# —: CHEMICAL KINETIC :—

Chemical kinetics ⇒ The Branch of chemistry in which be deal the study of the speed or the rate of chemical Reaction.

There are Three types of chemical Rxn

1- very fast reaction :- such type of chemical Reaction which take place withing $10^{-16}$ sec known as very fast Reaction. Practically the rate of rxn for such of rxn we can not calculated.

2- very slow Reaction ⇒ such type of chemical rxn which take place withing 2 days, mounts, week, years known as very slow reaction. Practically the rate of such type of rxn we ~~can~~ should not calculated.

3- modirate rate of reaction ⇒ Such type of chemical rxn which take place withing in a day, in Hours, in minite. Practically we can calculate the ~~su~~ Rate of such type of rxn.

③ Rate of dis appeance of C

① Rate of rxn

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

=

$$= -\frac{1}{2}\frac{\Delta[A]}{\Delta t} = +\frac{1}{4}\frac{\Delta[B]}{\Delta t} = +\frac{\Delta[C]}{\Delta t}$$

② Rate of appeance of B -

$B = 5\times10^{-4}$ mol $L^{-1}$ $sec^{-1}$

$$= +\frac{1}{4}\frac{\Delta[B]}{\Delta t}$$

$$= -\frac{1}{2}\times 5\times10^{-4}$$

$$\boxed{A = -2.5\times10^{-4}}$$

$= 1.25\times10^{-4}$ mol $L^{-1} sec^{-1}$

③ Rate of dis'appeance - of C

$$= +\frac{1}{4}\frac{\Delta[B]}{\Delta t} + C$$

$$= 1.25\times10^{-4} + C$$

$C = -1.25\times10^{-4}$ mol $L^{-1}$ $sec^{-1}$

Question

di composition of $N_2O_5$ is expresed by the following equation

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$$

if the rale of di-composition of $N_2O_5$ is $1.9\times10^{-3}$ mol $L^{-1}$ $min^{-1}$. find out the rale of formation of $NO_2$ and $O_2$.

if $\alpha+\beta = 0$, the rxn is known as zero order Rxn.

if $\alpha+\beta = 1$ the rxn is known as first order Rxn.

and similarlly

$\alpha+\beta = 2$ the rxn is known as second order Rxn.

## → Zero ORDER REACTION →

Such Type of chemical Rxn in which the sum of order of Rxn. is zero. Known as zero Order Rxn.

Let us consider a Rxn

$$A \longrightarrow \text{Product}$$

| | A | Product | |
|---|---|---|---|
| $t=0$ | $a$ | $0$ | initial |
| at time t | $(a-x)$ | $x$ | after time t |

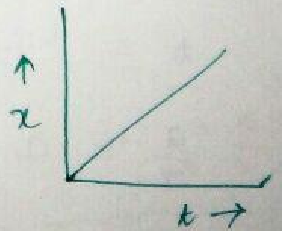
$$\text{rate of rxn} = K[A]^{\alpha}$$

$$\frac{-dA}{dt} = K[A]^{0}$$

$$\frac{-d(a-x)}{dt} = K(a-x)^{0}$$

$$\frac{dx}{dt} = K$$

$$\int_0^x dx = K\int_0^t dt$$



$$[x]_0^x = K[t]_0^t$$

$$\boxed{\underset{y}{\underset{\downarrow}{x}} = \underset{m}{\underset{\downarrow}{K}}\,\underset{x}{\underset{\downarrow}{t}}}$$

$y = m x$

**Question** Write down the expression for Rate of rxn for the following rxn.

ⓐ $2A + 3B \longrightarrow 3C + 2D$

rate of rxn = $-\frac{1}{2}\frac{\Delta[A]}{\Delta t} = -\frac{1}{3}\frac{\Delta[B]}{\Delta t} = +\frac{1}{3}\frac{\Delta[C]}{\Delta t} = +\frac{1}{2}\frac{\Delta[D]}{\Delta t}$

ⓑ $3A \longrightarrow 2B + C$

Rate of Rxn = $-\frac{1}{3}\frac{\Delta[A]}{\Delta t} = +\frac{1}{2}\frac{\Delta[B]}{\Delta t} = +\frac{\Delta[C]}{\Delta t}$

ⓒ $2HCl \longrightarrow H_2 + Cl_2$

Rate of Rxn = $-\frac{1}{2}\frac{\Delta[HCl]}{\Delta t} = +\frac{\Delta[H_2]}{\Delta t} = +\frac{\Delta[Cl_2]}{\Delta t}$

ⓓ $N_2 + 3H_2 \longrightarrow 2NH_3$

~~$-\Delta$~~

Rate of Rxn = $-\frac{\Delta[N_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = +\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$

dish appeance = $-\frac{\Delta[N_2]}{\Delta t} = -\frac{\Delta[H_2]}{\Delta t} = +\frac{\Delta[NH_3]}{\Delta t}$

dishappeance = $+\frac{\Delta[NH_3]}{\Delta t}$

Que $2A + B \longrightarrow 3C$ if the rate of apperance of C is $1.32 \times 10^{-4}$ mol/lit/sec Calculate

1) Rate of the rxn -

(ii) Rate of disapperence of A .

