

SURFACE CHEMISTRY

6.1 INTRODUCTION

Surface chemistry is the branch of physical chemistry which deals with the study of phenomena occurring at interfaces. The study of interfaces is of great significance for chemists because it finds applications in our daily life and industry. Mainly, surfaces play an important role in catalysis, colloid formation, chromatography etc. This chapter covers the fundamentals and applications of surface chemistry. Adsorption is the process of attachment of adsorbate molecules on the surface of adsorbent. This chapter explains the adsorption isotherms, adsorption of a gas and its catalytic reaction on solid surface. Adsorption of two gases and their catalytic reaction on solid surface and retardation process is also explained with the help of Langmuir adsorption isotherm. Eley-Rideal mechanism and Langmuir-Hinshelwood mechanisms to study some organic and inorganic reactions have been described in this chapter. Catalytic decomposition of ammonia is also described by the Tempkin adsorption isotherm in detail. The gas-solid interface is of great importance in catalysis. The current chapter also covers some basic physical aspects of catalysis, autocatalysis, enzyme catalysis and enzyme inhibition. Moreover comparative analysis of competitive, uncompetitive and non-competitive enzyme inhibitions is also discussed in this chapter.

6.2 ADSORPTION

When molecules of a substance come in contact with any solid surface its molecules get attached on it, this process of attachment of molecules is named as adsorption. In other words, "*attachment of particles of a substance on the surface of another substance is called adsorption.*" Adsorbate and adsorbent are basic components which are necessary for adsorption. Adsorbate is the substance which get attached to the other surface and the substance on which adsorption takes place is called adsorbent. Adsorption can be distinguished from absorption because in adsorption adsorbate molecules will attach at the surface while in case of absorption, molecules will penetrate into the body of adsorbent. So, "*the penetration of the molecules of a substance into the other substance is called absorption.*"

When adsorption and absorption takes place at same time then the process is known as sorption. The dyeing of cotton fibers is an example of sorption.

Types of Adsorption

There are two types of adsorption i.e. physical and chemical adsorption. Some distinguishing characteristics are given below

Physical Adsorption	Chemical Adsorption
<ol style="list-style-type: none"> Physical adsorption occurs through van-der Waal's forces. So, it is also known as physisorption. Physical adsorption is fast process. This is relatively weak adsorption. It has low value of heat of adsorption. Physical adsorption is mostly exothermic process. It is not specific. It depends only on the nature of adsorbate. It is usually multilayered adsorption. It decreases with rise of temperature. It is reversible process. Heat of adsorption is less than 40 kJ/mol. For example, Adsorption of oxalic acid on charcoal. 	<ol style="list-style-type: none"> Chemical adsorption occurs through chemical bonding. It is also known as chemisorption. Chemical adsorption is slow process. This is relatively strong adsorption. It has high value of heat of adsorption. The process of chemisorption may be exothermic or endothermic. It is highly specific. It depends on the nature of adsorbate and adsorbent. It is monolayered adsorption It increases with increase of temperature. It may be irreversible or reversible process. Heat of adsorption is greater than 80 kJ/mol. For example, H₂ adsorbed on Ni/Fe/Pt.

6.3 FACTORS AFFECTING ADSORPTION

(i) Nature of Adsorbate and Adsorbent

Adsorption depends upon the nature of adsorbate and adsorbent. The various groups of adsorbate and adsorbent are responsible for adsorption. For example polarity of both can cause force of attraction between them.

(ii) Surface Area

Surface area of the adsorbent has pronounced effect on the rate of adsorption. Adsorbent with greater surface to volume ratio possess greater extent of adsorption and vice versa. If substance is divided and subdivided further then we get small particles. This process will increase the surface area to volume ratio to a very large extent.

(iii) Temperature

Temperature affects the process of adsorption. For example in most cases chemical adsorption increases with the increase of temperature, while physical adsorption decreases with the increase of temperature.

(iv) Pressure/Concentration

Dynamic equilibrium exists between the adsorbed and desorbed gas molecules during adsorption process. So, according to Le-Chatlier's principle increase in pressure leads to higher rate of adsorption. When pressure is decreased it causes desorption.

6.4 ADSORPTION ISOTHERMS

Adsorption of a substance on the surface of another substance can be investigated under various conditions of temperature and pressure but in most studies relation between extent of adsorption and equilibrium pressure has been explored. When a gas starts to adsorb on a surface, initially its rate of desorption depends upon number of molecules adsorbed. With the increase of number of molecules adsorbed, rate of desorption increases. "When rate of adsorption becomes equal to the rate of desorption this state is called dynamic equilibrium." At dynamic equilibrium, the pressure is called equilibrium pressure. The process of adsorption and desorption in a close vessel is shown in Fig. 6.1 (a) at equilibrium. "The relation between extent of adsorption and equilibrium pressure at constant temperature is called adsorption isotherm."

6.4.1 Freundlich Adsorption Isotherm

Freundlich gave an empirical relation between extent of adsorption and pressure of gas at constant temperature in the form of an empirical equation which is given below

$$\frac{x}{m} = kP^{1/n} \quad (6.1)$$

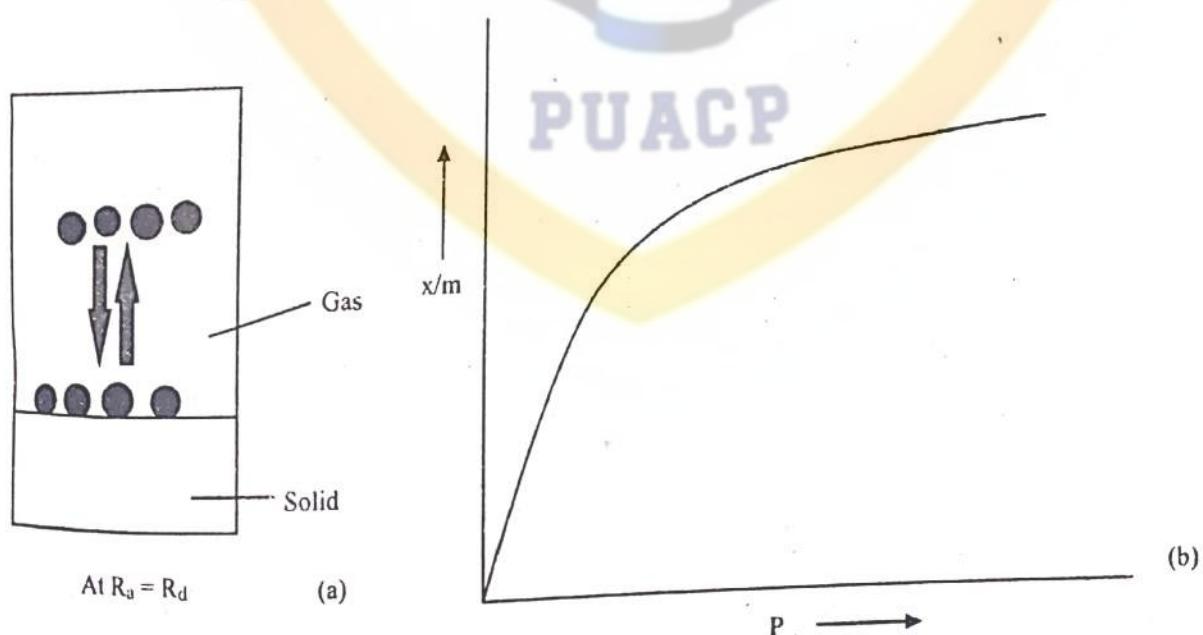


Fig. 6.1 (a) Adsorption desorption equilibrium
(b) x/m as a function of pressure of a gas at constant temperature

