3. Second Order Reactions

The reaction

$A+A \rightarrow$ Product (s)

Follows a second order kinetics if the rate is proportional to the square of the concentration of A i.e,

$-d[A]/dt=k[A]^2$ …………………………………..(32)

However, if the reaction is , $A+B \rightarrow$ Product (s)

the rate is proportional to the product of the concentration of each reactant

$-d[A]/dt=-d[B]/dt=\mathbf{dx}/dt=\mathbf{k}[A][B]$ …………………………………..(33)

where **dx**/dt is the rate of disappearance of A or B or appearance of the products. From eq. (32), $\mathbf{dx}/dt=k(a-x)^2$ ………………………………………..(34)

From eq. (33), $\mathbf{dx}/dt=k(a-x)(b-x)$ ………………………………………..(35)

In these equations a and b are the initial concentration of A and B in mol dm^{-3} respectively. In Eq.(35) if a=b, i.e, when the concentration of two reacting species are same, then the rate is given by eqn (34). Integrating this eqn we get

$$\int \mathbf{dx}/(a-x)^2=k\int dt$$

$$1/(a-x)=kt+I \quad \text{………………….(36)}$$

Where I is the constant of integration and its value can be obtained by applying the initial conditions, i.e., when t=0, x=0

$$I= 1/\mathbf{a}$$

Putting the of integration constant in Eq.(36), we get

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

$$\textbf{or,} \quad \mathbf{k=x/at(a-x)} \quad \text{…………. ….(37)}$$

From eq.(37), it is clear that k has units of $(time)^{-1}(concentration)^{-1}$.

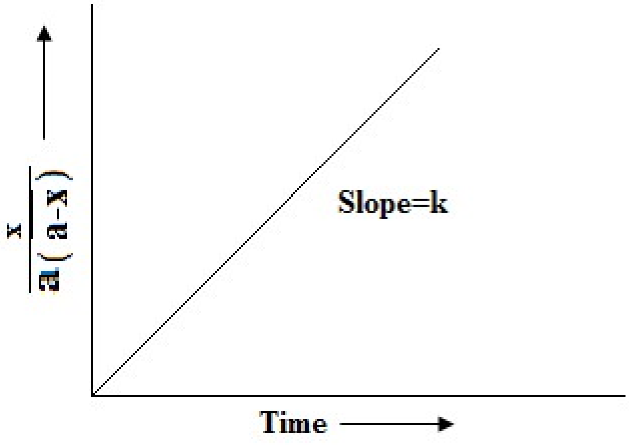

Figure 4: Plot of x/a(a-x) verses t

A plot of x/a(a-x) verses t should be a straight line passing through the origin with slop equal to k (**Fig 4**).

When the concentration of the reacting species are different, i.e.,a≠b, then the rate is given by Eq.(35),

$$dx/dt=k(a-x)(b-x)$$

separating the variable, we get

$$dx/(a-x)(b-x)=k\,dt \quad \ldots\ldots\ldots\ldots\ldots\ldots (38)$$

The expression **1**/(a-x) (b-x) can be resolved into partial fraction as

$1/(a-x)(b-x) = A/(a-x) + B/(b-x)$

$1/(a-x)(b-x)= \{A(b-x)+B(a-x)\}\{(a-x)(b-x)\}$

$1=A(b-x) +B(a-x)$

1=Ab+Ba

And –A-B=0

From this we get A=1/(b-a)

And B= 1/(a-b)

Hence, $1/(a-x)(b-x)=1/(b-a)(a-x) +1/(a-b)(b-x)$

$=1/(a-b)[\ 1/(b-x) - 1/(a-x)]$

Eq(38) becomes

$1/(a-b)[\ 1/(b-x) - 1/(a-x)]dx = kdt$

On integrating this equation, we get

$1/(a-b)[\ \int dx/(b-x) - \int dx/(a-x)]dx = k\int dt$

or, $1/(a-b)[\ -\ln(b-x) + \ln(a-x)]dx = kt + I$ …………………………… (39)

Again, when $t=0$, $x=0$, and therefore

$1/(a-b)[\ln(a/b)] = I$

Putting the value of I in eq (39), we obtain

$1/(a-b)[\ -\ln(b-x) + \ln(a-x)]dx = kt + 1/(a-b)[\ln(a/b)]$

or, $kt = 1/(a-b)\ln\{b(a-x)/a(b-x)\}$

$k = 2.303/(a-b)t \log\{b(a-x)/a(b-x)\}$ ………………………………… (40)