Rate of rxn $= -\frac{1}{2}\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t} = +\frac{1}{3}\frac{\Delta[C]}{\Delta t}$

Rate of apperence

$$= -\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{\Delta t} = +\frac{1}{3} \times 1.32 \times 10^{-4}$$

$= 0.44 \times 10^{-4}$ mol/lit/sec'

$= 4.4 \times 10^{-5}$ mol $L^{-1}$ $sec^{-1}$

Rate of disappearance -

$$4 \times 10^{-5} = -\frac{1}{2} \cdot \frac{\Delta[A]}{\Delta t}$$

$$8 \times 10^{-5} = -\frac{\Delta[A]}{\Delta t}$$

$$\boxed{8. \times 10^{-5} \text{ mol } L^{-1} \text{ sec}^{-1}}$$

Question a gaseous rxn $2A \longrightarrow 4B + C$ is carryed out in closed container. if the rate of appeance of B is $5 \times 10^{-4}$ mol $L^{-1}$ $sec^{-1}$

① find out the rate of rxn -

② rate of appeancen of A

Soln

$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2} O_2$

Rate of Rxn -

$$= -\frac{\Delta [N_2O_5]}{\Delta t} = +\frac{1}{2} \frac{\Delta [NO_2]}{\Delta t} = +\frac{1}{2} \frac{\Delta [O_2]}{\Delta t}$$

$$= + \frac{\Delta [O]}{\Delta t}$$

$N_2O_5 = 1.8 \times 10^{-3}$ mol $L^{-1}$ min$^{-1}$

Rate of formation of $NO_2$

$$= +\frac{1}{2} \frac{\Delta [NO_2]}{\Delta t}$$

$$= \frac{1}{2} \times 1.8 \times 10^{-3}$$

$NO_2$ $= 5.9 \times 10^{-3}$

$= 9 \times 10^{-4}$

$$= \frac{1}{2} \times 1.8 \times 10^{-3}$$

$= ~~3.6 \times 10^{-3}~~$

$= 0.9 \times 10^{-3}$

$= 9 \times 10^{-4}$ mol $L^{-1}$ min$^{-1}$

Rate of formation of $O_2$

$$= +\frac{1}{2} \frac{\Delta [O_2]}{\Delta t}$$

$$= + \frac{\Delta [O]}{\Delta t}$$

$= 2$

$= 2 \times 1.8 \times 10^{-3}$

$$\boxed{= 3.6 \times 10^{-3} \text{ mol } L^{-1} \text{ min}^{-1}}$$

Question = In the haber process $N_2 + 3H_2 \rightarrow 2NH_3$ the Rate of formation of $NH_3$ is $4.8 \times 10^{-3}$ mol $L^{-1}$ sec$^{-1}$ Calculate the rate of conjuesuption of Hydrogen

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

Rate of Rxn

$$= -\frac{\Delta[N_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = +\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$$

$NH_3 = 4.8 \times 10^{-3}$ mol $L^{-1}$ $sec^{-1}$

Rate of rxn $= \frac{1}{2} \times 4.8 \times 10^{-3}$

$= 2.4 \times 10^{-3}$ mol $L^{-1}$ $sec^{-1}$

Rate of consumeption of $H_2 = 3 \times 2.4 \times 10^{-4}$

$$\boxed{H_2 = 7.2 \times 10^{-4} \text{ mol } L^{-1} \text{ sec}^{-1}}$$

# Factor's which influance the Rate of Rxn ⇒

① Physical State of the Reactant ⇒

Any chemical Reaction depends on Collision of the Reactant. in gaseous State the Collision will be greater then solid and liquide. There for the rate of rxn in gaseous State greater then Solid or liqued.

Hence the order of Rate of rxn —

$$\boxed{\text{Gas} > \text{liqued} > \text{Solid}}$$

### 2- Concentration of the reactant ⇒

greater the conc. of the reactant greater will be the possivitijes. of Collision due to which rate of rxn Increase.

### #effect of tempreture :-

When be increase the temp the K.E of the reactant also increase due to which the possivities of Collision also increase. hence rate of rxn also increase.

### #Presence of catylist ⇒

Catylist can increased an dicrease the rate of chemical Rxn. if we used +ve catylist the rate of rxn increase.

Ex- $N_2 + 3H_2 \xrightarrow{Fe} 2NH_3$

Here Fe is a catylist which increase a rate of rxn. if we use (-ve) catylist the rate of rxn dicrease

Ex- $CHCl_3 + O_2 \xrightarrow{C_2H_5OH} COCl_2 + H_2O$

Here $C_2H_5OH$ at (-ve) catylist.

### #Surface Area ⇒

greater the surface Area of the redictent greater will the posivities of Collision b/w the reactant due to which rate of rxn increase.

## #Presence of sun light (effect of Radiations) विकिरण का प्रभाव

in the presence of sun light, the rate of rxn also increase.

$$\cancel{2HC} \quad H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$$

When any chemical rxn goes through in the presence of sun light, reactent break free radically.

## #Presence of Solvent →

for any chemical rxn we will use a sutable type at reactant. for any polar reaction we will use polar solvent and for non-polar reaction we will use non-polar solvent.

Ex– for neutralisation rxn we will use water for disolving acid ~~of~~ OR Base. in the presence of water escident base ionised an formation of Salt take place.

Ex– $\underset{(aq)}{BaCl_2} + \underset{(aq)}{H_2SO_4} \longrightarrow$

$BaCl_2 + \text{water}(H_2O) \longrightarrow Ba^{+2}\,Cl_2^{-2}$

$H_2SO_4 + H_2O \longrightarrow 2H^+ + SO_4^-$

$Ba^{+2} + SO_4^{-2} \longrightarrow BaSO_4 \downarrow$

~~When~~ Solvent can also change the product

When alkene react with HBr, addition Rxn take place a/c to markovnikof Rule. if this rxn take place in the presence of Per oxide

(Solvent), addition Rxn take place a/c to Antimorkovnikof Rule.

Ex = $CH_3-CH=CH_2+HBr \longrightarrow CH_3-CH_2-CH_3+HBr$

$CH_3-CH=CH_2+HBr \xrightarrow[R]{H_2O_2} CH_3-CH_2-CH_3+Br$

1 bromopropane

## # effect of Pressure ⇒

in case of solid or liqued reactants, Pressure does not change the rate of rxn.

but in case of gas, if we increase the pressure, the rate of rxn also increase becoz number of collision increase.

