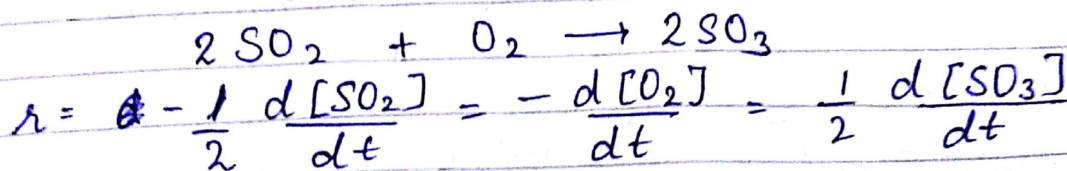
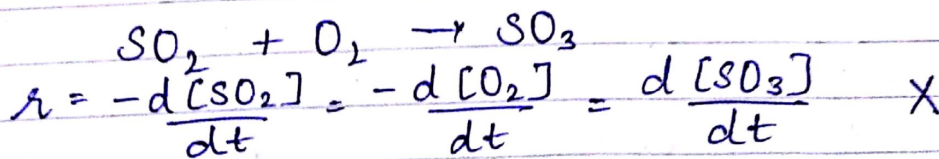
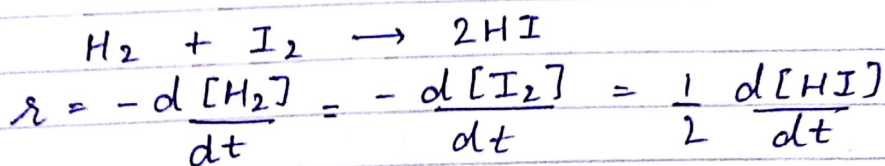
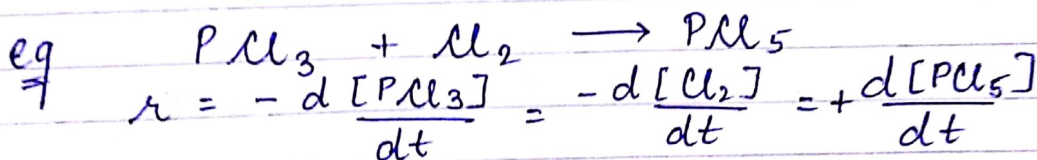
rate of appearance of C = $+\frac{d[C]}{dt}$

rate of appearance of D = $+\frac{d[D]}{dt}$

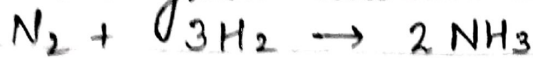
$$r = -\frac{1}{m_1} \frac{d[A]}{dt} = -\frac{1}{m_2} \frac{d[B]}{dt} = +\frac{1}{n_1} \frac{d[C]}{dt} = +\frac{1}{n_2} \frac{d[D]}{dt}$$

$r = \frac{\text{change in conc.}}{\text{time}}$

Unit : $\text{conc} \cdot \text{time}^{-1}$
 $\text{mol L}^{-1} \text{s}^{-1}$
 $\text{mol L}^{-1} \text{min}^{-1}$



Ques For the given reacⁿ



Rate of formation of ammonia is $2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
then find rate of disappearance of Hydrogen?

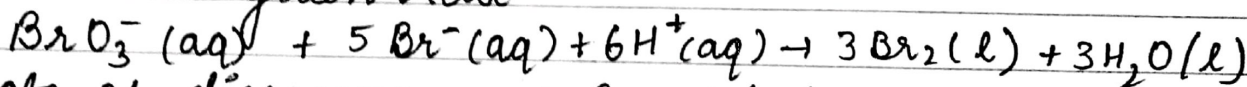
- ① $3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ ② $2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
③ $4 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ ④ $6 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

$$r = + \frac{1}{2} \frac{d[\text{NH}_3]}{dt} = - \frac{1}{3} \frac{d[\text{H}_2]}{dt}$$

$$= \frac{2 \times 10^{-4} \times 3}{2} = - \frac{d[\text{H}_2]}{dt}$$

$$- \frac{d[\text{H}_2]}{dt} = 3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

Ques for the given reacⁿ



rate of disappearance of Bromide ion.

① $\frac{d[\text{Br}^-]}{dt} = - \frac{3}{5} \frac{d[\text{Br}_2]}{dt}$ ② $\frac{d[\text{Br}^-]}{dt} = - \frac{5}{3} \frac{d[\text{Br}_2]}{dt}$

③ $\frac{d[\text{Br}^-]}{dt} = \frac{3}{5} \frac{d[\text{Br}_2]}{dt}$ ④ $\frac{d[\text{Br}^-]}{dt} = \frac{5}{3} \frac{d[\text{Br}_2]}{dt}$

$$- \frac{1}{5} \frac{d[\text{Br}^-]}{dt} = \frac{1}{3} \frac{d[\text{Br}_2]}{dt}$$

$$\frac{d[\text{Br}^-]}{dt} = - \frac{5}{3} \frac{d[\text{Br}_2]}{dt}$$

Ques $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$

If rate of disappearance of Hydrogen is $12 \text{ mol L}^{-1} \text{ s}^{-1}$ then find.

① rate of appearance of NH_3

$$- \frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

$$2 \times \frac{12^4}{3} = \frac{d[\text{NH}_3]}{dt}$$
$$8 = \frac{d[\text{NH}_3]}{dt}$$

② rate of disappearance of N_2

$$-\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt}$$

$$= \frac{12}{3} = 4$$

③ rate of reaⁿ

$$r = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = 4$$

Ques H_2 If rate of disappearance of Hydrogen is $6 \text{ g L}^{-1} \text{ s}^{-1}$ then solve above ques. again.

$$n = \frac{6 \text{ g}}{2} = 3 \text{ mol}$$

① $-\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$

$$\frac{3 \times 2}{3} = \frac{d[\text{NH}_3]}{dt}$$

$$\frac{d[\text{NH}_3]}{dt} = 2 \text{ mol L}^{-1} \text{ s}^{-1}$$

For Gas Reacⁿ

$$PV = nRT$$

$$C = \frac{n}{V} = \frac{P}{RT}$$

$$r = \frac{dc}{dt} = \frac{1}{V} \left(\frac{dn}{dt} \right) = \frac{1}{RT} \left(\frac{dP}{dt} \right)$$

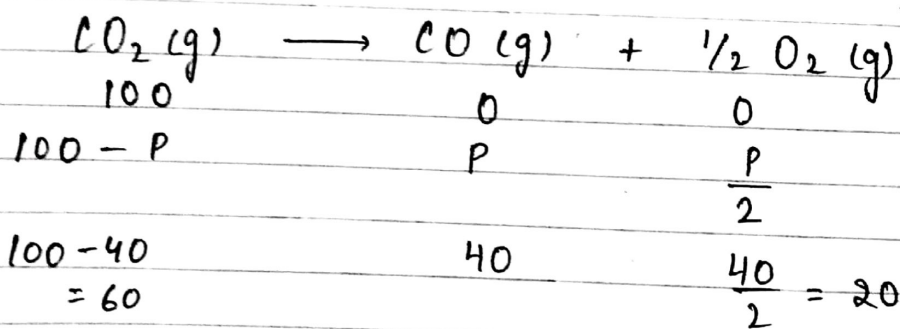
rate in terms of concⁿ

rate in terms moles

↳ rate in terms of Pr.

Ques $\text{CO}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ at 300 K gaseous reacⁿ shows ↑ in Pr. from 100 mm of Hg to 120 mm of Hg in 5 sec then find
① rate in terms of Pr.

$$r = \frac{1}{RT} \left(\frac{120 - 100}{5} \right) = \frac{1}{8.4 \times 300} \times \frac{20}{5} = \frac{4}{2520}$$



$$100 - P + P + \frac{P}{2} = 120$$

$$P = 40 \text{ mm of Hg}$$

$$r = \frac{dP}{dt} = - \left[\frac{d(P)}{dt} \right]_{\text{CO}_2}$$

$$= - \frac{[P_f - P_i]_{\text{CO}_2}}{t}$$

$$= - \frac{[60 - 100]}{5}$$
$$= 8 \text{ mm of Hg/s} = \frac{8}{760} \text{ atm/s}$$

② rate in terms of concⁿ.

$$r = \frac{dc}{dt} = \frac{1}{RT} \times \frac{dp}{dt}$$
$$= \frac{1}{0.08 \times 300} \left(\frac{8}{760} \right) \text{ mol L}^{-1} \text{ s}^{-1}$$
$$= \frac{1}{760 \times 3} \text{ mol L}^{-1} \text{ s}^{-1}$$

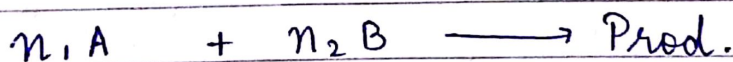
③ rate of disappearance of CO₂

$$\frac{-d[\text{CO}_2]}{dt} = r$$

$$\frac{-d[\text{CO}_2]}{dt} = \frac{1}{760 \times 3} \text{ mol L}^{-1} \text{ s}^{-1}$$

Rate of Law :- It representation of rate of reacⁿ
in terms of concⁿ of reactant

• It is an experimental concept.



accⁿ to Law of Mass Action

$$r \propto [A]^{n_1} [B]^{n_2}$$

accⁿ to experimental concept,

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

$r \rightarrow$ rate of reacⁿ

$k \rightarrow$ rate const.

$x \rightarrow$ order of reacⁿ w.r.t. A

$y \rightarrow$ order of reacⁿ w.r.t. B

$(x+y) \rightarrow$ order of overall reacⁿ

x & y may or may not be equal to n_1 & n_2 resp.

$$[A] = [B] = 1$$
$$r = k [1]^x [1]^y$$
$$r = k$$

Rate constant (k): Rate of reacⁿ when concⁿ of reactants is unity then rate is c/a rate constant or specific rate of reacⁿ.

- k depends upon:
- nature of reactant
 - temp.
 - catalyst

Note: Rate const. does not depend upon concⁿ.

Unit of k:

$$A \longrightarrow B$$
$$r = k [A]^n \quad n \rightarrow \text{order of reac}^n$$
$$\text{mol L}^{-1} \text{s}^{-1} = k [\text{mol L}^{-1}]^n$$
$$k = (\text{mol L}^{-1})^{1-n} \text{s}^{-1}$$

for zero order reac ⁿ n=0	Unit of k
for first order reac ⁿ n=1	$\text{mol L}^{-1} \text{s}^{-1}$
for 2 nd order reac ⁿ n=2	s^{-1}
	$\text{mol}^{-1} \text{L s}^{-1}$

Ques for which order unit of rate const. is same that of rate of reacⁿ?
n=0

Determination of rate law & order from exp. :-
Ques for the given reacⁿ $A + B \longrightarrow C + D$
following data is obtained

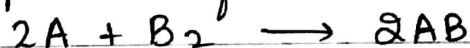
Exp. No.	[A] mol L ⁻¹	[B] mol L ⁻¹	rate (mol L ⁻¹ s ⁻¹)
1.	0.1	0.2	2 × 10 ⁻²
2.	0.2	0.2	8 × 10 ⁻²
3.	0.2	0.4	16 × 10 ⁻²

Find rate law & order of reacⁿ?

