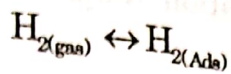


6.5 LANGMUIR ADSORPTION ISOTHERM FOR ADSORPTION OF SINGLE GAS SYSTEM

Adsorption of a gas on solid surface is described by Langmuir adsorption isotherm which is a relation between fractional surface coverage and pressure of gas. The adsorption of a gas on solid surface may be non dissociative and dissociative. The Langmuir adsorption isotherm for both type of adsorption is described here.

6.5.1 Langmuir Adsorption Isotherm for Non Dissociative Adsorption

The adsorption process during which gas molecules adsorbed as such without any dissociation is called non dissociative adsorption. Non dissociative adsorption of hydrogen on a solid surface can be written as



Rate of adsorption of a gas is directly proportional to pressure and fraction of unoccupied sites i.e.

$$R_{Ads} \propto P_A \quad (6.4)$$

$$R_{Ads} \propto (1-\theta) \quad (6.5)$$

On combining equation (6.4) and (6.5)

$$R_{Ads} = k_{Ads} (1-\theta) P_A \quad (6.6)$$

k_{ads} , is the rate constant for adsorption.

According to Arrhenius equation k_{ads} is the function of temperature and can be written as $k_{Ads} = b_1 e^{\frac{E_{Ads}}{RT}}$. Then equation (6.6) will become

$$R_{Ads} = b_1 e^{\frac{E_{Ads}}{RT}} (1-\theta) P_A \quad (6.7)$$

Rate of desorption is directly proportional to fractional surface coverage i.e.

$$R_{Des} \propto \theta$$

$$R_{Des} = k_{Des} \theta$$

$$k_{Des} = b_2 e^{\frac{E_{Des}}{RT}} \cdot \theta \quad (6.8)$$

At dynamic equilibrium, rate of adsorption becomes equal to the rate of desorption. So,

$$R_{Ads} = R_{Des}$$

By comparing equation (6.7) and (6.8) we get,

$$b_1 e^{\frac{E_{Ads}}{RT}} (1-\theta) P_A = b_2 e^{\frac{E_{Des}}{RT}} \cdot \theta$$

$$b_1 e^{\frac{E_{Ads}}{RT}} P_A - b_1 e^{\frac{E_{Ads}}{RT}} \theta P_A = b_2 e^{\frac{E_{Des}}{RT}} \cdot \theta$$

$$b_1 e^{-\frac{E_{Ads}}{RT}} P_A = b_1 e^{-\frac{E_{Ads}}{RT}} \theta P_A + b_2 e^{-\frac{E_{Des}}{RT}} \theta$$

$$b_1 e^{-\frac{E_{Ads}}{RT}} P_A = \theta \left\{ b_1 e^{-\frac{E_{Ads}}{RT}} P_A + b_2 e^{-\frac{E_{Des}}{RT}} \right\}$$

$$\theta = \frac{b_1 e^{-\frac{E_{Ads}}{RT}} P_A}{b_2 e^{-\frac{E_{Des}}{RT}} + b_1 e^{-\frac{E_{Ads}}{RT}} P_A}$$

Multiplying and dividing right hand side of equation by $b_2 e^{-\frac{E_{Des}}{RT}}$

$$\theta = \frac{b_1 e^{-\frac{E_{Ads}}{RT}} P_A / b_2 e^{-\frac{E_{Des}}{RT}}}{1 + \frac{b_1 e^{-\frac{E_{Ads}}{RT}} P_A}{b_2 e^{-\frac{E_{Des}}{RT}}}}$$

$$\theta = \frac{\frac{b_1}{b_2} e^{-\frac{E_{Ads}}{RT}} e^{-\frac{E_{Des}}{RT}} P_A}{1 + \frac{b_1}{b_2} e^{-\frac{E_{Ads}}{RT}} e^{-\frac{E_{Des}}{RT}} P_A}$$

$$\theta = \frac{\left(\frac{b_1}{b_2} \right) e^{-\frac{E_{Ads} - E_{Des}}{RT}} P_A}{1 + \left(\frac{b_1}{b_2} \right) e^{-\frac{E_{Ads} - E_{Des}}{RT}} P_A}$$

$$\theta = \frac{\left(\frac{b_1}{b_2} \right) e^{-\frac{(E_{Ads} - E_{Des})}{RT}} P_A}{1 + \left(\frac{b_1}{b_2} \right) e^{-\frac{(E_{Ads} - E_{Des})}{RT}} P_A} \quad (6.9)$$

And, $\Delta H_{Ads} = E_{Ads} - E_{Des}$ (6.10)

The quantity $E_{Ads} - E_{Des}$ is the heat of adsorption as shown in energy profile in Fig. 6.6.

Putting value of $(E_{Ads} - E_{Des})$ from equation (6.10) into equation (6.9), we get

$$\theta = \frac{\left(\frac{b_1}{b_2} \right) e^{-\frac{\Delta H_{Ads}}{RT}} P_A}{1 + \left(\frac{b_1}{b_2} \right) e^{-\frac{\Delta H_{Ads}}{RT}} P_A}$$

$$\left(\frac{b_1}{b_2}\right) e^{-\frac{\Delta H_{\text{Ads}}}{RT}} = b$$

So, above equation becomes

$$\theta = \frac{bP_A}{1 + bP_A} \quad (6.11)$$

b is the adsorption coefficient which depends upon the nature of adsorbate and adsorbent, it is temperature dependent and its units are Pa^{-1} .

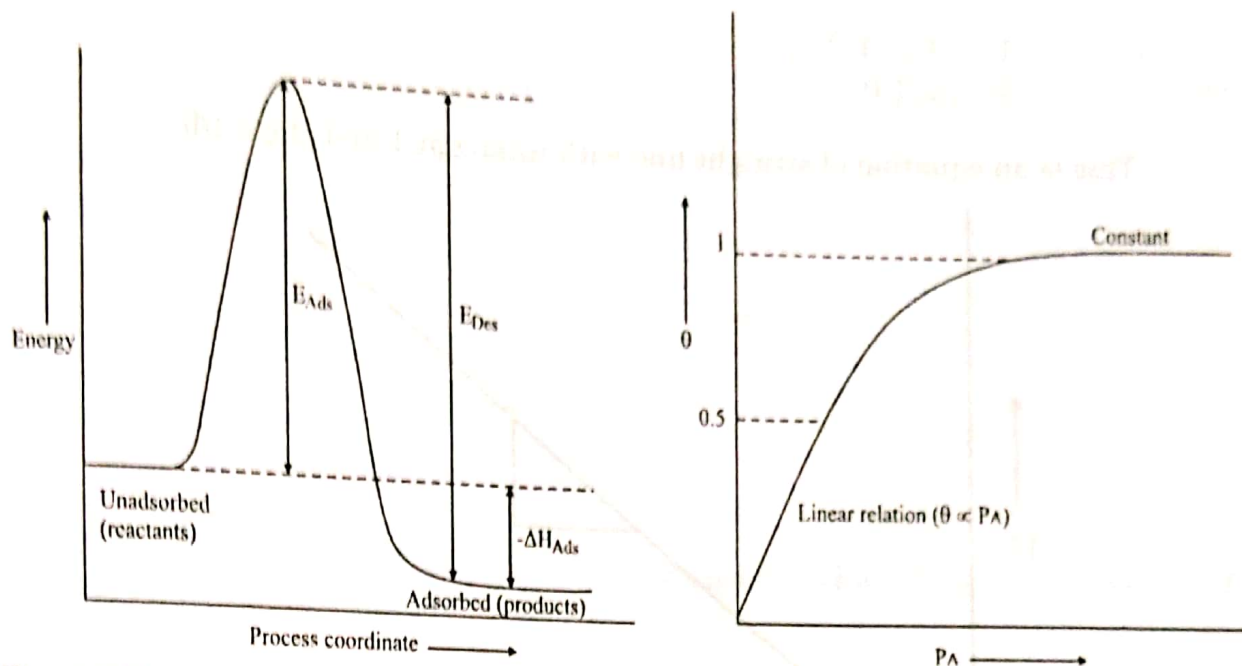


Fig. 6.6 Energy profile of adsorption and Fig. 6.7 θ as a function of pressure of gas A desorption processes