Where, P is the equilibrium pressure and x/m is the extent of adsorption i.e. amount of adsorbate adsorbed per unit mass of adsorbent. k and n are empirical constants which depend upon the nature of gas, solid and temperature, n is the dimensionless quantity but k has dimension of inverse of pressure. According to equation (6.1) extent of adsorption is a function of equilibrium pressure of gas as shown in Fig. 6.1 (b).

Equation (6.1) can be written in the form of equation of straight line as

$$\log \frac{x}{m} = \frac{1}{n} \log P + \log k \quad (6.2)$$

According to equation (6.2) $\log(x/m)$ is a linear function of $\log P$ whose slope and intercept are $1/n$ and $\log k$ respectively as shown in Fig. 6.2. This plot can be used for the determination of values of empirical constants n and k .

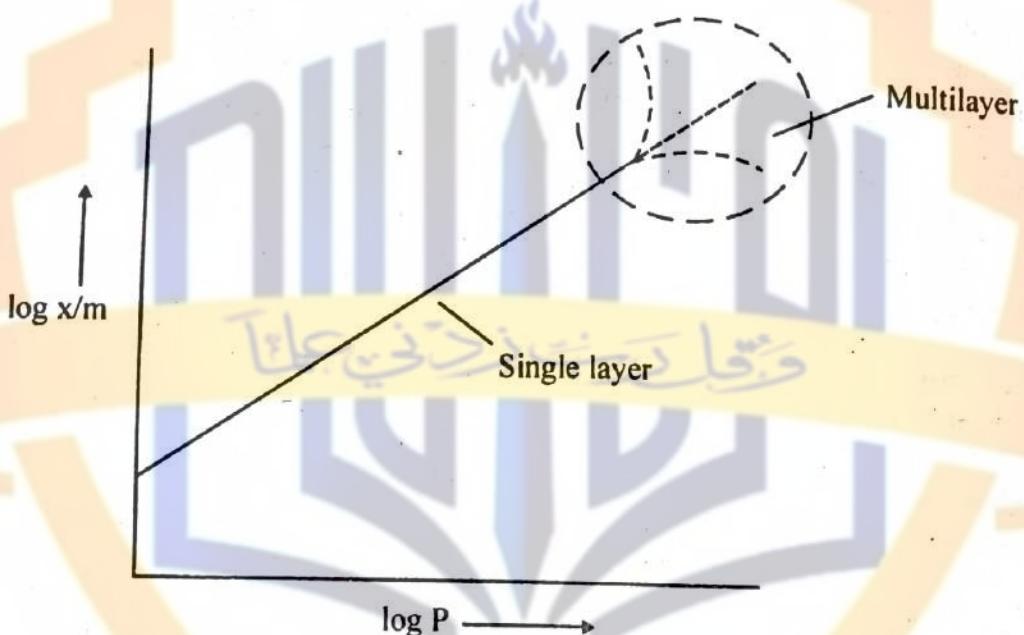


Fig. 6.2 Plot of $\log x/m$ versus $\log P$ with slight curvature at high pressure

When value of $1/n$ approaches to zero, then x/m becomes independent of pressure and $1/n$ approaches to one then x/m becomes a linear function of pressure of gas as shown in Fig. 6.3.

Freundlich adsorption isotherm for adsorption from solution to a solid surface can be written by replacing P with C in equation (6.1) as

$$\frac{x}{m} = kC^{\frac{1}{n}} \quad (6.3)$$

By taking log of equation (6.3)

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C$$

This equation can be used to study the adsorption of toxic material on biosorbent in aqueous medium. Water purification can be done by suitable adsorbent

using this equation. The value of n and k can be determined using plot as shown in Fig. 6.4.

