B. Sc. Hons Part III

PAPER : Physical Chemistry

TOPIC : Chemical Kinetics

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Kinetics of Third Order Reactions

A chemical reaction is said to be of third order if its rate depends on three concentration terms. In general, a third order reaction may be represented as :

(i) $3A \rightarrow$ Products

(ii) $2A + B \rightarrow$ Products

(iii) $A + B + C \rightarrow$ Products

A. Consider type (i) reaction :

$$3A \rightarrow \text{Products}$$

Suppose 'a' is the initial concentration of each reactant in moles/litre. Suppose 'x' is the concentration change after time 't'. Then the concentration of A at time t will be '(a-x)' moles/litre. Now, according to the law of mass action, the rate of such a reaction at time t is given by

$$\frac{dx}{dt} \propto (a-x)^3 \quad \text{or} \quad \frac{dx}{dt} = k\,(a-x)^3 \qquad -①$$

where k is the rate constant or velocity constant for the third order reaction.

On separating the variables equation ① becomes as

$$\frac{dx}{(a-x)^3} = k.dt \qquad —②$$

On integration, it gives

$$\frac{1}{2(a-x)^2} = kt + c \quad \text{—— (3)}$$

where c is the integration constant and its value is determined from the initial conditions of experiment, i.e. when $t=0$, $x=0$, then

$$C = \frac{1}{2a^2}$$

By substituting the value of C in equation (3) we get

$$\frac{1}{2(a-x)^2} = k.t + \frac{1}{2a^2} \quad \text{—— (4)}$$

or, $$k.t = \frac{1}{2(a-x)^2} - \frac{1}{2a^2}$$

or, $$k = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$$

or, $$k = \frac{1}{2t}\left[\frac{a^2-(a-x)^2}{a^2.(a-x)^2}\right]$$

$$= \frac{1}{2t}\left[\frac{a^2-a^2+2ax-x^2}{a^2.(a-x)^2}\right]$$

$$= \frac{1}{2t}\left[\frac{2ax-x^2}{a^2.(a-x)^2}\right]$$

or $$k = \frac{1}{2t}\left[\frac{x(2a-x)}{a^2(a-x)^2}\right] \quad \text{—— (5)}$$

This is the kinetic equation of the third order reaction when the concentration of three reactants is the same. This is also applicable to the reaction of the type $A+B+C \rightarrow$ Products if the initial molar concentrations of all the three reactants are same, i.e. equal to a.

B. Now we consider type (ii) reaction :

$$2A + B \longrightarrow \text{Products}$$

Suppose 'a' and 'b' are initial concentrations of

A and B respectively. Suppose 'x' is the concentration change after time 't'. Then the rate of reaction is given by

$$\frac{dx}{dt} = k\,(a-2x)^2(b-x) \quad \text{—— (6)}$$

where the amount of A decomposed at any instant is equal to $2x$ which is twice that of B.

On rearranging equation (6) we have

$$\frac{dx}{(a-2x)^2(b-x)} = k.dt$$

On integrating we get

$$\int \frac{dx}{(a-2x)^2(b-x)} = k.\int dt \quad \text{—— (7)}$$

On resolving $\frac{1}{(a-2x)^2(b-x)}$ into partial fraction, we have

$$\frac{1}{(a-2x)^2(b-x)} = -\frac{2}{(2b-a)^2(a-2x)} + \frac{2}{(2b-a)(a-2x)^2} + \frac{1}{(2b-a)^2(b-x)} \quad \text{—— (8)}$$

By using this partial fraction in the integration equation (7) we obtain

$$\int \frac{dx}{(a-2x)^2(b-x)} = -\frac{2}{(2b-a)^2}\int \frac{dx}{(a-2x)} + \frac{2}{(2b-a)}\int \frac{dx}{(a-2x)^2} + \frac{1}{(2b-a)^2}\int \frac{dx}{(b-x)}$$

$$= -\frac{2}{(2b-a)^2}\cdot\left(-\frac{1}{2}\right)\ln(a-2x) + \frac{2}{(2b-a)}\left(\frac{1}{2}\right)\left(\frac{1}{a-2x}\right) - \frac{1}{(2b-a)^2}\ln(b-x)$$

$$= \frac{1}{(2b-a)^2}\ln(a-2x) - \frac{1}{(2b-a)^2}\ln(b-x) + \frac{1}{(2b-a)}\left(\frac{1}{(a-2x)}\right)$$

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$$= \frac{1}{(2b-a)^2} \ln\left(\frac{a-2x}{b-x}\right) + \frac{1}{(2b-a)(a-2x)} = k.t + C$$
— (9)

