T.D.C 4th Sem (General)

Chemical Kinetics

Integrated rate equation of second order reaction

(a) When the two reactants are of same type.

$$A + A \rightarrow \text{Product}$$

Let "a" be the concentration of each reactant to start with and (a-x) their concentration after any time 't'. Then we have

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

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

In order to get the value of k, we integrate this expression

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

$$\Rightarrow \frac{1}{a-x} = Kt + C \text{ (constant of integration)} \rightarrow (1)$$

When $t=0$, $x=0$.

Substituting these values in the above equation we get $C = \frac{1}{a}$

Putting the value of c in the eqn (1)

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

$$\Rightarrow \frac{1}{a-x} - \frac{1}{a} = Kt \quad \text{or} \quad \frac{a-a+x}{a(a-x)} = \frac{x}{a(a-x)} = Kt$$

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

This is known as the rate equation for a 2nd order reaction.

(b) 2nd order reaction when the reactants are different

$$A + B \rightarrow Product$$

Let a and b be the initial concentration of A and B.

$$A + B \rightarrow Product$$
$$a \quad b \quad 0$$
At 't' sec $(a-x)$ $(b-x)$. x

where $(a-x)$, and $(b-x)$ are the concentration of A and B after t sec.

$$Rate = \frac{dx}{dt} \propto (a-x)(b-x).$$

$$\frac{dx}{dt} = k(a-x)(b-x) \quad [k \text{ is the rate constant}]$$

$$\frac{dx}{(a-x)(b-x)} = k\,dt \rightarrow (1)$$

We have,
$$\frac{1}{(a-x)(b-x)} = \frac{1}{(a-b)}\left[\frac{1}{b-x} - \frac{1}{a-x}\right] \quad \left[\text{using Partial fraction}\right]$$

Substituting the value in (1) and integration.

$$\int \frac{dx}{(a-x)(b-x)} = \frac{1}{a-b}\left[\int \frac{dx}{b-x} - \int \frac{dx}{a-x}\right] = k\int dt.$$

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

NOTES

C is the integration constant.

or
$$\frac{1}{(a-b)}\left[\ln\frac{(a-x)}{(b-x)}\right] = kt + C \rightarrow (2)$$

When $t = 0$, $x = 0$

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

Putting the value of C in Equn (2)

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

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

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

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

$$\boxed{\text{or } K = \frac{1}{(a-b)t}\ln\frac{b(a-x)}{a(b-x)}.}$$

This is the integrated rate equation for 2nd order reaction when $a \neq b$ & $a > b$.

For 2nd order reaction

Unit of K (rate constant)

$$K = time^{-1}\,conc^{-1}$$
$$= min^{-1}(mol/Litre)^{-1}$$
$$= min^{-1}\,mol^{-1}\,Litre.$$