$$r = k[A]^2[B]^2$$

$$2 \times 10^{-2} = k [$$

Ques The exp. data for the reacⁿ



Exp	[A]	[B]	rate (mol L ⁻¹ s ⁻¹)
1.	0.50	0.50	1.6 × 10 ⁻⁴
2.	0.5	1.00	3.2 × 10 ⁻⁴
3.	1.0	1.00	6.4 × 10 ⁻⁴

find rate law

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

$$1.6 \times 10^{-4} = k [0.50]^x [0.50]^y \quad \text{--- (1)}$$

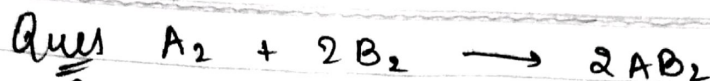
$$3.2 \times 10^{-4} = k [0.50]^x [1]^y$$

$$\textcircled{1} / \textcircled{2} \quad \left(\frac{1}{2}\right) = 1 \times \left(\frac{1}{2}\right)^y$$

$$6.4 \times 10^{-4} = k [1]^x [1]^y$$

$$\textcircled{2} / \textcircled{3} \Rightarrow \frac{1}{2} = \left(\frac{1}{2}\right)^x \quad \Rightarrow x = 1$$

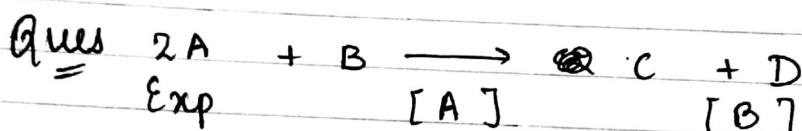
$$r = k[A]^1[B]^1$$



Exp.	$[A_2]$	$[B_2]$	rate ($\text{mol L}^{-1} \text{s}^{-1}$)
1.	0.1	0.1	5×10^{-2}
2.	0.2	0.2	$1 \times 10^{-1} = 10 \times 10^{-2}$
3.	0.2	0.4	2×10^{-1}

Find rate law.

$$r = k [A]^0 [B]^1$$



Exp	$[A]$	$[B]$	Initial rate of form of D (m s^{-1})
1.	0.1	0.1	6×10^{-3}
2.	0.3	0.2	7.2×10^{-2}
3.	0.3	0.4	2.88×10^{-1}
4.	0.4	0.1	2.40×10^{-2}

$$r \propto [A]^1 [B]^2$$

Ques The reacⁿ b/w A & B is first order w.r.t. to A & zero order w.r.t. B. Fill in the blanks in the following table

Exp	$[A] \text{ mol L}^{-1}$	$[B] \text{ mol L}^{-1}$	Initial rate $\text{mol L}^{-1} \text{min}^{-1}$
1.	0.1	0.1	2×10^{-2}
2.	0.2	0.2	4×10^{-2}
3.	0.4	0.4	8×10^{-2}
4.	0.1	0.2	2×10^{-2}

$$r = k [A]^1 [B]^0$$

Ques for the reacⁿ $2A + B \rightarrow A_2B$
 $r = k[A][B]^2$ where k is ~~2~~ $2 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$
 Cal. initial rate of reacⁿ when $[A] = 0.1 \text{ M}$ $[B] = 0.2 \text{ M}$
 Calc. rate of reacⁿ after conc. of A is reduced to 0.06 M

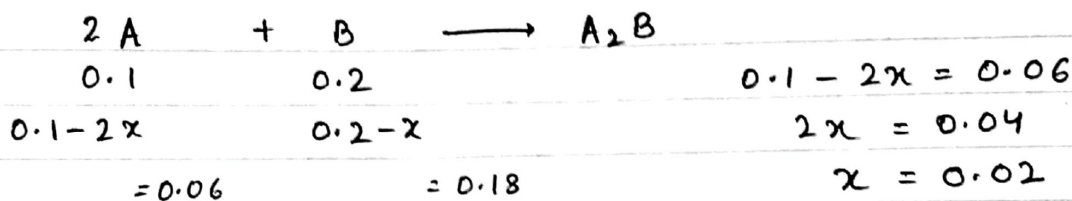
$$r = k[A][B]^2$$

$$= 2 \times 10^{-6} [0.1] [0.2]^2$$

$$= 2 \times 10^{-6} \times 0.1 \times 0.04$$

$$= 0.008 \times 10^{-6}$$

$$= 8 \times 10^{-9}$$

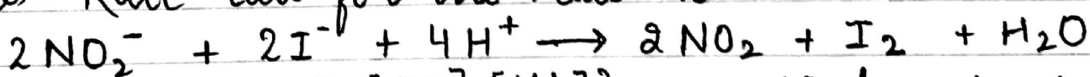


$$r = ~~k[A][B]^2~~ 2 \times 10^{-6} [0.06]^2 [0.18]$$

$$= 2 \times 10^{-6} \times 0.0036 \times 0.18$$

$$= 36 \times 36 \times 10^{-6} \times 10^{-6} =$$

Ques Rate law for the reacⁿ is



$r = k[\text{NO}_2^-][\text{I}^-][\text{H}^+]^2$ then find rate of reacⁿ if

- ① conc. of all reactant is doubled
- ② Vol. of reacⁿ mixture is doubled
- ③ pH of solⁿ ↑ by 1 unit.

$$r = k[\text{NO}_2^-][\text{I}^-][\text{H}^+]^2$$

$$r' = k[2\text{NO}_2^-][2\text{I}^-][2\text{H}^+]^2$$

$$r' = 16r$$

$$r'' = k \left[\frac{\text{NO}_2^-}{2} \right] \left[\frac{\text{I}^-}{2} \right] \left[\frac{\text{H}^+}{2} \right]^2$$

$$r'' = \frac{r}{16}$$

~~pH~~ $r'' = k[\text{NO}_2^-][\text{I}^-] \left[\frac{\text{H}^+}{10} \right]^2 = \frac{r}{100}$

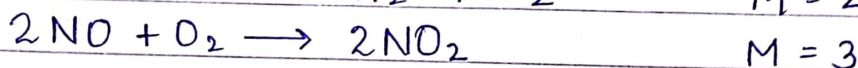
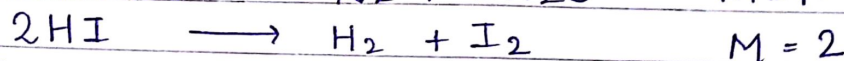
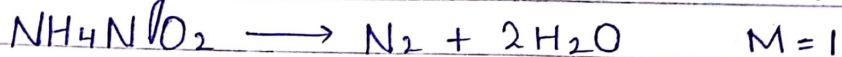
Molecularity of a Reacⁿ

no. of molecules / atoms / ions collide in an elementary reacⁿ is c/a molecularity of a Reacⁿ.

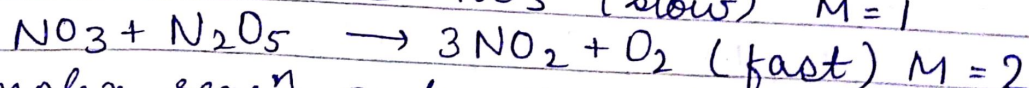
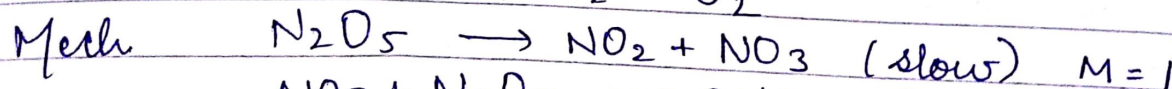
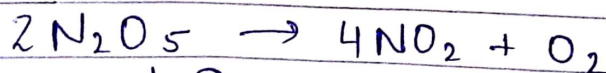
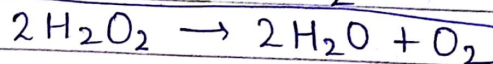
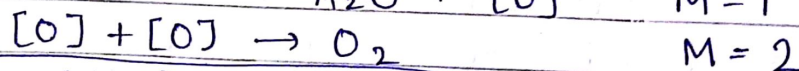
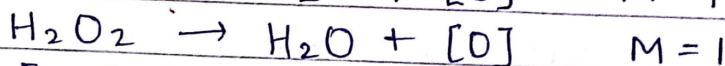
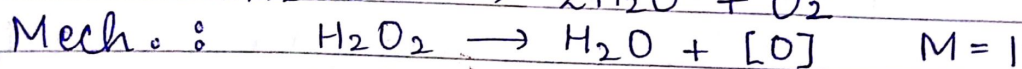
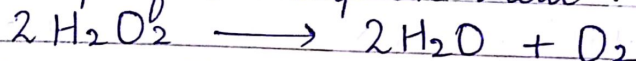
no. of atoms / molecules / ions colliding f. to form a product.

Type of reacⁿ :-

1. **Elementary Reacⁿ** : Single step reacⁿ.
no. of reacting species in an elementary reacⁿ c/a Molecularity.



Complex reaction : Molecularity is not defined for complex reacⁿ but defined for single step of a complex reacⁿ.

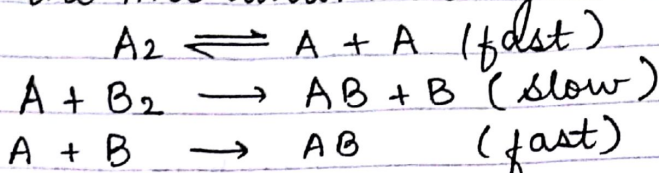


In complex reacⁿ order of reacⁿ is given by slow step

$$r = k [\text{N}_2\text{O}_5]^1$$

NEET-17

Ques A hypothetical reacⁿ $A_2 + B_2 \rightarrow 2AB$ follows
the mechanism as given below,



The order of overall reacⁿ is -

- ① 2 ② 1 ③ $1\frac{1}{2}$ ④ 0

$$r = k[A]^1[B_2]^1$$

intermediate should not be present rate law.

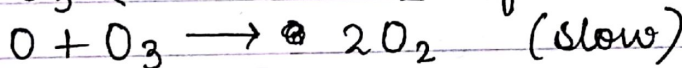
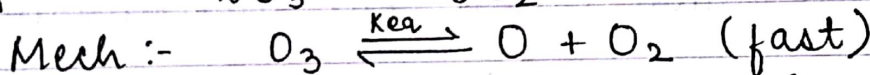
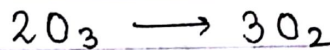
$$K_{eq} = \frac{[A]^2}{[A_2]}$$

$$[A] = K_{eq}^{1/2} [A_2]^{1/2}$$

Put in ①

$$\begin{aligned} r &= k \cdot K_{eq}^{1/2} [A_2]^{1/2} \\ &= k' [A_2]^{1/2} [B_2]^1 \end{aligned}$$

Ques



$$r = k[O][O_3]$$

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

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

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

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

$$\text{order} = 1$$

NEET-17

Ques Mechanism of

Note-① Molecularity can never be -ve, zero or fractional value.

② Molecularity is always less than or equal to 3.

Molecularity

→ It is total no. of atom/
ion/^{molecules} colliding in an
elementary reacⁿ.

- Theoretical concept
- Molecularity is not defined for complex reacⁿ
- Molecularity can never be -ve, zero, fractional

Order.

Sum of power of concⁿ
terms in k & t .

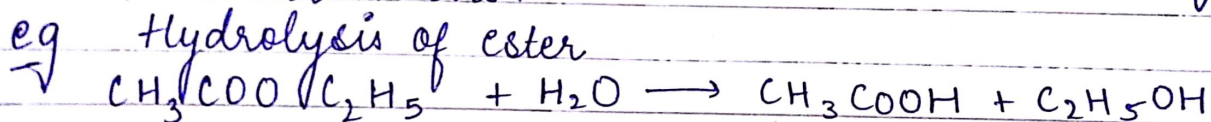
- Experimental
- Order is defined for elementary & complex reacⁿ.
- Order can be -ve, zero, +ve, fractional.

Note : For complex reacⁿ, order of reacⁿ is given by slow step and molecularity of slow step is same as the order of reaction.

