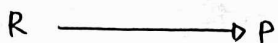


CHEMICAL KINETICS

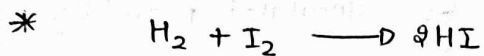
RATE OF RXN :- it can be expressed in terms of

- i) Rate of disappearance of Reactant
- ii) Rate of appearance of product

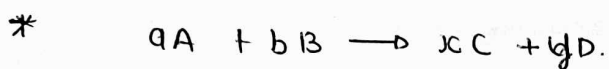


$$-\frac{\Delta[R]}{\Delta t} = \text{Rate of disappearance of Reactant}$$

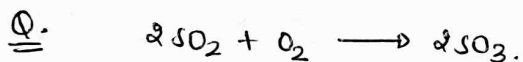
$$\frac{\Delta P}{\Delta t} = \text{Rate of Appearance of Product}$$



$$-\frac{\Delta[H_2]}{\Delta t} = -\frac{\Delta[I_2]}{\Delta t} = \frac{1}{2} \left[\frac{\Delta[HI]}{\Delta t} \right] = \text{Rate of RXN}$$



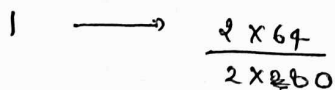
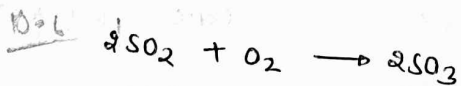
$$-\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{x} \frac{d[C]}{dt} = \frac{1}{y} \frac{d[D]}{dt}$$



① R.O.D for $SO_2(g)$ is $2.8 \text{ mol L}^{-1}\text{sec}^{-1}$ calculate rate of A of $SO_3(g)$.

$$SO_3 \text{ R.O.A for } SO_2 = 2.8 \text{ mol L}^{-1}\text{sec}^{-1}$$

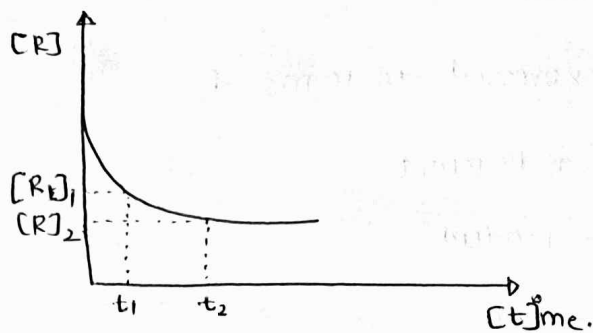
② R.O.A of $SO_3(g)$ is 4.8 kg/min . calculate R.O.D of $SO_2(g)$



$$\longrightarrow \frac{64}{64} \times 4.8 = 8 \times 0.48 =$$

$$\begin{array}{r} 1 \\ 4.8 \\ \hline 800 \\ 480 \\ \hline 320 \\ 80 \\ \hline 240 \\ 480 \\ \hline 800 \end{array}$$

* Average + instantaneous Rate :-



• Av. rate = $-\frac{[R]_2 - [R]_1}{t_2 - t_1}$

• instantaneous rate = slope at given instant
= $\tan \theta = \frac{d[R]}{dt}$

instantaneous rate can be calculated practically only

* Factors affecting Rate of rxn :-

- ① Nature of reactants.
- ② conc. of reactants
- ③ Temp.
- ④ surface area
- ⑤ presence of catalyst
- ⑥ presence of sunlight

* dependence of Rate on concentration of Reactants :-



[A]	[B]	Rate
0.1	0.1	2×10^{-2}
0.1	0.2	4×10^{-2}
0.2	0.1	8×10^{-2}

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

$x=2$
 $y=1$

$$\frac{R_1}{R_2} = \frac{2 \times 10^{-2}}{4 \times 10^{-2}} = \frac{k(0.1)^x(0.1)^y}{k(0.1)^x(0.2)^y}$$

$\frac{1}{2} = \left(\frac{1}{2}\right)^y$ $y=1$

$$\frac{R_1}{R_3} = \frac{1}{4} = \left(\frac{1}{2}\right)^x \quad \boxed{x=2}$$

* for above rxn acc. to data given rate is

$$\text{Rate} = k[A]^2[B]^1$$

→ Power to which conc. term in expressⁿ, experimentally ~~depen~~ determined rate law eq. has been raised is k/a "order of reactⁿ"



$$\text{Rate} = k[A]^x[B]^y \Rightarrow \text{Rate law eqn.}$$

x = order w.r.t A

y = order w.r.t B

x + y = overall order

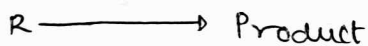
→ Rate law eq. can only be derived experimentally.

