

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. (16)

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 logarithms, we get-

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

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

- (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 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-

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

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

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

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

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

- 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 .

Examples of First-Order Reaction :-

1. Decomposition of Nitrogen Pentoxide :

This reaction occurs both in gas phase and in liquid phase.

(a) Decomposition of N_2O_5 in gaseous phase :- The equation can be represented as



Though this is a bimolecular reaction but experimentally found to be first-order and the rate law is given by

$$-\frac{d[N_2O_5]}{dt} = k[N_2O_5]$$

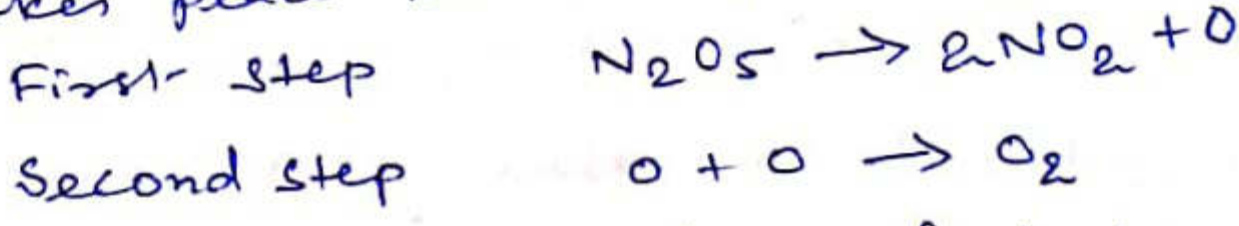
The process of reaction is monitored by measuring the pressure of N_2O_5 at various intervals of time. Let P_0 is the initial pressure of N_2O_5 (at $t=0$), P_t is the pressure after time t and P_∞ is the

pressure when the reaction is completed. Here 'a' will be equivalent to $P_{\infty} - P_0$ and '(a-x)' will be equivalent to $P_{\infty} - P_t$. Then

$$k = \frac{2.303}{t} \log \frac{P_{\infty} - P_0}{P_{\infty} - P_t}$$

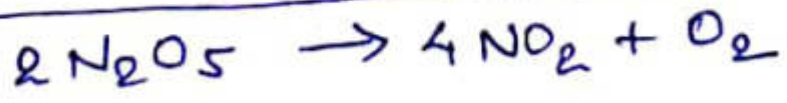
On substituting the values of $P_{\infty} - P_0$ and $P_{\infty} - P_t$ at different time intervals, t, the value of k is found to be constant. Thus this is a first-order reaction.

Actually the dissociation of N_2O_5 takes place in the following two steps:



Since second step is too fast, hence first step is the rate determining step. In principle, if a reaction takes place in various steps, the rate of reaction is determined by the slowest step.

(b) Decomposition of N_2O_5 in CCl_4 Solⁿ:



Both N_2O_5 and NO_2 are soluble in CCl_4 and remain in solution while O_2 evolved

is insoluble and its volume is measured time to time using a suitable device. When reaction is complete, no more oxygen is evolved.

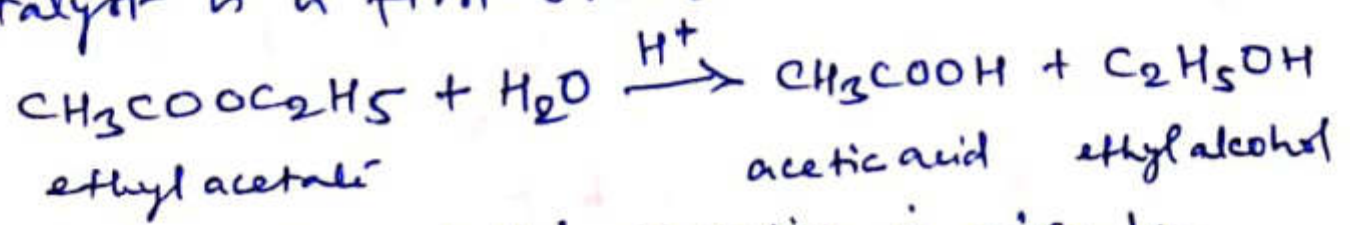
If V_t be the volume of O_2 at any time t and V_∞ be the final volume of O_2 when the reaction is completed, the V_∞ is a measure of the initial concentration (i.e. a) of N_2O_5 and $(V_\infty - V_t)$ is a measure of undecomposed N_2O_5 (i.e. $a-x$) remaining at time t . Thus

$$k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

On substituting values of V_∞ and $V_\infty - t$ at different time intervals, t , k can be calculated and is always found to be constant.

