Second order Reaction:-

Suppose a reaction follows second order kinetics -

eg $nA \longrightarrow$ Product.

now $\text{rate} = -\frac{1}{n}\frac{d[A]}{dt} \propto [A]^2$

$$-\frac{1}{n}\frac{d[A]}{dt} = K[A]^2$$

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

$nK = K_{obs}$ (a new constant called observed rate constant)

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

$$-\frac{d[A]}{[A]^2} = K_{obs}\,dt$$

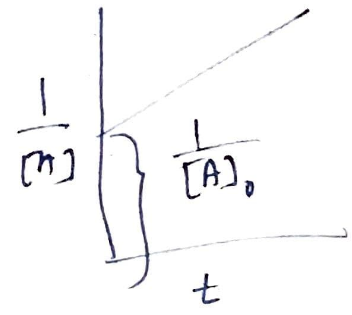
Intregrating both side with proper limit -

$$-\int_{[A]_0}^{[A]}\frac{d[A]}{[A]^2} = \int_0^t K_{obs}\cdot dt$$

$$\left[\frac{1}{[A]}\right]_{[A]_0}^{[A]} = K_{obs}[t]_0^t$$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = K_{obs}t$$

$$\frac{1}{[A]} = \frac{1}{[A]_0} + K_{obs}t$$



$$A \longrightarrow P$$

$t=0 \quad a \quad 0$

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

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

$$\int \frac{dx}{x^2} = \int k\,dt + C$$

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

$t = 0 \; ; \; x = 0$

~~t=t ; a~~ $\frac{1}{a} = K \times 0 + C$

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

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

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

$$t_{1/2} = \frac{1}{K}\,\frac{a/2}{a(a-a/2)} = \frac{1}{K}\,\frac{a/2}{a \times a/2}$$

$$= \frac{1}{ak}$$

Half life is inversely proportional to initial Concentration of reactant.

$$\begin{array}{lccc} & A + B & \rightarrow & \text{Product} \\ t=0 & a \quad b & & 0 \\ t=t & (a-x)\,(b-x) & & x \end{array}$$

$$\frac{dx}{dt} = K(1-x)(b-x)$$

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

$$\frac{1}{a-b}\left[\frac{1}{b-x} - \frac{1}{a-x}\right]dx = K\,dt$$

Intregrating both side.

$$\frac{1}{a-b}\left[-\ln(b-x) + \ln(a-x)\right] = Kt + C$$

$$\frac{1}{a-b}\ln\frac{a-x}{b-x} = kt + C$$

$t = 0$; $x = 0$

$$\frac{1}{a-b}\ln\frac{a}{b} = C$$

$$\frac{1}{a-b}\ln\frac{a-x}{b-x} = kt + \frac{1}{a-b}\ln\frac{a}{b}$$

$$\frac{1}{a-b}\left[\ln\frac{a-x}{b-x} - \ln\frac{a}{b}\right] = kt$$

$$\boxed{\frac{1}{a-b}\ln\frac{b(a-x)}{a(b-x)} = kt.}$$

This is for 2nd order reactn when two components is present.

When $b >> a$; ~~then~~ and x is very small.

$$\frac{1}{a-b}\ln\frac{\cancel{b}(a-x)}{a\cancel{b}} = kt$$

$$-\frac{1}{b}\ln\frac{a-x}{a} = kt \quad \text{or} \quad \ln\frac{a}{a-x} = k.b.t = k't.$$

ie when one component is very high compared to other component then the second order reaction act as a first order reaction, ~~it~~ it is called psuedo first order reactn.

eg hydrolysis of ester.

