B.Sc. (Hons) Part I

CHEMICAL KINETICS

Paper : I A Physical Chemistry

Dr. Om Prakash Singh
Department of Chemistry,
Maharaja College, Ara

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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

$$2\,N_2O_5(g) \longrightarrow 4\,NO_2(g) + O_2(g)$$

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:

First step $\quad N_2O_5 \rightarrow 2NO_2 + O$

Second step $\quad O + O \rightarrow O_2$

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:

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

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.

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O \xrightarrow{H^+} \underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{ethyl alcohol}}{C_2H_5OH}$$

The rate of this reaction is given by

$$\frac{dx}{dt} = k[CH_3COOC_2H_5][H_2O]$$

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

$$\frac{dx}{dt} = k[CH_3COOC_2H_5]$$

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 equal to $V_\infty - V_0$, $V_t - V_0$ 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

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\substack{\text{Glucose}\\ \text{Dextro}}}{C_6H_{12}O_6} + \underset{\substack{\text{Fructose}\\ \text{Laevo}}}{C_6H_{12}O_6}$$

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.

To be continued.....