x + y has no relation with a + b

13/12

* INTEGRATED RATE LAW EQUATION :-

① ZERO ORDER RXN



$$\text{Rate} = -\frac{d[R]}{dt} = k[R]^0$$

$$\int d[R] = \int -k dt$$

$$[R] = -kt + c$$

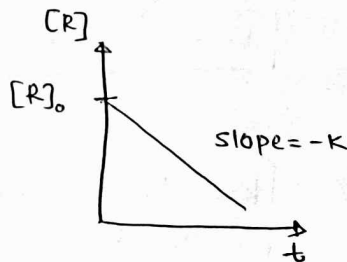
when t = 0

$$c = [R]_0$$

$$[R] = -kt + [R]_0$$

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

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



$t_{1/2}$ = Half life of RXN

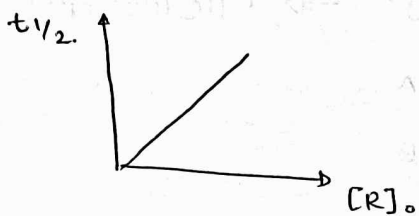
= Time interval during which half of reactants get consumed.

$$t_{1/2} = \frac{[R]_0 - [R]_0/2}{k}$$

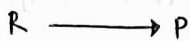
$$t_{1/2} = \frac{[R]_0}{2k}$$

Half life of zero order RXN depends upon initial conc. of reactants as

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



② 1st ORDER RXN :-



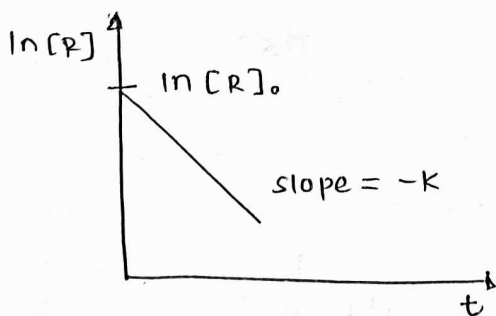
$$\text{Rate} = -\frac{d[R]}{dt} = k[R]$$

$$\int \frac{d[R]}{[R]} = \int -kt$$

$$\ln[R] = -kt + c$$

when $t=0$ ~~$c=0$~~ $c = \ln[R]_0$

$$\ln[R] = -kt + \ln[R]_0$$



$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

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

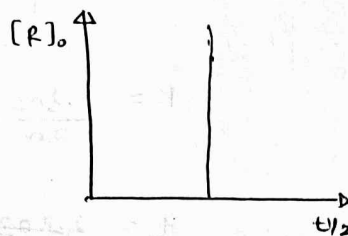
$t_{1/2}$ = Time interval during which half of reactant get completed.

$t_{1/2}$ = time after which $a-x = \frac{a}{2}$

$$x = \frac{a}{2}$$

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

$$t_{1/2} \propto ([R_0])^0$$



* 1st order rxn never gets completed

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

$$t = \infty$$

Time taken to get 50% completed = $t_{1/2} = \frac{0.693}{k}$

" " " " 100% " = ∞

★ Average life of Rxn :-

- it is a statistical life.
- may be defined as life spent by each molecule on an average.

$$t_{av} = \frac{n_1 t_1 + n_2 t_2 + n_3 t_3 \dots}{n_1 + n_2 + n_3}$$

$$t_{av.} = \frac{\sum nt}{\sum n}$$

$$t_{av.} = \frac{1}{k}$$

→ All radioactive disintegratⁿ follow 1st order kinetics.