## #Law of mass Action ⇒

Let us Consider a rxn a

$aA + bB \longrightarrow$ Product

A/c to Law of mass of Action rate is

$$\boxed{rate = K[A]^{\alpha}[B]^{\beta}}$$

Where K is Rate constant

Where sum of $\alpha$ & $\beta$

$\alpha+\beta$ Known as order of Rxn

Here $\alpha$ may or may not be equal to a Similarlly

$\beta$ may " " " be " " b.

$\boxed{x = K.t}$ $\longrightarrow$ ①

$a - (a-x) = Kt$

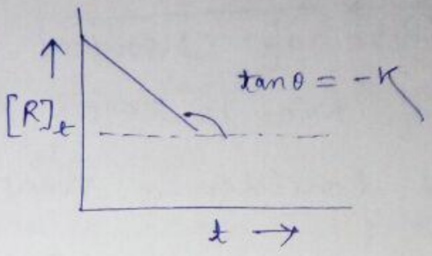
$[R]_0 - [R]_t = Kt$

$\boxed{[R]_t = [R]_0 - Kt}$ $\rightarrow$ ②

The graphical reporesention for eqn ②

$$\begin{array}{ccccc} [R]_t & = & [R]_0 & - & K\,t \\ \downarrow & & \downarrow & & \downarrow\;\downarrow \end{array}$$

$$\boxed{y = c - mx}$$



*Half life period ⇒

The required to reduced the initial concentration of the reactant to half of its initial value is Called half life period.

it is represented by $t_{1/2}$.

We known that

$$[R]_t = [R]_0 - Kt$$

$$[R]_0 = a$$

$$[R]_t = a/2$$

$$t = t_{1/2}$$

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

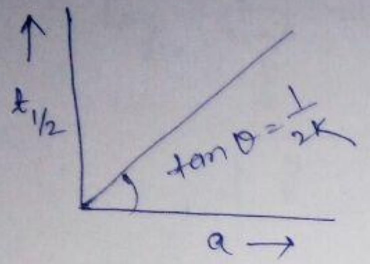
$$Kt_{1/2} = \frac{a}{2}$$

$$\boxed{t_{1/2} = a\left(\frac{1}{2K}\right)}$$

The graphical representation.

$$t_{1/2} = a\left(\frac{1}{2K}\right)$$

$$\boxed{y = x \quad m}$$



Que-
The rate constant afor a rexn of zero order is 0.003 mol $L^{-1}$ $sec^{-1}$. How long will it take for initial Con- A all from 0.1 M to 0.075 M.

$K = 0.003$

$a = 0.1$ M.

$(a-x) = 0.075$ M.

A ⟶ Product.

$x = Kt$

$[R]_0\ a = 0.1$ m

$[R]_t = 0.075$ M

$K = 0.003$

$[R]_t = [R]_0 - Kt$

$0.075 = 0.1 - 0.003t$

$0.003t = 0.025$

$$\boxed{t = 8.3 \text{ sec}}$$

$= .1 - .075 = 0.025$

$= \frac{0.025}{0.003} = 8.33$

## Ist order Rxn ⇒

Let us Consider a Reaction

$$A \longrightarrow \text{Product}$$

| | A | Product |
|---|---|---|
| Initial | $a$ | $0$ |
| at time t | $(a-x)$ | $x$ |

$$\text{rate} = K\,[A]^{r}$$

$$-\frac{dA}{dt} = K[A]^{1}$$

$$-\frac{d(a-x)}{dt} = K(a-x)$$

$$\frac{dx}{dt} = K(a-x)$$

$$\frac{dx}{a-x} = K\,dt$$

$$\int \left(\frac{1}{a-x}\right) dx = K\int dt$$

$$-\log_e (a-x) = Kt + c$$

$$t=0 \qquad x=0$$

$$-\log_e a = c$$

$$-\log_e (a-x) = Kt - \log_e a$$

$$Kt = \log_e a - \log_e (a-x)$$

$$Kt = \log_e \frac{a}{a-x}$$

$$\boxed{K = 2.303 \log_{10} \frac{a}{a-x}}$$

Ist order RxN

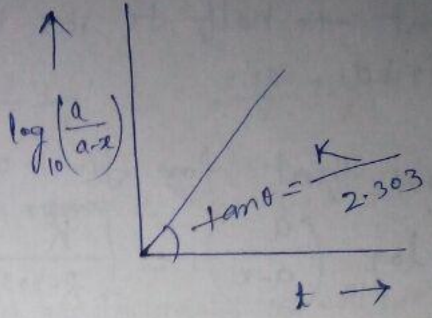
$$\boxed{Kt = 2.303 \log_{10} \frac{[R]_0}{[R]_t}}$$

1- graph -

$$2.303 \log_{10}\left(\frac{a}{a-x}\right) = Kt$$

$$\log_{10}\left(\frac{a}{a-x}\right) = \left(\frac{K}{2.303}\right) t$$

$$\boxed{\underset{y}{\underset{\downarrow}{\log_{10}\left(\frac{a}{a-x}\right)}} = \underset{m}{\underset{\downarrow}{\left(\frac{K}{2.303}\right)}} \underset{x}{\underset{\downarrow}{t}}}$$

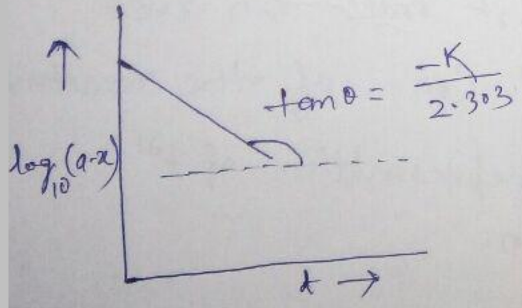


# graph - 2

$$Kt = 2.303 \log_{10} \frac{a}{a-x}$$

$$\left(\frac{K}{2.303}\right) t = \log_{10} a - \log_{10} (a-x)$$

$$\underset{y}{\underset{\downarrow}{\log_{10} (a-x)}} = \underset{c}{\underset{\downarrow}{\log_{10} a}} - \underset{m}{\underset{\downarrow}{\left(\frac{K}{2.303}\right)}} \underset{x}{\underset{\downarrow}{t}}$$