2. Hydrolysis of an Ester :-

The hydrolysis of ethyl acetate (or methyl acetate) in the presence of a mineral acid as catalyst is a first-order reaction.



The rate of this reaction is given by

$$\frac{dx}{dt} = k [\text{CH}_3\text{COOC}_2\text{H}_5] [\text{H}_2\text{O}]$$

But since water is present in large excess, its concentration is almost constant and therefore,

$$\frac{dx}{dt} = k [\text{CH}_3\text{COOC}_2\text{H}_5]$$

Hence the reaction is of the first order. Such types of reactions are also known as pseudo unimolecular reactions.

For studying the kinetics of this reaction, a known volume of ethyl acetate is mixed with a relatively large quantity of acid solution, say $N/2$ HCl. At various intervals of time, a known volume of the reaction mixture is titrated against a standard alkali solution. Hydrolysis of the ester produces acetic acid. Therefore, as the reaction proceeds, the volume of alkali required for titration goes on increasing.

If V_0 is the volume of alkali used to neutralise HCl at the start of the reaction (i.e. at $t=0$), V_t is the volume after time t and V_{∞} is the volume of alkali when the reaction is complete.

Here the initial concentration (a) of ethyl acetate will be $\frac{V_{\infty} - V_0}{V}$, $V_t - V_0$ will be the volume of alkali required to neutralise acetic acid formed at time t (i.e. x) and the concentration

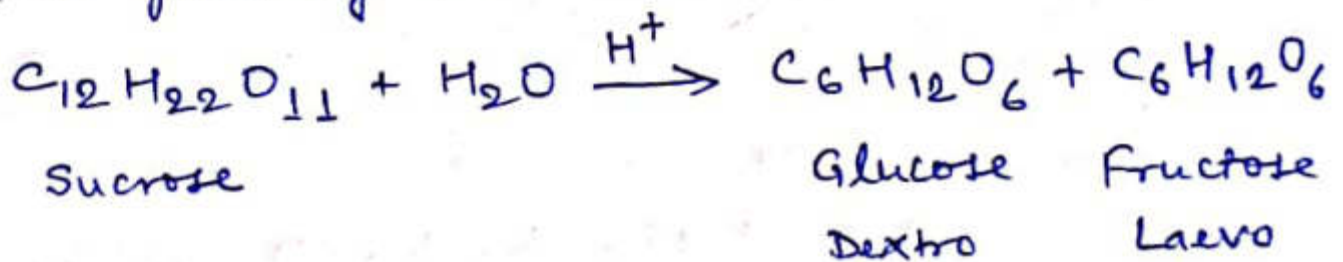
of ethyl acetate at any time t , i.e. $(a-x)$ will be equal to $(V_{\infty} - V_0) - (V_t - V_0) = V_{\infty} - V_t$.

Therefore, equation for the first-order reaction is written as

$$k = \frac{2.303}{t} \log \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$$

3. Inversion (or Hydrolysis) of Sucrose (or Cane Sugar) :-

The inversion of sucrose catalysed by dil. HCl is given by the reaction



and it follows the first order kinetics. The progress of the reaction is followed by noting the optical rotation of the reaction mixture with the help of a polarimeter at different intervals of time. The optical rotation goes on changing since glucose rotates the plane of polarised light to the right and fructose to the left. The change in rotation is proportional to the amount of sugar decomposed.

Let α_0 and α_{∞} be the angles of rotation at the start (i.e. $t=0$) and at the completion

of reaction, and α_t is the angle of rotation at any time t . Then $(\alpha_0 - \alpha_\infty)$ will be proportional to 'a' (the initial amount of sucrose) and $(\alpha_t - \alpha_\infty)$ will be proportional to 'a-x' (the amount of sucrose left at time t). Therefore, the rate equation becomes

$$k = \frac{2.303}{t} \log \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$$

If the experimental values of t , $(\alpha_0 - \alpha_\infty)$ and $(\alpha_t - \alpha_\infty)$ are substituted in the above equation, a constant value of k is obtained.

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To be continued.....