Pseudo first Order Reacⁿ :-

Reacⁿ in which order is one but molecularity is more than one.

eg Hydrolysis of ester



$\text{H}_2\text{O} = \text{excess}$

$$r = k [\text{CH}_3\text{COOC}_2\text{H}_5] [\text{H}_2\text{O}]$$

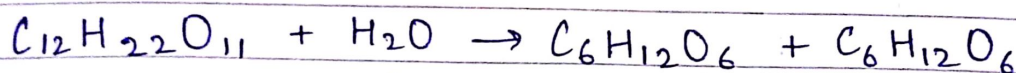
$[\text{H}_2\text{O}] = \text{const}$

$$r = k' [\text{CH}_3\text{COOC}_2\text{H}_5]^1$$

$M = 2$

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

Order = 1



$$r = k [\text{C}_{12}\text{H}_{22}\text{O}_{11}]^1 [\text{H}_2\text{O}]^0$$

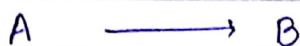
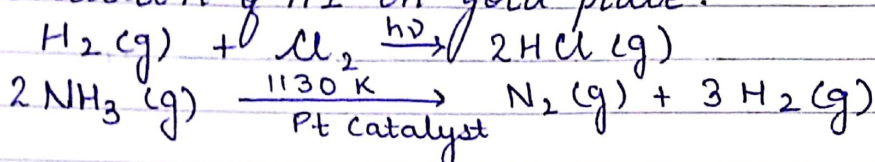
Order = 1

$M = 2$

Integrated Rate Equation

1. **Zero Order Reacⁿ**:- The reacⁿ in which rate of reacⁿ does not depend upon initial concⁿ of reactant.
 eg Enzyme catalyst reacⁿ
 Reacⁿ which takes place on metal surface.

Dissociation of HI on gold plate.



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

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

$$-\int_{c_0}^{c_t} d[\text{A}] = k \int_0^t dt$$

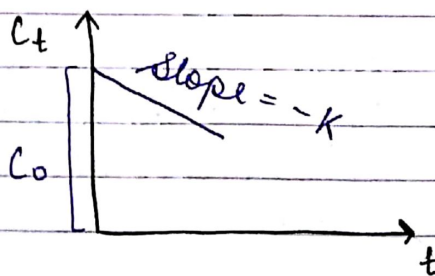
$$-[\text{A}]_{c_0}^{c_t} = k(t)_0^t$$

$$c_0 - c_t = kt$$

Concⁿ of A
of reactant
time 't'

$$c_t = c_0 - kt$$

$$y = c + mx$$



$$t = 0$$

$$a$$

$$0$$

$$t = t$$

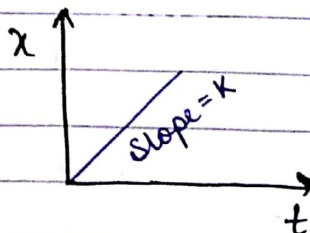
$$a - x$$

$$x$$

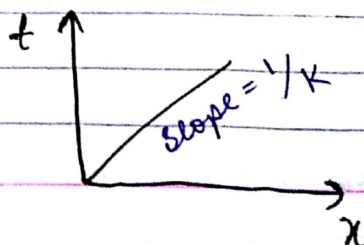
$$c_t = c_0 - kt$$

$$a - x = a - kt$$

$$x = kt$$



$$t = \frac{1}{k} x$$



$$C_t = C_0 - Kt$$

t_{complete} or $t_{100\%}$ → time taken to complete reacⁿ

$$C_t = 0$$

$$0 = C_0 - Kt_{100\%}$$

$$t_{100\%} = \frac{C_0}{K}$$

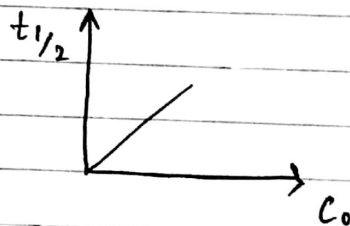
Half life of reacⁿ :- ($t_{1/2}$)
Half of reactant is converted into product

$$C_t = \frac{C_0}{2}$$

$$\frac{C_0}{2} = C_0 - Kt_{1/2}$$

$$t_{1/2} = \frac{C_0}{2K}$$

$$t_{1/2} \propto C_0$$



Que = $A \rightarrow B$ $r = K[A]^0$
If concⁿ of A is reduces from 0.1 M to 0.05 M
in 10 sec. Then Calculate

① time taken when concⁿ. reduce to 0.025 M

$$0.025 = 0.1 - Kt$$

$$Kt = 0.1 - 0.025$$

$$0.05 = 0.1 - K \times 10$$

$$10K = 0.1 - 0.05$$

$$10K = 0.05$$

$$K = \frac{0.05}{10} = 0.005$$

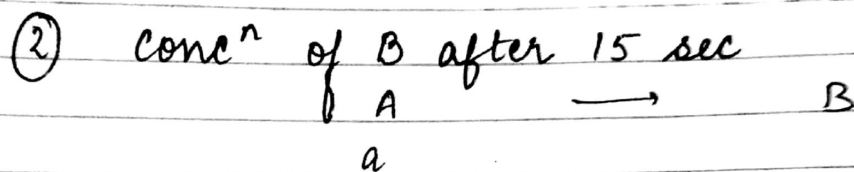
$$0.025 = 0.05 - 0.005 \times t$$

$$5 \times 10^{-3} t = 0.05 - 0.025$$

$$t = \frac{0.025}{0.005} = \frac{25}{5} = 5 \text{ sec}$$

$$\frac{0.050}{0.025} = 2$$

$$t = \frac{0.075 \times 10^{-3}}{5 \times 10^{-3}} = 15 \text{ sec}$$

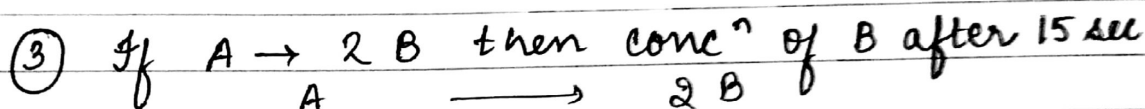


$$a \qquad \qquad \qquad x = 0.075$$

$$a - x = 0.025$$

$$0.1 - 0.025 = x$$

$$0.075 = x$$



$$A \longrightarrow 2B$$

$$a \qquad \qquad \qquad 0$$

$$a - x = 0.025 \qquad \qquad 2x$$

$$x = 0.075 \qquad \qquad \qquad = 2 \times 0.075$$

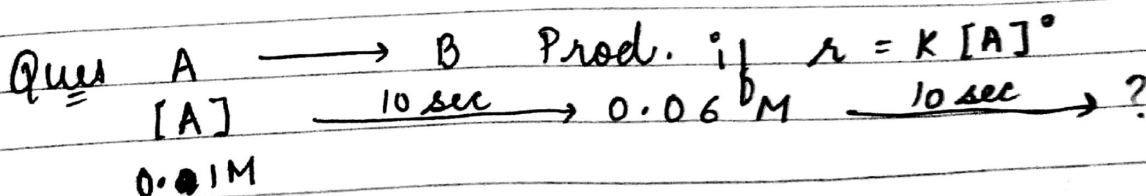
$$\qquad \qquad \qquad \qquad \qquad = 0.150$$

Ques For $A \rightarrow B$ ROR is given by $k = k[A]^0$. If half life of A was 10 sec. when initial concⁿ was 1M, calculate half life when initial concⁿ of A is 2M

$$t_{1/2} \propto C_0$$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{(C_0)_1}{(C_0)_2}$$

$$\frac{10}{(t_{1/2})_2} = \frac{1}{2} \Rightarrow (t_{1/2})_2 = 20 \text{ sec}$$



$$0.06 = 0.1 - k \times 10$$

$$10k = 0.1 - 0.06 = 0.04$$

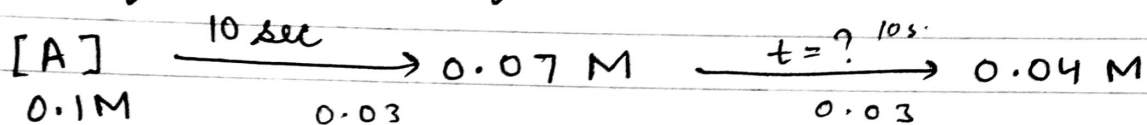
$$k = 0.004$$

$$C_t = 0.06 - 10 \times 4 \times 10^{-3} \quad \text{OR} \quad C_t = 0.1 - 4 \times 10^{-3} \times 20$$

$$= 0.06 - 4 \times 10^{-2}$$

$$= 0.02$$

Ques If $r = k[A]^0$ for reacⁿ $A \rightarrow B$



$$0.07 = 0.1 - 10k$$

$$10k = 0.1 - 0.07$$

$$10k = 0.03$$

$$k = 0.003$$

$$0.04 = 0.07 - 3 \times 10^{-3} t$$

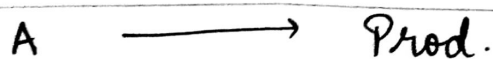
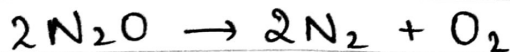
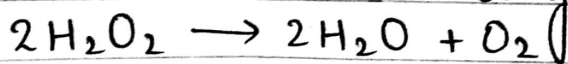
$$3 \times 10^{-3} t = 0.03$$

$$t = \frac{0.03}{0.003} = \frac{30}{0.3}$$

$$= 10 \text{ sec}$$

2. First Order Reacⁿ :- The reacⁿ in which ROR directly depends on initial concⁿ.

eg All radioactive decay.



$$r = k[A]$$

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

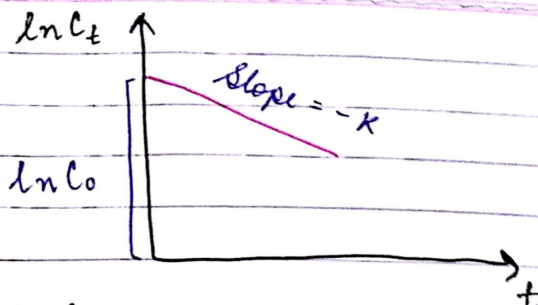
$$-\int_{c_0}^{c_t} \frac{d[A]}{[A]} = k \int_0^t dt$$

$$-\left[\ln A\right]_{C_0}^{C_t} = k [t]_0^t$$

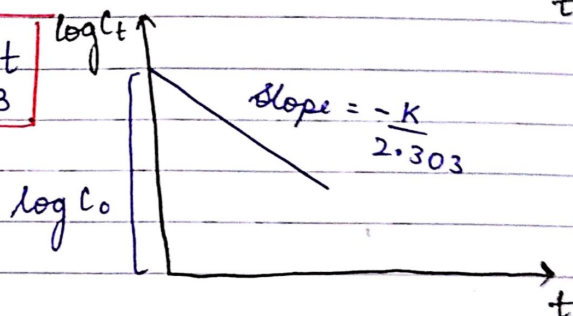
$$\ln C_0 - \ln C_t = kt$$

$$\ln C_t = \ln C_0 - kt$$

$$y = c + mx$$



$$\log C_t = \log C_0 - \frac{k}{2.303} t$$

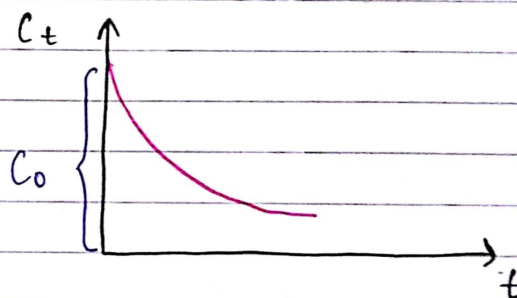


$$\ln C_t = \ln C_0 - kt$$

$$\ln \frac{C_t}{C_0} = -kt$$

$$\frac{C_t}{C_0} = e^{-kt}$$

$$C_t = C_0 e^{-kt}$$



$$\ln C_t = \ln C_0 - kt$$

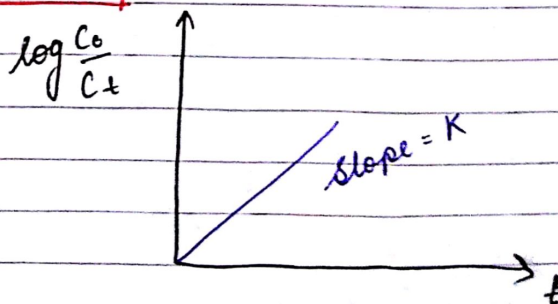
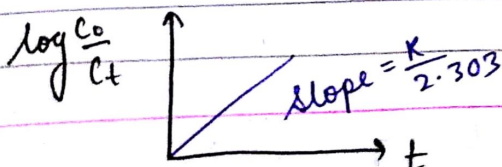
$$\log C_t = \log C_0 - \frac{k}{2.303} t$$

$$\log \frac{a}{a-x} = \log a - \frac{k}{2.303} t$$

$$\log \frac{a}{a-x} = \frac{kt}{2.303}$$

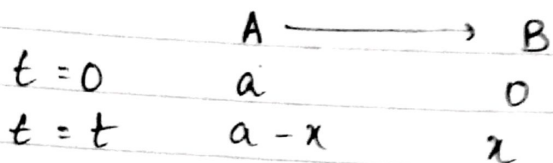
$$\ln \frac{C_0}{C_t} = kt$$

$$\log \frac{C_0}{C_t} = \frac{kt}{2.303}$$



$$Kt = \ln \frac{C_0}{C_t}$$

$$K = \frac{2.303}{t} \log \frac{C_0}{C_t}$$



$$K = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$t = \frac{2.303}{K} \log \frac{a}{a-x}$$