Calculation of Rate of Rxn ⇒

Let us consider a rxn

$$A \longrightarrow B$$

$$\text{Rate of Rxn} = \frac{\text{change in concentration}}{\text{Total time taken}}$$

$$= -\frac{\Delta[A]}{\Delta t} = +\frac{\Delta[B]}{\Delta t}$$

$$= -\frac{dA}{dt} = +\frac{dB}{dt}$$

$\left[-\frac{\Delta[A]}{\Delta t} = +\frac{\Delta[B]}{\Delta t}\right]$ is also known as avarage r
of Reaction.

While $\left[-\frac{dA}{dt} = +\frac{dB}{dt}\right]$ is Known as instaneous
of Reaction.

Let us consider a general rxn in which insto
-mentry its present -

$$mA \longrightarrow nB$$

$$\text{rate of rxn} = -\frac{1}{m}\frac{\Delta[A]}{\Delta t} = +\frac{1}{n}\frac{\Delta[B]}{\Delta t}$$

$$= -\frac{1}{m}\cdot\frac{dA}{dt} = +\frac{1}{n}\frac{dB}{dt}$$

Half life of first order Rxn ⇒

The required to reduced the initial Con- of the reactant to half to its initial value is called half life period.

We know that for first order Reaction:⇒

$$\log_{10}\left(\frac{a}{a-x}\right) = \left(\frac{K}{2.303}\right)t$$

for half life period

$x = a/2$

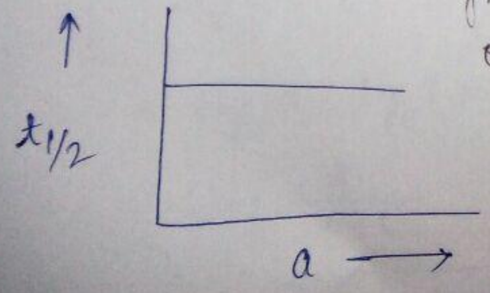
$t = t_{1/2}$

$$\log_{10}\left(\frac{a}{a-a/2}\right) = \frac{K}{2.303}\, t_{1/2}$$

$$\log_{10} 2 = K\, t_{1/2}$$

$$0.3010 = \frac{K\, t_{1/2}}{2.303}$$

By the help of above expression we can say that the half life period for first order rxn does not depents upon the initial Con- of the reactant



graphical representation of Ist order rxn.

## Second order Rxn ⇒

Let us Consider a rxn A give Product

$$A \longrightarrow \text{Product}$$

| | A | Product |
|---|---|---|
| initial | $a$ | $0$ |
| at time t | $a-x$ | $x$ |

$$\text{rate} = K[A]^2$$

$$-\frac{dA}{dt} = K[A]^2$$

$$-\frac{d(a-x)}{dt} = K(a-x)^2$$

$$\frac{dx}{dt} = K(a-x)^2$$

$$\frac{dx}{(a-x)^2} = K\,dt$$

$$\int \frac{1}{(a-x)^2}\,dx = K\int dt$$

$$\frac{1}{a-x} = Kt + c$$

$t=0$ , $x=0$

$$\frac{1}{a} = c$$

$$\frac{1}{a-x} = Kt + \frac{1}{a}$$

$$\boxed{Kt = \frac{1}{a-x} - \frac{1}{a}}$$

$$\int \frac{1}{(a-x)^2}\,dx$$

let $a-x = p$

$-dx = dp$

$$-\int \frac{1}{p^2}\,dp$$

$$-\int p^{-2}\,dp$$

$$-\frac{p^{-2+1}}{-2+1}$$

$$= \frac{1}{p}$$

$$= \frac{1}{(a-x)}$$

$$\int x^n\,dx$$

$$\frac{x^{n+1}}{n+1}$$

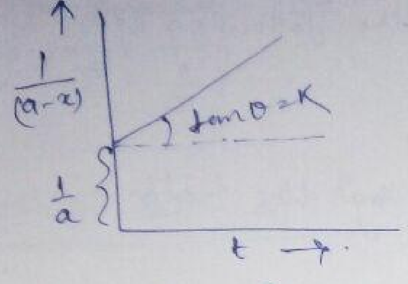
## # grophical representation for second order Rxn ⇒

$$Kt = \frac{1}{a-x} - \underset{\overset{\downarrow}{c}}{\frac{1}{a}}$$

$$mx = y$$

$$\underset{\overset{\downarrow}{y}}{\frac{1}{a-x}} = \underset{\overset{\downarrow\downarrow}{mx}}{Kt} + \underset{\overset{\downarrow}{c}}{\frac{1}{a}}$$

$$\boxed{y = mx + c}$$



## Half life Period for second order Rxn ⇒

The required to reduced the initial Concentration of the reactant to half of its initial value is called half life Period-

It is represented by 1/2.

we know that,

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

$$x = a/2$$

$$t = t_{1/2}$$

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

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

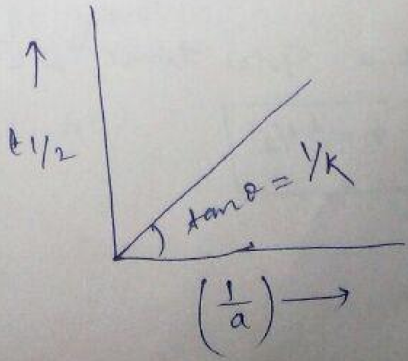
$$Kt_{1/2} = \frac{1}{a}$$

$$\boxed{t_{1/2} = \frac{1}{Ka}}$$

The graphical represention.

$$\underset{\overset{\downarrow}{y}}{t_{1/2}} = \underset{\overset{\downarrow\downarrow}{mx}}{\frac{1}{Ka}}$$

$$\boxed{y = mx}$$



Radio Active Decay ⇸

when an element looses its mass by the elimination of sum sutable rays (α-Ray, β-Ray, γ-Ray) known as Radio active Decay.

