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◆ Unit of Rate Constant

The differential rate expression for n^{th} order reaction is as follows:

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

$$\text{or, } k = \frac{dx}{(a-x)^n dt} = \frac{(\text{Concentration})}{(\text{Concentration})^n \text{ time}}$$

$$= (\text{Conc.})^{1-n} \text{ time}^{-1}$$

If concentration be expressed in mole L^{-1} and time in minutes, then

$$k = (\text{mole L}^{-1})^{1-n} \text{ min}^{-1}$$

For zero order reaction, $n=0$ and hence, $k = \text{mole L}^{-1} \text{ min}^{-1}$

For first order reaction, $n=1$ and hence,

$$k = (\text{mole L}^{-1})^0 \text{ min}^{-1} = \text{min}^{-1}$$

For second order reaction, $n=2$ and hence,

$$k = (\text{mole L}^{-1})^{-1} \text{min}^{-1} = \text{mole}^{-1} \text{L min}^{-1}$$

The rate constant of a first order reaction has only time in its units. It has no concentration term in the unit. This means the numerical value of k for a first order reaction is independent of the unit in which concentration is expressed. If concentration unit is changed, the numerical value of k for a first order reaction will not change. However, it would change with change in time. Say, k is $6.0 \times 10^{-3} \text{ min}^{-1}$ then it may also be written as $1 \times 10^{-4} \text{ s}^{-1}$, i.e., numerical value of k will decrease 60 times if time unit is changed from hour to minute or from minutes to second.

◆ Half-time or half-life period of a first order reaction:

The half-time of a reaction is defined as the time required to reduce the concentration of the reactant to half of its initial value. It is denoted by the symbol $t_{1/2}$. Thus,

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

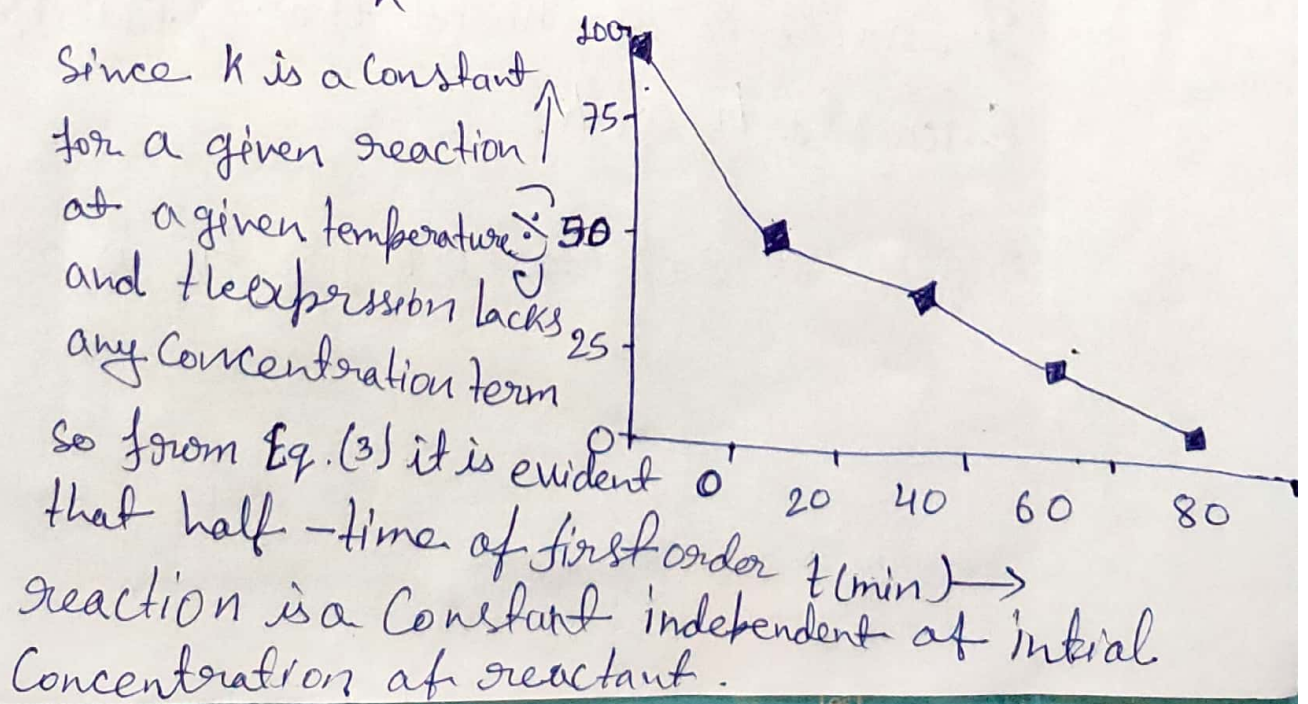
Putting these values in Eq. (2), we get

$$k = \frac{2.303}{t_{1/2}} \log \frac{a}{a - \frac{a}{2}} = \frac{2.303}{t_{1/2}} \log 2 = \frac{2.303}{t_{1/2}}$$

0.30103

$$(\because \log 2 = 0.30103)$$

$$t_{1/2} = \frac{0.693}{k} \quad \text{--- (3)}$$



This means if we start with 4 moles l^{-1} of a reactant. This means if we start with ~~by~~ first order kinetics, then after 20 minutes it is reduced to 2 moles l^{-1} . That is after 20 minutes from the start of reaction the concentration of the reactant will be 2 moles l^{-1} after 40 minutes the start of reaction, the concentration is 1 mole l^{-1} . After 60 minutes from the start of reaction, the concentration of the reactant will be reduced to 0.5 mol l^{-1} . In other words, if during 20 minutes 50% of the reaction completes, then 40 minutes 75%, in 60 minutes 85.5% of the reaction and so on, will complete as shown in the figure above.

Thus, fraction left after n half-lives = $\left(\frac{1}{2}\right)^n$

Concentration left after n half-lives = $[A] \left(\frac{1}{2}\right)^n [A]$

It is also to be noted that Eq. (3) helps to calculate $t_{1/2}$ or k .

A general expression for $t_{1/2}$ is as follows.