

Chemical Kinetics

⇒ Deals with determination of rate of reaction and mechanism of reaction

Rate of reaction ~~AB~~



$$\begin{aligned}\text{Rate of reaction} &= -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt} \\ &= K[A][B]\end{aligned}$$



$$\begin{aligned}\text{Rate} &= -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt} \\ &= K[A]^a[B]^b\end{aligned}$$

Order of Reaction

⇒ Sum of the powers of the concentration terms in rate expression

For example

$$\text{Rate} = K[A]^a[B]^b[C]^c$$

$$\text{Order} = a + b + c$$

$$\text{order} = 1 \text{ First order } R = K[A]$$

$$\text{order} = 2 \text{ Second order } R = K[A]^2$$

$$\text{order} = n$$

$$R = K[A]^n$$

Molecularity - No. of molecules in reaction



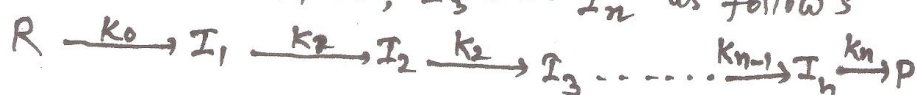
$$\text{Molecularity} = 2$$

Mechanism of Complex Reactions

Two approximations are generally used for elucidating the mechanism of a complex reaction.

1. The equilibrium approximation

Let us ~~now~~ consider a reaction in which reactant R gives the product P through the formation of a series of consecutive intermediates $I_1, I_2, I_3, \dots, I_n$ as follows



In order to derive the rate equation for this reaction,

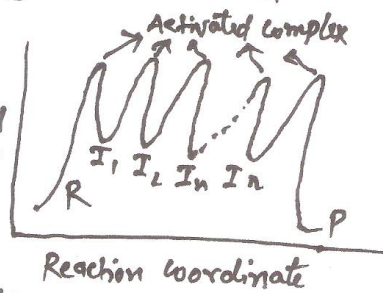
We assume that the rate determining step exists. The rate determining step is the

slowest in the sequence of reaction steps. It is further assumed that all the steps

preceding the rate determining step are in equilibrium



where K is the equilibrium constant



2. The steady state approximation

In a case where the reactions are investigated under such conditions that the slowest rate determining step does not exist, one assumes the steady state approximation (s.s.a.) for the transients or short-lived intermediates. In such a mechanism



The rate of formation of an intermediate is equal to the rate of its decomposition, so that

$$\frac{d[I_1]}{dt} = \frac{d[I_2]}{dt} = \frac{d[I_n]}{dt} = 0$$

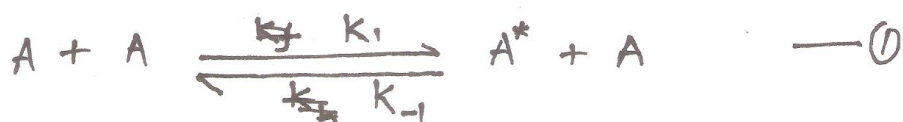
(2)

Lindeman Theory of Unimolecular Reactions

Let us consider the reaction



In gaseous reaction, of this type first order kinetics is followed. The mechanism of such reactions was proposed by F.A. Lindeman. According to Lindeman, a unimolecular reaction $A \longrightarrow P$ proceeds via the following mechanism



Where A^* is the energized A molecule which has acquired sufficient energy to decompose.

When two molecules of A collide, the kinetic energy of the second molecule is transferred to the first molecule and form A^* .

According to steady state approximation

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_{-1}[A][A^*] - k_2[A^*] = 0 \quad \text{--- (3)}$$

$$[A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2} \quad \text{--- (4)}$$

The rate of reaction is given by

$$r = -\frac{d[A]}{dt} = k_2[A^*] \quad \text{--- (5)}$$

(3)

From equation (4) and (5)

$$r = \frac{k_1 k_2 [A]^2}{k_{-1} [A] + k_2} \quad \text{--- (6)}$$

The rate law given by eq. (6) has no definite order. Thus we have to consider two limiting cases, depending upon which of the two terms in the denominator of eq. (6) is greater.