The Rate of Radio active Decay always will we 1st order. there for its will satisfy the following eqn –

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

Hence The radio active Decay defined by the help of following eqn.

$$\boxed{\lambda = \frac{2.303}{t} \log \frac{N_0}{N}}$$

where $\lambda$ is Decay constant

$N_0$ = initial amount of radio active element

$N$ = the amount of radio active element at time $t$.

$N$ and $N_0$ are also related by a following way

$$\boxed{N = N_0 \left(\frac{1}{2}\right)^n}$$

where $n$ = no. of half life.

~~Average life~~ = Total time ⇒ (T)

$$\boxed{T = n \times t_{1/2}}$$

~~Average life~~ ⇒ Total time (T)

$$\boxed{T = n \times t_{1/2}}$$

**Average life** ⇒ The reciprocal of decay constant is known as Average life. it is represented by $\tau$.

$$\boxed{\tau = \frac{1}{\lambda}}$$

**#Half life of Radio active Rxn** ⇒ $\boxed{t_{1/2} = \frac{0.693}{\lambda}}$

**#Relasionship b/w Average life and Half life** ⇒

$$\boxed{\tau = \frac{1}{\lambda}} \rightarrow ①$$

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

$$t_{1/2} = 0.693 \times \tau$$

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

$$\boxed{\tau = 1.44 \times t_{1/2}}$$

Question
Archaeologic remain of woodn Artifact was found to Contain 32% $C_{14}$ activity of what was accepted in freshlly cut wood. fine the age of wood if Half life of C-14 is 5760 year's.

Sol$^n$ $a = 100$
$a - x = 100 - 32 = 68\%$

$$K = \frac{2.303}{t} \log \frac{100}{68}$$

**Question** ⇒ If in 3160 years a radio active substance becomes 1/4 of the original amount find its Half life period.

**Sol^n** $t = 3160$ years $\qquad \lambda = \frac{1}{4}$ $\qquad N_0 = 100$, $N = 25$

$$\lambda = \frac{2.303}{3160} \log 4$$

$$= \frac{2.303 \times 0.6020 \ \cancel{.477}}{3160}$$

$$= .00072 \times \cancel{.477} \ .6020$$

$$= 0.000433$$

$$\lambda = \frac{1.386}{3160} = 0.00043$$

$\boxed{1580}$ Ans

st method)

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

$$\lambda = \frac{2.303}{t} \log \frac{N_0}{N} \frac{1}{1/4}$$

$$\lambda = \frac{2.303}{3160} \log 4$$

$$\frac{0.6930}{t_{1/2}} = \frac{2.303}{3160} \log 4$$

$$\frac{2.303 \log 2}{t_{1/2}} = \frac{2.303 \ \cancel{x} \cdot 2 \times \log 2}{3160}$$

$$2 t_{1/2} = 3160 = \frac{3160}{2}$$

$$t_{1/2} = 1580 \text{ year}$$

(IInd method)

$$N = N_0 \left(\frac{1}{2}\right)^n$$

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

$$x = 2$$

$$T = x \times t_{1/2}$$

$$3160 = 2 \times t_{1/2}$$

$$T = 1580 \text{ year}$$

A) Radio active element as Half life Period 13.3 Hour. after 79.8 Hour. What fraction of radio active element remain.

$t_{1/2} = 13.3$ Hrs $\rightarrow 1$

$N_0 = 100$

$N = ?$

$\lambda = ?$

$t_{1/2} = 79.8$ Hrs $\rightarrow 2$

$T = n \times t_{1/2}$

$79.8 = n \times 13.3$

$n = 6$

$N = N_0 \left(\frac{1}{2}\right)^n$

$N = 1 \left(\frac{1}{2}\right)^6$

$$\boxed{N = \frac{1}{64}}$$

* PSEUDO ORDER RXN :—

The reaction whose actual order is different from that accepted from by using rate low equation are called pseudo order Rxn.

Ex- $R-Cl + H_2O \longrightarrow R-OH + HCl$

The rate law expression for this reaction is -

rate $= K [R-Cl][H_2O]$

By the Help of this formula the order of reach should 2 but the actual order of rxn is - 1.

ex- $2HI \longrightarrow H_2 + I_2$

rate $= K [HI]^2$

By the help of above formula the order of Rxn is 2 but the acttual order of rection is 0.

Experimental method for Calculating the order of Reaxn/. →

## Initial Rate Method ⇒

let is consider a reacn $m_1 A + m_2 B \longrightarrow$ Product.

The rate of this rxn will be rate

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

Hence the order of reaction for the calculation of order Reacn we will take for rxn. exp- for Calcute $\alpha$ and 2 exp. for calculate $\beta$.