Equation (6.11) is a relation between fractional surface coverage and pressure of gas. According to equation (6.11) θ is a function of pressure of gas. Fig. 6.7 gives dependence of θ on pressure. The value of θ increases with the increase of pressure of gas for small range of pressure and it becomes independent of pressure at very high value of pressure. At this stage, all sites are occupied by gas molecules, that is why further increase of pressure has no effect on extent of adsorption.

Special Cases

(i) When P_A is low, then $1 + bP_A \approx 1$. So, equation (6.11) will become

$$\theta = bP_A$$

$$\theta \propto P_A$$

So, θ is a linear function of P_A .

(ii) When P_A is high, then $1 + bP_A \approx bP_A$. Then, equation (6.11) becomes

$$\theta = 1$$

So, fractional surface coverage is independent of available pressure. At this stage, adsorption or value only depends upon value of b . If weak adsorption

occurs, then b has low value and if strong adsorption occurs, then value of b will be high.

By taking inverse of equation (6.11)

$$\frac{1}{\theta} = \frac{1 + bP_A}{bP_A}$$

$$\frac{1}{\theta} = \frac{1}{bP_A} + 1$$

$$\frac{1}{\theta} = \left(\frac{1}{b}\right)\left(\frac{1}{P_A}\right) + 1$$

This is an equation of straight line with intercept 1 and slope $1/b$.

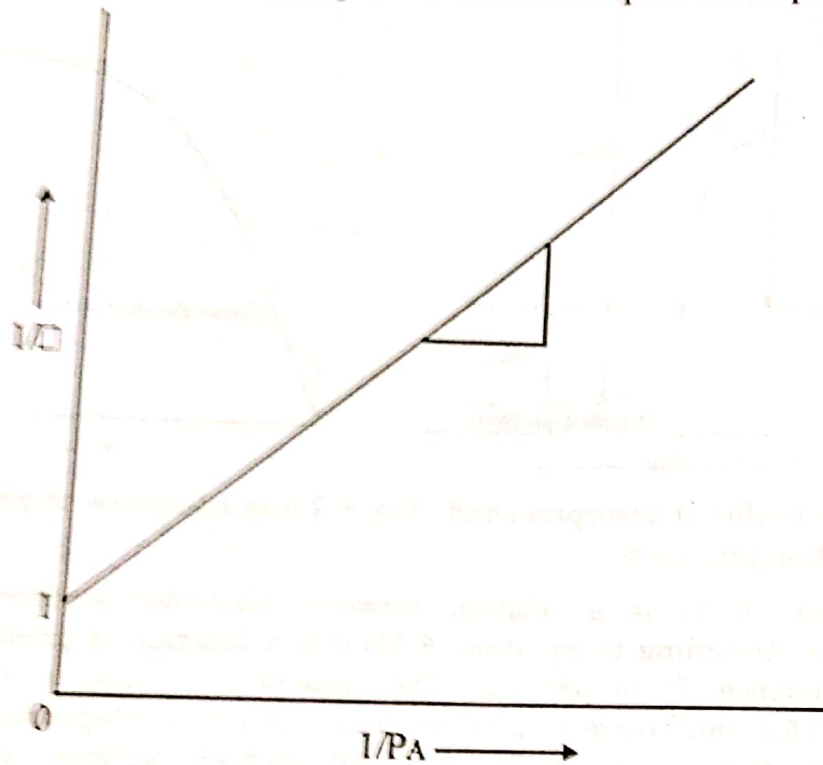


Fig. 6.8 Plot of $1/\theta$ versus $1/P_A$

Fig. 6.8 shows that $1/\theta$ is directly proportional to $1/P_A$. From the slope of this graph, value of b can be determined.

6.5.2 Langmuir Adsorption Isotherm for Dissociative Adsorption of a gas

The adsorption process during which dissociation of gas molecules takes place is called dissociative adsorption and for dissociative adsorption rate of adsorption is directly proportional to pressure and square of fraction of vacant sites of adsorbent i.e.

$$R_{\text{Ads}} \propto (1 - \theta)^2$$

$$R_{\text{Ads}} \propto P_A$$

On combining above both equations we get,

$$R_{\text{Ads}} = k_{\text{Ads}} (1 - \theta)^2 P_A \quad (6.12)$$

According to Arrhenius equation: $k_{\text{Ads}} = b_1 e^{-\frac{E_{\text{Ads}}}{RT}}$

So, equation (6.12) becomes

$$R_{\text{Ads}} = b_1 e^{-\frac{E_{\text{Ads}}}{RT}} P_A (1 - \theta)^2 \quad (6.13)$$

Rate of desorption is directly proportional to square of fractional surface coverage because two vacant sites are formed when a molecule of desorbed gas formed from adsorbed gas. It means it is second order reaction. Thus

$$\begin{aligned} R_{\text{Des}} &\propto \theta^2 \\ R_{\text{Des}} &= k_{\text{Des}} \theta^2 \end{aligned} \quad (6.14)$$

According to Arrhenius equation: $k_{\text{Des}} = b_2 e^{-\frac{E_{\text{Des}}}{RT}}$

So, equation (6.14) will become

$$R_{\text{Des}} = b_2 e^{-\frac{E_{\text{Des}}}{RT}} \theta^2 \quad (6.15)$$

E_{Ads} is the energy of activation for adsorption while, E_{Des} is the energy of activation for desorption process.

Initially rate of adsorption is greater than rate of desorption according to Langmuir, but rate of adsorption decreases with the passage of time because number of vacant sites decreases. Rate of desorption increases with time because number of occupied sites increases.