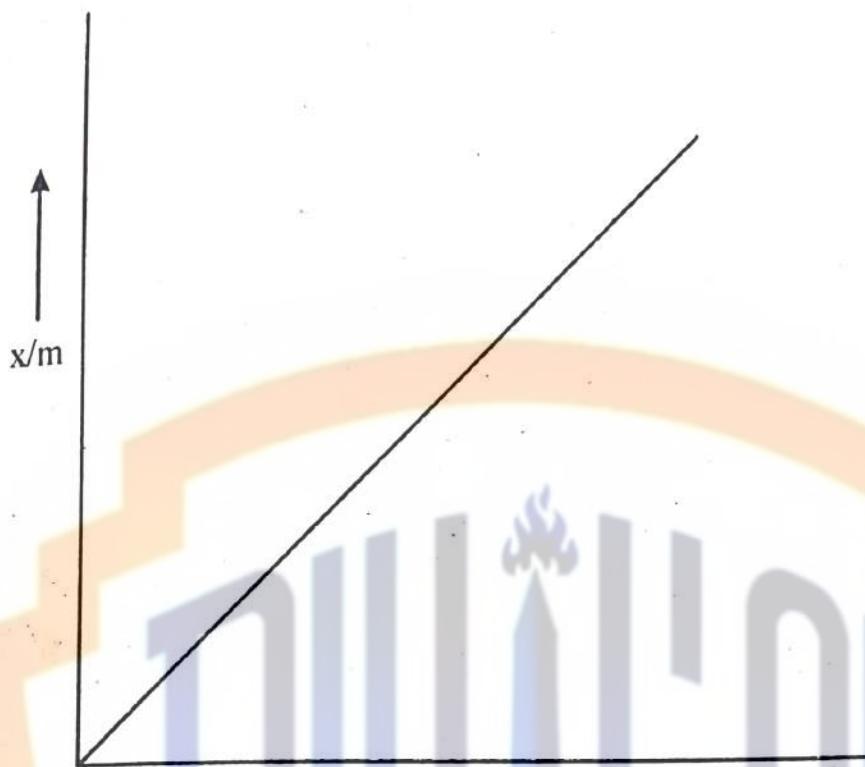


Fig. 6.3 Plot of x/m as a function of pressure when $n = 1$

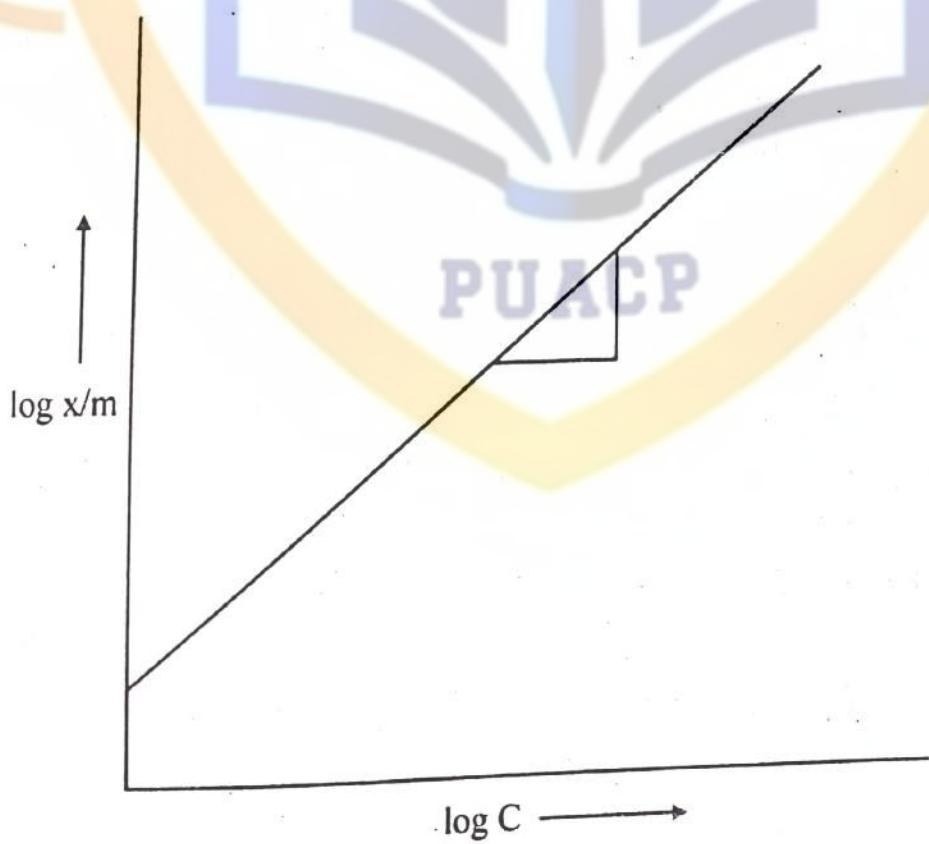


Fig. 6.4 Plot of $\log x/m$ versus $\log C$

6.4.2 Langmuir's Adsorption Isotherm

Langmuir was an American physical chemist who worked on adsorption of gases on solid surface. He also derived "adsorption isotherm" and got noble prize in chemistry in 1932. The postulates on which Langmuir's adsorption isotherm is based are given below.

Postulates

- (i) Each adsorbent has specific equivalent sites for adsorption.
 - (ii) Adsorbate molecule attach to these sites.
 - (iii) One molecule of adsorbate can adsorb on one site of adsorbent.
 - (iv) There is no interaction between molecules of adsorbate adsorbed.
 - (v) Rate of adsorption is relatively high as compared to rate of desorption at initial stages.
 - (vi) Rate of adsorption becomes equal to rate of desorption at dynamic equilibrium as shown in Fig. 6.5.
 - (vii) Fractional surface coverage (θ), a new dimensionless quantity is equal to the ratio of number of sites covered to total number of sites i.e.
- $$\theta = \frac{\text{no. of sites occupied}}{\text{total no. of sites}}$$
- (viii) Rate of adsorption depends upon the equilibrium pressure of gas (adsorbate) and fraction of available sites and rate of desorption depends upon the fraction of sites covered.

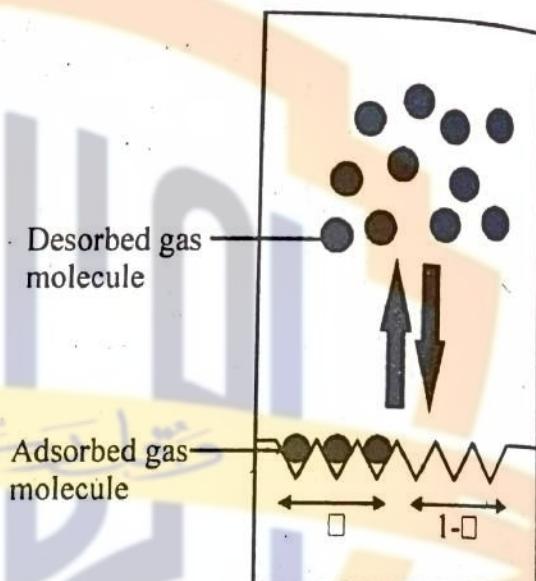


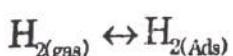
Fig. 6.5 Dynamic equilibrium exists between adsorbed and desorbed molecules

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.

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

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

On combining equation (6.4) and (6.5)

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

k_{ads} is the rate constant for adsorption.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\theta = \frac{b_1 e^{-\frac{E_{A_{ds}}}{RT}} P_A / b_2 e^{-\frac{E_{D_{es}}}{RT}}}{1 + \frac{b_1 e^{-\frac{E_{A_{ds}}}{RT}} P_A}{b_2 e^{-\frac{E_{D_{es}}}{RT}}}}$$

$$\theta = \frac{\frac{b_1}{b_2} e^{\frac{E_{D_{es}} - E_{A_{ds}}}{RT}} P_A}{1 + \frac{b_1}{b_2} e^{\frac{E_{D_{es}} - E_{A_{ds}}}{RT}} P_A}$$

$$\theta = \frac{\left(\frac{b_1}{b_2}\right) e^{\frac{E_{D_{es}} - E_{A_{ds}}}{RT}} P_A}{1 + \left(\frac{b_1}{b_2}\right) e^{\frac{E_{D_{es}} - E_{A_{ds}}}{RT}} P_A}$$

$$\theta = \frac{\left(\frac{b_1}{b_2}\right) e^{-\frac{(E_{A_{ds}} - E_{D_{es}})}{RT}} P_A}{1 + \left(\frac{b_1}{b_2}\right) e^{-\frac{(E_{A_{ds}} - E_{D_{es}})}{RT}} P_A} \quad (6.9)$$

And, $\Delta H_{A_{ds}} = E_{A_{ds}} - E_{D_{es}}$ (6.10)

The quantity $E_{A_{ds}} - E_{D_{es}}$ is the heat of adsorption as shown in energy profile in Fig. 6.6.