If $k_{-1} [A] \gg k_2$ then

$$r = \frac{k_1 k_2 [A]^2}{k_{-1} [A]} \quad \text{--- (7)}$$

$$r = \frac{k_1 k_2 [A]}{k_{-1}} \quad \text{--- (7)}$$

which is first-order reaction. In a gaseous reaction, this is the high-pressure limit because at very high pressure, $[A]$ is very large so that

$$k_1 [A] \gg k_2$$

If $k_2 \gg k_{-1} [A]$ then from eq. (6)

$$r = \frac{k_1 k_2 [A]^2}{k_2} \quad \text{--- (8)}$$

$$r = k [A]^2 \quad \text{--- (8)}$$

which is rate equation for second order. This is the low pressure limit. The experimental rate is defined as

$$r = k_{uni} [A] \quad \text{--- (9)}$$

where k_{uni} is the unimolecular rate constant from eq. (8) and (9)

$$k_{uni} =$$

(4)

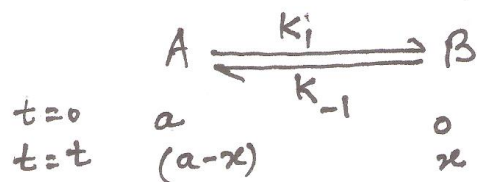
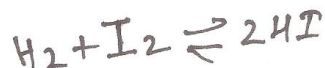
$$K_{uni} = \frac{k_1 k_2 [A]}{k_{-1} [A] + k_2} = \frac{k_1 k_2}{k_{-1} + \frac{k_2}{[A]}}$$

Kinetics of Complex Reactions

The study of chemical kinetics becomes highly ~~complex~~ complicated due to the occurrence of complex reactions which involves more than one steps. Important among them are as follows.

1. Opposing or Reversible Reactions

Let us consider an opposing reaction in which the forward as well as the reverse reactions are of first-order.



Rate of formation of B is given as

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

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

(5)

$$K_1(a - x_e) - K_{-1}x_e = 0$$

$$K_1(a - x_e) = K_{-1}x_e$$

$$K_{-1} = \frac{K_1(a - x_e)}{x_e} = \frac{K_1 a}{x_e} - K_1 \quad (2)$$

From eq. (1) and (2) we have

$$\frac{dx}{dt} = K_1(a - x) - K_{-1}\left(\frac{a - x_e}{x_e}\right)x$$

$$\frac{dx}{dt} = K_1 \frac{(x_e - x)a}{x_e} \quad \text{--- } 3$$

$$\frac{dx}{(x_e - x)} = \frac{a}{x_e} K_1 dt$$

on integration, we get

$$-\ln(x_e - x) = \frac{a}{x_e} (K_1 t + I) \quad \text{--- } (3)$$

where I is the constant of integration

$$-\frac{x_e}{a} \ln(x_e - x) = K_1 t + I \quad \text{--- } (4)$$

at $t=0$ $x=0$ so

$$I = -\frac{x_e}{a} \ln x_e \quad \text{--- } (5)$$

From eq. (4) and (5) we get

$$-\frac{x_e}{a} \ln(x_e - x) = K_1 t - \frac{x_e}{a} \ln x_e$$

$$K_1 t = \frac{x_e}{a} \ln \frac{x_e}{(x_e - x)}$$

(6)

$$k_1 = \frac{x_e}{at} \ln \left(\frac{x_e}{(x_e - x)} \right) \quad (6)$$

Eq. (6) gives k_1 in terms of easily measurable quantities

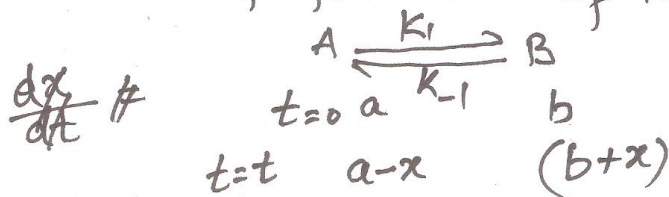
From Eq. (2) we have

$$k_1 + k_{-1} = \frac{a}{x_e} \cdot \frac{x_e}{at} \ln \left(\frac{x_e}{x_e - x} \right) =$$

$$\boxed{k_1 + k_{-1} = \frac{1}{t} \ln \left(\frac{x_e}{x_e - x} \right)} \quad (7)$$