General unit of K,

$$litre^{n-1}\ mole^{1-n}\ sec^{-1}$$

$n = 2$ → $litre\ mole^{-1}\ sec^{-1}$

$n = 1$ → sec^{-1}

$n = 0$ → $litre^{-1}\ mole\ sec^{-1}$

—∘—

n^{th} order reaction:-

Suppose a reaction A → Product follows n^{th} order reaction -

So rate $$-\frac{d[A]}{dt} = K[A]^n$$

or $$-\int \frac{d[A]}{[A]^n} = \int K\,dt$$

or $$-\int [A]^{-n}\,d[A] = \int K\,dt$$

or $$-\frac{1}{1-n}[A]^{1-n} = Kt + C$$ [C = integrating constant]

or $$\frac{1}{n-1}[A]^{1-n} = Kt + C$$

When $t = 0$; Concentration of reactant $[A]_0$

$$\therefore\ C = \frac{1}{n-1}[A]_0^{1-n}$$

$$Kt = \frac{1}{n-1}\left\{[A]^{1-n} - [A]_0^{1-n}\right\}$$

$$\therefore\ K = \frac{1}{(n-1)t}\left\{[A]^{1-n} - [A]_0^{1-n}\right\}$$

Similarly

$$\begin{array}{lcc} & A & \rightarrow P \\ t=0 & a & 0 \\ t=t & (a-x) & x \end{array}$$

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

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

Integrating both side

$$\frac{1}{1-n}(a-x)^{1-n} = Kt + C$$

when $t = 0$; $x = 0$

$$\therefore\ C = \frac{1}{1-n}a^{1-n}$$

Now,

$$Kt = \frac{1}{(1-n)}\left\{(a-x)^{1-n} - a^{1-n}\right\}$$

Now,

$$t = \frac{1}{(1-n)K}\left\{(a-x)^{1-n} - a^{1-n}\right\}$$

At half life; $x = a/2$

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

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

$$= \frac{1 \times a^{1-n}}{(1-n)K}\left\{\left(\frac{1}{2}\right)^{1-n} - 1\right\}$$

Everything is constant except 'a'

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

Determination of Order of a reaction:-

Method :1 Differential Method

Suppose the order of a reaction is 'n'. Now for the same reaction we arrange two sets of same starting having different innitial concentration say C_1 + C_2.

Now $-\frac{dc_1}{dt} = K C_1^n$ and $-\frac{dc_2}{dt} = K C_2^n$

Now

$$\frac{-\frac{dc_1}{dt}}{-\frac{dc_2}{dt}} = \left(\frac{C_1}{C_2}\right)^n$$

$$\therefore \frac{\frac{dc_1}{dt}}{\frac{dc_2}{dt}} = \left(\frac{C_1}{C_2}\right)^n$$

taking 'log' on both side

$$\log\left(\frac{dc_1}{dt}\right) - \log\left(\frac{dc_2}{dt}\right) = n\left[\log C_1 - \log C_2\right]$$

$$n = \frac{\log\left(\frac{dc_1}{dt}\right) - \log\left(\frac{dc_2}{dt}\right)}{\log C_1 - \log C_2}$$

Now we can determine 'n'..

Method of half-life

we know that for a 'n' order reaction

$$t_{1/2} = \text{Const.} \times a^{1-n}$$

or $$t_{1/2} = \frac{\text{Constant}}{a^{n-1}}$$

where 'a' is innitial concentration

Now if $t'_{1/2}$ & $t''_{1/2}$ ~~is~~ are the half life of the reactant at innitial concentration C_1 & C_2 respectively, then

$$t'_{1/2} = \frac{k'}{C_1^{n-1}} \quad \text{and} \quad t''_{1/2} = \frac{k'}{C_2^{n-1}}$$

or $$\frac{t''_{1/2}}{t'_{1/2}} = \left(\frac{C_1}{C_2}\right)^{n-1}$$

now $$\log\left(\frac{t''_{1/2}}{t'_{1/2}}\right) = (n-1)\log(C_1/C_2)$$

or $$(n-1) = \frac{\log\left(\frac{t''_{1/2}}{t'_{1/2}}\right)}{\log(C_1/C_2)}$$

or $$n = 1 + \frac{\log(t''_{1/2}/t'_{1/2})}{\log(C_1/C_2)}$$

'n' can be determined now.