

## Kinetics of complex reactions:-

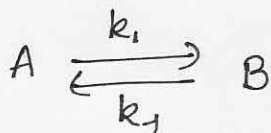
The study of chemical kinetics become highly complicated due to the occurrence of complex reactions which involves more than one step. Important among such reactions are the following:-

- 1) ~~to~~ Opposing or Reversible Reactions
- 2) Consecutive reactions
- 3) chain reactions

① Kinetics of opposing or Reversible Reactions:- The kinetics of such reactions are usually studied in the initial stages of process when the products are too low a concentration to set up the opposing reaction at a noticeable rate.

However, when the opposite reaction also takes at a comparable rate, the problem becomes complicated and the rate constant obtained is not quite reliable.

consider the opposing reaction in which the forward as well as the reverse reaction are both first-order:-



where  $k_1$  and  $k_{-1}$  are rate constants of the forward and reverse reactions, respectively.

Let  $a$  be the initial concentration of the reactant A.  
(It is assumed that initially the concentration of B = 0)

Then, after time,  $t$ , the concentration of A will be  $(a-x)$  and that of the product B will be  $x$ .

The rate of forward reaction is equal to  $k_1(a-x)$  while that of the ~~reverse~~ reverse reaction is  $k_{-1}x$ .  
Hence, the net rate of the formation of B is given by:-

$$\frac{dx}{dt} = k_1(a-x) - k_{-1}x \quad \text{--- (1)}$$

If  $x_e$  is the concentration of B at equilibrium when the net rate is zero, then,

$$k_1(a-x_e) - k_{-1}x_e = 0$$

$$\text{or } k_1(a-x_e) = k_{-1}x_e \quad \text{--- (2)}$$

$$\text{or } k_{-1} = k_1(a-x_e)/x_e \quad \text{--- (3)}$$

substituting for  $k_{-1}$  in equation (1) we have

$$\frac{dx}{dt} = k_1(a-x) - k_1 \frac{(a-x_e)}{x_e}$$

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

separating the variables, we have

$$\frac{dx}{x_e - x} = \frac{a}{x_e} k_1 dt \quad \text{--- (5)}$$

Integrating, we get

$$-\ln(x_e - x) = \frac{a}{x_e} (k_1 t + I) \quad \text{--- (6)}$$

where  $I$  is the constant of integration

$$\text{or } -\frac{x_e}{a} \ln(x_e - x) = k_1 t + I \quad \text{--- (7)}$$

At  $t=0$ ,  $x=0$ , so that

$$I = -\frac{x_e}{a} \ln x_e \quad \text{--- (8)}$$

(At  $t=0$ ,  $x=0$ , so that)

Hence, substituting for  $I$  in eq. (7)

$$-\frac{x_e}{a} [\ln(x_e - x)] = k_1 t - \frac{x_e}{a} \ln x_e$$

$$\text{or } \underline{k_1 t} = \frac{x_e}{a} \ln \left( \frac{x_e}{x_e - x} \right) \text{ or } k_1 = \frac{x_e}{at} \ln \left( \frac{x_e}{x_e - x} \right) \quad \text{--- (9)}$$

In eq. (9) gives  $k_1$  in terms of easily measurable quantities

From eq. ~~(3)~~ (3), we have

$$(1 + k_{-1}) = k_1 \frac{a}{x_e} = \frac{1}{t} \ln \left( \frac{x_e}{x_e - x} \right) \quad \text{--- (10)}$$

Thus, from a knowledge of  $k_1$ ,  $a$  and  $x_e$ , the rate constant  $k_{-1}$  for the reverse reaction can be calculated.

Now suppose that initially a small amount of B, say  $b$  moles, is present. Then, the net rate of formation of B, say  $b$  moles, is ~~present~~ ~~then~~, given by

$$\frac{dx}{dt} = k_1(a - x) - k_{-1}(b + x) \quad \text{--- (11)}$$

since at equilibrium,  $\frac{dx}{dt} = 0$ , hence