At dynamic equilibrium, rate of adsorption become equal to the rate of desorption as given below

$$R_{\text{Ads}} = R_{\text{Des}}$$

$$b_1 e^{-\frac{E_{\text{Ads}}}{RT}} (1 - \theta)^2 P_A = b_2 e^{-\frac{E_{\text{Des}}}{RT}} \theta^2$$

$$b_1^{1/2} e^{-\frac{E_{\text{Ads}}}{2RT}} (1 - \theta) P_A^{1/2} = b_2^{1/2} e^{-\frac{E_{\text{Des}}}{2RT}} \theta$$

$$b_1^{1/2} e^{-\frac{E_{\text{Ads}}}{2RT}} P_A^{1/2} - b_1^{1/2} e^{-\frac{E_{\text{Ads}}}{2RT}} \theta P_A^{1/2} = b_2^{1/2} e^{-\frac{E_{\text{Des}}}{2RT}} \theta$$

$$b_2^{1/2} e^{-\frac{E_{\text{Des}}}{2RT}} \theta + b_1^{1/2} e^{-\frac{E_{\text{Ads}}}{2RT}} \theta P_A^{1/2} = b_1^{1/2} e^{-\frac{E_{\text{Ads}}}{2RT}} P_A^{1/2}$$

$$\theta \left(b_2^{1/2} e^{-\frac{E_{\text{Des}}}{2RT}} + b_1^{1/2} e^{-\frac{E_{\text{Ads}}}{2RT}} P_A^{1/2} \right) = b_1^{1/2} e^{-\frac{E_{\text{Ads}}}{2RT}} P_A^{1/2}$$

$$\theta = \frac{b_1^{1/2} e^{-\frac{E_{Ads}}{2KT}} P_A^{1/2}}{1 + b_1^{1/2} e^{-\frac{E_{Ads}}{2KT}} P_A^{1/2}} \quad (6.16)$$

Divide above equation numerator and denominator by $b_1^{1/2} e^{-\frac{E_{Ads}}{2KT}}$

$$\theta = \frac{\left(\frac{b_1}{b_2}\right)^{1/2} e^{-\frac{(E_{Des} - E_{Ads})}{2KT}} P_A^{1/2}}{1 + \left(\frac{b_1}{b_2}\right)^{1/2} e^{-\frac{(E_{Des} - E_{Ads})}{2KT}} P_A^{1/2}} \quad (6.17)$$

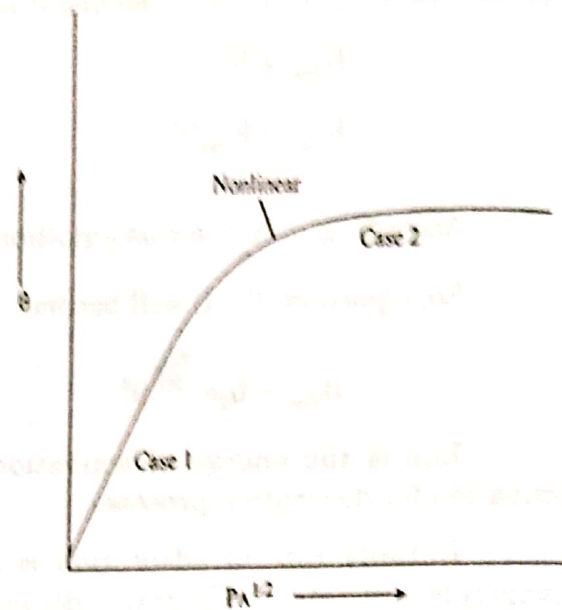
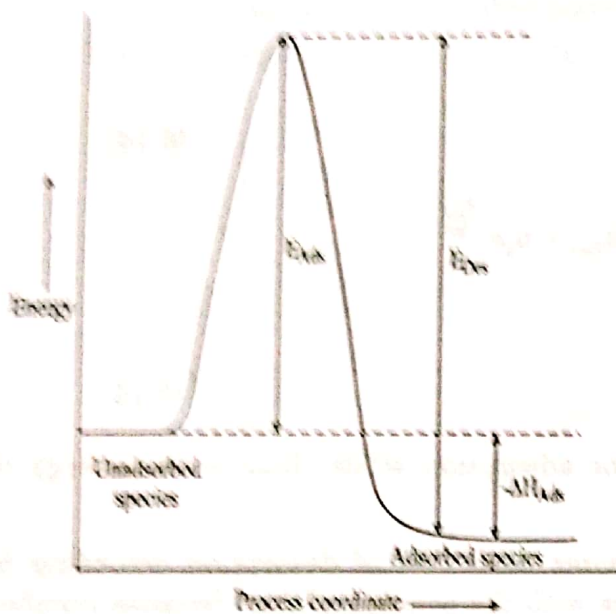


Fig. 6.9 Energy profile of adsorption of a gas Fig. 6.10 Plot of θ as a function of $P_A^{1/2}$

ΔH_{Ads} denotes enthalpy of adsorption according to Fig. 6.9. ΔH_{Ads} is equal to

$$\Delta H_{Ads} = E_{Ads} - E_{Des} \quad (6.18)$$

Putting value of $(E_{Ads} - E_{Des})$ from equation (6.18) into equation (6.17)

$$\theta = \frac{\left(\frac{b_1}{b_2}\right)^{1/2} e^{-\frac{\Delta H_{Ads}}{2KT}} P_A^{1/2}}{1 + \left(\frac{b_1}{b_2}\right)^{1/2} e^{-\frac{\Delta H_{Ads}}{2KT}} P_A^{1/2}} \quad (6.19)$$

If, $\left(\frac{b_1}{b_2}\right)^{1/2} e^{-\frac{\Delta H_{Ads}}{2KT}} = b'$

Then equation (6.19) will become

$$\theta = \frac{bP_A^{1/2}}{1 + bP_A^{1/2}} \quad (6.20)$$

According to above relation, fractional surface coverage is the function of pressure of gas A as given below

$$\theta = f(P_A)$$

Special Cases

(i) When P_A is low, then $1 + bP_A^{1/2} \approx 1$

So, equation (6.20) becomes

$$\theta = bP_A^{1/2}$$

$$\theta \propto P_A^{1/2}$$

It means θ is directly proportional to $P_A^{1/2}$ (Fig. 6.10).

(ii) When P_A is high, then $1 + bP_A^{1/2} \approx P_A^{1/2}$. So, equation (6.20) becomes

$$\theta = 1$$

It means θ is independent of pressure when P_A is high (Fig. 6.10).

By taking inverse of equation (6.20)

$$\frac{1}{\theta} = \frac{1 + bP_A^{1/2}}{bP_A^{1/2}}$$

$$\frac{1}{\theta} = \frac{1}{bP_A^{1/2}} + 1$$

According to above equation $1/\theta$ is a linear function of $1/P_A^{1/2}$ whose slope equal to $1/b$, and intercept equal to 1 as shown in Fig. 6.11.

On comparison of equations (6.11) and (6.20) of non-dissociative and dissociative adsorption respectively, it is concluded that θ is more dependent on pressure for non dissociative adsorption but θ is less dependent on pressure for dissociative adsorption as shown in Fig. 6.12.

$$\frac{d[\text{HBr}]}{dt} = \frac{2k_2 \left(\frac{k_1}{k_3} \right)^2 [\text{H}_2][\text{Br}_2]^{1/2}}{1 + \frac{k_4[\text{HBr}]}{k_3[\text{Br}_2]}}$$

$$\frac{d[\text{HBr}]}{dt} = \frac{k[\text{H}_2][\text{Br}_2]^{1/2}}{1 + \frac{k'[\text{HBr}]}{[\text{Br}_2]}}$$

The above equation shows the similar relation between the reaction rate and the reactant concentration as was found experimentally. Here

$$k = 2k_2 \left(\frac{k_1}{k_3} \right)^2 \quad \text{and} \quad k' = \frac{k_4}{k_3}$$

When $t = 0$, then $[\text{HBr}] = 0$

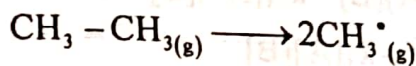
$$\frac{d[\text{HBr}]}{dt} = k[\text{H}_2][\text{Br}_2]^{1/2}$$

Overall reaction order is 1.5 and the rate of formation of HBr is maximum at this point.