**Exp-1** $r_1 = K [A_1]^{\alpha} [B_1]^{\beta}$

**Exp-2** $r_2 = K [A_2]^{\alpha} [B_1]^{\beta}$

$$\frac{r_1}{r_2} = \frac{[A_1]^{\alpha}}{[A_2]^{\alpha}}$$

$$\frac{r_1}{r_2} = \left\{ \frac{[A_1]^{\cancel{\alpha}}}{[A_2]^{\cancel{\alpha}}} \right\}^{\alpha}$$

Exp-3 $r_3 = K [A_3]^{\alpha} [B_3]^{\beta}$

Exp-4 $r_4 = K [A_4]^{\alpha} [B_4]^{\beta}$

$$\frac{r_3}{r_4} = \left\{ \frac{[B_3]}{[B_4]} \right\}^{\beta}$$

**Question→** for a rxn in which A and B $A + B \longrightarrow C$ Accordin to the following way—

| Exp. | [A] mol $L^{-1}$ | [B] mol $L^{-1}$ | rate (mol $L^{-1}$ $sec^{-1}$) |
|---|---|---|---|
| 1 | 0.03 | 0.03 | $0.3 \times 10^{-4}$ |
| 2 | 0.06 | 0.06 | $1.2 \times 10^{-4}$ |
| 3 | 0.09 | 0.09 | $2.7 \times 10^{-4}$ |

**Sol^n** rate $= K[A]^{\alpha}[B]^{\beta}$

$$0.3 \times 10^{-4} = K[0.03]^{\alpha}[0.03]^{\beta} \longrightarrow ①$$

$$1.2 \times 10^{-4} = K[0.06]^{\alpha}[0.06]^{\beta} \longrightarrow ②$$

$$2.7 \times 10^{-4} = K[0.09]^{\alpha}[0.09]^{\beta} \longrightarrow ③$$

$$\frac{1.2 \times 10^{-4}}{0.3 \times 10^{-4}} = \left(\frac{0.06}{0.03}\right)^{\alpha}\left(\frac{0.06}{0.03}\right)^{\beta}$$

$$4 = 2^{\alpha} \cdot 2^{\beta}$$

$$4 = 2^{\alpha+\beta}$$

$$2^2 = 2^{\alpha+\beta}$$

$$\boxed{\alpha + \beta = 2}$$

**Question** for the Rxn $2NO + Cl_2 \longrightarrow 2NOCl$ following datas are obtened. find out the order of Rxn as well as rate law expresion for this reacn.

| Exp | [NO] | [$Cl_2$] | Rate (mol $L^{-1}$ $sec^{-1}$) |
|---|---|---|---|
| 1 | 0.01 | 0.01 | $1.2 \times 10^{-4}$ |
| 2 | 0.01 | 0.02 | $2.4 \times 10^{-4}$ |
| 3 | 0.02 | 0.02 | $9.6 \times 10^{-4}$ |

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

$1.2\times10^{-4} = K[0.01]^{\alpha}[0.01]^{\beta} \rightarrow ①$

$2.4\times10^{-4} = K[0.01][0.02]^{\beta} \rightarrow ②$

$9.6\times10^{-4} = K[0.02][0.02]^{\beta} \rightarrow ③$

from eqn $\frac{②}{①}$

$$\frac{\overset{2}{\cancel{2.4}}\cancel{\times10^{-4}}}{\cancel{1.2\times10^{-4}}} = \left[\frac{(0.01)}{(0.01)}\right]^{\alpha}\left(\frac{0.02}{0.01}\right)^{\beta}$$

$$2 = 1^{\alpha}\,2^{\beta}$$

$$2^{1} = 2^{\beta}$$

$$\boxed{\beta = 1}$$

from eqn $\left(\frac{3}{1}\right)$

$$\frac{\overset{8}{\cancel{9.6\times10^{-4}}}}{\cancel{1.2\times10^{-4}}} = \left(\frac{0.02}{0.01}\right)^{\alpha}\left(\frac{0.02}{0.01}\right)^{\beta}$$

$$8 = 2^{\alpha}\cdot2^{\beta}$$

$$8 = 2^{\alpha+\beta}$$

$$(2)^{3} = 2^{\alpha+\beta}$$

$$\boxed{\alpha+\beta = 3}$$

Put the value —

$$\alpha + 1 = 3$$

$$\alpha = 3-1$$

$$\boxed{\alpha = 2}$$

$$\boxed{\text{rate} = K[NO]^{2}[Cl_2]^{1}}$$

## ② Half life Period method ⇒

for any chemical Reaction the half life Period depends on the intial Constration of the reactant according to following equation.

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

Where n is order of Reaction

let us consider a Reaction

$$A \longrightarrow \text{Product.}$$

Let $a_1$ is the intial Consentration of the reactant A, the half life period at this time will be $(t_{1/2})$.

$$\boxed{(t_{1/2})_1 \propto \frac{1}{a^{n-1}}} \longrightarrow ①$$

let $a_2$ is the another initial Concentration of this reactant the half life period at this time will be $(t_{1/2})_2$ -

$$\boxed{(t_{1/2})_2 \propto \frac{1}{a_2^{n-1}}} \longrightarrow ②$$

By eqn ① and ②

$$\boxed{\frac{(t_{1/2})_2}{(t_{1/2})_1} = \left(\frac{a_1}{a_2}\right)^{n-1}}$$

By the help of this expression we confinded the reaction for Gaseous · Reactant -

$$\boxed{\frac{(t_{1/2})_2}{(t_{1/2})_1} = \left(\frac{P_1}{P_2}\right)^{n-1}}$$

**Question** At the certain temp. the half life period for the decomposition of ammonia give following Result.

| Pressure (mmHg) | Half life period (second) |
|---|---|
| 6667 | 3.52 |
| 13333 | 1.92 |
| 26666 | 1 |

find out the order of this Reaction-

$$\frac{(t_{1/2})_2}{(t_{1/2})_1} = \left(\frac{P_1}{P_2}\right)^{n-1}$$

$$\frac{\cancel{26666}^{\,2}}{\cancel{13333}} = \left(\frac{2}{1}\right)^{n-1}$$

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

$$(n-1) = 1$$

$$\boxed{n = 1+1 = 2} \qquad n \approx 2$$

**Question**⇒ The Half life period for the thermal decomposition of $PH_3$ give following data.

| Pressure (mmHg) | Half life (Hour) |
|---|---|
| 70 | 84 |
| 79 | 84 |
| 37.5 | 84 |

Solⁿ

$$\frac{(t_{1/2})_2}{(t_{1/2})_1} = \left(\frac{P_1}{P_2}\right)^{n-1}$$

$$\frac{\cancel{70}^{35}}{\cancel{38}_{19}} = \left(\frac{84}{84}\right)^{n-1}$$

$$\gamma^{0} = (1)^{n-1}$$

$$(n-1) = 0$$

$$\boxed{n = 1} \quad \underline{n \approx 1} \text{ Answer}$$

* III^rd Method

* Ostwalt Isolation Method ⇒

Let us consider a reaction $m_1A + m_2B \longrightarrow$ Product -

Let the rate law expression for this reaction is -

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

where $\alpha + \beta$ is order of reacⁿ.

