⟹ Kinetics of Third order Reaction

A reaction is said to be of the third order if the rate of reaction depends upon three concentration terms.

Let us consider a simple third order reaction

$$3A \longrightarrow \text{Products}$$

Let the initial concentration of A = a moles litre^{-1} and after time t, x moles reacted. Therefore, the conn. of A becomes (a−x).

The rate law.

$$\frac{dx}{dt} = K(a-x)^3 \quad \text{——— (1)}$$

Rearranging equation (1),

$$\frac{dx}{(a-x)^3} = K\,dt \quad \text{——— (2)}$$

on integration, it gives

$$\frac{1}{2(a-x)^2} = Kt + I \quad \text{——— (3)}$$

where I = Integration constant

I is evaluated by putting x = 0 and t = 0

Thus

$$I = \frac{1}{2a^2}$$

Putting the value of I in eqn. (3) we write

$$Kt = \frac{1}{2(a-x)^2} - \frac{1}{2a^2}$$

$$\therefore \boxed{K = \frac{1}{t} \cdot \frac{x(2a-x)}{2a^2(a-x)^2}}$$

This eqn. is the Integrated rate equation for a third order reaction.

⇒ Examples of third order Reaction

① $2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$

② $2NO + O_2 \longrightarrow 2NO_2$

③ $2NO + Cl_2 \longrightarrow 2NOCl$

⇒ Half-life of a Third order Reaction

The time taken for any fraction of the reaction to be completed is inversely proportional to the square of the initial concentration.

e.g.

The time taken for half of the reaction to be completed i.e. half period may be calculated as

When $x = \frac{a}{2}$ and $t = t_{1/2}$

Putting this value in Third order reaction, we get

$$K = \frac{1}{t} \cdot \frac{x(2a-x)}{2a^2(a-x)^2}$$

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

or, $$t_{1/2} = \frac{1}{2K}\left(\frac{a/2 \cdot 3a/2}{a^2 \cdot a^2/4}\right)$$

or, $$t_{1/2} = \frac{1}{2K} \cdot \frac{3}{a^2}$$

i.e. $t_{1/2} \propto \frac{1}{a^2}$ i.e. Half-life period is inversely proportional to the square of initial conc.

⇒ Unit of Third order Reaction

The rate constant ~~constant~~ for a third order reaction is

$$K = \frac{1}{t} \cdot \frac{x(2a-x)}{2a^2(a-x)^2}$$

or, $$K = \frac{\text{Conc}^{n} \times \text{Conc}^{n}}{(\text{Conc}^{n})^2 \times (\text{Conc}^{n})^2} \times \frac{1}{\text{time}}$$

$$= \frac{1}{(\text{concentration})^2} \times \frac{1}{\text{time}}$$

$$= \frac{1}{(\text{mol/litre})^2} \times \frac{1}{\text{time}}$$

Thus the unit of K for the third order reaction are

$$\boxed{\text{mol}^{-2}\, l^{2}\, \text{time}^{-1}}$$