5.14 UNIMOLECULAR GAS PHASE REACTIONS

In such type of reactions, the reactants as well as the products exist in gaseous state. As the name indicates, in these reactions only one reactant molecule is involved in the rate determining step and the order of reaction is also 1. Such reactions can be exemplified with a number of rearrangement and decomposition reactions, a few of which are given below

Decomposition of ethane and also that of ethyl iodide involves unimolecular gas phase reaction.



Another such example is the isomerization of cyclopropane shown as below

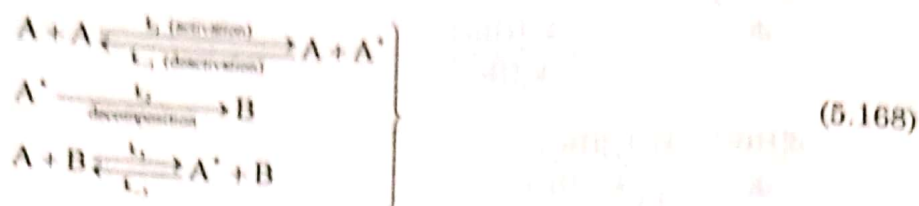


5.14.1 Kinetics of Unimolecular Gas Phase Reactions

To study the kinetics of such reactions, let us consider a reaction in which a reactant A transforms into the product B after passing through a series of elementary reactions. Single line reaction for the transformation of A into B can be written as



This reaction is supposed to involve the following mechanism according to Lindmann theory



This mechanism reveals that the reactant A transforms into the product B after passing through an intermediate form i.e. A^* . The first step shows a reversible reaction involving the activation of A to form an activated complex A^* and the deactivation of this complex to give back the reactant again. In the second step, the activated complex decomposes to form the product B which then activates the molecules of the reactant to form the activated complex in the third step. The second step is the slowest of all and is, therefore, the rate determining step.

The rate of the reaction written in equation (5.167) in terms of the rate of change of the concentration of the product with respect to time can be written using the rate determining step of the mechanism shown in equation (5.168) as shown below

$$\frac{d[B]}{dt} = k_2[A^*] \quad (5.169)$$

Where the concentration of A^* , the reaction intermediate, can be determined by using steady state approximation. The rate of change of the concentration of A^* with respect to time can be written from the mechanism as follows

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*] + k_3[A][B] - k_{-3}[A^*][B]$$

Applying steady state approximation, we get

$$k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*] + k_3[A][B] - k_{-3}[A^*][B] = 0$$

$$[A^*]\{k_{-1}[A] + k_2 + k_{-3}[B]\} = k_1[A]^2 + k_3[A][B]$$

$$[A^*] = \frac{k_1[A]^2 + k_3[A][B]}{k_{-1}[A] + k_2 + k_{-3}[B]}$$

Putting the value of $[A^*]$ in equation (5.169), we get

$$\frac{d[B]}{dt} = \frac{k_2 \{k_1[A]^2 + k_3[A][B]\}}{k_{-1}[A] + k_2 + k_{-3}[B]} \quad (5.170)$$

Let the concentrations of A and B be 'a' and '0' initially and after a certain time 't' the concentrations change into a - x and x respectively. Hence putting the values of the available concentrations of A and B in equation (5.170), we get

$$\frac{dx}{dt} = \frac{k_2 \{k_1(a-x)^2 + k_3(a-x)(x)\}}{k_{-1}(a-x) + k_2 + k_{-3}(x)}$$

Since the forward reactions of both the first and the third step involve the activation of A while the backward reactions involve the deactivation of A*, hence k_3 can be assumed to be equal to k_1 and k_{-3} be equal to k_{-1} , therefore replacing k_3 by k_1 and k_{-3} by k_{-1} in the above equation, we get

$$\frac{dx}{dt} = \frac{k_2 \{k_1(a-x)^2 + k_1(a-x)(x)\}}{k_{-1}(a-x) + k_2 + k_{-1}(x)}$$

$$\frac{dx}{dt} = \frac{k_2(k_1a^2 + k_1x^2 - 2k_1ax + k_1xa - k_1x^2)}{k_{-1}a - k_{-1}x + k_2 + k_{-1}x}$$

$$\frac{dx}{dt} = \frac{k_2(k_1a^2 - k_1ax)}{k_{-1}a + k_2}$$

$$\frac{dx}{dt} = \frac{k_1k_2a(a-x)}{k_{-1}a + k_2} \quad (5.171)$$

Let $\frac{k_1k_2a}{k_{-1}a + k_2} = k'$ (5.172)

Hence equation (5.171) will become

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

Hence unimolecular gas phase reactions are first order reactions and the first order rate constant k' depends upon the initial pressure of the gas.

For small value of a i.e. when the pressure is low, then $k_{-1}a + k_2 \approx k_2$, applying this condition to equation (5.172), we get

$$k' = \frac{k_1k_2a}{k_2}$$

$$k' = k_1a$$

The above equation shows that at low pressure, k' is directly proportional to a , hence increasing the concentration of A increases the rate of the reaction and vice versa.

For large values of a i.e. when the pressure is high, then $k_{-1}a + k_2 \approx k_{-1}a$, hence equation (5.172) will become

$$k' = \frac{k_1k_2a}{k_{-1}a}$$

$$k' = \frac{k_1k_2}{k_{-1}}$$

As we know that $(k_1/k_{-1}) = K_1$, where K_1 is the equilibrium constant for first step, the above equation will become

$$k' = K_1 k_2$$

Hence at high pressure, the rate of the reaction is independent of a . The variation in the value of k' with the change in the initial concentration (pressure) of the gas is shown in Fig. 5.19.

Taking reciprocal on both sides of equation (5.172), we get

$$\frac{1}{k'} = \frac{k_{-1}a + k_2}{k_1 k_2 a}$$

$$\frac{1}{k'} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1 a}$$

This is the equation of straight line in intercept form, where $1/a$ is the independent variable and $1/k'$ is the dependent variable. k_1 can be calculated by taking the reciprocal of the slope of the plot $1/a$ versus $1/k'$. Dividing the intercept by the slope gives the value of Hinshelwood i.e. k_{-1}/k_2 .

