

Paper : Physical Chemistry

Topic : Chemical Kinetics

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First Order Reactions

Consider a first-order reaction represented by



As per rate laws, the rate of this reaction is directly proportional to the concentration of A. i.e.

$$\text{Rate} = - \frac{d[A]}{dt} \propto [A]$$

$$\text{or } r = - \frac{d[A]}{dt} = k[A] \quad \text{--- (1)}$$

where  $k$  is proportionality constant - or rate constant - of this reaction. If we put  $[A] = 1$ , above expression becomes

$$r = k$$

It means rate constant  $k$  can also be called the specific reaction rate or specific velocity constant - for the first-order equation

if the concentration of reactant is taken as unity.

Suppose that at the beginning of the reaction (at  $t=0$ ), the concentration of A is  $a$  moles per litre. If after time  $t$ ,  $x$  moles per litre of A have changed into products. Therefore, remaining concentration of A at time  $t$  will be  $(a-x)$  moles/litre.

Putting the value  $(a-x)$  for the concentration of A at time  $t$  in eqn. ① we get-

$$-\frac{d(a-x)}{dt} = k(a-x)$$

$$\begin{aligned} \text{But } -\frac{d(a-x)}{dt} &= -\frac{da}{dt} - \left(-\frac{dx}{dt}\right) \\ &= 0 + \frac{dx}{dt} \quad (a \text{ is a constant}) \end{aligned}$$

so above equation can be written as

$$\frac{dx}{dt} = k(a-x) \quad \text{--- ②}$$

This equation gives the rate of first order reaction in terms of initial concentration of the reactant and the concentration of the reactant decomposed. On separating the variables we get-

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

By integrating this equation we get-

$$\int \frac{dx}{(a-x)} = \int k \cdot dt$$

$$-\ln(a-x) = kt + I \quad \text{--- (3)}$$

where I is the integration constant.

When  $t=0$ , then  $x=0$ , by putting these values in equation (3) we get-

$$I = -\ln a$$

Now substituting the value of I in equation (3) we get-

$$-\ln(a-x) = kt - \ln a$$

$$\text{or } \ln a - \ln(a-x) = kt$$

$$\text{or } \ln \frac{a}{(a-x)} = kt$$

$$\text{or, } k = \frac{1}{t} \ln \frac{a}{a-x} \quad \text{--- (4)}$$

This is the kinetic equation of the first-order reaction.

Changing it into common logarithm, we get-

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \quad \text{--- (5)}$$



$$\text{or, } t = \frac{2.303}{k} \log \frac{a}{a-x} \quad - (6)$$

The value of  $k$  can be found by substituting the values of  $a$  and  $(a-x)$  observed experimentally at time interval  $t$  during the course of reaction.

Sometimes the integrated rate law in the following form is also used:

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

where  $x_1$  and  $x_2$  are the amounts of reactants decomposed at time intervals  $t_1$  and  $t_2$  respectively.

Units of First-Order Rate Constant :-

The rate constant of a first-order reaction is given by equation (5) above i.e.

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$\Rightarrow \frac{2.303}{\text{second}} \log \frac{\text{moles/litre}}{\text{moles/litre}}$$

$$\Rightarrow \frac{1}{\text{second}} = \text{s}^{-1}$$

Units of 1st order rate constant is  $\text{s}^{-1}$ . Thus the rate constant for the first order is independent of concentration.

Half-Life of a Reaction ( $t_{1/2}$ ) :-

Reaction rates can also be expressed in terms of half-life or half-life period. It is defined as the time required for the concentration of a reactant to decrease to just half of its initial value. In another words half-life is the time required for one-half of the reaction to be completed. It is denoted by the symbol  $t_{1/2}$  or  $t_{0.5}$ .

Half-life of a First-Order Reaction :-

Consider the integrated rate equation (eqn 5) for a first-order reaction

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

By the definition when  $t = t_{1/2}$ , then  $x$  will be equal to half of the initial concentration  $a$ , i.e.  $x = a/2$ . On putting these values in above equation we get -

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

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

$$\left[ \frac{\frac{a}{2a-a}}{2} = \frac{a}{a/2} = \frac{2a}{a} = 2 \right]$$

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

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

From this equation, we say that -  
 (i) half-life for a first order reaction is independent of the initial concentration of the reactant, and  
 (ii) it is inversely proportional to the rate constant,  $k$ .

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