1st Order



$$r = K[A]$$

$$-\frac{1}{n} \frac{d[A]}{dt} = K[A]$$

$$-\int_{C_0}^{C_t} \frac{d[A]}{[A]} = nK \int_0^t dt$$

$$\ln C_0 - \ln C_t = nKt$$

$$[\ln[A]]_{C_0}^{C_t} = -nKt$$

$$C_t = C_0 e^{-nKt}$$

Ques $2A \rightarrow B + C$ If unit of rate const. is min^{-1} then write which is correct.

- ① $C_t = 2C_0 e^{-kt}$
- ✓ ② $C_t = C_0 e^{-2kt}$
- ③ $C_t = \frac{1}{2} C_0 e^{-kt}$
- ④ $C_t = C_0 e^{-kt/2}$

$$t = \frac{2.303}{K} \log \frac{C_0}{C_t} \quad \text{OR} \quad t = \frac{2.303}{K} \log \frac{a}{a-x}$$

~~Equation~~ $t_{1/2}$
 $C_t = C_0/2$

$$t_{1/2} = \frac{2.303}{K} \log \frac{C_0}{C_0/2}$$

$$t_{1/2} = \frac{2.303}{K} \log 2$$

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

↳ for 1st Order Reacⁿ $t_{1/2}$ does not depend upon initial concⁿ.

t_{complete} OR $t_{100\%}$
 $C_t = 0$

$$t_{100\%} = \frac{2.303}{K} \log \frac{C_0}{0}$$

$$t_{100\%} = \infty$$

$t_{75\%}$ $x = 75\%$ of a
 $x = 0.75a$

$$t_{75\%} = \frac{2.303}{K} \log \frac{a}{a-0.75a}$$

$$= \frac{2.303}{K} \log 4$$

$$= 2 \left(\frac{2.303}{K} \log \right) = \frac{1.386}{K}$$

$$t_{75\%} = 2 \times t_{1/2}$$

$t_{2/3}$ $x = \frac{2}{3} a$

$$t_{2/3} = \frac{2.303}{K} \log \frac{a}{a-2/3a}$$

$$= \frac{2.303}{K} \log 3$$

$$t_{2/3} = t_{1/2} \frac{\log 3}{\log 2}$$

$t_{1/3}$

$$x = a/3$$

$$t = \frac{2.303}{K} \log \frac{a}{a - a/3}$$

$$= \frac{2.303}{K} \log \frac{3}{2}$$

$$= \frac{2.303}{K} (0.47 - 0.30)$$

$$= \frac{2.303}{K} \times 0.17 = \frac{.39151}{K}$$

$$\frac{2 \frac{17}{57}}{34}$$

~~log~~

$t_{1/4}$

$$x = a/4$$

$$t = \frac{2.303}{K} \log \frac{a}{a - a/4}$$

$$\frac{2.303}{K} \log \frac{4}{3}$$

$$\frac{2.303}{K} (0.60 - 0.47)$$

$$t_{1/4} = \frac{2.303}{K} (0.13)$$

For 1st Order reactⁿ :-

① $t_{99\%}$

$$x = 0.99a$$

$$t = \frac{2.303}{K} \log \frac{a}{a - 0.99a}$$

$$= \frac{2.303}{K} \log \frac{100}{0.01}$$

$$= \frac{2.303}{K} 2 \log 10$$

$$= \frac{4.606}{K} = \frac{2}{\log 2} t_{1/2}$$

(2) $t_{99.9\%}$ $x = 0.999 a$

$$t = \frac{2.303}{k} \log \frac{a}{a - 0.999 a}$$

$$= \frac{2.303}{k} \log \frac{1000}{0.001 a}$$

$$\frac{2.303}{k} 3 \log 10 = \frac{3}{\log 2} t_{1/2}$$

$$t = \frac{6.909}{k}$$

(3) $t_{90\%}$

$$t = \frac{2.303}{k} \log \frac{a}{a - 0.90 a}$$

$$\log \frac{100}{0.1 a}$$

$$t = \frac{2.303}{k} = \frac{t_{1/2}}{\log 2}$$

(4) $t_{99.9\%}$
 $t_{99\%}$

$$= \frac{6.909}{k} \times k$$

$$= \frac{6.909}{4.606} = \frac{\frac{2.303}{k} \log \frac{a}{a - 0.999 a}}{\frac{2.303}{k} \log \frac{a}{a - 0.99 a}}$$

$$\frac{\log \frac{a}{0.001 a}}{\log \frac{a}{0.01 a}} = \frac{\log 1000}{\log 100} = \frac{3}{2}$$

(5) $t_{60\%}$
 $t_{40\%}$

$$= \frac{\frac{2.303}{k} \log \frac{a}{a - 0.60 a}}{\frac{2.303}{k} \log \frac{a}{a - 0.40 a}} = \frac{\log \frac{1}{0.4}}{\log \frac{1}{0.6}}$$

$$= \frac{\log \frac{5}{2}}{\log \frac{5}{3}} = \frac{\log 5 - \log 2}{\log 5 - \log 3}$$

Ques If 60% of a 1st order reacⁿ was completed in 60 min, 50% of the same reacⁿ would be complete in time? [take $\log 4 = 0.6$
 $\log 5 = 0.69$]

- ① 50 min ② 45 min ③ 60 min ④ 40 min

$$\frac{t_{60\%}}{t_{50\%}} = \frac{\frac{2.303}{k} \log \frac{a}{a-0.60a}}{\frac{2.303}{k} \log \frac{a}{a-0.50a}}$$

$$= \frac{\log \frac{a}{0.40a}}{\log \frac{a}{0.50a}} = \frac{\log \frac{100}{40}}{\log \frac{100}{50}}$$

$$= \frac{\log 10 - \log 4}{\log 10 - \log 5} = \frac{1 - 0.60}{1 - 0.69}$$

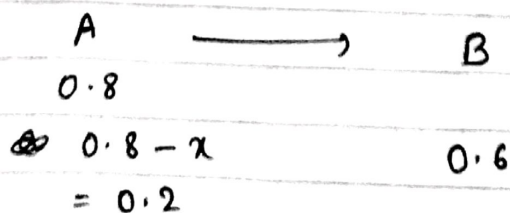
$$= \frac{0.40}{0.31} = \frac{40}{31}$$

$$\frac{60}{t_{50\%}} = \frac{40}{31}$$

$$t_{50\%} = \frac{31 \times 60}{40} = \frac{93}{2} = 46.5$$

Ques The reacⁿ $A \rightarrow B$ follows 1st order Kinetics. The time taken for 0.8 mole of A to produce 0.6 mol of B is 1 hr. What is time taken for conversion of 0.9 mole of A to 0.675 mole B?

- ① 0.25 h ② 2 h ③ 1 h ④ 0.5 h



$$t = \frac{2.303}{k} \log \frac{0.8}{0.2}$$

$$t = \frac{2.303}{K} 2 \log 2 \quad \text{--- (1)}$$

$$\begin{array}{ccc} A & \longrightarrow & B \\ 0.9 & & 0.675 \\ 0.9 - 0.675 & & 0.675 \\ = 0.2205 & & \end{array}$$

$$\begin{aligned} t &= \frac{2.303}{K} \log \frac{0.9}{0.2205} \times 100\% \\ &= \frac{2.303}{K} \log \frac{90}{22.05} \\ &= \frac{2.303}{K} (\log 45 - \log 11) \\ &= \frac{2.303}{K} [\log 5 \times 9 - \log 11] \\ &= \frac{2.303}{K} [(\log 5 + 2 \log 3) - \log 11] \\ &= \frac{2.303}{K} [(0.69 + 2 \times 0.47) - 1.043] \\ &= \frac{2.303}{K} [0.69 + 0.94 - 1.043] \\ &= \frac{2.303}{K} [1.63 - 1.043] \end{aligned}$$

$$= \frac{2.303}{K} \times 0.587$$

$$= \frac{2.303}{K} \times 0.587 \quad \text{--- (2)}$$

$$\frac{t_1}{t_0} = \frac{\frac{2.303}{K} 2 \times 0.30}{\frac{2.303}{K} \times 0.587} = \frac{0.60}{0.587}$$

$$\frac{1}{t_0} = 1 \Rightarrow t_0 = \frac{1}{1}$$

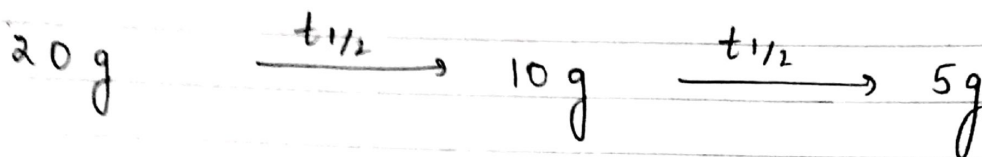
NCERT
2019

Ques

$A \rightarrow B$ For given reacⁿ sp. reacⁿ rate is given 10^{-2} sec^{-1} . How much time will it take for 20g reactant to reduce 5g?

$$r = k[A]$$

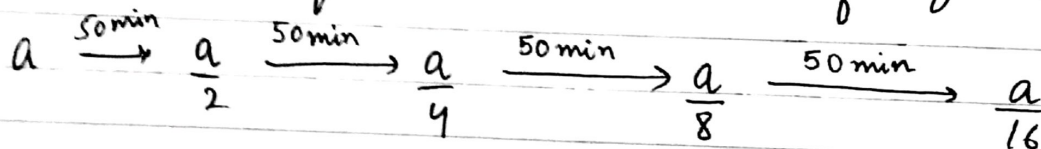
$$k = 10^{-2} \text{ s}^{-1}$$



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

$$= 2 \times \frac{0.693}{10^{-2}} = 1.386 \times 10^2 \\ = 138.6 \text{ sec}$$

Ques Half life Period of 1st order reacⁿ is 50 min. What % of reactant will be left after 200 min?



for 1st order reacⁿ
after n half life = $\frac{a}{2^n}$ reactant is left

Ques The rate constⁿ of reacⁿ is 2.303 min^{-1} . Find what % of initial concⁿ would convert into product after 1 min and what will be rate of reacⁿ after 1 min. if initial conc. is given 1M

$$[a_0] = 1 \text{ M}$$

$$[a] = 1 - 0.9 = 0.1$$

$$r = k[A] \\ = 2.303 \times 0.1$$

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EX. 9.5
NEET 2018

$$t_{90} = \frac{2.303}{k} \log \frac{C_0}{C_t}$$

$$1 = \frac{2.303}{2.303} \log \frac{a}{a-x}$$

$$\log \frac{a}{a-x} = 1$$

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

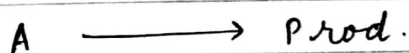
$$10a - 10x = a$$

$$9a = 10x$$

$$x = \frac{9a}{10} = 0.9a = 90\% \text{ of } a$$

Ques What is unit of rate for 1st order reaction?

