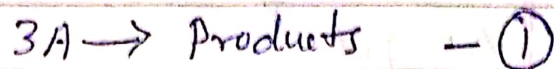


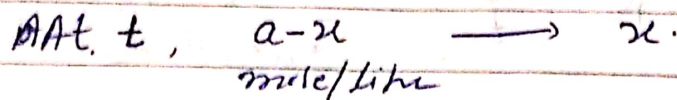
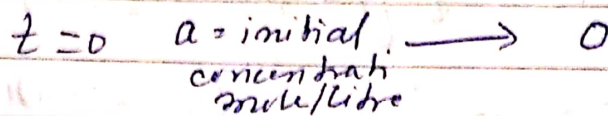
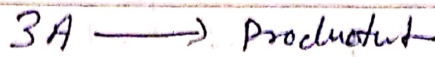
BSc. III (Hons) - PAPER-V, Chemistry.
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Kinetics of third order reaction.

Let us consider third order reaction of following types.



Type I -



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

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

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

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

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

$C = \text{Integration Constant}$

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

putting value of C in equation ① we get

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

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

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

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

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

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

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

For type II



$$t=0 \quad a \quad b = 0$$

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

From rate law equations

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

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

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

~~$$k_3 = \frac{1}{t(a-2b)} \left[\ln \frac{2x(2b-a)}{a(a-2x)} + \ln \frac{b(a-2x)}{a(b-x)} \right]$$~~

$$k_3 = \frac{1}{t(a-2b)} \left[\ln \frac{2x(2b-a)}{a(a-2x)} + \ln \frac{b(a-2x)}{a(b-x)} \right]$$

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

Half life period of third order reaction.

The third order reaction is

$$k_3 = \frac{1}{2t} \left[\frac{x(2a-x)}{a^2(a-x)^2} \right]$$

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

$$\Rightarrow k_3 = \frac{1}{2 \cdot t_{1/2}} \left[\frac{\frac{a}{2} \left[2a - \frac{a}{2} \right]}{a^2 \left(a - \frac{a}{2} \right)^2} \right]$$

$$\Rightarrow k_3 = \frac{1}{2t_{1/2}} \left[\frac{\frac{a}{2} \times \frac{3a}{2}}{a^2 \times \frac{a^2}{4}} \right]$$

$$\Rightarrow \text{~~scribble~~}$$

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

$$\Rightarrow t_{1/2} = \frac{1}{2k} \times \frac{3}{a^2} = \text{~~scribble~~ } \frac{1}{a^2}$$

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

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

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

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

$$k_3 = \frac{1}{2t} \left[\frac{x(2a-x)}{a^2(a-x)^2} \right]$$

⇒

$$k_3 = \frac{1}{2 \text{ sec}} \times \frac{\text{mole/litre} \times \text{mole/litre}}{(\text{mole/litre})^2 \cdot (\text{mole/litre})^2}$$

$$\Rightarrow k_3 = \frac{1}{2 \text{ sec}} \times \frac{1}{(\text{mole/litre})^2}$$

$$\Rightarrow \boxed{\text{Unit of } k_3 \text{ is } (\text{mole/litre})^{-2} \cdot \text{sec}^{-1}}$$