Putting value of $(E_{A_{ds}} - E_{D_{es}})$ from equation (6.10) into equation (6.9), we get

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

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

So, above equation becomes

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

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

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.

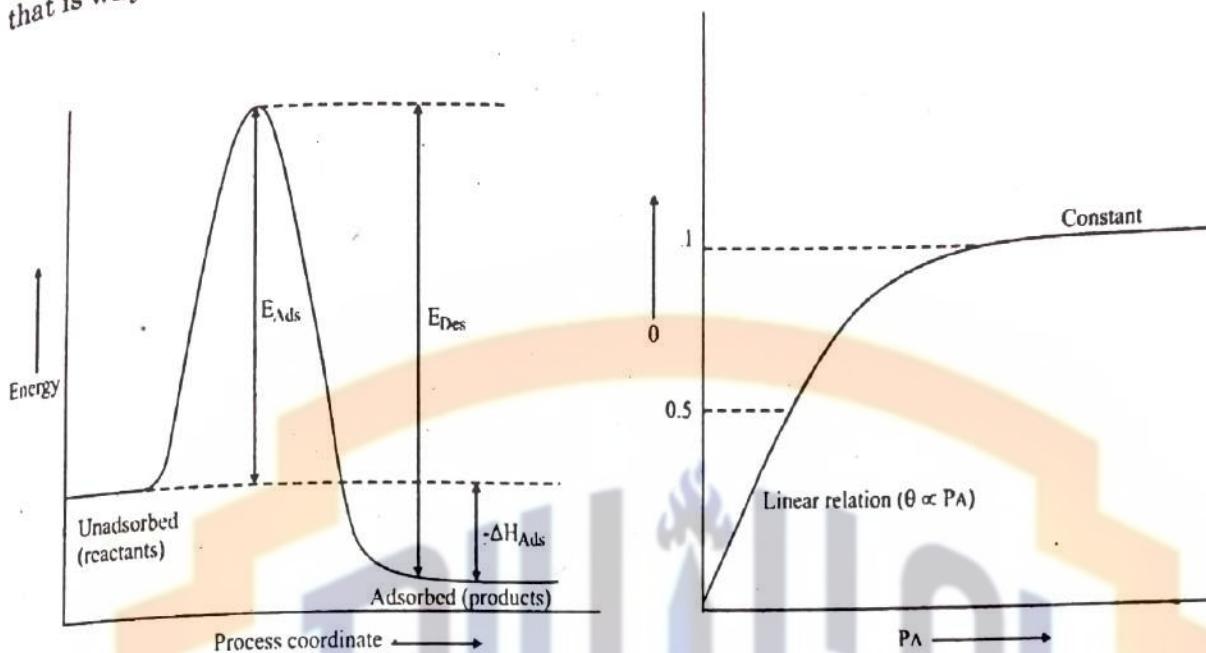


Fig. 6.6 Energy profile of adsorption and Fig. 6.7 θ as a function of pressure of gas A desorption processes

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 $1/b$.

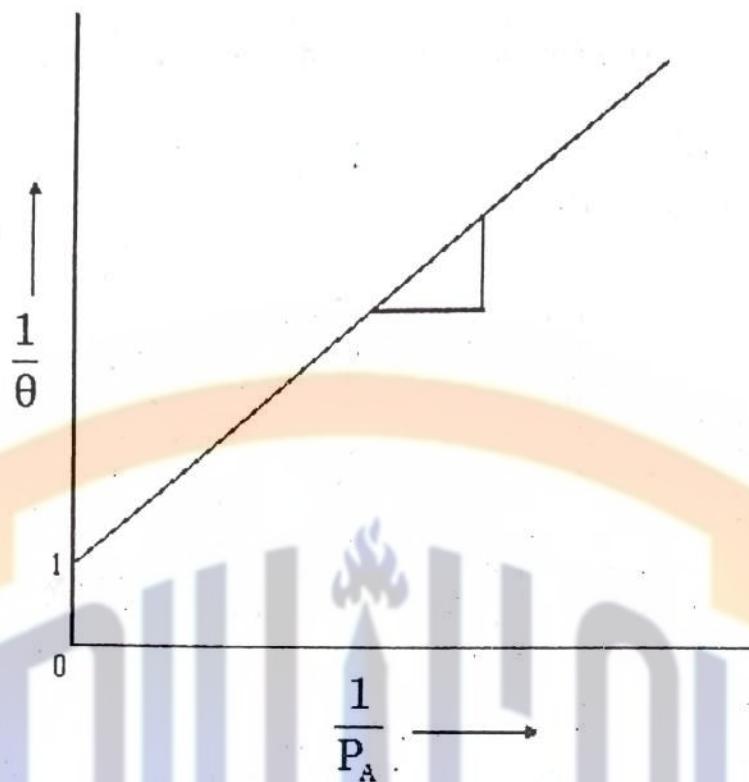
Fig. 6.8 Plot of $1/\theta$ versus $1/P_A$

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

$$R_{Des} \propto \theta^2$$

$$R_{Des} = k_{Des} \theta^2$$

(6.14)

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

So, equation (6.14) will become

$$R_{Des} = b_2 e^{-\frac{E_{Des}}{RT}} \theta^2$$

(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

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

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

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

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

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

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

$$\theta = \frac{b_1^{\frac{1}{2}} e^{-\frac{E_{Ads}}{2RT}} P_A^{\frac{1}{2}}}{b_2^{\frac{1}{2}} e^{-\frac{E_{Des}}{2RT}} + b_1^{\frac{1}{2}} e^{-\frac{E_{Ads}}{2RT}} P_A^{\frac{1}{2}}} \quad (6.16)$$

Divide above equation numerator and denominator by $b_2^{\frac{1}{2}} e^{-\frac{E_{Des}}{2RT}}$

