

Kinetics of complex reactions

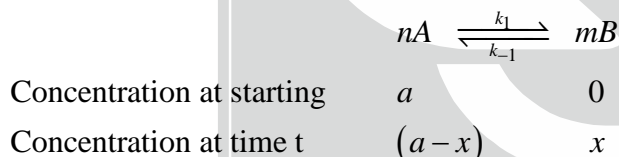
The study of chemical kinetics becomes highly complicated due to the occurrence of complex reactions which involve more than one step. Important among such reactions are the following categories:

1. Reversible Reactions
2. Consecutive Reactions
3. Chain Reactions

Kinetics of Reversible Reactions

In a reversible process, if the rate of backward reaction is much less as compared to the rate of forward reaction, the equilibrium will be far away from the starting end and the reaction may be found to follow a simple and straight forward path as discussed earlier. However, when the reaction rates are appreciable for both the forward and backward directions, the kinetics must be taken into consideration for both the direction.

Let us consider a simple reaction,



where k_1 and k_{-1} are rate constants for forward and backward directions, respectively.

$$\text{Rate of forward reaction} = k_1 (a - x)^n$$

$$\text{Rate of backward reaction} = k_{-1} (x)^m$$

The net rate of formation of products will be the difference between the two, i.e.

$$\text{Net rate of reaction} = \frac{dx}{dt} = k_1 (a - x)^n - k_{-1} (x)^m \quad \dots (1)$$

At equilibrium, the rate of forward reaction is equal to the backward reaction and, therefore, net rate of reaction will be zero. Thus, at equilibrium when $x = x_e$ (concentration of B, measured separately)

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

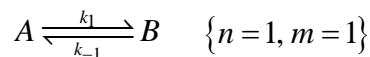
Or,
$$k_{-1} = \frac{k_1 (a - x_e)^n}{(x_e)^m} \quad \dots (2)$$

Substituting the value of k_{-1} from equation (1), in (2), we get

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

Or,
$$\frac{dx}{dt} = \frac{k_1}{x_e^m} \left[(a-x)^n x_e^m - (a-x_e)^n x^m \right] \quad \dots (3)$$

If reaction is simple first order in both therefore, i.e.



equation (3) reduces to

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

which on integration gives

$$k_1 = \frac{x_e}{at} \ln \left(\frac{x_e}{x_e - x} \right) \quad \dots (4)$$

The measurement of x at different times would give the value of k_1 . The value of k_{-1} can be obtained with the help of equation (2), which reduces to

$$k_{-1} = \frac{k_1(a-x_e)}{(x_e)} \quad \dots (5)$$

An alternate expression may also be used if the equilibrium concentration x_e is not known. Equation (1) for above simple reaction can be reduced to

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

On integration, we get

$$t = -\frac{1}{(k_1 + k_{-1})} \ln \{k_1 a - (k_1 + k_{-1})x\} + z$$

The value of integration constant z is obtained as follows:

When $t = 0, x = 0;$
$$z = \frac{1}{(k_1 + k_{-1})} \ln(k_1 a)$$

Substituting the value of z and rearranging, gives

$$(k_1 + k_{-1}) = \frac{1}{t} \ln \left(\frac{k_1 a}{k_1 a - (k_1 + k_{-1})x} \right) \quad \dots (6)$$

again, equilibrium constant $K = k_1 / k_{-1}$ and, therefore, equation (6) can be written in terms of K as

$$k_{-1} = \frac{1}{t(K+1)} \ln \left(\frac{Ka}{Ka - (K+1)x} \right) \quad \dots (7)$$

Thus, with the help of equations (6) and (7), the values of k_1 and k_{-1} can be obtained.

For a given reaction at constant temperature, the equilibrium concentrations, i.e. $(a - x_e)$ and x_e attain the definite values depending on the value of a and therefore, $\frac{a}{x_e}$ can be considered to be a constant under these conditions. The differential equation can be written as

$$\frac{dx}{dt} = k_2(x_e - x) \quad \left[\text{where, } k_2 = \frac{k_1 a}{x_e} \right] \quad \dots (8)$$

Equation (8) on integration and rearrangement becomes

$$k_2 = \frac{1}{t} \ln \left(\frac{x_e}{x_e - x} \right) \quad \dots (9)$$

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

Or, $\frac{k_1}{k_{-1}} = \frac{a - x_e}{x_e}$

Or, $\frac{k_1 + k_{-1}}{k_1} = \frac{a}{x_e}$

Therefore, $k_1 + k_{-1} = \frac{k_1 a}{x_e} = k_2$

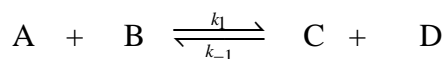
Thus, equation (9) becomes

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

Therefore, the reaction will behave like a first order with $(k_1 + k_{-1})$ as the rate constant and x_e as the initial concentration in place of a .