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

Let us now suppose that initially a small amount of B say b moles, is present. Then the net rate of formation of B is given by



$$\frac{dx}{dt} = k_1(a-x) - k_{-1}(b+x) \quad (8)$$

at equilibrium $\frac{dx}{dt} = 0$, $x = x_e$

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

(7)

$$K_{-1} = \frac{K_1(a-x_e)}{(b+x_e)} \quad \text{--- (9)}$$

From Eq. (8) and (9)

$$\begin{aligned} \frac{dx}{dt} &= K_1(a-x) - K_{-1} \frac{(a-x_e)(b+x_e)}{(b+x_e)} \\ &= K_1 \left[\frac{(a+b)}{(b+x_e)} \right] (x_e - x) \end{aligned}$$

Separating the variables

$$\left[\frac{(b+x_e)}{(a+b)} \right] \left[\frac{dx}{(x_e - x)} \right] = K_1 dt \quad \text{--- (10)}$$

Integration of eq. (10) gives

$$\frac{(b+x_e)}{(a+b)} \left[-\ln(x_e - x) \right] = K_1 t + I \quad \text{--- (11)}$$

Since at $t=0$, $x=0$, we have

$$I = \frac{(b+x_e)}{(a+b)} \left[-\ln x_e \right] \quad \text{--- (12)}$$

from Eq. (11) and (12) we have

$$K_1 = \frac{(b+x_e)}{t(a+b)} \ln \frac{x_e}{(x_e - x)} \quad \text{--- (13)}$$

From Eq. (9) we have

(8)

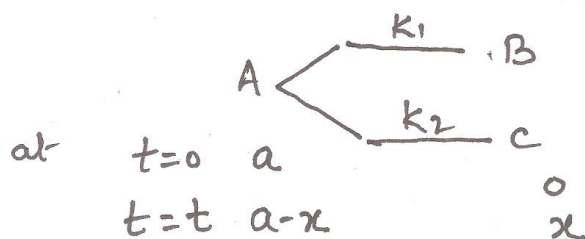
$$x_e = \frac{k_1 a - k_{-1} b}{k_1 + k_{-1}} \quad \text{--- (14)}$$

Substituting the value of x_e from eq. (14) in eq. (13) we get

$$(k_1 + k_{-1}) = \frac{1}{t} \ln \frac{x_e}{(x_e - x)} \quad \text{--- (15)}$$

We see that eq. (15) is similar to eq. (7) which is obtained when no B was present initially.

② Kinetics of Side or Parallel Reaction.



Net rate of reaction,

$$\begin{aligned}
 \frac{dx}{dt} &= k_1(a-x) + k_2(a-x) \\
 &= (k_1 + k_2)(a-x)
 \end{aligned}$$

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

where $K = k_1 + k_2$

⑨

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

on integration we get-

$$-\ln(a-x) = kt + I, \quad I = \text{Integration constant} \quad (2)$$

$$\text{at } t=0 \quad x=0$$

$$I = -\ln a \quad \text{--- } (3)$$

from (2) and (3)

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

$$\ln \frac{a}{(a-x)} = kt$$

$$k = \frac{1}{t} \ln \frac{a}{(a-x)} \quad \text{--- } (4)$$

Amount of B = The rate of formation of B $\frac{d[B]}{dt} = k_1(a-x)$
 Amount of C = rate of formation of C $\frac{d[C]}{dt} = k_2(a-x)$

$$\Rightarrow \frac{[B]}{[C]} = \frac{k_1}{k_2} = k'$$

$$\boxed{k_1 = k_2 k'} \quad \text{--- } (5)$$

Since $k = k_1 + k_2$

$$\text{So } k = k_2 k' + k_2$$

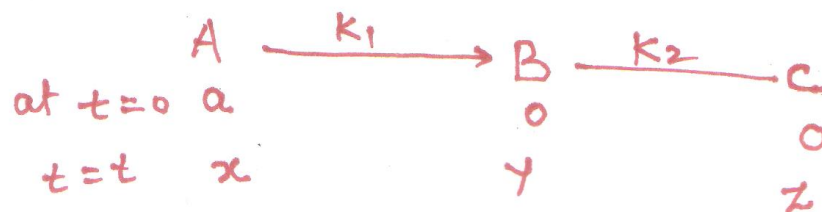
$$\boxed{k_2 = \frac{k}{(1+k')}} \quad (6)$$