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

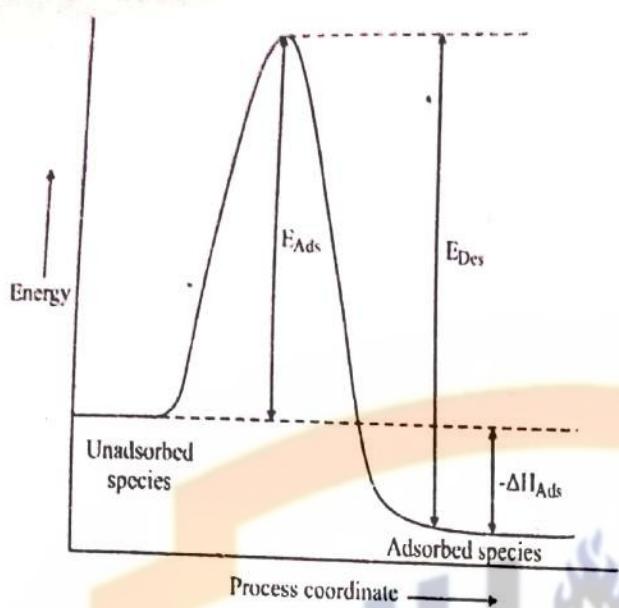
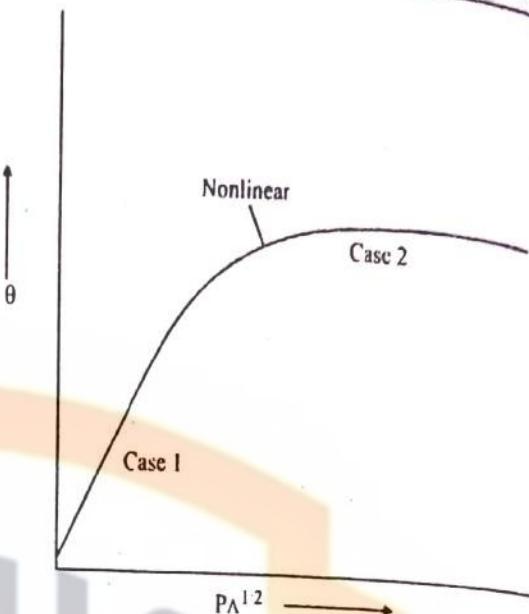


Fig. 6.9 Energy profile of adsorption of a gas

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

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

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

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

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

Then equation (6.19) will become

$$\theta = \frac{b' P_A^{\frac{1}{2}}}{1 + b' P_A^{\frac{1}{2}}} \quad (6.20)$$

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 $1 + b' P_A^{\frac{1}{2}} \approx 1$

So, equation (6.20) becomes

$$\theta = b' P_A^{1/2}$$

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

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

(ii) When P_A is high, then $1 + b' P_A^{1/2} \approx P_A^{1/2}$. 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)

$$\frac{1}{\theta} = \frac{1 + b' P_A^{1/2}}{b' P_A^{1/2}}$$

$$\frac{1}{\theta} = \frac{1}{b' P_A^{1/2}} + 1$$

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.

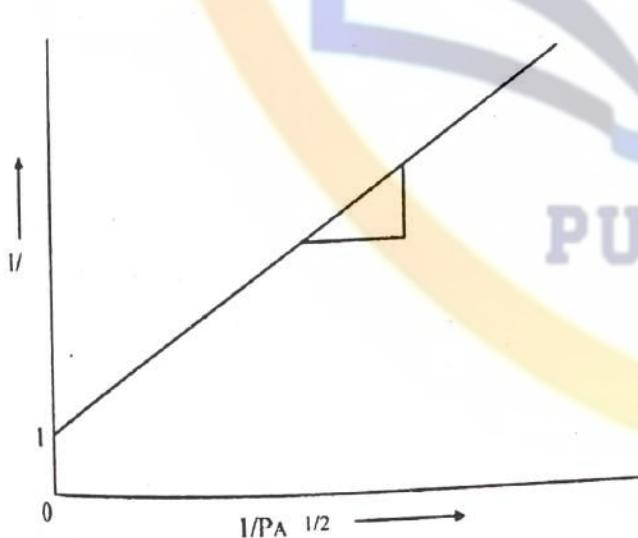


Fig. 6.11 Plot of $1/\theta$ versus $1/P_A^{1/2}$ with intercept 1

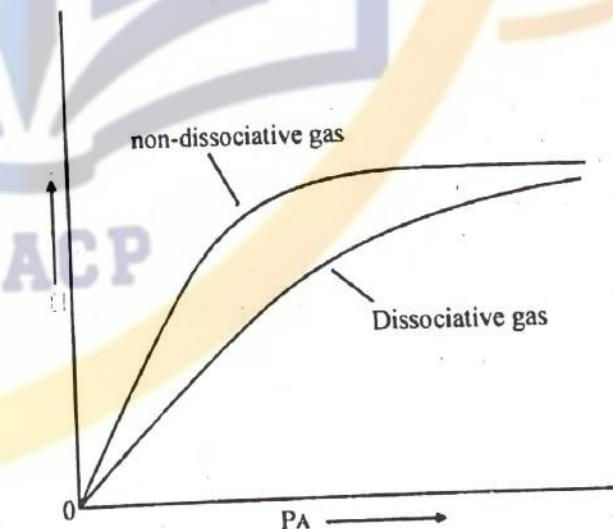


Fig. 6.12 Plot showing dependence of θ on P_A for dissociative and non-dissociative adsorption

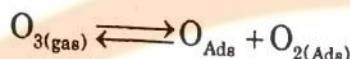
Limitations

The Langmuir adsorption isotherm gives a quantitative explanation of the adsorption. The mechanism of chemical adsorption can also be explained with the help of Langmuir equation. The Langmuir adsorption isotherm gives a satisfactory

theoretical explanation of a large number of experimental results. But it also has some limitations as Langmuir adsorption isotherm assumes that surface is capable of adsorbing one molecule thick layer. But in actual practice, there are chances of multilayer formation. According to this theory, the saturation value of adsorption should be independent of temperature. But experiments show that saturation value decreases with the rise of temperature. This theory holds good only at low pressure.

Example 6.1

Adsorption of ozone on solid surface takes place according to following scheme



Write down Langmuir adsorption isotherm for the adsorption.

Solution

According to the reaction given above, ozone is dissociated into two species, therefore Langmuir isotherm for the adsorption of ozone will be

$$\theta = \frac{b' P_{\text{O}_3}^{1/2}}{1 + b' P_{\text{O}_3}^{1/2}}$$

Example 6.2

Adsorption of ozone on solid surface takes place according to following scheme



Write down Langmuir isotherm for the adsorption of ozone.

Solution

Ozone is dissociated into three oxygen atoms as given in above equation, therefore Langmuir adsorption isotherm is

$$\theta = \frac{b'' P_{\text{O}_3}^{1/3}}{1 + b'' P_{\text{O}_3}^{1/3}}$$

Comments: If a gas dissociates into greater number of atoms, then dependence of θ on pressure of gas decreases.

6.6 APPLICATION OF LANGMUIR ADSORPTION ISOTHERM FOR SINGLE SYSTEM

The Langmuir adsorption isotherm for single system can be used for the determination of isosteric enthalpy of adsorption (ΔH_θ) and for the study of catalytic reaction of gas on solid surface.

