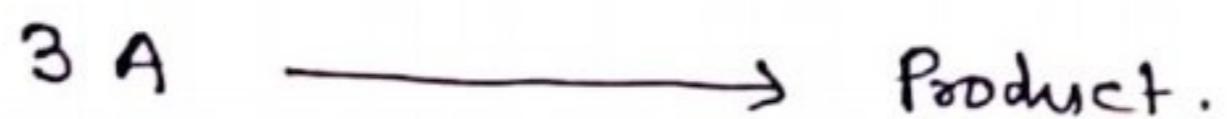


* Expressions of rate Constant for 3rd order Reaction:-



Initial
Conc²

a mole/litre

0

after

t sec.

$(a-x)$ mole/litre

x

It is a 3rd order reaction.

$$\therefore \frac{dx}{dt} \propto [A]^3$$

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

where k = rate constant of 3rd order reaction.

On rearranging and integrating —

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

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

where, I = Integration Constant.

When $t=0 \quad x=0$

\therefore Eqⁿ — (1) becomes —

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

Putting the value of I in Eqⁿ — (1) we get —

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

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

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

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

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

$\text{Eq } (2)$ 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 -

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

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

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

(17)

$$\therefore t_{1/2} = \frac{1}{k} \times \frac{3/2 \times 9/2}{2a^2 \times (\frac{9}{2})^2}$$

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

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

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

(2) Unit of 3rd order rate -

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

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

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

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

(3) Examples of 3rd order reaction -

(i) Reduction of Ferric chloride to Stanous chloride -



(2) Oxidation of nitric oxide



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From
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