- ① s^{-1}
- ② $\text{mol L}^{-1} s^{-1}$
- ③ $\text{mol}^{-1} \text{L s}^{-1}$
- ④ mol L^{-1}



$$\ln C_0 - \ln C_t = kt$$

$$\ln C_t = \ln C_0 - kt$$

at time t_1 , $[A] = (C_t)_1$

t_2 $[A] = (C_t)_2$

$$\ln (C_t)_1 = \ln C_0 - kt_1 \quad \text{--- (1)}$$

$$\ln (C_t)_2 = \ln C_0 - kt_2 \quad \text{--- (2)}$$

$$\text{①} - \text{②} \quad \ln (C_t)_1 - \ln (C_t)_2 = -kt_1 + kt_2$$

$$* \quad k = \frac{2.303}{t_2 - t_1} \log \frac{(C_t)_1}{(C_t)_2}$$

1st Order Gaseous Reacⁿ :-



Imp NEET 2018

Ques The initial concⁿ of N_2O_5 in following first order reaction.
 $N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$ was $1.24 \times 10^{-2} \text{ mol L}^{-1}$ at 318 K.
 The concⁿ of N_2O_5 after 60 min. was $0.20 \times 10^{-2} \text{ mol L}^{-1}$ Calculate rate const. of the reacⁿ at 318 K.

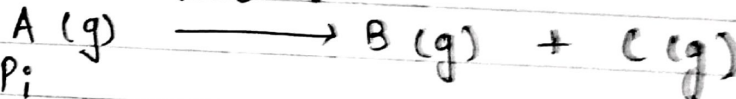
$$k = \frac{2.303}{t_2 - t_1} \log \frac{(C)_1}{(C)_2}$$

$$= \frac{2.303}{60 - 0} \log \frac{1.24 \times 10^{-2}}{0.20 \times 10^{-2}}$$

$$= \frac{2.303}{60} \log \frac{124}{20} = \frac{2.303}{60} \log 6.2 = \frac{2.303}{60} \times 0.75$$

$$k = 0.0304 \text{ min}^{-1}$$

1st Order Gaseous Reacⁿ :-



$t=0$

P_i

$t=t$

$P_i - x = P_A$

x

x

$P_i \rightarrow$ initial Pr. of container

$P_t \rightarrow$ total Pr. at time t

$$P_t = P_i - x + x + x$$

$$P_t = P_i + x$$

$$x = P_t - P_i$$

$$k = \frac{2.303}{t} \log \frac{P_i}{P_A}$$

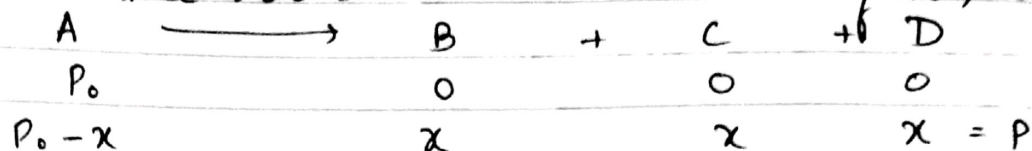
$$k = \frac{2.303}{t} \log \frac{P_i}{P_i - x}$$

$$k = \frac{2.303}{t} \log \frac{P_i}{P_i - (P_t - P_i)}$$

$$k = \frac{2.303}{t} \log \frac{P_i}{2P_i - P_t}$$

Ques $A \rightarrow B + C + D$ is a 1st order homogenous gaseous reacⁿ. Initial pr. of the reactant is P_0 & Pressure the reactant mixture at time 't' is P

Determine rate const in terms of P_0, P & t ?



$$P_0 - x + x + x + x = P$$

$$x = \frac{P - P_0}{2}$$

$$K = \frac{2.303}{t} \log \frac{P_i}{P_i - x}$$

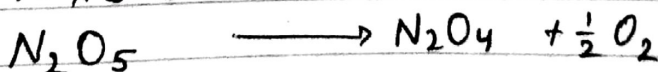
$$\frac{2.303}{t} \log \frac{P_0}{P_0 - \left(\frac{P - P_0}{2}\right)}$$

$$= \frac{2.303}{t} \log \frac{2P_0}{3P_0 - P}$$

Ques The decomposition of N_2O_5 in carbon tetra chloride was followed by measuring the vol. O_2 gas evolved. The vol. of O_2 gas obtained at the end of the reacⁿ was 100 cm^3 . In 500 min, 90 cm^3 of O_2 evolved. for the reacⁿ given first order reacⁿ rate const would be.

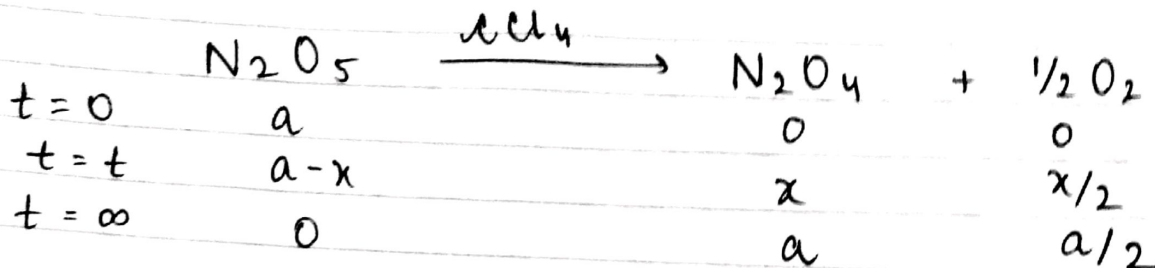
① $\frac{2.303}{500} \text{ min}^{-1}$ ② $\frac{2.303}{500} \log \frac{100}{90} \text{ min}^{-1}$ ③ $\frac{2.303}{500} \log \frac{90}{100} \text{ min}^{-1}$

④ $\frac{100}{10 \times 500} \text{ min}^{-1}$



t	0	100 cm^3
500 min	$a - x$	90 cm^3

$$\frac{k_1}{k_2} = \frac{2.303}{t}$$



$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$PV = nRT$$

$$V \propto n$$

at $t=t$ Vol. of O_2 $V_t \propto x/2$ — (1)

$t=\infty$ Vol. of O_2 $V_\infty \propto a/2$ — (2)

$$(2) - (1) \quad V_\infty - V_t \propto \frac{a-x}{2} \quad \text{--- (3)}$$

$$(2) / (3) \quad \frac{a/2}{a-x/2} \propto \frac{V_\infty}{V_\infty - V_t}$$

$$\frac{a}{a-x} \propto \frac{V_\infty}{V_\infty - V_t}$$

$$k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t} \quad **$$

$V_\infty \rightarrow$ Vol. of O_2 at $t = \infty$

$$V_\infty = 100 \text{ cm}^3$$

$V_t \rightarrow$ Vol. of O_2 at $t = t$

$$V_t = 90 \text{ cm}^3$$

$$k = \frac{2.303}{500} \log \frac{100}{100-90}$$

$$k = \frac{2.303}{500} \text{ min}^{-1}$$

2nd Order Reaction :-



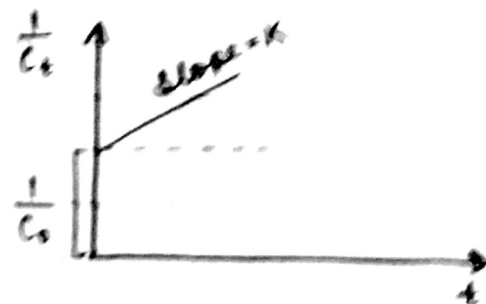
$$r = k[A]^2$$

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

$$-\int_{C_0}^{C_t} \frac{d[A]}{[A]^2} = k \int_0^t dt$$

$$-\left[-\frac{1}{[A]}\right]_{C_0}^{C_t} = kt$$

$$\boxed{\frac{1}{C_t} - \frac{1}{C_0} = kt}$$

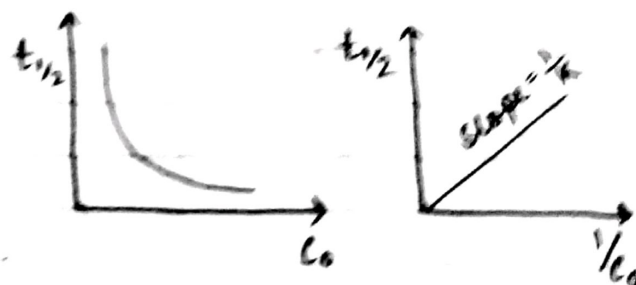


Half life $C_t = C_0/2$

$$\frac{2}{C_0} - \frac{1}{C_0} = k t_{1/2}$$

$$t_{1/2} = \frac{1}{k C_0}$$

$$\boxed{t_{1/2} \propto \frac{1}{C_0}}$$



Unit of k

$$k = \frac{1}{t_{1/2} C_0}$$

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

3rd Order Reaction :-



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

$$-\int_{C_0}^{C_t} \frac{d[A]}{[A]^3} = k \int_0^t dt$$

$$-\left[-\frac{1}{2} \frac{1}{[A]^2}\right]_{C_0}^{C_t} = kt$$

$$\boxed{\frac{1}{C_t^2} - \frac{1}{C_0^2} = 2kt}$$

3rd order

$$\frac{1}{C_t^{3-1}} - \frac{1}{C_0^{3-1}} = (3-1) K t$$

nth order

$$\frac{1}{C_t^{n-1}} - \frac{1}{C_0^{n-1}} = (n-1) K t$$

not valid for 1st Order Reaction

Half life for nth Order

$$\frac{1}{\left(\frac{C_0}{2}\right)^{n-1}} - \frac{1}{C_0^{n-1}} = (n-1) K t_{1/2}$$

$$\frac{2^{n-1} - 1}{C_0^{n-1}} = (n-1) K t_{1/2}$$

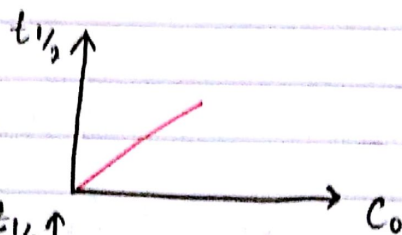
$$t_{1/2} = \frac{1}{(n-1) K} \left[\frac{2^{n-1} - 1}{C_0^{n-1}} \right]$$

n=3 $t_{1/2} = \frac{3}{2 K C_0^2}$

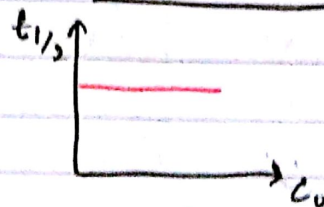
$t_{1/2} \propto \frac{1}{C_0^{n-1}}$

$t_{1/2} \propto \frac{1}{C_0^{n-1}}$

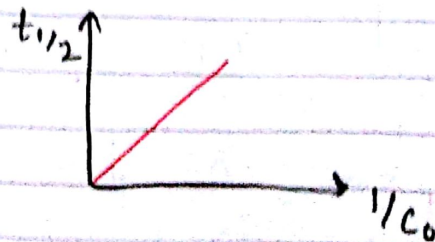
Zero Order n=0 $t_{1/2} \propto C_0$



1st Order n=1 $t_{1/2} \propto C_0^0$



2nd Order n=2 $t_{1/2} \propto \frac{1}{C_0}$



3rd Order $n=3$ $t_{1/2} \propto \frac{1}{C_0^2}$

$$t_{1/2} \propto \frac{1}{C_0^{n-1}}$$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left[\frac{(C_0)_2}{(C_0)_1} \right]^{n-1}$$

