Class ⇒ B.Sc. (Hons) Part I
Subject ⇒ Chemistry
Chapter ⇒ Chemical Kinetics
Topic ⇒ First order reaction

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First order reaction

A reaction is said to be of the first order if the rate of the reaction depends upon one concentration term only.

Let us consider a first order reaction

$$A \longrightarrow \text{Products}$$

Suppose that at the beginning of the reaction. $t=0$, the concentration of A is a moles per litre.

If after time t, x moles of A have changed, the concentration of A is $a-x$.

Then the first order reaction, the rate of reaction, dx/dt is directly proportional to the concentration of the reactant.

Thus,

$$\frac{dx}{dt} \propto (a-x)$$

or

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

Where K is called the rate constant or the specific reaction rate for the reaction of the first order.

$$\frac{dx}{a-x} = K\,dt \quad \text{——— (1)}$$

Integration of the expression (1) gives

$$\int \frac{dx}{a-x} = \int k\,dt$$

or $-\ln(a-x) = kt + I$ ——— (2)

Where I is the constant of integration.

The constant k may be evaluated by putting $t=0$ and $x=0$.

Thus,

$$I = -\ln a$$

Substituting this value in equation (2) we get

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

or $\ln \frac{a}{a-x} = kt$ ——— (3)

or $k = \frac{1}{t} \ln \frac{a}{a-x}$

Changing into common logarithms

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \quad \text{——— (4)}$$

This equation is called the first order 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 decomposed at time intervals t_1 and t_2 respectively from the start

Units of First order Rate Constant

The rate constant for the first order reaction is independent of the concentration. It has the unit

$$\text{time}^{-1}$$

Examples of first order Reaction

① Decomposition of N_2O_5 in CCl_4 Solution ⇒

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$$

If V_t the volume of O_2 at any time t and V_∞ the final volume of oxygen when the reaction is completed. The V_∞ is a measure of the initial conc^n of N_2O_5 and $(V_\infty - V_t)$ is a measure of undecomposed N_2O_5 $(a-x)$ remaining at time t. Thus,

$$K = \frac{2.303}{t} \log_{10} \frac{V_\infty}{V_\infty - V_t}$$

Putting the value of V_∞, $(V_\infty - V_t)$ at different time intervals t. The value of K is found to be constant. Thus, it is a reaction of the first order.

② Decomposition of Benzene diazonium chloride $(C_6H_5N=NCl)$ in water ⇒

$$C_6H_5N=NCl + H_2O \longrightarrow C_6H_5OH + N_2 + HCl$$

Let V_∞ be the volume of N_2 measured at the end of the reaction and ~~volume~~ V_t be the volume at any time t, then

$$a \propto V_\infty$$

$$(a-x) \propto (V_\infty - V_t)$$

Substituting the values of a and $(a-x)$ in the first order reaction, we get

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

The value of K is found to be constant. ~~This~~ Thus, it a first order reaction.

③ Decomposition of H_2O_2 in aqueous soln.

$$H_2O_2 \xrightarrow{Pt} H_2O + O$$

④ Hydrolysis of an ester i.e. Ethyl acetate or methyl acetate in the presence of a mineral

acid as catalyst, is a first order reaction.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

Ethyl acetate — Acetic acid — Ethyl alcohol.

5. Inversion of cane sugar (sucrose) is catalysed with dil. HCl is a first order reaction.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

Glucose (Dexto-rotatory) — fructose (laevo-rotatory)