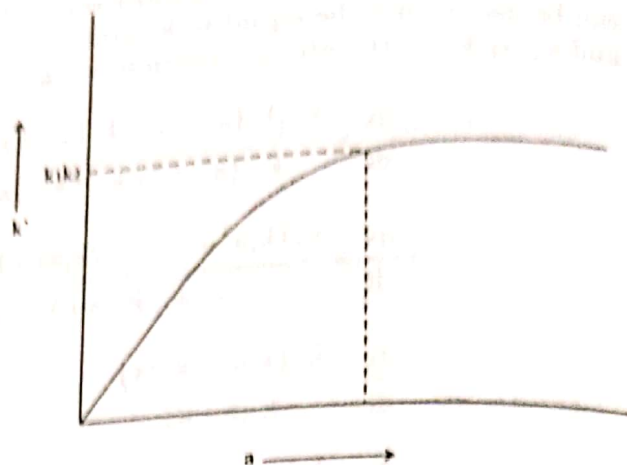
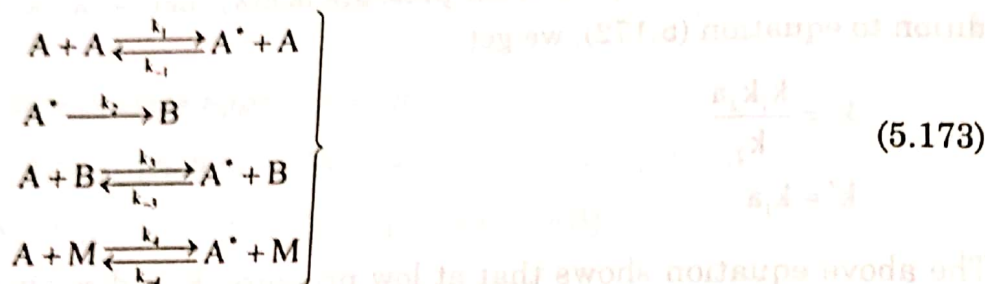


Fig. 5.19 Variation of the rate constant for a unimolecular gas phase reaction with the initial pressure of gas

5.14.2 Unimolecular Gas Phase Reactions in the Presence of an Inert Gas

Lindmann proposed the following mechanism for reaction (5.167) in the presence of an inert gas M.



This mechanism involves four steps, the first three of which are similar to those in the mechanism (5.168). The fourth step involves a reversible reaction in which activation and deactivation of A takes place in the presence of an inert gas M.

The rate of reaction in terms of the rate of formation of the product B is given by

$$\frac{dB}{dt} = k_2 [A^*] \quad (5.174)$$

Where A^* is the reaction intermediate and its concentration cannot be determined experimentally. Hence, steady state approximation is used for this purpose.

The rate of formation of A^* , using the mechanism (5.173) is given by

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*] + k_3[A][B] - k_{-3}[A^*][B] + k_4[A][M] - k_{-4}[A^*][M]$$

Applying steady state approximation, we get

$$k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*] + k_3[A][B] - k_{-3}[A^*][B] + k_4[A][M] - k_{-4}[A^*][M] = 0$$

$$k_{-1}[A^*][A] + k_2[A^*] + k_{-3}[A^*][B] + k_{-4}[A^*][M] = k_1[A]^2 + k_3[A][B] + k_4[A][M]$$

$$[A^*]\{k_{-1}[A] + k_2 + k_{-3}[B] + k_{-4}[M]\} = k_1[A]^2 + k_3[A][B] + k_4[A][M]$$

$$[A^*] = \frac{k_1[A]^2 + k_3[A][B] + k_4[A][M]}{k_{-1}[A] + k_2 + k_{-3}[B] + k_{-4}[M]}$$

Putting the value of A^* in equation (5.174), we get

$$\frac{d[B]}{dt} = \frac{k_2\{k_1[A]^2 + k_3[A][B] + k_4[A][M]\}}{k_{-1}[A] + k_2 + k_{-3}[B] + k_{-4}[M]} \quad (5.175)$$

Let the concentrations of A and B be 'a' and '0' initially and after a certain time 't' the concentrations change into a - x and x respectively. Hence putting the values of the available concentrations of A and B in equation (5.175), we get

$$\frac{dx}{dt} = \frac{k_2\{k_1(a-x)^2 + k_3(a-x)(x) + k_4(a-x)[M]\}}{k_{-1}(a-x) + k_2 + k_{-3}(x) + k_{-4}[M]}$$

$$\frac{dx}{dt} = \frac{k_2(a-x)\{k_1(a-x) + k_3(x) + k_4[M]\}}{k_{-1}(a-x) + k_2 + k_{-3}(x) + k_{-4}[M]}$$

Replacing k_1 by k_3 and k_{-1} by k_{-3} in the above equation, we get

$$\frac{dx}{dt} = \frac{k_2(a-x)\{k_3(a-x) + k_1(x) + k_4[M]\}}{k_{-1}(a-x) + k_2 + k_{-1}(x) + k_{-4}[M]}$$

$$\frac{dx}{dt} = \frac{k_2(a-x)(k_3a - k_1x + k_1x + k_4[M])}{k_{-1}a - k_{-1}x + k_{-1}x + k_2 + k_{-4}[M]}$$

$$\frac{dx}{dt} = \frac{k_2(k_3a + k_4[M])}{k_{-1}a + k_2 + k_{-4}[M]}(a-x) \quad (5.176)$$

Let $\frac{k_2(k_3a + k_4[M])}{k_{-1}a + k_2 + k_{-4}[M]} = k'' \quad (5.177)$

Hence equation (5.176) will become

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

The above equation shows that the reaction is first order. k' depends on the concentration (pressure) of M as well as the initial concentration of A.

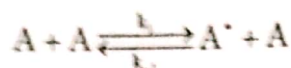
Example 5.24

Using reaction mechanism indicated in equation (5.173), prove that

$$\frac{k_1}{k_{-1}} = \frac{k_2}{k_{-2}} = \frac{k_4}{k_{-4}}$$

Solution

The first step of the reaction mechanism shown in equation (5.173) is



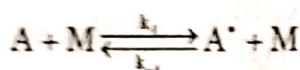
$$\frac{k_1}{k_{-1}} = \frac{[A^*][A]}{[A][A]} = \frac{[A^*]}{[A]} \quad (\text{i})$$

The third step of the mechanism 5.173 involves the following reaction



$$\frac{k_2}{k_{-2}} = \frac{[A^*][B]}{[A][B]} = \frac{[A^*]}{[A]} \quad (\text{ii})$$

Similarly from the last step of the mechanism 5.173, we have



$$\frac{k_4}{k_{-4}} = \frac{[A^*][M]}{[A][M]} = \frac{[A^*]}{[A]} \quad (\text{iii})$$

Hence from equation (i), (ii) and (iii), we can conclude that

$$\frac{k_1}{k_{-1}} = \frac{k_2}{k_{-2}} = \frac{k_4}{k_{-4}}$$

5.15 BASIC EXPERIMENTAL METHODS OF KINETICS

To make an experimental study of the kinetics of a reaction, certain parameters must be taken under consideration. Temperature, for example, must remain same throughout the experiment as the rate constant is dependent upon temperature. Similarly, if two solutions are mixed together for the reaction to take place, the mixing should be homogeneous. Stoichiometry of the reaction should be

Taking natural logarithm on both sides of the above equation, we get

$$\ln A = \ln\left(\frac{k_B T}{h}\right) + \frac{\Delta S^\ddagger}{R} + \ln e$$

$$\Delta S^\ddagger = \left\{ \ln A - \ln\left(\frac{k_B T}{h}\right) - 1 \right\} R$$

Putting values in the above equation, we get

$$\Delta S^\ddagger = \left\{ \ln(1.537 \times 10^{17}) - \ln\left(\frac{(1.38 \times 10^{-23})(298)}{6.626 \times 10^{-34}}\right) - 1 \right\} (8.3143)$$

$$\Delta S^\ddagger = (39.573 - 29.457 - 1)(8.3143) = 75.79 \text{ J mol}^{-1} \text{ K}^{-1}$$

We know that, $\Delta H^\ddagger = E_a - RT$

Putting the values in the above equation, we get

$$\Delta H^\ddagger = 1.285 \times 10^5 - (8.3143 \times 298) = 1.26 \times 10^5 \text{ J mol}^{-1}$$

5.18 REACTIONS IN SOLUTIONS

Solution phase reactions may be classified into diffusion controlled and activation controlled reactions depending upon whether the diffusion or activation step serves as the rate limiting step. Another basis of classification is the nature of reaction i.e. whether the reaction involves transfer of electrons namely redox reactions or exchange of protons/hydroxyl ions namely acid base reactions. The reactions in solution are very fast as compared to those in gas phase due to the solvent cage effect. Molecules of different reactants are in a cage of the molecules of solvent and collide with each other many times and are converted into products in very short interval of time but in gas phase reaction the probability of collision of the molecules of reactants is less as compared to that in solution.

