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BSc III (HONS) – PAPER-V, Chemistry.
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Kinetics of third order reaction.

Let us consider third order reaction of following types.

$$3A \rightarrow \text{Products} \quad —(1)$$

$$2A + B \rightarrow \text{Products}.$$

Type I –

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

$t = 0$ a = initial concentration mole/litre $\longrightarrow$ 0

At t, $a - x$ mole/litre $\longrightarrow$ x.

According to law of rate reaction

$$\frac{dx}{dt} \propto (a-x)^3$$

$$\Rightarrow \frac{dx}{(a-x)^3} \propto dt.$$

$$\Rightarrow \frac{dx}{(a-x)^3} = K\,dt$$

Integrating both side we get

$$\Rightarrow \int \frac{dx}{(a-x)^3} = \int K\,dt$$

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

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At $t=0$, $x=0$ then equation (1) will be

$$\frac{1}{2(a-0)^2} = 0 \times C$$

C = Integration Constant

$$\Rightarrow C = \frac{1}{2a^2}$$

putting value of C in equation (1) we get

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

$$\Rightarrow k = \frac{1}{t}\left[\frac{1}{2(a-x)^2} - \frac{1}{2a^2}\right]$$

$$\Rightarrow K = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$$

$$\Rightarrow K = \frac{1}{2t}\left[\frac{a^2 - (a^2 + x^2 - 2ax)}{a^2(a-x)^2}\right]$$

$$\Rightarrow K = \frac{1}{2t}\left[\frac{a^2 - a^2 - x^2 + 2ax}{a^2(a-x)^2}\right]$$

$$\Rightarrow \boxed{K = \frac{1}{2t}\left(\frac{x(2a-x)}{a^2(a-x)^2}\right]}$$

This is rate constant for third order reaction of type $3A \rightarrow$ Products.

For type II

$$2A + B \rightarrow \text{products}$$

t = 0   a   b   –   0

At t $a-2x$ $(b-x)$ x

From rate law equation

$$\frac{dx}{dt} \propto (a-2x)^2 (b-x)$$

$$\Rightarrow \frac{dx}{dt} = K (a-2x)^2 (b-x) \quad \text{— (iii)}$$

Separating the variable in eqn (iii) integrating we get

$$\int \frac{dx}{(a-2x)^2 (b-x)} = K_3 \int dt$$

After integration we get

~~$K_3 = \frac{1}{t(a-2b)^2} \left[\frac{2x(2b-a)}{a(b-2x)} \ln \right]$~~

$$K_3 = \frac{1}{t(a-2b)} \left[\ln \frac{2x(2b-a)}{a(a-2x)} + \ln \frac{b(a-2x)}{a(b-x)} \right]$$

This is required rate constant of reaction of third order of type $2A + B =$ Products.

Half life period of third order reaction :—

The third order reaction is

$$K_3 = \frac{1}{2t}\left[\frac{x(2a-x)}{a^2(a-x)^2}\right]$$

At $t = t_{1/2}$, $x = \frac{a}{2}$

$$\Rightarrow K_3 = \frac{1}{2 \cdot t_{1/2}}\left[\frac{\frac{a}{2}\left[2a-\frac{a}{2}\right]}{a^2\left(a-\frac{a}{2}\right)^2}\right]$$

$$\Rightarrow K_3 = \frac{1}{2t_{1/2}} = \left[\frac{\frac{a}{2} \times \frac{3a}{2}}{a^2 \times \frac{a^2}{4}}\right]$$

$\Rightarrow$

$$\Rightarrow t_{1/2} = \frac{1}{2K} \times \frac{\frac{3}{4}a^2}{\frac{a^4}{4}}$$

$$\Rightarrow t_{1/2} = \frac{1}{2K} \times \frac{3}{a^2} = \frac{\quad}{a^2}$$

$$\Rightarrow t_{1/2} = \frac{3}{2} \times \frac{1}{K} \times \frac{1}{a^2}$$

$$\Rightarrow t_{1/2} = \text{Constant}\ \frac{1}{a^2}$$

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

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The time required to complete a definite fraction (half) of third order reaction is inversely proportional to the ~~square~~ square of the initial concentration of the reactant.

Unit of third order reaction constant —

Rate constant equation of third order is

$$K_3 = \frac{1}{2t}\left[\frac{x(2a-x)}{a^2(a-x)^2}\right]$$

$$\Rightarrow K_3 = \frac{1}{2 \cdot sec} \times \frac{mole/litre \times mole/litre}{(mole/litre)^2 \cdot (mole/litre)^2}$$

$$\Rightarrow K_3 = \frac{1}{2 sec} \times \frac{1}{(mole/litre)^2}$$

$\Rightarrow$ Unit of K_3 is $(mole/litre)^{-2} \cdot sec^{-1}$