Q. calculate time required to get 90% of Rxn completed if same 1st order rxn takes 20 min to get 50%

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

$$k = \frac{2.303}{20} \times 0.303$$

$$t = \frac{2.303 \log 10 - \log 9}{2.303 \times 0.303} \times 20$$

$$\frac{1 - 0.6}{0.303} \times 20$$

$$\frac{0.4}{0.3} \times 20$$

$$t = \frac{1 \times 20}{0.303}$$

$$t = 66.6 \text{ min.}$$

0.6
20 x 6
10

Q. A gaseous reactⁿ



Follow 1st order kinetics ; $P_0 \rightarrow$ initial pressure $P_t =$ Total Press. at time t
correct expressⁿ for its Rate const. is/are

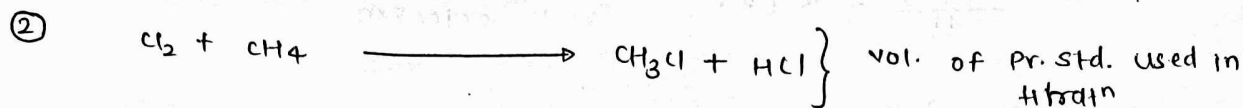
i) $k = \frac{2.303}{t} \log \frac{2P_0}{3P_0 - P_t}$

ii) $k = \frac{2.303}{t} \log \frac{3P_0}{2P_0 - P_t}$

iii) $k = \frac{2.303}{t} \log \frac{P_0}{P_t}$

iv) $k = \frac{2.303}{t} \log \frac{P_0}{P_0 - t}$

Ex ①



$$K = \frac{2.303}{t} \log \frac{Q_\infty - Q_0}{Q_\infty - Q_t}$$

Ans. $K = \frac{2.303}{t} \log \frac{3P_0 - P_0}{3P_0 - P_t}$

Q. d-2-Bromo butene having specific rotation of $+26^\circ$ was treated with Alc. KOH to get 2-Butene, an optically inactive compound. This rxn was monitored using polarimeter tube.

If optical rotatⁿ of sample des by 60% during 20 min. calculate Half life of rxn.

sol.

$$K = \frac{2.303}{t} \log \left[\frac{Q_\infty - Q_0}{Q_\infty - Q_t} \right]$$

$$= \frac{2.303}{20} \log \frac{0 - 26}{0 - 10.4}$$

$$K = \frac{2.303}{20} \times 0.4$$

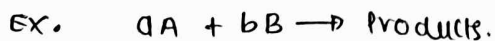
$$t_{1/2} = \frac{0.693}{K}$$

* order of rxn is an experimental quantity
 • may be -ve/+ve/ fractional/ zero.

→ How to predict order of rxn :-

① If rxn is elementary → Each step is complete होने वाली rxn.

$$\text{Stoichiometric coeff.} = \text{order of rxn}$$



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

$$\text{order} = a + b$$

ii) using unit of rate constant

$$\text{Rate} = \frac{-d[R]}{dt} = k [R]^n \quad \text{For } n^{\text{th}} \text{ order rxn}$$

$$\left[\frac{\text{conc.}}{\text{time}} \right] = k (\text{conc.})^n$$

$$k = (\text{con.})^{1-n} (\text{time})^{-1}$$
$$= [\text{mol} \cdot \text{L}^{-1}]^{1-n} \text{sec}^{-1}$$

For zero order rxn unit of $k = \text{mol} \cdot \text{L}^{-1} \text{sec}^{-1}$

1st order " " " " = ~~sec~~ sec^{-1}

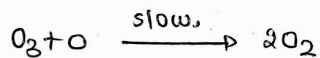
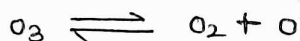
2nd order " " " " = $\text{mol}^{-1} \text{L} \text{sec}^{-1}$

nth " " " " = $\text{mol}^{1-n} \text{L}^{n-1} \text{sec}^{-1}$

③ using given mechanism of rxn :-



Mechanism



$$\text{Rate} = k [\text{O}_3] [\text{O}] \quad \left. \vphantom{\text{Rate}} \right\} \text{Applying steady state approximat}^n \text{ over } [\text{O}]$$

$$K_{\text{eq}} = \frac{[\text{O}_2][\text{O}]}{[\text{O}_3]}$$

$$[\text{O}] = \frac{K_{\text{eq}} [\text{O}_3]}{[\text{O}_2]}$$

$$\text{Rate} = k K_{\text{eq}} [\text{O}_3]^2 [\text{O}_2]^{-1}$$

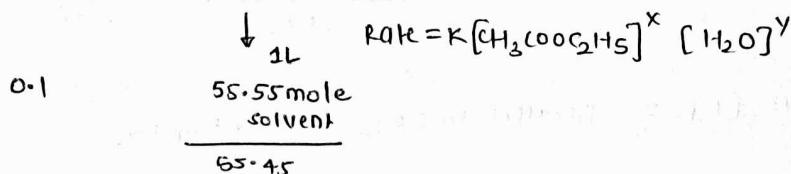
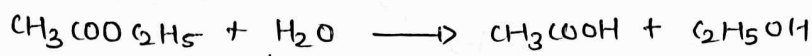
overall order = 1

④ Initial ^{Rate} Method :- $aA + bB \rightarrow \text{Product}$.