6.6.1 Determination of Isosteric Enthalpy of Adsorption (ΔH_0)

The variation of pressure of a gas with temperature for a particular fractional surface coverage can be used to determine the enthalpy of adsorption called isosteric enthalpy of adsorption which is represented by ΔH_0 .

We know that,

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

$$\theta(1 + bP_A) = bP_A$$

$$\theta + (bP_A)\theta = bP_A$$

$$\theta = bP_A(1 - \theta)$$

$$bP_A = \frac{\theta}{(1 - \theta)}$$

By taking natural logarithm on both sides of above equation

$$\ln(bP_A) = \ln\left(\frac{\theta}{1 - \theta}\right) \quad (6.21)$$

As $b = k_{\text{Ads}}/k_{\text{Des}}$, so b depends upon temperature because k_{Ads} and k_{Des} are dependent on temperature. Then, relation (6.21) will be

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

By differentiating above equation with respect to T at constant θ , we get

$$\left(\frac{\partial \ln P_A}{\partial T}\right)_\theta + \left(\frac{\partial \ln b}{\partial T}\right)_\theta = \frac{\partial}{\partial T} \left(\ln \frac{\theta}{1 - \theta}\right)_\theta \quad (6.22)$$

As θ is constant so, $\frac{\partial}{\partial T} \left(\ln \frac{\theta}{1 - \theta}\right)_\theta = 0$. Then equation (6.22) will be,

$$\begin{aligned} \left(\frac{\partial \ln P_A}{\partial T}\right)_\theta + \left(\frac{\partial \ln b}{\partial T}\right)_\theta &= 0 \\ \left(\frac{\partial \ln P_A}{\partial T}\right)_\theta &= -\left(\frac{\partial \ln b}{\partial T}\right)_\theta \end{aligned} \quad (6.23)$$

As we know that,

$$\Delta F = -RT \ln K \quad (6.24)$$

According to thermodynamics; $\Delta F = \Delta H_\theta - T\Delta S$. So, equation (6.24) will be

$$\Delta H_\theta - T\Delta S = -RT \ln b$$

$$\ln b = -\frac{\Delta H_\theta}{RT} + \frac{T\Delta S}{RT}$$

$$\ln b = -\frac{\Delta H_\theta}{RT} + \frac{\Delta S}{R}$$

Differentiating the above equation with respect to T, we get

$$\begin{aligned}\left(\frac{\partial \ln b}{\partial T}\right) &= -\frac{\Delta H_\theta}{R} \frac{\partial}{\partial T}(T^{-1}) + 0 \\ \left(\frac{\partial \ln b}{\partial T}\right) &= +\frac{\Delta H_\theta}{RT^2} \quad (6.25)\end{aligned}$$

Relation (6.25) is called Vant's Hoff equation. By putting the value of $\left(\frac{\partial \ln b}{\partial T}\right)$ from equation (6.25) in equation (6.23), we get

$$\begin{aligned}\left(\frac{\partial \ln P_A}{\partial T}\right)_\theta &= -\frac{\Delta H_\theta}{RT^2} \\ \partial \ln P_A &= -\frac{\Delta H_\theta}{R} \frac{\partial T}{T^2} \quad (6.26)\end{aligned}$$

Integrating equation (6.26), we get

$$\begin{aligned}\int \partial \ln P_A &= -\frac{\Delta H_\theta}{R} \cdot \int \frac{\partial T}{T^2} \\ \ln P_A &= +\frac{\Delta H_\theta}{R} \frac{1}{T} + c \quad (6.27)\end{aligned}$$

Where, c is the constant of integration. So, equation (6.27) is an equation of straight line in intercept form. The value of isosteric enthalpy of adsorption can be determined from the slope of the plot of $\ln P_A$ as a function of $1/T$ at constant θ as shown in Fig. 6.13.

The value and sign of ΔH_θ depends upon the nature of interaction between adsorbate and adsorbent. For negative value of enthalpy of adsorption, variation of $\ln P_A$ with $1/T$ is shown in Fig. 6.14.

The value of ΔH_θ is an approximation. Langmuir isotherm does not give an exact value of ΔH_θ because all sites of adsorbent are not equal, so ΔH_θ for every site is different. Moreover occupied sites show hindrance for molecules of adsorbate to fill the vacant sites of adsorbent.

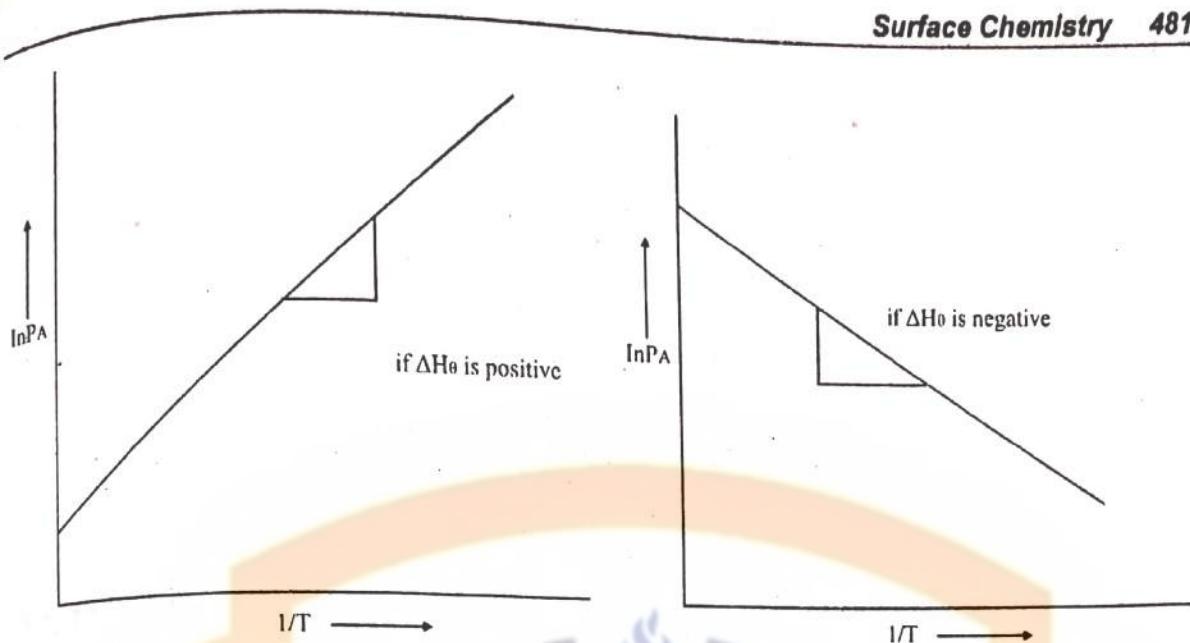


Fig. 6.13 Plot of $\ln P_A$ versus $1/T$ when isosteric enthalpy has positive value

Fig. 6.14 Plot of $\ln P_A$ versus $1/T$ when isosteric enthalpy has negative value

Example 6.3

The pressure required to saturate a particular surface was measured at two different temperatures as given below

$$P_1 = 250 \text{ Pa at } 25^\circ\text{C}, P_2 = 350 \text{ Pa at } 50^\circ\text{C}.$$

Calculate the isosteric enthalpy of adsorption.

