

* Expression of rate constant for 3rd order Reaction:-



Initial Conc ⁿ	a mole/litre	0
after t sec.	(a-x) mole/litre	x

It is a 3rd order reaction.

∴ $\frac{dx}{dt} \propto [A]^3$

∴ $\frac{dx}{dt} = k(a-x)^3$

Where k = rate constant of 3rd order reaction.

On rearranging and integrating -

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

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

Where, I = Integration Constant.

When t = 0 x = 0

∴ Eqⁿ (1) becomes -

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

putting the value of I in Eqⁿ (1) we get -

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

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

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

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

$$\therefore k = \frac{1}{t} \times \frac{(2a-x)x}{2a^2 (a-x)^2} \quad \text{--- (2)}$$

Eqⁿ - (2) is the expression of rate constant for 3rd order reaction.

Characteristics of 3rd order reaction -

① Half life time (t_{1/2}) -

from 3rd order kinetics -

$$k = \frac{1}{t} \times \frac{(2a-x)x}{2a^2 (a-x)^2}$$

When t = t_{1/2}, x = a/2

$$k = \frac{1}{t_{1/2}} \times \frac{(2a - a/2)^{a/2}}{2a^2 (a - a/2)^2}$$

$$t_{1/2} = \frac{1}{k} \times \frac{3^{1/2} \times a^{1/2}}{2a^2 \times \left(\frac{a}{2}\right)^2}$$

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

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

Thus, half life period of 3rd order reaction is inversely proportional to the square of the initial concentration.

② Unit of 3rd order reaction -

$$k = \frac{1}{t} \times \frac{(2a-x)x}{2a^2(a-x)^2}$$

$$k = \frac{1}{\text{sec}} \times \frac{\text{Conc}^2 \times \text{Conc}}{(\text{Conc}^2)^2 \times (\text{Conc}^2)^2}$$

$$k = \frac{1}{\text{sec}} \times \frac{1}{(\text{mol/L})^2}$$

$$k = \text{mol}^{-2} \text{ Liter}^2 \text{ sec}^{-1}$$

③ Examples of 3rd order reaction -

(i) Reduction of Ferric chloride to Stannous chloride -



② Oxidation of nitric oxide



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from
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chemistry.