5.18.1 Diffusion Controlled and Activation Controlled Reactions

Consider a bimolecular reaction of the type



in which reactants A and B approach each other by diffusion and form an encounter pair AB in the presence of a solvent.

The rate of such a reaction is given by

$$\frac{d[P]}{dt} = k_2[A][B] \quad (5.239)$$

The reaction (5.238) is supposed to involve the following mechanism



Very first step of the mechanism involves the formation of an encounter pair AB which then, following two different paths, decomposes to give the reactants again in the second step and transforms into the product in the third step.

The third step of the mechanism is the rate determining step as it is the slowest of all. Hence the rate of the reaction in terms of the formation of the product P is given by

$$\frac{d[P]}{dt} = k_1'[AB] \quad (5.241)$$

The expression for the rate of formation of AB can be written using the mechanism (5.240) as

$$\frac{d[AB]}{dt} = k_1[A][B] - k_{-1}[AB] - k_1'[AB]$$

Applying steady state approximation we get

$$k_1[A][B] - k_{-1}[AB] - k_1'[AB] = 0$$

$$[AB](k_{-1} + k_1') = k_1[A][B]$$

$$[AB] = \frac{k_1[A][B]}{k_{-1} + k_1'}$$

Putting this value of [AB] in equation (5.241), we get

$$\frac{d[P]}{dt} = \frac{k_1'k_1[A][B]}{k_{-1} + k_1'} \quad (5.242)$$

Comparing equation (5.239) and equation (5.242), the value of k_2 comes out to be

$$k_2 = \frac{k_1k_1'}{k_{-1} + k_1'} \quad (5.243)$$

If k_1' is very much greater than k_{-1} , then the denominator of the above equation will reduce to k_1' , applying this condition to equation (5.243), we get

$$k_2 = k_1$$

The above equation shows that k_2 depends on the diffusion step of mechanism (5.240) therefore, diffusion is the rate controlling step under this condition. Such reactions are called diffusion controlled reactions. Detailed discussion of diffusion controlled reaction is beyond the scope of this book.

If k_1' is very much smaller than k_{-1} , then the denominator in the equation (5.243) will reduce to k_{-1} , applying this condition to equation (5.243), we get

$$k_2 = \frac{k_1 k_3}{k_2} = K_1 k_3$$

The above equation shows the dependence of k_2 on the rate constant for third step of the mechanism (5.240). This reaction involves the formation of product that is activation controlled reaction. Here, we will discuss the factors affecting the rate of activation controlled reactions on the basis of transition state theory.

According to transition state theory, the rate of an activation controlled reaction depends on the following factors.

Solvent Effect

The effect of solvent on the rate of a reaction can be explained in terms of the entropy of activation using transition state theory. The relation between k_2 and ΔS^\ddagger is given in equation (5.233). According to this relation, the positive value of ΔS^\ddagger favors the reaction whereas the negative value decreases the value of k_2 . Moreover, an increase in the positive value of ΔS^\ddagger increases the rate of reaction while an increase in the negative value of ΔS^\ddagger decreases the value of k_2 .

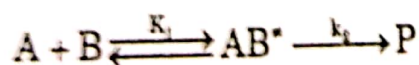
The value of ΔS^\ddagger is purely associated with the nature of solvent. For example, the formation of activated complex from the reactants having similar charges is accompanied by a decrease in the entropy of activation and hence the rate of reaction decreases. The entropy decreases due to the fact that the magnitude of the charge on the activated complex is greater than that on the reactants due to which a greater number of polar molecules of the solvent get arranged, surrounding the molecules of activated complex. Hence the degree of randomness decreases, decreasing the entropy of activation and lowering the reaction rate.

In case of the reactants with opposite charges, the magnitude of the charge on the activated complex, so formed, will be less, offering less home for the polar molecules of the solvent and promoting disorderness due to which the entropy of activation increases and hence the rate of reaction increases.

The entropy of a reaction between two neutral species in aqueous medium depends upon the difference in the polarity of the activated complex and that of the reactants. If the activated complex has more polarity than the reactants, then the entropy of activation will decrease, decreasing the rate of the reaction, whereas the reactions with the reactants and the activated complex of same polarity proceed without any change in the entropy of activation.

Effect of Hydrostatic Pressure

Consider the following reaction



If the volume of activated complex is less than that of the reactants, then the change in the volume of activation i.e. the volume of activated complex minus the volume of reactants will be negative indicating that a high pressure will shift equilibrium towards right and the rate of reaction will increase.

If the volume of activated complex is greater than that of the reactants, then the volume change will be positive and in this case, an increase in pressure will shift the equilibrium towards left decreasing the rate of reaction.

According to transition state theory, we know that

$$k_2 = \frac{k_B T}{h} e^{-\frac{\Delta F^\ddagger}{RT}}$$

Taking natural logarithm on both sides of the above equation, we get

$$\ln k_2 = \ln \frac{k_B T}{h} - \frac{\Delta F^\ddagger}{RT}$$

$$\ln k_2 = \ln \frac{k_B T}{h} - \frac{1}{RT} (F^\ddagger - F_R)$$

Differentiating the above equation with respect to pressure at constant temperature, we get

$$\left(\frac{\partial \ln k_2}{\partial P} \right)_T = 0 - \frac{1}{RT} \left[\left(\frac{\partial F^\ddagger}{\partial P} \right)_T - \left(\frac{\partial F_R}{\partial P} \right)_T \right]$$

Since the rate of change of free energy with respect to pressure at constant temperature is equal to volume, so

$$\left(\frac{\partial \ln k_2}{\partial P} \right)_T = -\frac{1}{RT} [V^\ddagger - V_R]$$

$$\left(\frac{\partial \ln k_2}{\partial P} \right)_T = -\frac{1}{RT} \Delta V^\ddagger$$

Separating the variables in the above equation and integrating it, we get

$$\int \partial \ln k_2 = -\frac{\Delta V^\ddagger}{RT} \int \partial P$$

$$\ln k_2 = -\frac{\Delta V^\ddagger P}{RT} + \text{constant} \quad (5.244)$$

Applying initial conditions, i.e. when $P = 0$, then $k_2 = k_2^\circ$, to the above equation, we get

$$\ln k_2^\circ = \text{constant}$$

Putting this value of the constant of integration in equation (5.244), we get

$$\ln k_2 = -\frac{\Delta V^\ddagger P}{RT} + \ln k_2^\circ$$

$$\ln \frac{k_2}{k_2^\circ} = -\frac{\Delta V^\ddagger P}{RT} \quad (5.245)$$

This is the equation of straight line passing through origin, where $\ln(k_2/k_1)$ is the dependent variable and P is the independent variable. A plot of $\ln(k_2/k_1)$ versus P gives a straight line, the slope of which can be used to calculate the change in the volume of activation. It is evident from equation (5.245) that if the volume change is negative, then an increase in pressure increases the value of k_2 , as a result the rate of reaction increases, whereas a positive volume change causes the rate constant to decrease with the increase in pressure and hence decreases the rate of the reaction.