Ques

Find Order of Reacⁿ

Initial conc ⁿ	$t_{1/2}$
2M	10 min
4M	5 min

$$t_{1/2} \propto \frac{1}{C_0}$$

$$\frac{10}{5} = \left(\frac{4}{2} \right)^{n-1}$$

$$(2)^1 = (2)^{n-1}$$

$$n-1 = 1$$

$$n = 2$$

Ques Find order of Reacⁿ

Initial concⁿ

Initial conc ⁿ	$t_{1/2}$
2M	10 min
4M	10 min

$$\frac{10}{10} = \left(\frac{4}{2} \right)^{n-1}$$

$$2^0 = 2^{n-1}$$

$$2 = 2^n$$

$$n = 1$$

Ques Find order of Reacⁿ

initial concⁿ

initial conc ⁿ	$t_{1/2}$
5M	10 min
10M	20 min

$$\frac{10}{20} = \left(\frac{10}{5}\right)^{n-1}$$

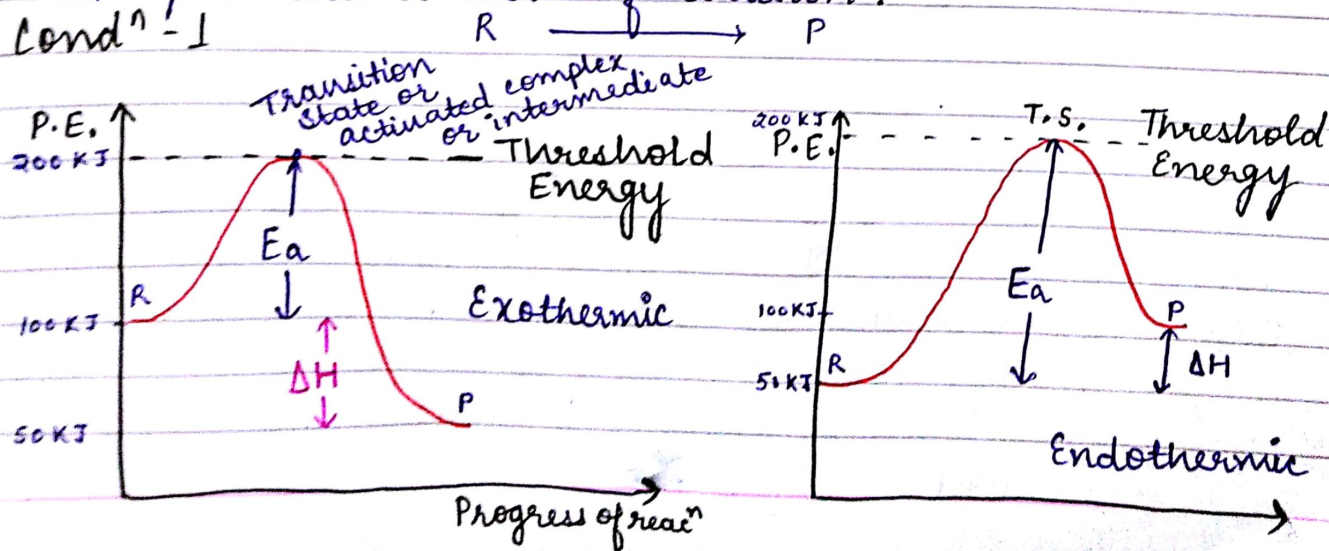
$$\frac{1}{2} = (2)^{n-1}$$

$$2^0 = 2^n$$

$$n = 0$$

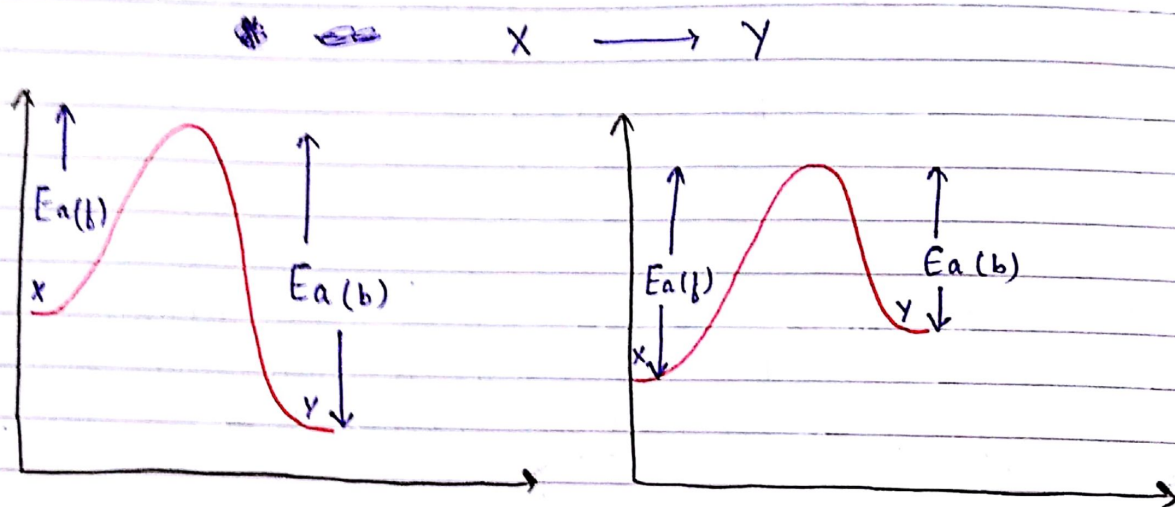
Collision Theory of Chemical Reacⁿ :-

- Accⁿ to this theory, for a reacⁿ to occur there must be effective collision b/w reacting molecule.
- Total no. of collision per sec. per unit volume is c/a collision frequency.
- For gaseous reacⁿ, collision frequency is very high i.e. 10^{25} to 10^{28} collisions/sec/ m^3 but only a small fraction of these collisions are capable to convert reactant into product. These collisions are c/a effective collisions.
- For effective collision, 2 condⁿ must be satisfied.
 1. Reactant molecule must possess a min^m amt. of energy.
 2. Proper orientation of collision.



Threshold Energy :- Min^m amt. of energy required to proceed a reacⁿ.

Activation Energy :- Min^m amt. of energy required by reactant to convert into product.



$$\Delta H = E_a(f) - E_a(b)$$

$$\Delta H = -ve$$

exothermic

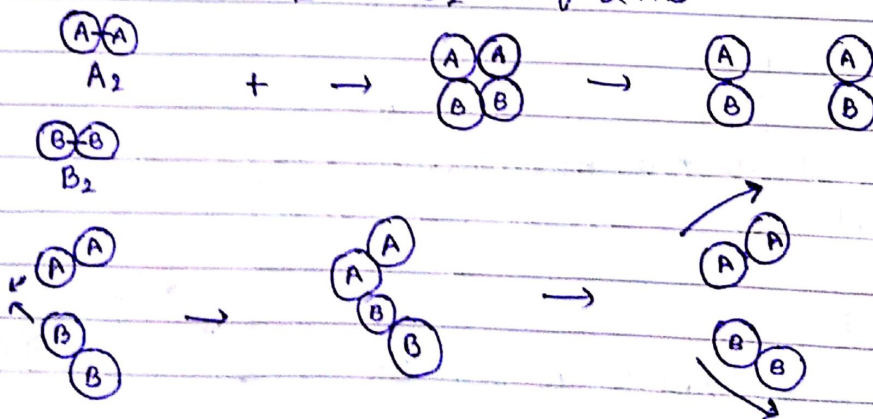
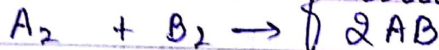
$$\Delta H = E_a(f) - E_a(b)$$

$$\Delta H = +ve$$

Endothermic

Condⁿ - II

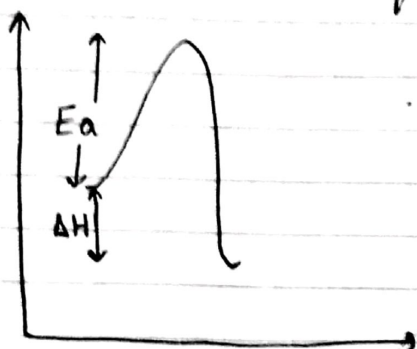
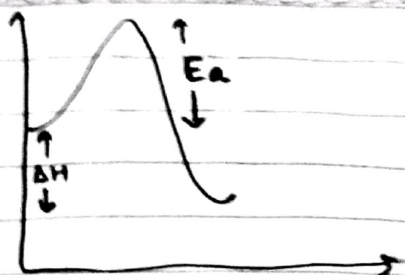
Orientation of Collision



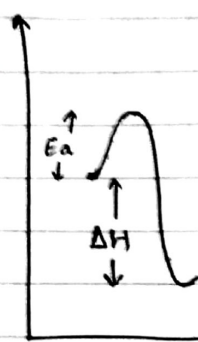
Note. Collision theory is only applicable for bimolecular gaseous reacⁿs.

Ques: for an exothermic reacⁿ

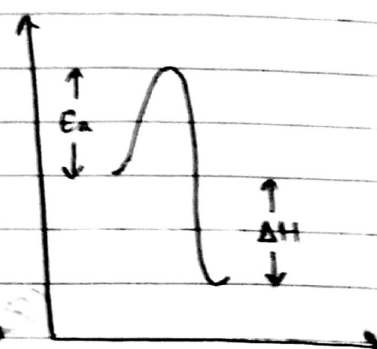
- ① $E_a > \Delta H$
- ② $E_a < \Delta H$
- ③ $E_a = \Delta H$
- ④ ~~all any one of possible~~



$E_a > \Delta H$



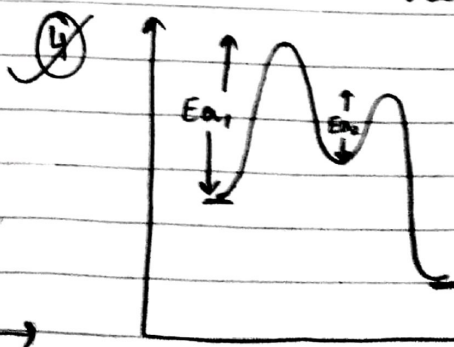
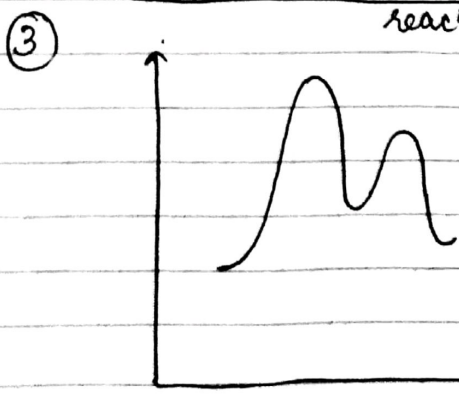
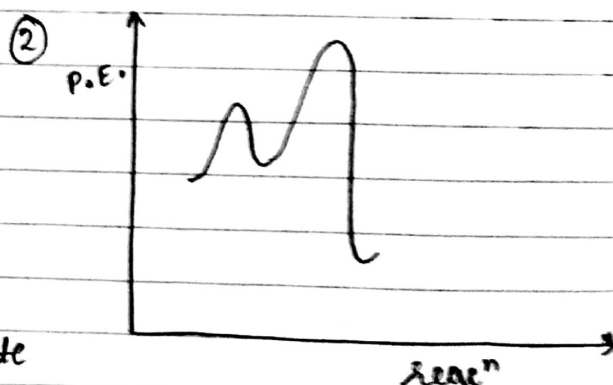
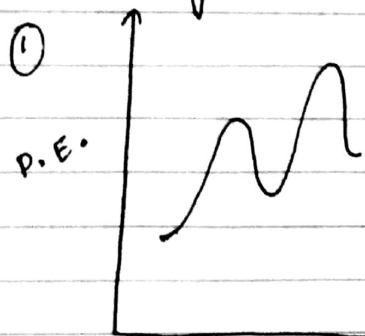
$\Delta H > E_a$



$E_a = \Delta H$

Ques An exothermic reacⁿ takes place in 2 steps
 $X + Y \longrightarrow Z$ (slow) $E_{a1} > E_{a2}$
 $Z \longrightarrow X + Y$ (fast) $\Delta H = -ve$

which graph explain the above reacⁿ!



