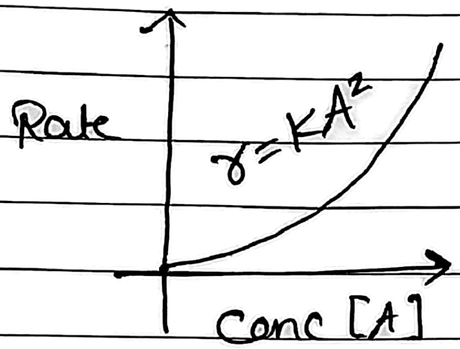
Chemical Kinetics – 07

Second, Third & n^{th} Order Kinetics

Second Order :

$$A \longrightarrow \text{Products}$$

$$\text{rate} = r = K[A]^2$$



Integrated Rate Law $\quad A \longrightarrow \text{Product}$

$$r = K[A]^2$$

$$r = \frac{-1}{1}\frac{dA}{dt}$$

$$\frac{-1}{1}\frac{dA}{dt} = K[A]^2$$

$$\int_{A_0}^{A} \frac{dA}{A^2} = \int_0^t -K\,dt$$

Let at $t=0 \quad t=t$
$A = A_0 \quad A = A$

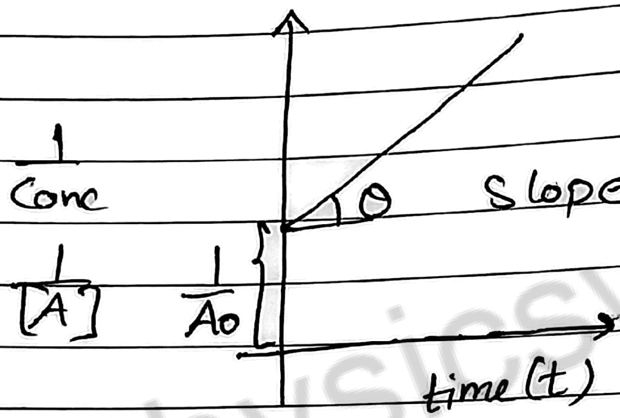
$$\left[-\frac{1}{A}\right]_{A_0}^{A} = -K(t)_0^t$$

$$\frac{1}{A} - \frac{1}{A_0} = Kt$$

$$\boxed{t = \frac{1}{K}\left[\frac{1}{A} - \frac{1}{A_0}\right]}$$

$$\frac{1}{A} = Kt + \frac{1}{A_0}$$

Plot of $\frac{1}{\text{Conc}}$ v/s time



slope $= \tan\theta = K$

<u>Half Life</u> :

at $t = t_{1/2}$ $\quad A = \frac{A_0}{2}$

$$t = \frac{1}{K}\left[\frac{1}{A} - \frac{1}{A_0}\right]$$

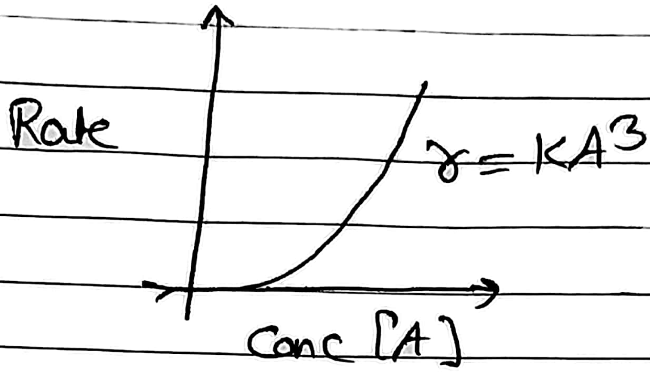
$$t_{1/2} = \frac{1}{K}\left[\frac{1}{A_0/2} - \frac{1}{A_0}\right]$$