[A]	[B]	Rate
0.1	0.1	2×10^{-2}
0.1	0.2	4×10^{-2}
0.2	0.1	8×10^{-2}

$$\text{Rate} = k [A]^2 [B]^1$$

⑤ By Flooding of reactant :-



If one of the reactant is used in excess its conc. remains almost const.

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

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

such rxn which due to presence of one of reactant in excess appear 1st order although actually it was 2nd order, is called "Pseudo First-order Rxn"

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

$$\text{order} = 2$$

But H_2O in excess

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

$$\text{order} = 1$$

Now pseudo 1st order

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

= pseudo 1st order rate const.

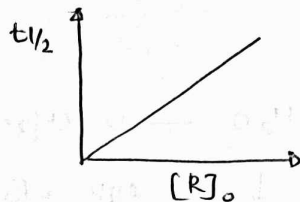
22/02

⑥ using half life of reactant

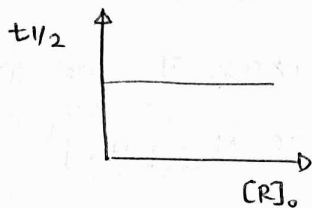
For n^{th} order rxn

$$t_{1/2} \propto [R]_0^{1-n}$$

if $t_{1/2}$ vs $[R]_0 =$ straight line passing through \Rightarrow "zero order"



$t_{1/2}$ vs $[R]_0 =$ parallel to $[R]_0 \Rightarrow$ 1st order.



⑦ K is calculated at diff. time interval:-

use integrated rate law eq. of '0' order to calculate K at diff. interval.

* if $K = \text{const.} \Rightarrow$ order = 0

$K \neq \text{const.} \Rightarrow$ order = try for 1st order.

$$\Rightarrow \boxed{K = \frac{2.303}{t} \log \frac{a}{(a-x)}} \Rightarrow \text{at diff interval apply here}$$

* if $K = \text{const.} \Rightarrow$ order = 1

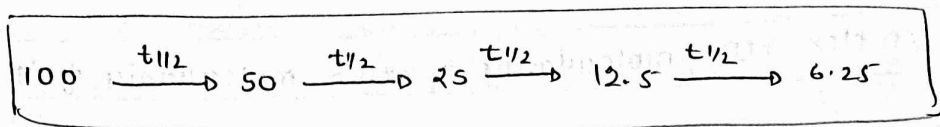
$K \neq \text{const.} \Rightarrow$ const. \Rightarrow Try for 2nd order

Apply $\boxed{\frac{1}{[R]} = \frac{1}{[R]_0} + Kt}$

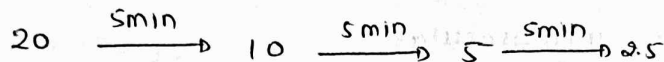
Q. A rxn reduce conc. of reactant A from 20 mol/L to 5 mol/L in 10 min + upto 2.5 mol/L in next 5 min order of rxn will be.

Sol.

①



1st order rxn



∴ 1st order rxn.

②

$$k = \frac{2.303}{10} \log \frac{20}{5}$$

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

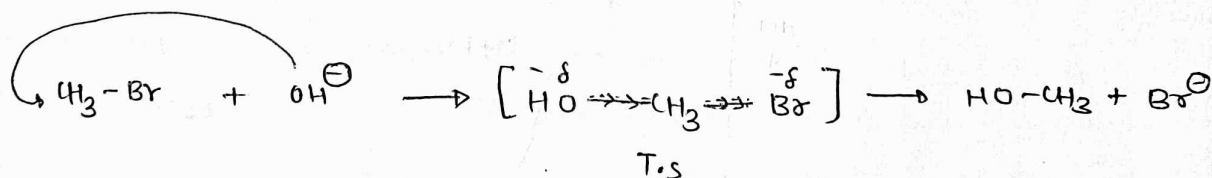
$$k = \frac{2.303}{5} \log \frac{5}{2.5}$$

