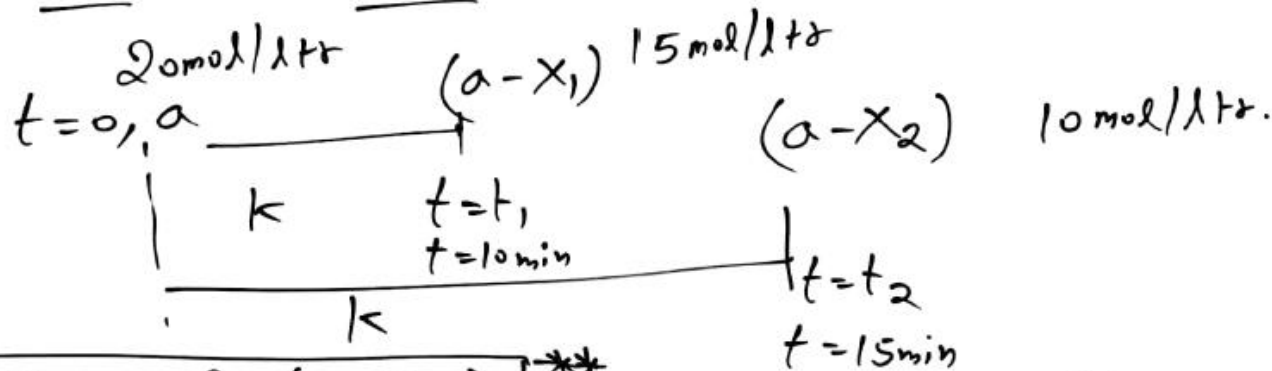


Interval Formula of 1<sup>st</sup> order Reaction



$$k = \frac{2.303}{t_2 - t_1} \log \left( \frac{a - x_1}{a - x_2} \right)$$

Here  $t_1$  &  $t_2 \Rightarrow$  time  
 $(a - x_1) \Rightarrow$  Conc. at time  $t_1$   
 $(a - x_2) \Rightarrow$  - - - at time  $t_2$   
 $k \Rightarrow$  rate constant of 1<sup>st</sup> order  
 $\text{ex n. } (\text{sec}^{-1} / \text{min}^{-1} / \text{hr}^{-1})$

General integrated rate equation ( $n^{\text{th}}$  order rate eq.)  $\div$

$$k t = \frac{1}{(n-1)} \left[ \frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right]; \quad n \neq 1$$

Here  $\Rightarrow n$  is order of rxn;  $t \rightarrow$  time;  $a \rightarrow$  initial Conc.

$k \rightarrow$  rate constant ;  $(a-x) \rightarrow$  Conc. at time  $t$ .

Half life of  $n^{\text{th}}$  order rxn  $\div t \rightarrow t_{1/2}$

$$x = a/2;$$

$$a-x = a - a/2 = a/2$$

Put in given eq.

$$k t_{1/2} = \frac{1}{(n-1)} \left[ \frac{1}{(a/2)^{n-1}} - \frac{1}{a^{n-1}} \right]$$

$$k t_{1/2} = \frac{1}{(n-1)} \left[ \frac{2^{n-1}}{a^{n-1}} - \frac{1}{a^{n-1}} \right]$$

$$k t_{1/2} = \frac{1}{(n-1)} \left[ \frac{2^{n-1} - 1}{a^{n-1}} \right]$$

~~\*\*\*~~  $t_{1/2} \Rightarrow$  Half life.

$$\# \quad t_{1/2} \propto \frac{1}{a^{n-1}}$$

# If  $a \rightarrow a_1$ ,  $t_{1/2} \rightarrow (t_{1/2})_1$ ,  
 $a \rightarrow a_2$ ,  $t_{1/2} \rightarrow (t_{1/2})_2$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left( \frac{a_2}{a_1} \right)^{n-1} \quad \text{***}$$

II<sup>nd</sup> order Reaction

① Integrated rate eq. :- By using n<sup>th</sup> order R<sub>exn</sub> integrated rate eq.

$$kt = \frac{1}{(n-1)} \left[ \frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right]; n \neq 1$$

For n=2 (second order R<sub>exn</sub>)

$$kt = \frac{1}{2-1} \left[ \frac{1}{(a-x)^{2-1}} - \frac{1}{a^{2-1}} \right]$$

$$kt = 1 \left[ \frac{1}{(a-x)} - \frac{1}{a} \right] \Rightarrow kt = \left[ \frac{a - (a-x)}{a \cdot (a-x)} \right]$$

$$kt = \frac{a - a + x}{a \cdot (a-x)} \Rightarrow \boxed{kt = \frac{x}{a \cdot (a-x)}} \rightarrow \text{II}^{\text{nd}} \text{ order Here } \rightarrow x \rightarrow \text{dissociated Conc. at time } t$$

k → rate Const. of II<sup>nd</sup> order R<sub>exn</sub>.

t → time  
a → initial conc.