$$\boxed{t_{1/2} = \frac{1}{KA_0}}$$

Third order Kinetics

$$A \longrightarrow \text{Products}$$

$$\text{Rate} = r = K[A]^3$$



Integrate Rate Law

$$A \longrightarrow \text{Products}$$

$$r = K[A]^3$$

$$r = -\frac{1}{1}\frac{dA}{dt}$$

$$-\frac{1}{1}\frac{dA}{dt} = K[A]^3$$

$$\int_{A_0}^{A} \frac{dA}{A^3} = \int_{0}^{t} -K\,dt$$

$$\left[-\frac{1}{2A^2}\right]_{A_0}^{A} = -K(t)_0^t$$

$$\frac{1}{2A^2} - \frac{1}{2A_0^2} = Kt$$

$$\boxed{t = \frac{1}{2K}\left[\frac{1}{A^2} - \frac{1}{A_0^2}\right]}$$

Second

$$t = \frac{1}{K}\left[\frac{1}{A} - \frac{1}{A_0}\right]$$

Third

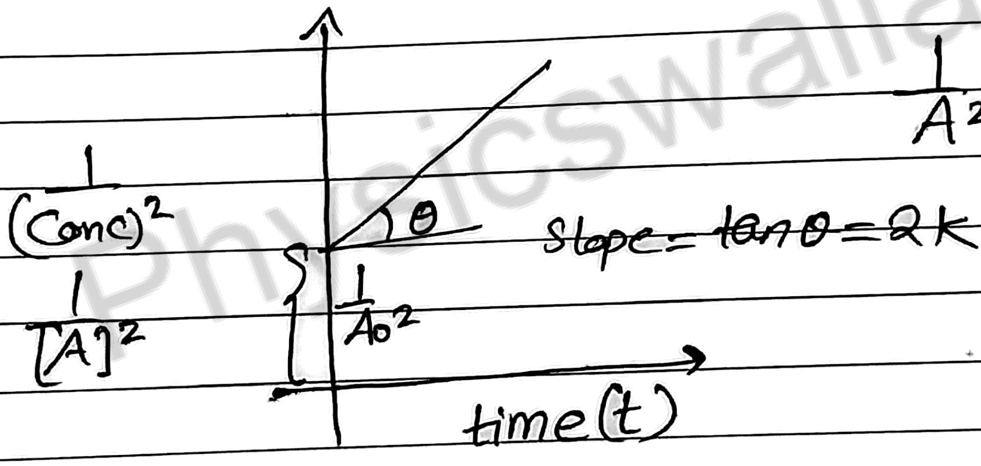
$$t = \frac{1}{2K}\left[\frac{1}{A^2} - \frac{1}{A_0^2}\right]$$

for n^{th} order

$$\boxed{t = \frac{1}{(n-1)K}\left[\frac{1}{A^{(n-1)}} - \frac{1}{A_0^{(n-1)}}\right]}$$ for $n \geq 2$

Graph of $\frac{1}{A^2}$ v/s time for 3^{rd} Order

$$\frac{1}{A^2} = 2Kt + \frac{1}{A_0^2}$$



Half Life:

at $t = t_{1/2}$ $A = \frac{A_0}{2}$

$$t_{1/2} = \frac{1}{2K}\left[\frac{1}{(A_0/2)^2} - \frac{1}{(A_0)^2}\right]$$

$$\boxed{t_{1/2} = \frac{3}{2KA_0^2}}$$

Second

$$t_{1/2} = \frac{1}{KA_0}$$

Third

$$t_{1/2} = \frac{3}{2KA_0^2}$$

First

$$t_{1/2} = \frac{0.693}{K}$$

Zero

$$t_{1/2} = \frac{A_0}{2K}$$

for any order: $\boxed{t_{1/2} \propto (A_0)^{1-n}}$ Remember

for $n \geq 2$ $\quad t_{1/2} = \frac{(2^{n-1} - 1)}{(n-1)K(A_0)^{n-1}}$

Fourth Order Kinetics

$$t = \frac{1}{3K}\left[\frac{1}{A^3} - \frac{1}{A_0^3}\right]$$

$$t_{1/2} \propto A_0^3$$

$$t_{1/2} = \cancel{2}\ \frac{7}{3KA_0^3}$$

Fifth order ÷ $\quad t = \frac{1}{4K}\left[\frac{1}{A^4} - \frac{1}{A_0^3}\right]$

$$t_{1/2} = \frac{15}{4KA_0^4}$$ - - - - - -