Reversible reaction when both the opposing processes are second order:

Let us consider a general reaction,



Concentration at starting $a \quad b \quad c \quad d$

Concentration at time $t \quad (a - x) \quad (b - x) \quad (c + x) \quad (d + x)$

The net rate of reaction can be written as

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

Or, $\frac{1}{k_{-1}} \frac{dx}{dt} = K(a - x)(b - x) - (c + x)(d + x)$, where $K = \frac{k_1}{k_{-1}}$

$$\begin{aligned}
 &= K[ab - (a+x)x + x^2] - [cd + (c+d)x + x^2] \\
 &= (K-1)x^2 - K\{(a+b) + (c+d)\}x + K(ab - cd)
 \end{aligned}$$

Or,

$$\begin{aligned}
 \frac{1}{k_{-1}(K-1)} \frac{dx}{dt} &= x^2 - \frac{K\{(a+b) + (c+d)\}}{K-1}x + \frac{K(ab - cd)}{K-1} \\
 &= x^2 - Lx + M \quad \dots (12)
 \end{aligned}$$

where,

$$L = \frac{K\{(a+b) + (c+d)\}}{K-1} \quad \text{and} \quad M = \frac{K(ab - cd)}{K-1}$$

Again, equation (12) can be written as

$$\begin{aligned}
 \frac{1}{k_1 - k_{-1}} \frac{dx}{dt} &= \left(x - \frac{L - \sqrt{L^2 - 4M}}{2} \right) \left(x - \frac{L + \sqrt{L^2 - 4M}}{2} \right) \\
 &= (x - A)(x - B)
 \end{aligned}$$

Where,

$$A = \frac{1}{2}(L - \sqrt{L^2 - 4M}) \quad \text{and} \quad B = \frac{1}{2}(L + \sqrt{L^2 - 4M})$$

The above equation can also be written as $\frac{dx}{(x-A)(x-B)} = (k_1 - k_{-1}) dt$

which, on integrating and rearranging, gives

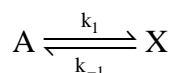
$$k_1 - k_{-1} = \frac{1}{t(A-B)} \ln \left(\frac{B(x-A)}{A(x-B)} \right)$$

Since, $K = \frac{k_1}{k_{-1}}$, knowing the value of equilibrium constant, k_1 and k_{-1} can be determined.

Problem: For a reversible chemical reaction $A \xrightleftharpoons[k_{-1}]{k_1} X$ in which both the forward and reverse reactions are first order and the initial concentration of A is a_0 and the equilibrium concentration of X is x_e , the value of k_{-1} in terms of k_1 is given by

- (a) $k_1(a_0 - x_e)$ (b) $k_1 a / x_e$ (c) $k_1(a_0 - x_e) / x_e$ (d) $k_1 x_e / (a_0 - x_e)$

Soln.



$$a_0 \quad 0$$

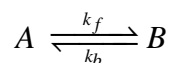
At $t = t$ $a_0 - x$ x

At equilibrium $a_0 - x_e$ x_e

$$\frac{k_1}{k_{-1}} = \frac{x_e}{a_0 - x_e}; \quad k_{-1} = \frac{k_1(a_0 - x_e)}{x_e}$$

Correct option is (c)

Problem: Find the values of k_f and k_b for reaction,



$$\text{If } [A]_0 = 0.30 \text{ mol dm}^{-3} \quad [A]_e = 0.172 \text{ mol dm}^{-3}$$

$$[A]_{10} = 0.285 \text{ and } [A]_{100} = 0.21 \text{ M}$$

Soln.
$$\frac{k_f}{k_b} = \frac{a - x_e}{x_e} = \frac{0.30 - 0.172}{0.172} = 0.744$$

$$\text{Again, } \frac{a}{a - x_e} k_f t = \ln \left\{ \frac{a - x_e}{x_t - x_e} \right\}$$

$$\frac{0.30}{0.30 - 0.172} k_f 10 = \ln \left\{ \frac{0.30 - 0.172}{0.285 - 0.172} \right\}$$

$$k_f = 5.31 \times 10^{-3} \text{ sec}^{-1}$$

$$k_{f \text{ average}} = 5.25 \times 10^{-3} \text{ sec}^{-1}$$

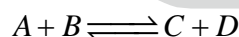
$$k_b = \frac{5.25 \times 10^{-3}}{0.744} = 7.05 \times 10^{-3} \text{ sec}^{-1}$$

Principle of Microscopic reversibility:

The equilibrium constant K_{eq} of the reaction, $A \rightleftharpoons B$ given by

$$K_{eq} = \frac{k_f}{k_b} \quad \dots (1)$$

The above relation was derived from the principle that at equilibrium the rate of forward reaction is equal to the rate of backward reaction. In fact, equation (1) is applicable to all types of one-step elementary reversible reactions. For example, consider a reaction of the type second-order opposed by second-order i.e.



At equilibrium, we will have

Rate of forward reaction = Rate of backward reaction

$$k_f [A]_{eq} [B]_{eq} = k_b [C]_{eq} [D]_{eq}$$

Hence,
$$K_{eq} = \frac{[C]_{eq} [D]_{eq}}{[A]_{eq} [B]_{eq}} = \frac{k_f}{k_b}$$

The principle that for one-step elementary reaction at equilibrium, the rate of forward reaction is equal to the rate of backward reaction, is known as **the principle of microscopic reversibility**. This principle helps us in establishing the connection between the equilibrium constant of an elementary reaction and the rate constants of its forward and backward processes. If a reaction mechanism involves more than one elementary process, each elementary process follows the principle of microscopic reversibility. For example, the reaction,



involves the following two elementary reactions.