(a-x) → conc. at time t

Half life of II<sup>nd</sup> order rxn:

$$t \rightarrow t_{1/2}, \quad x = a/2; \quad \boxed{a-x = a - \frac{a}{2} = a/2}$$

Put in II<sup>nd</sup> order integrated rate eq.

$$k t_{1/2} = \frac{a/2}{a \cdot \left(\frac{a}{2}\right)} \Rightarrow \boxed{t_{1/2} = \frac{1}{a \cdot k}} \quad ***$$

# Half life of II<sup>nd</sup> order rxn. is inversely proportional to initial conc.

Q.1 90% of 1<sup>st</sup> order rxn was completed in 10 hr.  
When will 99.9% reaction complete.

Sol.  $k_{90\%} = k_{99.9\%}$

$$\frac{2.303}{10} \log\left(\frac{100}{100-90}\right) = \frac{2.303}{t} \log\left(\frac{100}{100-99.9}\right)$$

$$\frac{1}{10} \log\left(\frac{100}{10}\right) = \frac{1}{t} \log\left(\frac{1000}{0.1}\right)$$

$$\frac{1}{10} \cdot 1 = \frac{1}{t} \log(10)^3 \Rightarrow \frac{1}{10} = \frac{3}{t} \log 10$$

$$t = 3 \cdot 10 \cdot 1 \Rightarrow \boxed{t = 30 \text{ hr}} \text{ Ans.}$$

Q.2) 20% of I<sup>st</sup> order reaction was completed in 5 min. when will 60% of reaction complete?

Sol.  $k_{20\%} = k_{60\%}$

$$\frac{2.303}{5} \log\left(\frac{100}{100-20}\right) = \frac{2.303}{t} \log\left(\frac{100}{100-60}\right)$$

$$\frac{1}{5} \cdot \log\left(\frac{100}{80}\right) = \frac{1}{t} \log\left(\frac{100}{40}\right)$$

$$\frac{1}{5} [\log 10 - \log(2)^3] = \frac{1}{t} [\log 10 - \log(2)^2]$$

$$\frac{1}{5} [1 - 3 \times 0.30] = \frac{1}{t} [1 - 2 \times 0.30]$$

$$\frac{1}{5} [1 - 0.90] = \frac{1}{t} [1 - 0.60] \Rightarrow \frac{1}{5} \times 0.10 = \frac{1}{t} \times 0.4$$

$$t = 5 \times 4 \Rightarrow \boxed{t = 20 \text{ min}} \text{ Ans.}$$

$$\left. \begin{aligned} (1) \log(m \cdot n) &= \log m + \log n \\ (2) \log\left(\frac{m}{n}\right) &= \log m - \log n \\ (3) \log m^n &= n \log m \end{aligned} \right\}$$

$$\left. \begin{aligned} \log 2 &= 0.30 \\ \log 3 &= 0.48 \\ \log 5 &= 0.70 \\ \log 7 &= 0.84 \end{aligned} \right\}$$



Q.3 For 1<sup>st</sup> order rxn Half life is 6 min. Cal. the rate constant of 1<sup>st</sup> order rxn.

Sol.  $t_{1/2} = 6 \text{ min} \quad | \quad t_{1/2} = \frac{0.693}{k} \Rightarrow k = \frac{0.693}{6}$   
 $k = ?$

$k = 0.1155 \text{ min}^{-1}$

Q.4. A 1<sup>st</sup> order reaction was 90% complete in 40 min. Cal. Half life of the reaction.

Sol. given  $t_{90\%} = 40 \text{ min.}$   
 $t_{1/2} = ?$

$k = \frac{2.303}{t} \log \left( \frac{a}{a-x} \right)$

$k = \frac{2.303}{40} \log \left( \frac{100}{100-90} \right)$

$k = \frac{2.303}{40} \log \left( \frac{100}{10} \right) \Rightarrow k = \frac{2.303}{40}$

$t_{1/2} = \frac{0.693}{k} \Rightarrow t_{1/2} = \frac{2.303 \log 2}{2.303} \times 40$

$t_{1/2} = 0.30 \times 40$

$= 3 \times 4$   
 $t_{1/2} = 12 \text{ min}$



Q.5. If the initial Conc. of reactants are double then Half life becomes Half. Cal. order of reaction.

Sol. let;  $a_1 \rightarrow a$ ;  $(t_{1/2})_1 \rightarrow (t_{1/2})$   
 $a_2 \rightarrow 2a$ ;  $(t_{1/2})_2 \rightarrow \frac{(t_{1/2})}{2}$

$$\boxed{\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}}$$

$$\frac{t_{1/2}}{\frac{t_{1/2}}{2}} = \left(\frac{2a}{a}\right)^{n-1}$$

$$2 = 2^{n-1} \Rightarrow 1 = n-1$$

II<sup>nd</sup> order //

$$\boxed{n = 1 + 1 = 2}$$