From (5)

$$\boxed{k_1 = \frac{k k'}{1+k'}}$$

①

Consecutive Reaction



Rate of disappearance of A

$$\text{So } a = x + y + z$$

$$-\frac{dx}{dt} = k_1 x$$

$$-\frac{dx}{x} = k_1 dt$$

on integration

$$-\ln x = k_1 t + I \quad \text{--- (1)}$$

$$\text{at } t=0 \quad x=a$$

$I = \text{integration const}$

$$-\ln a = I \quad \text{--- (2)}$$

from (1) and (2)

$$-\ln x = k_1 t - \ln a$$

$$k_1 t = \ln \frac{a}{x}$$

$$\frac{x}{a} = e^{-k_1 t}$$

$$x = a e^{-k_1 t} \quad \text{--- (3)}$$

~~Rate of formation of B~~
~~Rate of formation accumulation of B~~

Rate of formation of C

$$\frac{dz}{dt} = k_2 y \quad \text{--- (4)}$$

(2)

Rate of accumulation of B

$$\frac{dy}{dt} = -\frac{dx}{dt} - \frac{dz}{dt}$$

$$= K_1 x - K_2 y$$

$$= K_1 a e^{-K_1 t} - K_2 y \quad \left(\text{Put the value of } x \text{ from eq. (3)} \right)$$

$$\frac{dy}{dt} + K_2 y = K_1 a e^{-K_1 t} \quad \text{--- (5)}$$

multiplying both side by $e^{K_2 t}$ we get

$$\left(\frac{dy}{dt} + K_2 y \right) e^{K_2 t} = K_1 a e^{-K_1 t} \cdot e^{K_2 t}$$

$$= K_1 a e^{(K_2 - K_1)t}$$

$$d[y \cdot e^{K_2 t}] = K_1 a e^{(K_2 - K_1)t} dt \quad \text{--- (6)}$$

on integrating eq. (6) we get

$$y \cdot e^{K_2 t} = K_1 a \frac{e^{(K_2 - K_1)t}}{(K_2 - K_1)} + I \quad \text{--- (7)}$$

at $t=0$, $y=0$ from eq. (7)

$$0 = K_1 a \frac{e^0}{(K_2 - K_1)} + I$$

$$I = -\frac{K_1 a}{(K_2 - K_1)} \quad \text{--- (8)}$$

from (7) and (8)

$$y \cdot e^{K_2 t} = K_1 a \frac{e^{(K_2 - K_1)t}}{K_2 - K_1} - \frac{K_1 a}{K_2 - K_1}$$

(3)

$$y = \frac{k_1 a}{(k_2 - k_1)} \left[e^{k_2 t} \cdot e^{-k_1 t} \cdot e^{-k_2 t} - e^{-k_2 t} \right]$$

$$y = \frac{k_1 a}{(k_2 - k_1)} \left[e^{-k_1 t} - e^{-k_2 t} \right] \quad \text{--- (9)}$$

Since $a = x + y + z$

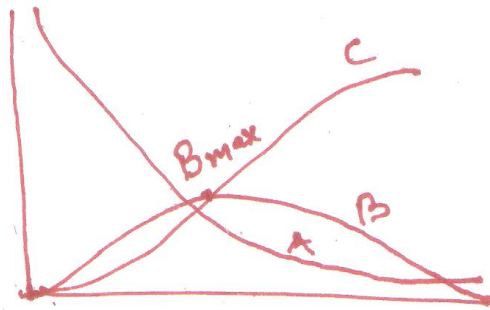
$$z = a - x - y \quad \text{--- (10)}$$

Putting the value of x and y we get

$$z = a - a e^{-k_1 t} - \frac{k_1 a}{(k_2 - k_1)} \left[e^{-k_1 t} - e^{-k_2 t} \right] \quad \text{from (3) and (9)}$$

$$z = a \left[k_2 - k_1 - k_2 e^{-k_1 t} + \cancel{k_1} e^{-k_1 t} - \cancel{k_1} e^{-k_2 t} + k_1 e^{-k_2 t} \right]$$

$$z = a \left[(k_2 - k_2 e^{-k_1 t}) - (k_1 - k_1 e^{-k_2 t}) \right] \quad \text{--- (11)}$$