Example 5.32

Prove that $\left[\frac{\partial F}{\partial P}\right]_T = V$

Solution

We know

$$F = H - TS$$

Since $H = E + PV$

So $F = E + PV - TS$

Taking differential of the above equation, we get

$$dF = dE + PdV + VdP - TdS - SdT$$

We know

$$dQ = dE + PdV$$

So $dF = dQ + VdP - TdS - SdT$

We know $\frac{dQ}{T} = dS$, $dQ = TdS$, so

$$dF = TdS + VdP - TdS - SdT$$

$$dF = VdP - SdT$$

Hence proved, at constant temperature

$$\left[\frac{\partial F}{\partial P}\right]_T = V$$

Example 5.33

Calculate the volume of activation for a chemical reaction $A + B \xrightarrow{k_2} P$ using the following data.

P (Pa)	k_2 ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) at 25 °C
2×10^5	1×10^{-6}
3×10^9	2×10^{-6}

Solution

We know that

$$\ln k_2 = -\frac{\Delta V_{\ddagger} P}{RT} + \ln k_2^{\circ}$$

For the rate constant $(k_2)_1$ at pressure P_1 , the above equation can be written as

$$\ln(k_2)_1 = -\frac{\Delta V_{\ddagger} P_1}{RT} + \ln k_2^{\circ} \quad (\text{i})$$

Similarly for the rate constant $(k_2)_2$ at pressure P_2 , we have

$$\ln(k_2)_2 = -\frac{\Delta V_{\ddagger} P_2}{RT} + \ln k_2^{\circ} \quad (\text{ii})$$

Subtracting equation (ii) from equation (i), we get

$$\ln \frac{(k_2)_1}{(k_2)_2} = \frac{\Delta V_{\ddagger}}{RT} (P_2 - P_1)$$

$$\Delta V_{\ddagger} = \frac{RT}{(P_2 - P_1)} \ln \frac{(k_2)_1}{(k_2)_2}$$

Putting the given values in the above equation, we get

$$\Delta V_{\ddagger} = \frac{(8.3143)(298)}{(3 \times 10^9 - 2 \times 10^5)} \ln \frac{(1 \times 10^{-6})}{(2 \times 10^{-6})} = -5.72 \times 10^{-7} \text{ m}^3 \text{ mol}^{-1}$$

Effect of Dielectric Permittivity of the Solvent

Rates of the reactions in solution also depend on the dielectric constant of the medium in which the charged species are being reacted. A mathematical relation between the dielectric constant of the medium and the rate constant of the reaction can be derived as given below:

Taking natural logarithm of equation (5.232), we get

$$\ln k_2 = \ln \frac{k_B T}{h} - \frac{\Delta F^{\ddagger}}{RT}$$

$$\ln k_2 = \ln \frac{k_B T}{h} - \frac{1}{RT} (\Delta F_{(C)}^{\ddagger} + \Delta F_{(N.C)}^{\ddagger}) \quad (5.246)$$

Where $\Delta F_{(C)}^*$ and $\Delta F_{(N.C)}^*$ represent the Coulombic and non-Coulombic activation energies respectively.

According to the Coulomb's law, the force of attraction between two charges A and B in vacuum is given by

$$F = \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r^2}$$

Where, Z_A and Z_B represent the charges on A and B respectively, r is the separation between the charged species and ϵ_0 is the permittivity of free space.

As the charges are immersed in a solvent, therefore the relative permittivity, ϵ_r of the medium should also be introduced. Hence the above equation will become

$$F = \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r^2 \epsilon_r}$$

Coulombic interaction energy (measured in Joules) is obtained by multiplying the force of attraction with the separation r i.e.

$$E = Fr = \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r \epsilon_r}$$

Multiplying the above equation by Avogadro's number gives the value of Coulombic activation energy i.e.

$$\Delta F_{(C)} = EN_A = \frac{Z_A Z_B e^2 N_A}{4\pi\epsilon_0 r \epsilon_r}$$

Putting this value of $\Delta F_{(C)}$ in equation (5.246), we get

$$\ln k_2 = \ln \frac{k_B T}{h} - \frac{1}{RT} \left(\frac{Z_A Z_B e^2 N_A}{4\pi\epsilon_0 r \epsilon_r} + \Delta F_{(N.C)}^* \right)$$

$$\ln k_2 = -\frac{Z_A Z_B e^2 N_A}{4\pi\epsilon_0 r RT} \left(\frac{1}{\epsilon_r} \right) + \ln \frac{k_B T}{h} - \frac{\Delta F_{(N.C)}^*}{RT} \quad (5.247)$$

When ϵ_r approaches infinity, then k_2 is equal to $\ln \frac{k_B T}{h} - \frac{\Delta F_{(N.C)}^*}{RT}$ and it is called the rate constant for infinite dielectric constant and it is denoted by k_2° , so

$$\ln k_2 = \ln k_2^\circ - \frac{Z_A Z_B e^2 N_A}{4\pi\epsilon_0 r RT} \left(\frac{1}{\epsilon_r} \right)$$

This is the equation of straight line in intercept form that shows the dependence of the rate constant k_2 on the dielectric constant ϵ_r of the solvent. It is clear from the equation that an increase in ϵ_r increases the value of k_2 which, in turn, increases the rate of the reaction. Non-Coulombic activation energy can be calculated from the intercept i.e.

$$\text{Intercept} = \ln \frac{k_A T}{h} - \frac{\Delta F_{\text{act}}^\ddagger}{RT}$$

$$\left(\ln \frac{k_A T}{h} - \text{Intercept} \right) RT = \Delta F_{\text{act}}^\ddagger$$

The value of r can be calculated from the slope of the plot of $\ln k_2$ versus $1/t_c$.

Effect of Ionic Strength (Primary Salt Effect)

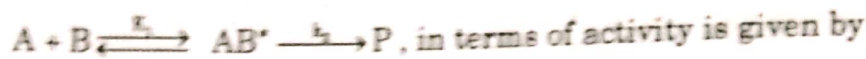
Lowry Bronsted and Bjerrum, using Debye Huckle Theory, studied the effect of ionic strength on the rate of a reaction keeping all other variables constant.

Activity, a_i of a substance, i , is directly related to its concentration, c_i , as given by the following expression

$$a_i = \gamma_i c_i \quad (5.248)$$

where γ_i is the activity coefficient of the substance i .