Solution

At pressure P_1 and temperature T_1 equation (6.27) will be

$$\ln P_1 = \frac{\Delta H_0}{R} \frac{1}{T_1} + c \quad (6.27a)$$

At temperature T_2 pressure is P_2 then, equation (6.27) will be

$$\ln P_2 = \frac{\Delta H_0}{R} \frac{1}{T_2} + c \quad (6.27b)$$

Subtracting equation (6.27a) from equation (6.27b), we get

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_0}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{P_1}{P_2} = \frac{\Delta H_0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{P_1}{P_2} = \frac{\Delta H_0}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\Delta H_0 = R \left(\frac{T_1 T_2}{T_2 - T_1} \right) \left(\ln \frac{P_1}{P_2} \right)$$

By putting values in above equation from given data we can find the isosteric enthalpy of adsorption as

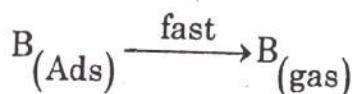
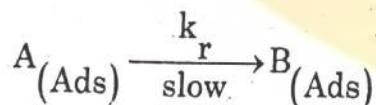
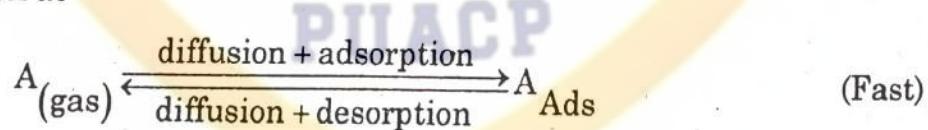
$$\Delta H_0 = 8.3143 \left[\frac{(298)(323)}{323 - 298} \right] \left(\ln \frac{250}{350} \right) = -10.77 \text{ kJ mol}^{-1}$$

6.6.2 Catalytic Reaction of Gas Adsorbed on Solid Surface

The most important feature of Langmuir adsorption isotherm is its application to explain the catalytic reaction of a gas on solid surface. Catalytic reaction of gas on metal surface involve following steps

- Diffusion of reactants towards catalyst surface.
- Adsorption of reactants on solid surface.
- Product formation on catalyst surface.
- Desorption of product gas.
- Diffusion of product gas into the reaction vessel from catalyst surface. This phenomenon is depicted by pictorial diagram as shown in Fig. 6.15.

According to above steps scheme of catalytic reaction of gas A to generate gas B can be written as



Where, k_r is the heterogeneous rate constant.

Rate of reaction is directly proportional to fractional surface coverage of adsorbed gas A.

$$\text{Rate of reaction} \propto \theta_A$$

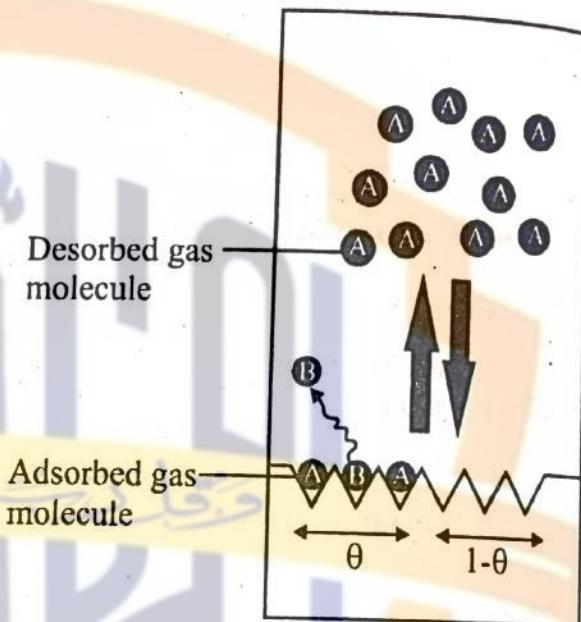


Fig. 6.15 Pictorial diagram of catalytic reaction of two gases on solid surface

$$\text{Rate} = k_r \theta_A \quad (6.28)$$

According to Langmuir adsorption isotherm for non dissociative adsorption, we know $\theta_A = \frac{bP_A}{1 + bP_A}$. So, equation (6.28) will be

$$\text{Rate} = k_r = \frac{bP_A}{1 + bP_A} \quad (6.29)$$

Nature of gas, whether it is strongly, moderately or weakly adsorbed on catalyst surface, highly affects kinetics of catalytic reactions. Thus kinetics of catalytic reaction can be discussed in two separate cases as given below

(i) When Reactant Gas is Weakly Adsorbed

If gas is weakly adsorbed it means b is very low. So. $1 + bP_A \approx 1$ put this value in equation (6.29) we get,

$$\text{Rate} = k_r bP_A \quad (6.30)$$

$$\text{Rate} \propto P_A$$

Hence, reaction is of first order, if b is very low.

$$-\frac{dP_A}{dt} = \text{Rate of consumption of gas A}$$

So, equation (6.30) can be written in terms of rate of consumption of gas A

$$-\frac{dP_A}{dt} = k_r bP_A \quad (6.31)$$

By separating variables and integrating equation (6.31) we get,

$$-\int \frac{dP_A}{P_A} = k_r b \int dt \quad (6.32)$$

$$-\ln P_A = k_r bt + c \quad (6.33)$$

Applying boundary conditions, when $t = 0$ then $P_A = P_i$. Physically, it is said that when reaction just starts then pressure has its maximum value equal to initial pressure of gas.

So, $-\ln P_i = c$, by putting value of c in equation (6.33) we get,

$$\begin{aligned} -\ln P_A &= k_r bt - \ln P_i \\ -\ln P_A + \ln P_i &= k_r bt \\ \ln \frac{P_i}{P_A} &= k_r bt \end{aligned} \quad (6.34)$$

Results concluded from equation (6.34) are as follows

- (i) Equation (6.34) is straight line equation passing through origin.