At $t=0$, $x=0$, then the value of integration constant C will be

$$C = \frac{1}{(2b-a)^2} \ln\left(\frac{a}{b}\right) + \frac{1}{(2b-a)a} \quad \text{— (10)}$$

On substituting the value of C in equation (9) we get

$$\frac{1}{(2b-a)^2} \ln\left(\frac{(a-2x)}{(b-x)}\right) + \frac{1}{(2b-a)(a-2x)} = kt + \frac{1}{(2b-a)^2} \ln\left(\frac{a}{b}\right) + \frac{1}{(2b-a)a}$$

or, $$k.t = \frac{1}{(2b-a)^2} \ln \frac{b(a-2x)}{a(b-x)} + \frac{1}{(2b-a)}\left(\frac{a-(a-2x)}{a(a-2x)}\right)$$

or, $$k = \frac{1}{t(2b-a)^2}\left[\ln \frac{b(a-2x)}{a(b-x)} + \frac{(2b-a)\cdot 2x}{a(a-2x)}\right]$$
— (11)

This is the kinetic equation of the third order reaction of the type (ii).

C. Now consider the type (iii) reaction :

$$A + B + C \longrightarrow \text{Products}$$

Suppose a, b and c are the initial concentrations of A, B and C respectively. Suppose x is the concentration change after time t from the commencement of the reaction. Then the rate of the reaction is given by

$$\frac{dx}{dt} = k(a-x)(b-x)(c-x) \quad \text{— (12)}$$

On separating the variables we get

$$\frac{dx}{(a-x)(b-x)(c-x)} = k.dt \quad \text{— (13)}$$

On integrating this equation using partial fraction resolution we get-

$$k = \frac{1}{t} \frac{(b-c)\ln\frac{(a-x)}{a} + (c-a)\ln\frac{(b-x)}{b} + (a-b)\ln\frac{(c-x)}{c}}{(a-b)(b-c)(c-a)} \quad \text{—— (14)}$$

This is the kinetic equation of the third order reaction of the type (iii).

<u>Units of the Third Order Reaction constant k :-</u>

From equation (5) we have

$$k = \frac{1}{2t} \frac{x(2a-x)}{a^2(a-x)^2}$$

$$= \frac{1}{sec} \times \frac{moles/litre \times moles/litre}{(moles/litre)^2 \times (moles/litre)^2}$$

$$= (moles/litre)^{-2} sec^{-1}$$

$$= litre^2 \, moles^{-2} \, sec^{-1}$$

Thus, the unit of k for the third order reaction is $(moles/litre)^{-2} sec^{-1}$.

<u>Half-life Period of Third Order Reaction :-</u>

Following the definition of half-life,

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

On putting these values in equation (5) we get-

$$k = \frac{1}{2t_{1/2}} \frac{\frac{a}{2}(2a - \frac{a}{2})}{a^2(a - \frac{a}{2})^2}$$

or $$t_{1/2} = \frac{1}{2k} \cdot \frac{\frac{a}{2} \cdot \frac{3a}{2}}{a^2 \cdot \frac{a^2}{4}}$$

$$= \frac{1}{2k} \cdot \frac{1}{a^2}$$

or $$t_{1/2} \propto \frac{1}{a^2} \quad \text{—— (15)}$$

Thus, the half-life period of the third order reaction is inversely proportional to the square of the initial concentration.

Similarly it can be proved that the time taken for the completion of any definite fraction of a reaction varies inversely as the square of the initial concentration.

Examples of Third Order Reactions :-

There are very few (only five) examples of third order reactions in the gaseous phase and each example involves two molecules of nitric oxide as one of the reactants and the other reactant is a molecule of either chlorine, bromine, oxygen, hydrogen or deuterium. These reactions are:

(a) $2NO + Cl_2 \rightarrow 2NOCl$

(b) $2NO + Br_2 \rightarrow 2NOBr$

(c) $2NO + O_2 \rightarrow 2NO_2$

(d) $2NO + H_2 \rightarrow N_2O + H_2O$

(e) $2NO + D_2 \rightarrow N_2O + D_2O$

Some examples of third order reaction in solutions are the interaction of stannous chloride and ferric chloride, oxidation of ferrous sulphate in water, the reaction between benzoyl chloride and alcohol in ether solution, reaction of triphenyl methyl (trityl) chloride with methanol in dry benzene etc. e.g.

$$2FeCl_3(aq) + SnCl_2(aq) \rightarrow 2FeCl_2(aq) + SnCl_4(aq)$$

To be continued ......