Factors affecting rate of Reacⁿ :-

1. Nature of Reactant : For different reactant, Bond Energy are different hence rates are different.
2. Physical state of Reactant
rate \rightarrow solid $<$ liq. $<$ gas
3. Size of reactant molecule (if reactant is solid)
as size of reactant molecule \downarrow surface area \uparrow rate \uparrow
4. Concⁿ. of Reactant :
as conc. of reactant \uparrow no. of molecules per unit vol. \uparrow collision frequency \uparrow eff. collision \uparrow rate \uparrow
5. Pressure : If reactant solid or liq. Pressure does not effect rate. ^{For} gaseous reacⁿ :-
 $P \uparrow$ no. of collision per unit vol. \uparrow collision frequency \uparrow eff. collision \uparrow rate \uparrow
6. ~~Rate~~ Temperature : For exothermic as well as endothermic reacⁿ, as $T \uparrow$ $r \uparrow$
as $T \uparrow$ K.E. of molecules \uparrow no. of molecules crossing energy barrier \uparrow $r \uparrow$

Note : Rise in T does not alter E_a but no. of molecules crossing the energy barrier \uparrow hence $r \uparrow$

\rightarrow for every 10°C rise in Temp. \uparrow es the rate of reacⁿ 2 to 3 times.

Temp. Coefficient (μ) : It is ratio of rate const. of reacⁿ at diff. temp. which is differ by 10°C or 10K

$$\mu = \frac{k_{T+10}}{k_T}$$

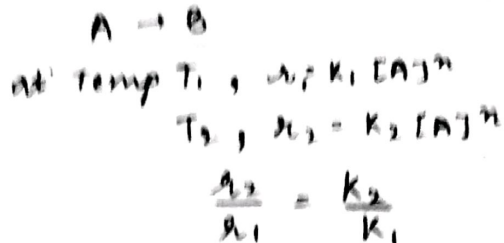
If μ is not given, $\mu = 2$ लेना है

If T is not given,

$$T = 25^\circ\text{C}$$

$$\frac{k_2}{k_1} = (\mu)^{\frac{T_2 - T_1}{10}}$$

$$\boxed{\frac{r_2}{r_1} = \frac{k_2}{k_1} = (\mu)^{\frac{T_2 - T_1}{10}}}$$



If temp. of reacⁿ. is increased from T_1 to T_2 then its rate become ~~$\mu^{\frac{T_2 - T_1}{10}}$~~ $\mu^{\frac{T_2 - T_1}{10}}$ times of initial rate.

Ques Temp. of a reacⁿ is ↑ from 10°C to 60°C then how many times rate of reacⁿ will be

- ① 16 times ② 64 times ③ 32 times ④ 8 times

$$r' = \mu^{\frac{50}{10}} r$$

$$= \mu^5 r$$

$$= 2^5 r = 32$$

Ques for reacⁿ carried out at 25°C its rate ↑ by 40°C then its rate becomes _____ rate

$$r' = (2)^{\frac{40}{10}} r$$

$$= 2^4 r$$

$$= 16r$$

Relation b/w Temp. & rate const.

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

Arrhenius eqⁿ

A → Arrhenius const / Preexponential factor / Frequency Factor

E_a → activation energy

R → universal Gas const.

T → temp.

K → rate const.

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

$\frac{K}{A}$ → Fraction of molecule having energy $\geq E_a$
or
Boltzman Factor

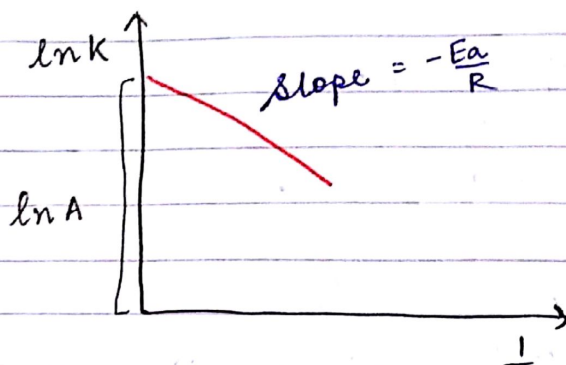
$$K = A e^{-E_a/RT}$$

as $T \uparrow$ $K \uparrow$
 $T \rightarrow \infty$

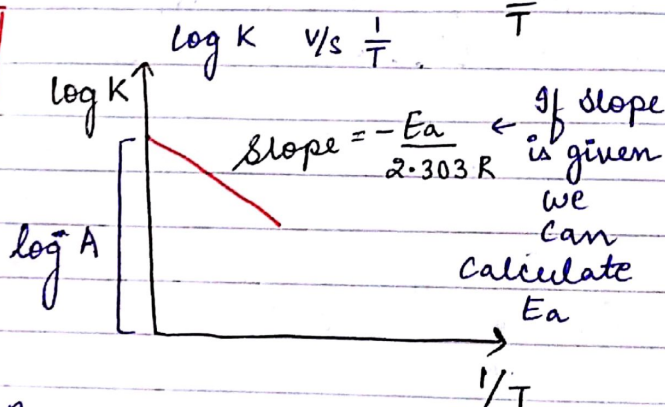
$$K = A$$

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

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



$$\log_{10} K = \log_{10} A - \frac{E_a}{2.303RT}$$



~~log K~~ = ~~do~~ for a reactⁿ
at temp T_1

$$\log K_1 = \log A - \frac{E_a}{2.303RT_1} \quad \text{--- (1)}$$

$$\text{at Temp } T_2 \quad \log K_2 = \log A - \frac{E_a}{2.303RT_2} \quad \text{--- (2)}$$

$$\text{(2) - (1)} \quad \log K_2 - \log K_1 = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

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

Ques for a reactⁿ $\log_{10} K$ is plotted against $1/T$ & it gives a straight line with a slope -6000 . Calculate the activation energy of the reactⁿ in (Kcal/mol)

41

SX

$$\begin{array}{r} 3 \quad 300,330 \\ 5 \quad 100,110 \\ \hline 4 \quad 20,72 \\ 5 \quad 1,22 \\ \hline 1104 \end{array}$$

$$\text{slope} = -6000$$

$$\text{slope} = -\frac{E_a}{2.303 R}$$

$$+6000 = +\frac{E_a}{2.303 \times 2}$$

$$6000 \times 2 \times 2.303 = E_a$$

$$12 \times 2303 \times 48 \times 2.303 = E_a$$

$$27636 \text{ cal/mol} \times 1104 = E_a = 27.636 \text{ Kcal/mol}$$

$$\begin{array}{r} 2 \quad 48 \\ 23 \\ \hline 144 \\ 96 \times \\ \hline 1104 \end{array}$$

Ques for a reacⁿ, Rate of reacⁿ becomes 8 times when temp. of reacⁿ is rised from 27°C to 57°C. Determine Energy of activation in Kcal/mol

$$\log \frac{r_2}{r_1} = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\frac{r_2}{r_1} = 8$$

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

$$\log 8 = \frac{E_a}{2.303 R} \left[\frac{1}{300} - \frac{1}{330} \right]$$

$$3 \log 2 = \frac{E_a}{2.303 \times 2} \left[\frac{330 - 300}{300 \times 330} \right]$$

$$3 \times 0.30 = \frac{E_a}{4.606} \left[\frac{30}{300 \times 330} \right]$$

$$E_a = 0.90 \times 3300 \times 4.606$$

$$= 9 \times 33 \times 46.06$$

$$= 297 \times 46.06$$

$$\approx 13662 \text{ cal/mol} \approx 13.662 \text{ Kcal/mol}$$

$$\begin{array}{r} 2 \\ 5 \quad 297 \\ \hline 1182 \\ 1188 \times \\ \hline 13662 \end{array}$$

Ques for a 1st order reacⁿ at 27°C the concⁿ of reactant is reduced to half initial value after 50 min. If temp. is kept 37°C then concⁿ of reactant becomes half of its initial value in 10 min. Calculate E_a.

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

$$K_1 = \frac{0.693}{50} \quad \text{--- (1)}$$

$$K_2 = \frac{0.693}{10} \quad \text{--- (2)}$$

$$\frac{K_2}{K_1} = \frac{\frac{0.693}{10}}{\frac{0.693}{50}} = \frac{50}{10} = \frac{5}{1}$$

$$\log \frac{5}{1} = \frac{E_a}{2.303 \times 2} \left[\frac{1}{300} - \frac{1}{310} \right] \quad \left| \begin{array}{l} 0.69 \times 4.606 \times 9300 = E_a \\ 6.9 \times 46.06 \times 93 = E_a \\ 7 \times 46 \times 93 = E_a \\ E = 651 \times 46 = 29946 \text{ cal/mol} \end{array} \right.$$

$$0.69 = \frac{E_a}{4.606} \left[\frac{10}{300 \times 310} \right]$$

Ques The rate const. for the reactⁿ is related to temp. as $\log k = 15 - \frac{10^6}{T}$. Determine 'A' & 'E_a'

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$$\log k = 15 - \frac{10^6}{T}$$

$$\log A = 15$$

$$A = 10^{15}$$

$$\frac{E_a}{2.303R} = 10^6$$

$$E_a = 10^6 \times 2.303 \times 2$$

$$E_a = 4.606 \times 10^6$$

Ques The activation Energy for the reactⁿ
 $2HI(g) \rightarrow H_2(g) + I_2(g)$ is $46.06 \text{ kcal mol}^{-1}$
at 500 K . Cal. fraction of molecules of reactant having energy level equal to or greater than E_a ?