B_{\max}

(4)

$$\text{for } B_{\max} \quad \frac{dy}{dt} = 0$$

$$\frac{d}{dt} \left[\frac{ak_1}{(k_2 - k_1)} (e^{-k_1 t} - e^{-k_2 t}) \right] = 0$$

$$\frac{ak_1}{(k_2 - k_1)} \left[-k_1 e^{-k_1 t} + k_2 e^{-k_2 t} \right] = 0$$

Since $\frac{ak_1}{(k_2 - k_1)}$ is constant so

$$-k_1 e^{-k_1 t} + k_2 e^{-k_2 t} = 0$$

$$k_2 e^{-k_2 t} = k_1 e^{-k_1 t}$$

$$\frac{k_1}{k_2} = e^{(k_1 - k_2)t}$$

$$\ln \frac{k_1}{k_2} = \ln e^{(k_1 - k_2)t}$$
$$= (k_1 - k_2)t$$

$$t_{\max} = \frac{1}{(k_1 - k_2)} \ln \frac{k_2}{k_1} \quad \text{--- (12)}$$

For B

B_{max}

(5)

$$Y = \frac{K_1 a}{K_2 - K_1} \left[e^{-K_1 t} - e^{-K_2 t} \right] \quad \text{--- (9)}$$

$$e^{-K_2 t} = e^{-K_2 \cdot \frac{1}{(K_1 - K_2)} \ln \frac{K_1}{K_2}} \quad \left(\begin{array}{l} \text{Putting the} \\ \text{value of } t_{\text{max}} \\ \text{from eq. (12)} \end{array} \right)$$

$$= e^{\ln \left(\frac{K_1}{K_2} \right) \frac{-K_2}{(K_1 - K_2)}}$$

$$= \left(\frac{K_1}{K_2} \right)^{\frac{-K_2}{(K_1 - K_2)}}$$

$$e^{-K_2 t} = \left(\frac{K_2}{K_1} \right)^{\frac{K_2}{(K_1 - K_2)}} \quad \text{--- (13)}$$

Similarly

$$e^{-K_1 t} = \left(\frac{K_2}{K_1} \right)^{\frac{K_1}{(K_1 - K_2)}} \quad \text{--- (14)}$$

From eq. (9), (13) and (14) we get

$$Y = \frac{K_1 a}{K_2 - K_1} \left[\left(\frac{K_2}{K_1} \right)^{\frac{K_1}{K_1 - K_2}} - \left(\frac{K_2}{K_1} \right)^{\frac{K_2}{K_1 - K_2}} \right]$$

$$= \frac{K_1 a}{(K_2 - K_1)} \cdot \left(\frac{K_2}{K_1} \right)^{\frac{K_2}{K_1 - K_2}} \left[\left(\frac{K_2}{K_1} \right)^{\frac{K_1}{K_1 - K_2} - \frac{K_2}{K_1 - K_2}} - 1 \right]$$

$$= \frac{K_1 a}{K_2 - K_1} \cdot \left(\frac{K_2}{K_1} \right)^{\frac{K_2}{K_1 - K_2}} \left[\frac{K_2}{K_1} - 1 \right]$$

$$= \frac{K_1 a}{(K_2 - K_1)} \cdot \left(\frac{K_2}{K_1} \right)^{\frac{K_2}{K_1 - K_2}} \left[\frac{(K_2 - K_1)}{K_1} \right]$$

$$Y_{\text{max}} = a \left(\frac{K_2}{K_1} \right)^{\frac{K_2}{K_1 - K_2}}$$