* Calculation for $\alpha$ ⇒

Let us consider $[A_1]$ is the concentration of the reactant A at this time the concentration of [B] is too large so that the rate of Rxn depends only the concentration of [A].

$$r_1 = K[A_1]^{\alpha} \longrightarrow ①$$

Let $[A_2]$ is the concentration of the reactent [A] and at this time the concentration of [B] is too, large, so that the rate of reacⁿ depends only the concentration of [A].

$$r_2 = K[A_2]^\alpha \longrightarrow ②$$

By equation ① and ②

$$\frac{r_1}{r_2} = \left[\frac{A_1}{A_2}\right]^\alpha$$

we can find out the value of $\alpha$.

* Calculation for $\beta \Rightarrow$

Let us consider $[A_1]$ is the concentration of the reactant A at this time the concentration of [B] is too large so that the rate of reaction depends only the concentration of [A].

$$r_1 = K[A_1]^\beta \longrightarrow ①$$

let $[A_2]$ is the concentration of the reactant [A] and at this time the concentration of [B] is too large, so that the rate of reaction depends only the concentration of [A]

$$r_2 = K[A_2]^\beta \longrightarrow ②$$

By equation ① and ②

$$\frac{r_1}{r_2} = \left[\frac{A_1}{A_2}\right]^\beta$$

we can find out the Value of $\beta$.

# * Van't Hoff differential method ⇒

—————— x ——————

Let us consider rxn

$$\begin{array}{llcc} & A & \longrightarrow & \text{Product} \\ t=0 & a & & 0 \\ \text{at } t=t_1 & (a-x) & & x \\ \text{at } t=t_2 & (a-y) & & y \end{array}$$

$$\boxed{\begin{aligned} \text{Let } c_1 &= (a-x) \\ c_2 &= (a-y) \end{aligned}}$$

$$\text{rate} = K[A]^n \quad , \quad \text{rate} = K[B]^n$$

$$-\frac{d(a-x)}{dt_1} = K[a-x]^n \qquad -\frac{d(a-y)}{dt_2} = K[a-y]^n$$

$$\boxed{-\frac{dc_1}{dt_1} = Kc_1^n} \rightarrow ① \qquad \boxed{-\frac{dc_2}{dt_2} = Kc_2^n} \rightarrow ②$$

By eqn ① and ②

$$-\frac{dc_1}{dt_1} = Kc_1^n \rightarrow 1$$

$$-\frac{dc_2}{dt_2} = Kc_2^n \rightarrow ②$$

∴ dividing ① and ②

$$\frac{-\frac{dc_1}{dt_1}}{-\frac{dc_2}{dt_2}} = \frac{\cancel{K}c_1^n}{\cancel{K}c_2^n}$$

$$\frac{-\frac{dc_1}{dt_1}}{-\frac{dc_2}{dt_2}} = \left(\frac{c_1}{c_2}\right)^n$$

equating log both side -

$$\log\left(-\frac{dc_1}{dt_1}\right) - \log\left(-\frac{dc_2}{dt_2}\right) = n\left[\log c_1 - \log c_2\right]$$

$$\boxed{n = \frac{\log\left(-\frac{dc_1}{dt_1}\right) - \log\left(-\frac{dc_2}{dt_2}\right)}{\log c_1 - \log c_2}}$$

Where $n$ = order of rxn.

## *Activation ENERGY ⇒

The minimum amount of energy which must be associatede with molicules for collision, Known as threshold energy. (देहली आग्रावे)

The axis energy which is given to the reactant To aquare the threshold energy Know as activation energy. it is representate By. Ea.

⊙ Calculation of activation energy ⇒

The Ea is Calculaleted by the hellp of Arrhenius equaction.

$$\boxed{K = A \cdot e^{-\frac{Ea}{RT}}}$$

Where - K = Rate Constant

A = Arrhenius constant OR frequncy factor

Ea = activation Energy.

T = Absolute temp -

R = 8.314 J K$^{-1}$ mol$^{-1}$

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

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

$$\log_e K = \log_e A - \frac{Ea}{RT} \log_e e$$

$\therefore \log_e e = 1$

$$\log_e K = \log_e A - \frac{Ea}{RT}$$

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

Activation energy

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

imp. formula -

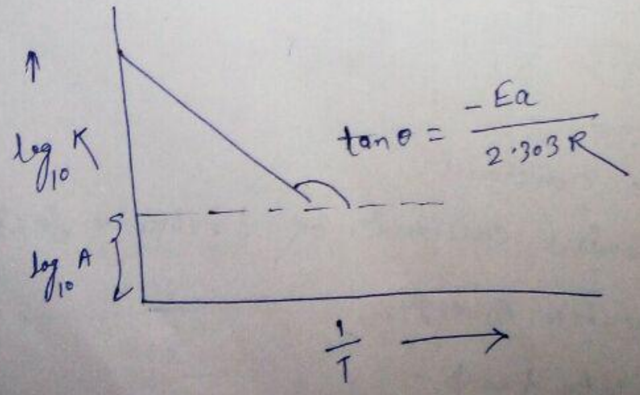
* graphical Representation ⇒

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

$$\log_{10} K = \log_{10} A - \left(\frac{Ea}{2.303 R}\right) \frac{1}{T}$$

$$\downarrow \quad \downarrow \quad \downarrow \quad \downarrow$$

$$\boxed{y = c - m \quad x}$$



$$\tan\theta = \frac{-Ea}{2.303 R}$$

$$\boxed{Ea = \frac{2.303 \times R \times T_1 \times T_2}{T_2 - T_1} \log \frac{K_2}{K_1}}$$

Let us consider for a reaction $T_1$ is temprature ~~atleast~~ which the value of rate constant $K_1$.

