

## First order Reaction

A reaction is said to be of first order if its rate is determined by the change of one concentration term only



	Time	Concentration
Initial	T = 0	a
Final	T = t	(a - x)

$$\therefore \frac{dx}{dt} = K(a - x)$$

$$\text{On integrating } \int \frac{dx}{a-x} = K \int dt \text{ we get } -\log_e (a-x) = Kt + C$$

$$\therefore \text{ at } t = 0 \quad x = 0 \quad \therefore C = -\log_e a$$

$$\therefore -\log_e (a - x) = Kt - \log_e a$$

$$\text{or } Kt = \log_e \frac{a}{a-x}$$

$$\text{Rate equation for first order reaction: } Kt = 2.303 \log \frac{a}{a-x}$$

Here  $[A]_0 = a$  (Initial Concentration)

$$[A]_0 = (a - x) \text{ (Remaning concentration)}$$

By rearranging the equation, we get

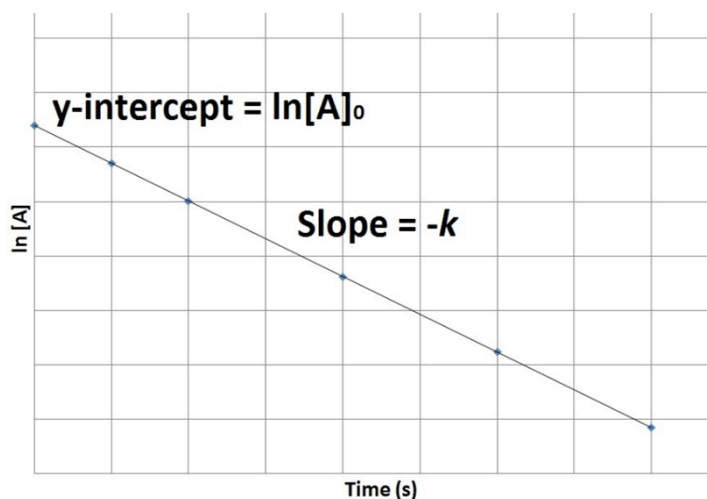
$$\frac{kt}{2.303} = \log \frac{[A]_0}{[A]_0}$$

$$\text{or } \frac{kt}{2.303} = \log[A]_0 - \log[A]$$

$$\text{or } \log[A] = \frac{-kt}{2.303} + \log[A]_0$$

The graph between  $\log[A]$  and time 't' is a straight line, and the slope of this line is given by

$$\text{Slope} = -\frac{k}{2.303}$$



**Half-life of a reaction:** Half-life of first order reaction does not depend upon initial concentration of the reactants.

For 1<sup>st</sup> order reaction:  $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$

From the above expression we get:  $t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$

when  $t = t_{1/2}$  then  $[A] = \frac{1}{2}[A]_0$

therefore  $t_{1/2} = \frac{2.303}{k} \log \frac{[A]_0}{\frac{1}{2}[A]_0} = \frac{2.303}{k} \log 2$

or  $t_{1/2} = \frac{0.693}{k}$

## Units of rate constant for reactions of different orders

(i) For zero order reactions

Rate  $= \frac{dx}{dt} = k[A]^0$ ;  $k = \text{mol L}^{-1} \text{sec}^{-1}$ .

(ii) For first order reactions

Rate  $= k[A] = \frac{dx}{dt}$ ; hence  $k \cdot [\text{mol L}^{-1}] = \left( \frac{\text{mol}}{\text{L-sec}} \right)$   
 $\therefore k = (\text{sec}^{-1})$ .

(iii) For second order reactions

Rate  $= k[A]^2 = \frac{dx}{dt}$ ;  $k \left( \frac{\text{mol}}{\text{L}} \right)^2 = \left( \frac{\text{mol}}{\text{L-sec}} \right)$   
Hence  $k = \text{L mol}^{-1} \text{sec}^{-1}$ .