B. Sc. Hons Part III

Paper : Physical Chemistry
Topic : Chemical Kinetics

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

...... continued from page ⑬

Kinetics of Complex Reactions :—

Only a few reactions are straight forward, i.e., first or second or third order reactions. There are many reactions both in nature and in the laboratory, which do not take place strictly according to the equation derived. These reactions involve two or more side reactions in addition to the actual reactions and thus the kinetics of such reactions is complicated. Such reactions are known as complex reactions. In complex reactions, the side reactions take place simultaneously along the main reaction. So the complex reactions are also known as simultaneous reactions. Complex reactions proceed in a series of steps instead of a single step and the rate of overall reaction is in accordance with the stoichiometric equation for that reaction.

Followings are the important complex reactions:—

1. Reversible or Opposing Reactions :—

So far it has been assumed that a reaction takes place in the forward direction only. But, there are certain reactions in which the products of a chemical reaction react to form the original reactants. Such reactions are known as counter, reversible or opposing reactions. Initially, the rate of forward reaction is very large which decreases with passage of time and the rate of backward or reverse reaction is zero which increases with passage of time. A stage is reached when two rates become equal. This situation is called the chemical equilibrium. It is dynamic in nature, i.e., all the species are reacting at the rate at which they are being formed.

In reversible or opposing reactions, the net rate of the reaction will be influenced by both the forward and backward rates and thus causes a serious disturbance in the measurement of reaction velocity. Let us consider the various cases of opposing reactions.

<u>case I</u> :- Consider a simplest case of this type in which both forward and backward reactions are of the first order.

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

where k_1 and k_2 represent the first order rate constants for the forward and backward reactions respectively. Let 'a' be the initial concentration of the reactant A. It is assumed that initially the concentration of reactant B is equal to zero. After a time 't', 'x' mols of A have decomposed to form B. Then, the concentration of A at time t is $(a-x)$ and the concentration of B at the same time is 'x'. Thus,

Rate of the forward reaction $= k_1(a-x)$
Rate of the backward reaction $= k_2 x$

The overall rate of reaction (i.e. the net rate of production of B) is given by

Rate of Reaction = Rate of forward reaction − Rate of backward reaction i.e. $$\frac{dx}{dt} = k_1(a-x) - k_2 x \quad \text{—①}$$

At equilibrium, the net rate is zero, i.e. $\frac{dx}{dt} = 0$.
Thus
$$k_1(a-x_e) - k_2 x_e = 0$$
or
$$k_1(a-x_e) = k_2 x_e$$
or,
$$k_2 = \frac{k_1(a-x_e)}{x_e} \quad \text{—②}$$

where x_e is the concentration at equilibrium.

Substituting the value of k_2 from equation ② in equation ①, we get

$$\frac{dx}{dt} = k_1(a-x) - \frac{k_1}{x_e}(a-x_e).x$$
$$= k_1 a - k_1 x - \frac{k_1 a x}{x_e} + \frac{k_1 x x_e}{x_e}$$
$$= k_1 a - k_1 a.\frac{x}{x_e} = k_1 a\left(1-\frac{x}{x_e}\right)$$
or
$$\frac{dx}{dt} = k_1 a\frac{(x_e-x)}{x_e} \quad \text{—③}$$

Separating the variables, we get

$$\frac{dx}{(x_e-x)} = \frac{k_1 a}{x_e}.dt \quad \text{—④}$$

Integrating this equation, we get

$$-\ln(x_e-x) = \frac{k_1 a}{x_e}.t + C \quad \text{—⑤}$$

where C is the integration constant.

At $t=0$, $x=0$, so that $C = -\ln x_e$ —⑥

Substituting this value in equation ⑤ we get

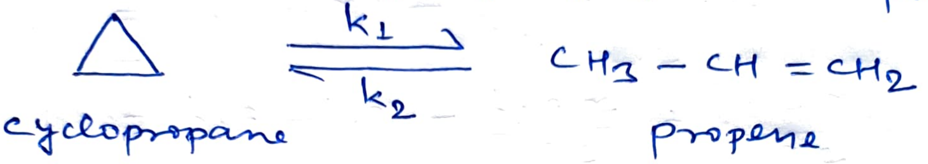
$$-\ln(x_e-x) = \frac{k_1 a}{x_e}.t - \ln x_e$$
or,
$$\ln x_e - \ln(x_e-x) = \frac{k_1 a}{x_e}t$$
or
$$\ln\frac{x_e}{x_e-x} = \frac{k_1 a}{x_e}.t$$
or,
$$k_1 = \frac{x_e}{at}\ln\left(\frac{x_e}{x_e-x}\right) \quad \text{—⑦}$$

Therefore, the value of k_1 can be calculated by using the above equation if x_e, x and t are known. The value of x can be calculated by noting the progress of the reaction at different time intervals 't' before the equilibrium is attained. When the equilibrium is attained, the determination of concentration gives the value of x_e.

By substituting the value of k_1 in equation ② the value of k_2 can be obtained.

Examples :-

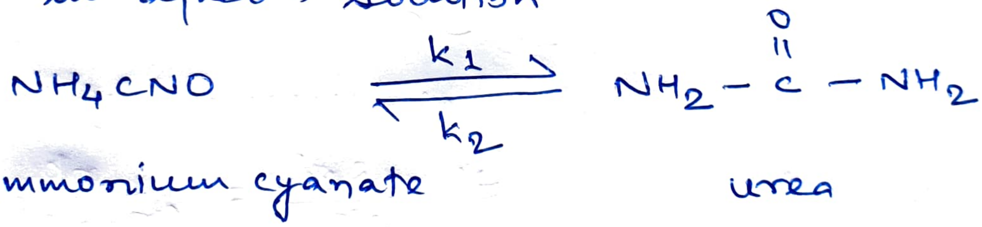
(a) Isomerisation of cyclopropane into propene.



$$\triangle \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CH_3-CH=CH_2$$

cyclopropane propene

(b) Isomerisation of ammonium cyanate into urea in aqueous solution



$$NH_4CNO \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NH_2-\overset{\overset{O}{\parallel}}{C}-NH_2$$

ammonium cyanate urea

...... to be continued