$$k = \frac{2.303}{5} \log 2.$$

MOLECULARITY OF RXN:-

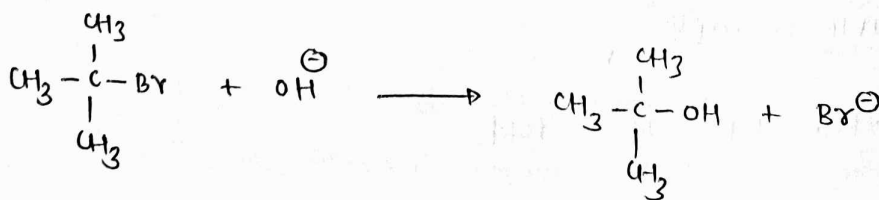
⇒ it is the no. of reactant molecules which collide simultaneously in order to happen a chemical rxn.

Ex. I

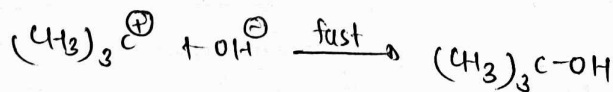
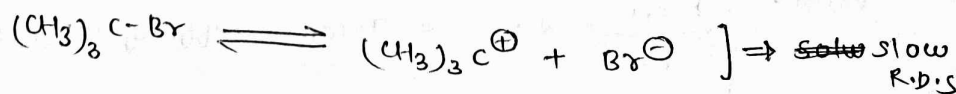


- one step rxn
- Attack + departure simultaneous } Elementary = 2.

Ex. II



Step



Two step rxn complex rxn.

* Molecularity is studied for elementary rxn's.

* Molecularity has no sense for a complex rxn

* for a complex rxn, molecularity of rxn = molecularity of its rds

for Ex (II) molecularity of r.d.s = 1

Rxn = unimolecular

* Molecularity = 0 \Rightarrow not possible

= fractional \rightarrow not possible

= -ve \rightarrow " "

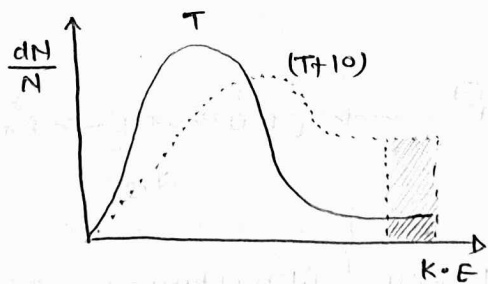
* Most common molecularity are 1 + 2.

* Effect of temp on rate of rxn:-

\rightarrow Rate of rxn \uparrow es with \uparrow es of temp.

\rightarrow on increasing temp. no. of molecules capable of crossing energy barrier increases

This \uparrow es ROR.



\rightarrow on \uparrow esing temp. of system by 10°C no. of molecules crossing energy barrier becomes double or triple.

\rightarrow This \uparrow es ROR by 2 to 3 fold.

\rightarrow $\frac{k_{T+10}}{k_T} = 2 \text{ to } 3 = \text{Temp. coeff. of rxn rate}$

* Quantitatively Arrhenius proposed an empirical relatⁿ to explain temp. dependence of rate

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

K = Rate const.

A = Arrhenius factor

E_a = Activation energy

R = Gas const.

T = Absolute temp.

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

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

E_a = +ve Always.

in Equil.

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303RT}$$

ΔH = -ve/+ve

COLLISION THEORY OF REACTION RATE:-

→ For a rxn to happen, there should be collisions b/w reactant molecules.

→ Z_{AB} = collision freq. = No. of collision taking place per unit volume per unit time

$$\text{Rate} \propto Z_{AB}$$

→ Not every collision is capable of product formatⁿ. Those collision which crosses energy barrier will ~~be~~ form product. This is k/a "effective collision".

$e^{-E_a/RT}$ = fractⁿ of molecules capable of crossing energy barrier.

$$\text{Rate} \propto Z_{AB} \cdot e^{-E_a/RT}$$

→ Not every collision with sufficient energy will form product unless reactant colliding with each other are properly orientated.

Thus.

$$\text{Rate} \propto P Z_{AB} \cdot e^{-E_a/RT}$$

P = probability of collision b/w reactant molecules with proper orientatⁿ.