The equilibrium constant for the first part of the reaction



$$K_1 = \frac{a_{AB^\ddagger}}{a_A a_B}$$

Using equation (5.248), the above equation can also be written as

$$K_1 = \frac{[AB^\ddagger] \gamma_{AB^\ddagger}}{[A] \gamma_A [B] \gamma_B}$$

$$[AB^\ddagger] = \frac{K_1 [A] [B] \gamma_A \gamma_B}{\gamma_{AB^\ddagger}}$$

Putting this value of $[AB^\ddagger]$ in equation (5.228), we get

$$\frac{d[P]}{dt} = \frac{k_2 K_1 [A] [B] \gamma_A \gamma_B}{\gamma_{AB^\ddagger}} \quad \text{or } K_1 \{A\} \{B\} = \frac{d[P]}{dt} \quad (5.249)$$

Comparing equation (5.230) and equation (5.249), the value of k_2 comes out to be

$$k_2 = \frac{k_2 K_1 \gamma_A \gamma_B}{\gamma_{AB^\ddagger}} \quad (5.250)$$

For a very dilute solution, the activity coefficients of the species involved can be taken as unity, hence the above equation will become

$$k_2^\circ = k_2 K_1$$

where k_2° represents the rate constant for a very dilute solution. Putting this value of $k_2 K_1$ in equation (5.250), we get

$$k_2 = \frac{k_2^\circ \gamma_A \gamma_B}{\gamma_s} \quad (5.251)$$

Where k_2 is a function of activity coefficients of the reactants as well as that of the activated complex, whereas k_2° is independent of the activity coefficient as it is that value of rate constant at which activity coefficients of all the species are unity.

According to Debye-Huckle limiting law, we know that

$$\log \gamma_i = -0.51 \frac{Z_i^2 \sqrt{I}}{1 + \sqrt{I}} \quad (5.252)$$

For specie A, this law can be written as

$$\log \gamma_A = -0.51 \frac{Z_A^2 \sqrt{I}}{1 + \sqrt{I}} \quad (5.252a)$$

For specie B, we have

$$\log \gamma_B = -0.51 \frac{Z_B^2 \sqrt{I}}{1 + \sqrt{I}} \quad (5.252b)$$

Similarly for transition state, we can write

$$\log \gamma_s = -0.51 (Z_A + Z_B)^2 \frac{\sqrt{I}}{1 + \sqrt{I}} \quad (2.253)$$

Taking natural logarithm of equation (5.251), we get

$$\log k_2 = \log k_2^\circ + \log \gamma_A + \log \gamma_B - \log \gamma_s$$

Putting the value of $\log \gamma_A$, $\log \gamma_B$ and $\log \gamma_s$ from equation (5.252a), (5.252b) and (2.253) respectively in the above equation, we get

$$\log k_2 = \log k_2^\circ - 0.51 \frac{Z_A^2 \sqrt{I}}{1 + \sqrt{I}} - 0.51 \frac{Z_B^2 \sqrt{I}}{1 + \sqrt{I}} + 0.51 (Z_A + Z_B)^2 \frac{\sqrt{I}}{1 + \sqrt{I}}$$

$$\log k_2 = \log k_2^\circ - 0.51 \frac{\sqrt{I}}{1 + \sqrt{I}} [Z_A^2 + Z_B^2 - (Z_A + Z_B)^2]$$

$$\log k_2 = \log k_2^\circ - 0.51 \frac{\sqrt{I}}{1 + \sqrt{I}} [Z_A^2 + Z_B^2 - Z_A^2 - Z_B^2 - 2Z_A Z_B]$$

$$\log k_2 = \log k_2^\circ - 0.51 \frac{\sqrt{I}}{1 + \sqrt{I}} (-2Z_A Z_B)$$

$$\log k_2 = \log k_2^\circ + 1.022 Z_A Z_B \frac{\sqrt{I}}{1 + \sqrt{I}} \quad (5.254)$$

Equation (5.254) is known as Bronsted-Bejerrum equation which indicates that $\log k_2$, and hence the rate of reaction, is dependent on the ionic strength of the solution. The effect of ionic strength on the rate of a reaction can be explained more

conveniently by assuming T to be very very small so that $1 + \sqrt{I}$ can be taken approximately equal to 1. Hence equation (5.254) will become

$$\log k_2 = \log k_2^0 + 1.022Z_A Z_B \sqrt{I} \quad (5.255)$$

Equation (5.255) is the equation of straight line in intercept form. Plotting $\log k_2$ versus \sqrt{I} gives three types of graphs depending on the nature of charges on A and B as shown in Fig. 5.33. If the reaction takes place between two species having similar charges, then the presence of the ions of some ionic specie between the two reactant ions decreases the electrostatic forces of repulsion between them and hence increases the rate of reaction. Therefore, a straight line with positive slope is obtained in this case. Whereas for the reactants having opposite charges, the presence of the ions of some ionic specie between the ions of the reactants decreases the forces of attraction between them, thus decreases the rate of reaction. Hence, in this case, the slope of the plot will be negative. If one of the reactants is neutral, then ionic strength has no effect on the rate constant of that reaction as there are no electrostatic forces between the reactants and hence, the slope of the plot will be zero.

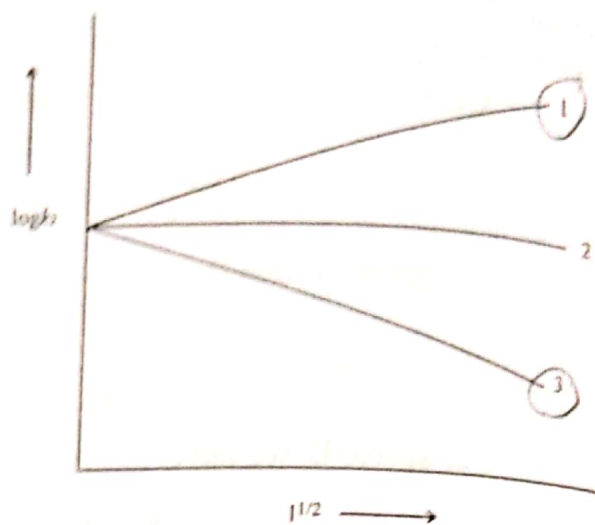


Fig. 5.33 Variation in the value of $\log k_2$ with $I^{1/2}$ (1) when the reactants have similar charges, (2) when the reactants are neutral, (3) when the reactants have opposite charges

Example 5.34

Discuss the effect of ionic strength on the rate constant of the following reaction on the basis of equation (5.255).

- (i) $\text{CH}_2\text{ICOOH} + \text{CNS}^- \longrightarrow \text{CH}_2(\text{CNS})\text{COOH} + \text{I}^-$
- (ii) $\text{CH}_2\text{BrCOO}^- + \text{S}_2\text{O}_3^{2-} \longrightarrow \text{CH}_2(\text{S}_2\text{O}_3)\text{COO}^- + \text{Br}^-$
- (iii) $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+} + \text{OH}^- \longrightarrow [\text{Co}(\text{NH}_3)_5\text{OH}]^{2+} + \text{Br}^-$

Solution

- (i) $Z_A Z_B = 0$, hence the value of k_2 is independent of ionic strength.
- (ii) $Z_A Z_B = 2$, hence the value of k_2 increases with the increase in ionic strength.
- (iii) $Z_A Z_B = -2$, hence the value of k_2 decreases with the increase in ionic strength.