Let at Temp – $T_2$ the value of Rate of constant $K_2$

at the time 'T' Arrhenius equation are –

$$\log_{10} K_1 = \log_{10} A - \frac{Ea}{2.303 R T_1} \longrightarrow 1$$

$$\log_{10} K_2 = \log_{10} A - \frac{Ea}{2.303 R T_2} \quad — 2$$

$$\log_{10} K_2 - \log_{10} K_1 = \frac{-Ea}{2.303 R T_2} + \frac{Ea}{2.303 R T_1}$$

$$\boxed{\log_{10}\left(\frac{K_2}{K_1}\right) = \frac{Ea}{2.303 R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]}$$

Arrhenius equation most formula

Question ⇒ The value of rate constant increases for 4 times the temp changes for 300 K to ~~4~~ 320 K find out the activation energy

$$\log_{10}\left(\frac{K_2}{K_2}\right) = \frac{Ea}{2.303 R}\left[\frac{1}{300} - \frac{1}{320}\right]$$

$$\log_{10}\left(\frac{32\cancel{0}}{30\cancel{0}}\right) = \frac{Ea}{2.303 \times 8.314}\left[\right.$$

$$\log_{10}(1.06) = \frac{Ea}{5038.20}\left[0.0033 - 0.0031\right]$$

$$= \frac{Ea}{5038.20} \times 0.0002$$

Sue Calculate the pressure in atm, exceted by $10^{23}$ gas particles each of mass $10^{-22}$ g in a container of volume 1 litre. The rms speed is $10^5$ cm/s. what the total kinetic energy (in cal) of these particles? what must be the temprature?

$V = 1000 = 1$ Letre, $m = 10^{-22}$, $n = 10^{23}$, $c = 10^5$

Sol$^n$ $PV = \frac{1}{3} mnc^2$

$P \times 1000 = \frac{1}{3} \times 10^{-22} \times 10^{23} \times 10^5 \times 10^5$

$P = \frac{10^8}{3}$ dynes per cm$^2$.

1 atm $= 76$ cm $= (76 \times 13.6 \times 981)$ dynes/cm$^2$

$P = \frac{10^8}{3} \times \frac{1}{76 \times 13.6 \times 981} = 33$ atm

Total KE of molecules $= \frac{1}{2} \times (\text{total mass}) \times c^2$

$= \frac{1}{2} \times 10^{-22} \times 10^{23} \times (10^5)^2$ ergs

$= \frac{1}{2} \times \frac{10^{-22} \times 10^{23} \times 10^{10}}{4.184 \times 10^7}$

$= 1195$ cal

(1 cal $= 4.184 \times 10^7$ ergs)

Now, number of moles $= \frac{10^{23}}{\text{Av. Const}} = \frac{10^{23}}{6.022 \times 10^{23}}$

$n = \frac{1}{6.022}$

again we have,

$KE = \frac{3}{2} nRT$

$1195 = \frac{3}{2} \times \frac{1}{6.022} \times 2 \times T$

$\boxed{T = 2398.7 \text{ K}}$

**Example 1-** The rate law for the decomposition of $N_2O_5(l)$ is rate $= K[N_2O_5]$ where $K = 6.22 \times 10^{-4}\ \text{sec}^{-1}$. Calculate half-life of $N_2O_5(l)$ and the number of seconds it will take for an initial concentration of $N_2O_5(l)$ of 0.100 M ~~of~~ to drop to 0.0100 M.

**Soln** Ⓐ Calculate the half-life-

$$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{6.22 \times 10^{-4}\ \text{sec}^{-1}} = 0.111 \times 10^{4}$$

$$= 1.11 \times 10^{3}\ \text{sec}$$

Ⓑ Calculation of time in second for drop of $[N_2O_5]$ from 0.100 M to 0.0100 M.

$$K = \frac{2.303}{t} \log \frac{[N_2O_5]_0}{[N_2O_5]_t}$$

$$t = \frac{2.303}{K} \log \frac{[N_2O_5]_0}{[N_2O_5]_t}$$

Substituting values-

$$t = \frac{2.303}{6.22 \times 10^{-4}} \log \frac{[0.100]}{[0.0100]}$$

$$= \frac{2.303}{6.22 \times 10^{-4}} \times 1$$

$$= 0.370 \times 10^{4}$$

$$\boxed{t = 3.70 \times 10^{3}\ \text{sec}}$$

## Radio Active Decay ⇸

when an element looses its mass by the elimination of sum sutable rays ($\alpha$-Ray, $\beta$-Ray, $\gamma$-Ray) known as Radio active Decay.

The Rate of Radio active Decay always will we 1st order. there for its will satisfy the following eqn-

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

Hence The radio active Decay defined by the help of following eqn.

$$\boxed{\lambda = \frac{2.303}{t} \log \frac{N_0}{N}}$$

where $\lambda$ is Decay constent

$N_0$ = initial amount of radio active element

$N$ = the amount of radio active element at time t.

$N$ and $N_0$ are also related by a following way

$$\boxed{N = N_0 \left(\frac{1}{2}\right)^n}$$

where $n$ = no. of half life.

~~Aeverage life =~~ Total time → (T)

$$\boxed{T = n \times t_{1/2}}$$

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~~Average life~~ = Total time ⇒ (T)

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