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Ex.26 Initial Concentrations of both the reactants of a second order reaction are equal and 60% of the reaction gets completed in 3000 seconds. How much time will be taken in 20% completion of the reaction?

Sol: $k_2 = \frac{1}{t} \frac{x}{a(a-x)}$

Suppose, $a = 1$ $\quad k_2 = \frac{1}{3000} \frac{0.6}{1(1-0.6)}$

$= \frac{1}{3000} \frac{0.6}{0.4}$

Now, for 20% completion

$k_2 = \frac{1}{t} \frac{x}{a(1-x)}$

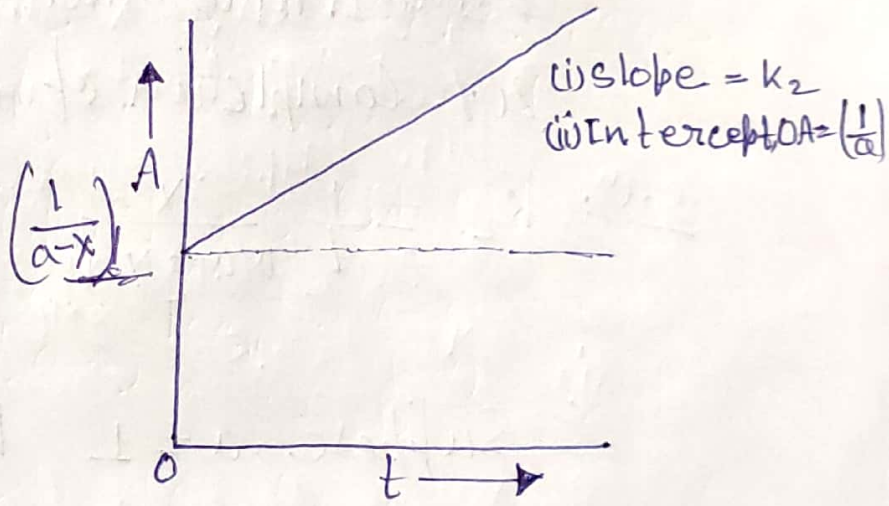
$\frac{1}{3000} \frac{0.6}{0.4} = \frac{1}{t} \frac{(0.2)}{1(1-0.2)}$

This is an example of pseudo first order reaction.

Equation for second order reaction can be rewritten as

$$\frac{a}{(a-x)} = k_2 t + \frac{1}{a}$$

- Graphical Representation



In general for n^{th} order reaction.

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

In general for n^{th} order reaction.

$$t_{1/2(n)} = \frac{2^{n-1}-1}{(n-1)k_n (a)^{n-1}} \quad (n \geq 2)$$

$$\Rightarrow t_{1/2(n)} \propto \frac{1}{a^{n-1}} \Rightarrow t_{1/2(n)} \propto a^{(1-n)}$$

$$\frac{1}{3000}\ \frac{0.6}{0.4} = \frac{1}{t}\ \frac{1}{4}$$

$$t = \frac{3000}{0.6}\ \frac{0.4}{4}$$

$$t = 500 \text{ second}$$

EX.27 A second order reaction requires 70 minutes to change the concentration of reactants from 0.08 M to 0.01 M. How much time will it require to become 0.04 M.

Sol^{n}. For second order reaction

when, $(a-x) = 0.01$

$$k_2 = \frac{x}{t \cdot a(a-x)}$$

$$k_2 = \frac{0.07}{70\ 0.08\ (0.01)}$$

$$(a-x) = 0.04$$

$$k_2 = \frac{0.04}{t\ 0.08\ (0.04)}$$

From the equation (1) and (2)

$$\frac{0.07}{70\ 0.08\ (0.01)} = \frac{0.04}{t\ \ 0.08\ (0.04)}$$

$$t = 10 \text{ minutes}$$

16. THIRD ORDER REACTION:

A reaction is said to be of third order if its rate is determined by the variation of three concentration terms. When the concentration of all the three reactants is same or three molecules of the same reactant are involved, the rate expression is given as

(i) $2NO + O_2 \rightleftharpoons 2NO$ (ii) $A + B + C \rightarrow$ Product

Rate Constant of third order reaction

$$k_3 = \frac{1}{t} \cdot \frac{x(2a-x)}{2a^2(a-x)^2}$$

Half life Period

$$t_{1/2} = \frac{3}{2ka^3}$$

Thus half life is inversely proportional to the square of initial Concentration.