$t = 2.303/(a-b)k \log\{b(a-x)/a(b-x)\}$ ………………………………… ..(41)

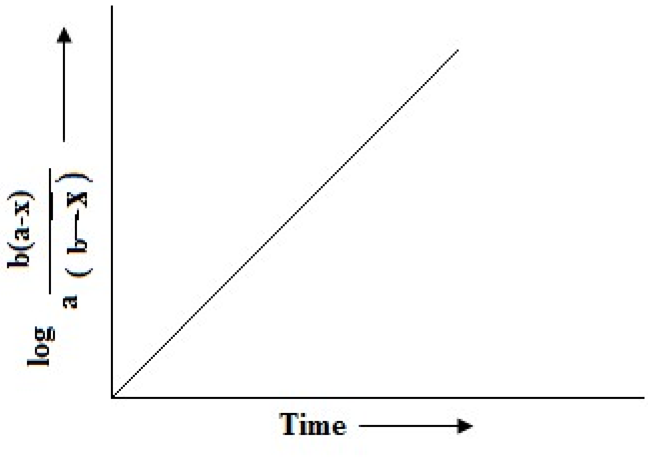

Fig 5: Plot of log {b(a-x)/a(b-x)} vs t

The eq (41) shows that the plot of log $\{b(a-x)/a(b-x)\}$ versus t for such a reaction would be straight line passing through the origin and the slope of the line is equal to $k(a-b)/2.303$.

In the reaction A+B → Products, if the concentration of one of the reactants is taken in large excess, the reaction then becomes kinetically of first order. This can be shown as follows.

Let b be the excess concentration, i.e., $b>>a$ or x, so that $a-b \approx -b$ and $b-x \approx b$

Therefore eq (40) reduces to

$k= -2.303/bt \log b(a-x)/ab$

$=-2.303/bt \log (a-x)/a$

$=2.303/bt \log a/(a-x)$

Since B is the reactant present in excess, so its concentration b may be taken as almost constant and hence the above equation is equivalent to that for a first order reaction (23)

Half-Life Period for a Second Order Reaction

The half -life period for a second order reaction in which the reactants are identical or different but have equal initial concentration can be calculated using Eq.(37). However, the half-life period cannot be calculated for reactions where concentrations of A and B are different as both A and B will have different times for half conversion.

Thus in equation,

$$\mathbf{k=x/at(a-x)}$$

when $t=t_{1/2}$, $x=a/2$, we get $k=(a\backslash 2)/ t_{1/2}. a. (a-a/2)$

$t_{1/2}=1/ka$ ………………. ……..……..(42a)

$t_{1/2} \infty 1/a$ ………………. ……..……..(42b)

The half-life period ($t_{1/2}$) for a second order reactions is inversely proportional to the first power of the initial concentration for the reactant. Knowing $\mathbf{t_{1/2}}$ and a, k is readily calculated from Eq.(42).A practical consequence of second order reaction is that the species which decay by second order reactions may persist in low concentrations for long time because their half-lifes are long when their concentration are low.

Example of 2nd order Reactions:

(i) The saponification of an ester is an example of a second order reaction.

$CH_3COOC_2H_5 + OH^- \rightarrow CH_3COO^- + C_2H_5OH$

(ii) Decomposition of HI

$2HI \rightarrow H_2 + I_2$

General Expression for the Rate of a Reaction

Reactions in which one reactant is involved may be represented as

$$nA \rightarrow Product(s)$$

The rate equation of such reactions is given as, $dx/dt = k(a-x)^n$ ……….. (43)

Integration of eq (43) becomes,

$$\int_0^x dx/(a-x)^n = \int_0^t k.dt$$

$1/(n-1)[1(a-x)^{n-1} - 1/a^{n-1}] = kt$ …………………………… (44)

This equation holds for all values of n except for n=1. When n=1, (n-1)=0, the equation becomes indeterminate.

The half-life period($t_{1/2}$) for a reaction of of nth order is given by

$t_{1/2} = (2^{n-1} - 1)/\{(n-1)a^{n-1}.k\}$

or $t_{1/2} \infty 1/a^{n-1}$ ……………………………………….. (45)