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

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

$$\frac{k}{A} = f$$

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

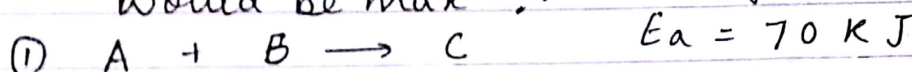
$$\ln f = - \frac{E_a}{RT}$$

$$2.303 \log_{10} f = - \frac{23.03}{2 \times 500} \times 10^3$$

$$\log_{10} f = \frac{-23.03 \times 2 \times 10}{2.303} = \frac{-2.303 \times 20}{2.303}$$
$$= -20$$

$$f = 10^{-20}$$

Ques for which of the following reacⁿ K_{320}/K_{310} would be max^m :-



$$\frac{K_{320}}{K_{310}} \propto E_a$$

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

↖ unitless

unit of A = unit of K
for eg : 1st order
unit of A = sec^{-1}

Derivation of Arrhenius Equation :-

Based upon 2 theories :-

1. Kinetic Theory of Gases
2. Collision Theory

Kinetic Theory of Gas

Accⁿ to KTG, all molecules do not have equal energy
so there will be fraction of activated molecule
having energy

Fraction of activated molecule $f = e^{-E_a/RT}$

$$r \propto f$$

Collision Theory :-

Collision per unit time per unit vol. \rightarrow collision frequency.
(Z)

$$r \propto Z$$

$$r \propto fZ$$

$$k \propto fZ$$

(P) \rightarrow Probability of Proper orientation / orientation factor /
steric factor

$$k = PfZ$$

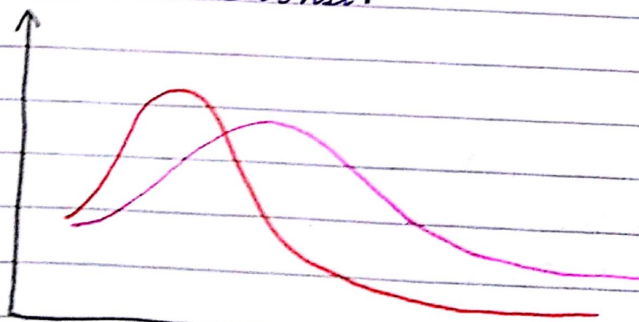
$$k = PZf$$

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

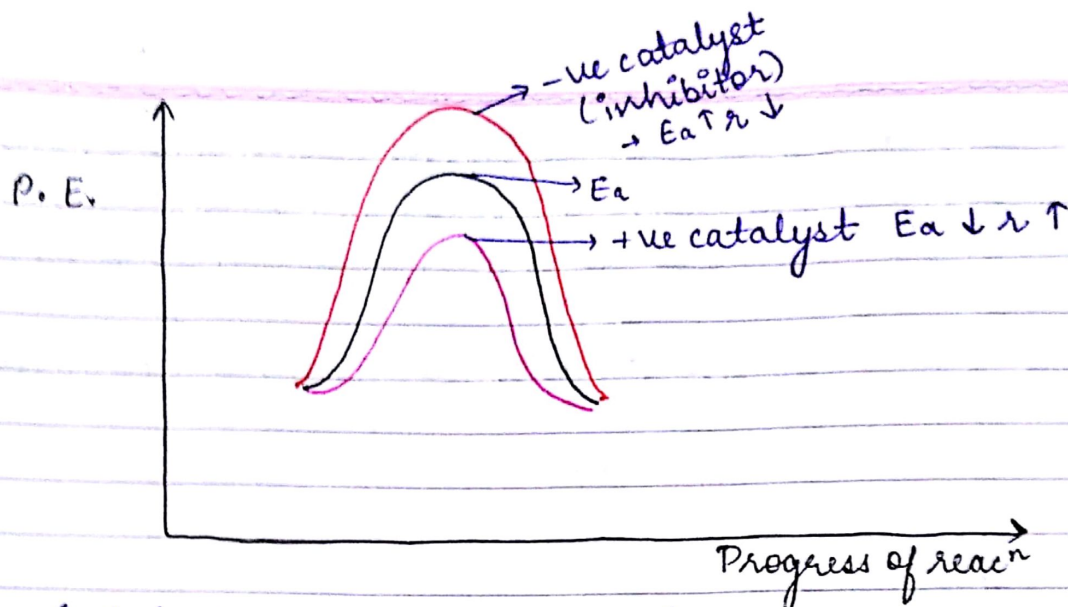
$$A = PZ$$

Arrhenius const.

$\frac{N_e}{N_T}$

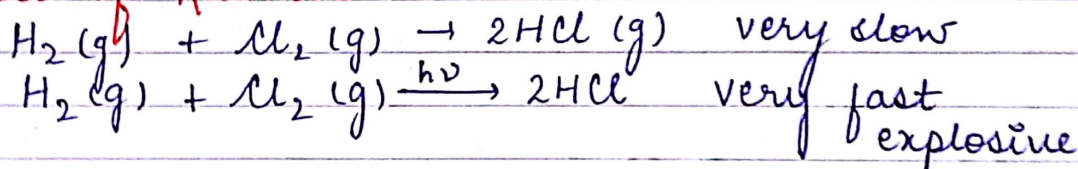


Effect of Catalyst :- Catalyst provide an
alternate path



Catalyst \rightarrow generally transition metals
becoz \rightarrow they provide more surface area
 \rightarrow they have variable O.S.

Effect of Radiation :



Ques A hydrogenation reaction is carried out at 500K. If same reaction is carried out in presence of a catalyst at same rate. The temp. required is 400K. Calculate the activation energy of the reaction. ~~it lowers~~ ~~the~~ activation energy by 20 kJ mol^{-1}

① with catalyst = 80 ② without catalyst = 100
 $r = \text{same}$ $k = \text{same}$

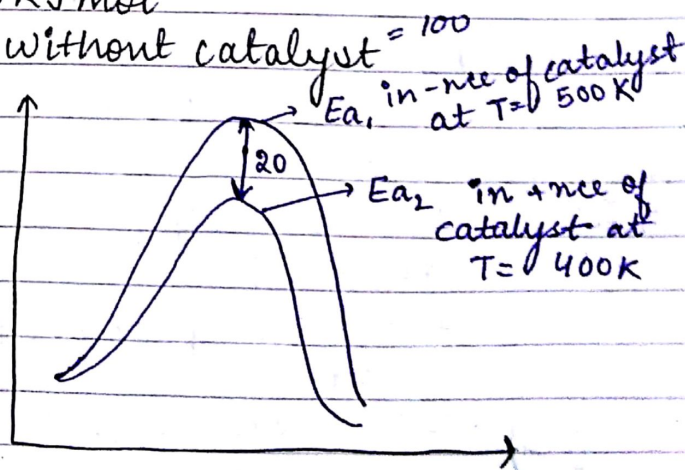
$$Ae^{-E_{a1}/RT_1} = Ae^{-E_{a2}/RT_2}$$

$$\frac{E_{a1}}{RT_1} = \frac{E_{a2}}{RT_2}$$

$$\frac{E_{a1}}{500} = \frac{E_{a1} - 20}{400}$$

$$4E_{a1} = 5E_{a1} - 100$$

$$E_{a1} = 100$$



Ques A reacⁿ takes place in 3 steps. The rate const are k_1, k_2 & k_3 . The overall rate const. of reacⁿ is $k = \frac{k_1 k_3}{k_2}$. If energy of activation are 80, 40 & 20 KJ mol⁻¹ resp. calculate overall energy of activation.

$$E_{a1} = 80 \quad E_{a2} = 40 \quad E_{a3} = 20$$

$$E_a = \frac{E_{a1} E_{a3}}{E_{a2}} = \frac{80 \times 20}{40} = 40$$

$$k = \frac{k_1 k_3}{k_2}$$

$$A e^{-E_a/RT} = \frac{k_2}{A_1 e^{-E_{a1}/RT} A_2 e^{-E_{a2}/RT}}$$

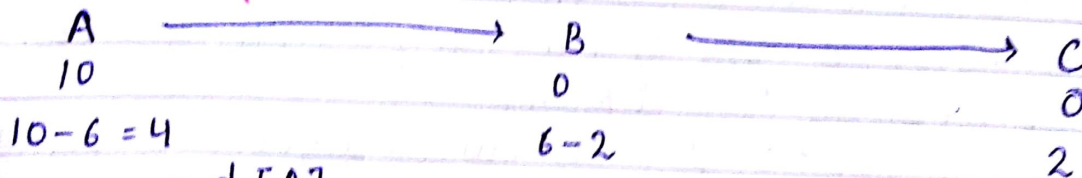
$$A e^{-E_a/RT} = \left(\frac{A_1 A_3}{A_2} \right) e^{-\frac{1}{RT} (E_{a1} - E_{a2} + E_{a3})}$$

$$A = \frac{A_1 A_3}{A_2}$$

$$E_a = E_{a1} - E_{a2} + E_{a3} = 80 - 40 + 20 = 60$$

Some important Points :-

1. Series Reacⁿ :-

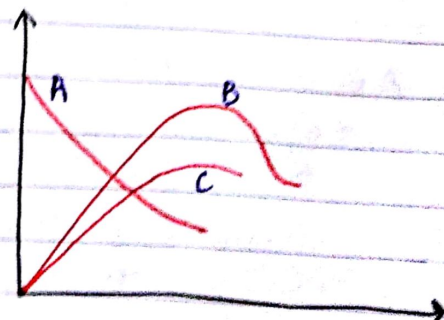


$$-\frac{d[A]}{dt} = k[A]$$

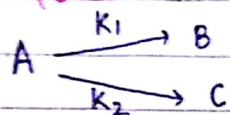
$$\frac{d[C]}{dt} = k[B]$$

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

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



2. Parallel Reacⁿ :



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

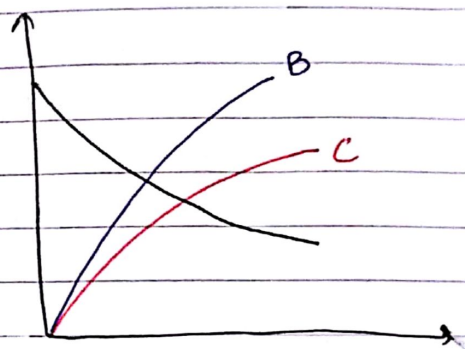
$$r = k_2 [B] = -\frac{d[A]}{dt} = \frac{d[C]}{dt}$$

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

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

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

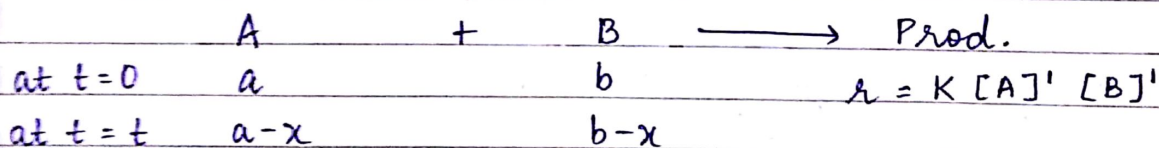
$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} + \frac{d[C]}{dt}$$



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

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

For 2nd Order reacⁿ :-



Integrated rate eqⁿ

$$kt = \frac{2.303}{(a-b)} \log \frac{b(a-x)}{a(b-x)} \quad a > b$$

$$kt = \frac{2.303}{(b-a)} \log \frac{a(b-x)}{b(a-x)} \quad b > a$$

Exception : for the reacⁿ $NO + \frac{1}{2}O_2 \rightarrow NO_2$

on ↑sing Temp. rate of reacⁿ ↓
it is an eq of -ve Temp. coeff. reacⁿ

generally $\mu = \frac{k_{T+10}}{k_T} \quad \mu > 1$

For this reacⁿ $k_T > k_{T+10} \quad \mu < 1$

Only for A.II.

Calculation of α :- (D.O.D) ^{From} ~~for~~ Wilhelmy eqⁿ

$t = 0$ A $\xrightarrow{\text{Prod.}}$

$$a = C_0$$

$$a - x = C_t$$

$$\alpha = \frac{x}{a}$$

$$a = C_0 \quad \text{--- (1)}$$

$$a - x = C_t \quad \text{--- (2)}$$

(1) & (2)

$$a - (a - x) = C_0 - C_t$$

$$x = C_0 - C_t$$

$$\alpha = \frac{x}{a} = \frac{C_0 - C_t}{C_0}$$

$$\alpha = 1 - \frac{C_t}{C_0}$$

Wilhelmy eqⁿ

$$C_t = C_0 e^{-kt}$$

$$\frac{C_t}{C_0} = e^{-kt}$$

$$\alpha = 1 - e^{-kt}$$

Radioactive decay - 1st order

$$C_t = C_0 e^{-kt}$$

$$N = N_0 e^{-\lambda t}$$

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

$N_0 \rightarrow$ no. of initial nuclei

$N \rightarrow$ no. of nuclei at time 't'

$$t_{avg} = \frac{1}{\lambda}$$

$$\frac{t_{avg}}{t_{1/2}} = \frac{1}{0.693} = 1.44$$

$$t_{avg} = 1.44 t_{1/2}$$

Que If $t_{1/2}$ of a radioactive substance is 100 Yr then find out ratio of N_0/N after 144 Yrs.

$$\frac{N_0}{N} = e^{-\lambda t}$$