- (ii) Plot of $\ln P_i/P_A$ versus t as shown in Fig. 6.16.
 (iii) The value of k_r can be determined from slope i.e.

$$\text{Slope} = k_r b$$

$$k_r = \frac{\text{slope}}{b}$$

- (iv) Expression of half life of gas A can be derived as

$$t = t_{1/2} \text{ at } P_A = P_i/2$$

Applying this condition to equation (6.34), we get

$$\ln \frac{P_i}{P_i/2} = k_r b t_{1/2}$$

$$k_r b t_{1/2} = \ln 2$$

$$t_{1/2} = \frac{1}{k_r b} \ln 2$$

$$t_{1/2} = \frac{0.693}{k_r b} \quad (6.35)$$

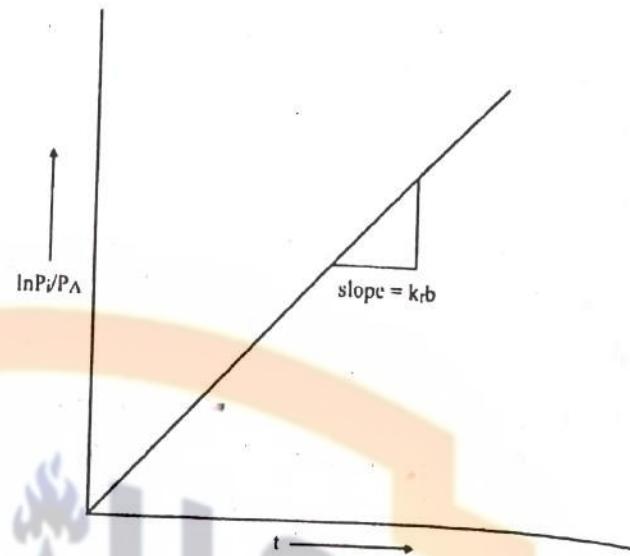


Fig. 6.16 $\ln P_i/P_A$ as a function of time

Results can be drawn from equation (6.35) as follows: $t_{1/2}$ is function of b , $t_{1/2}$ is inversely proportional to b and it is independent of P_A . With change in temperature, k_r and b changes which in turn causes a change in $t_{1/2}$.

- (v) Units of k_r can be determined as

$$k_r = \frac{1}{bt} \ln \frac{P_i}{P_A}$$

$$k_r = \text{Pa/s}$$

- (vi) The pressure of gas as a function of time can be expressed as

$$\frac{P_i}{P_A} = e^{k_r bt}$$

$$\frac{P_A}{P_i} = e^{-k_r bt}$$

$$P_A = P_i e^{-k_r bt} \quad (6.36)$$

According to equation (6.36), value of P_A decreases with increase of time exponentially as shown in Fig. 6.17.

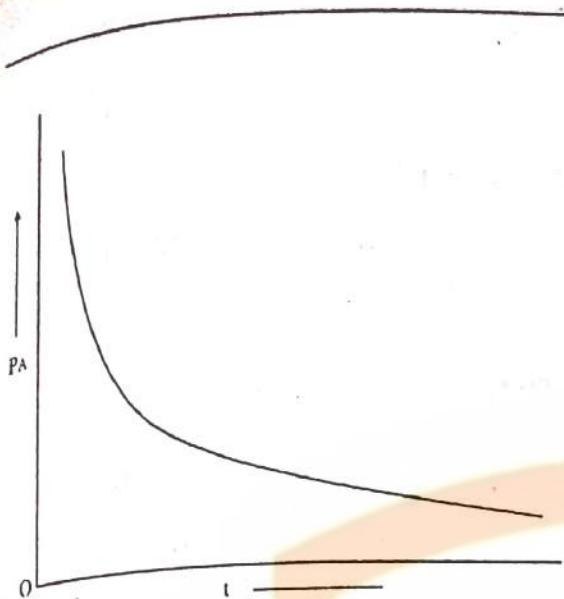


Fig. 6.17 Plot of pressure of gas A versus t in exponential form

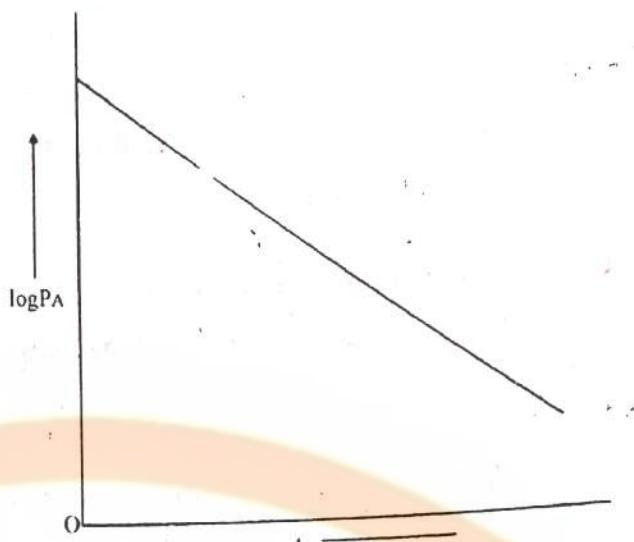


Fig. 6.18 Plot of $\log P_A$ versus t

(vii) By converting natural logarithm into common log of equation (6.34), we get

$$2.303 \log \frac{P_i}{P_A} = k_r b t$$

$$\log \frac{P_i}{P_A} = \frac{k_r b t}{2.303}$$

$$\log P_i - \log P_A = \left(\frac{k_r b}{2.303} \right) t$$

$$\log P_A - \log P_i = \left(-\frac{k_r b}{2.303} \right) t$$

$$\log P_A = \log P_i - \left(\frac{k_r b}{2.303} \right) t$$

This is an equation of straight line with intercept and having negative slope as shown in Fig. 6.18. The slope of the plot can be used to determine the value of k_r and intercept can be used to determine the value of initial pressure.

Relation between Homogenous and Heterogeneous Rate Constants

The kinetic rate equation for homogeneous 1st order reaction is

$$\ln \frac{P_i}{P_A} = kt \quad (6.37)$$

This is the rate law or kinetic rate equation for homogeneous 1st order reaction.

The kinetic rate equation for heterogeneous 1st order reaction is

$$\ln \frac{P}{P_A} = k_r b t \quad (6.38)$$

By comparing equation (6.37) and (6.38), we get

$$k = k_r b \quad (6.39)$$

Relation between $(E_a)_{w.a}$ and E_r

According to Arrhenius equation, we know

$$k = A e^{-\frac{E_a}{RT}} \quad (6.40)$$

Taking natural log of above equation,

$$\ln k = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln(A) \quad (6.41)$$

Differentiating equation (6.41) with respect to $1/T$

$$\begin{aligned} \frac{d \ln k}{d \frac{1}{T}} &= -\frac{E_a}{R} \frac{d}{d \frac{1}{T}} \left(\frac{1}{T} \right) + 0 \\ \frac{d \ln k}{d \frac{1}{T}} &= -\frac{E_a}{R} \\ E_a &= -R \frac{d \ln k}{d \frac{1}{T}} \end{aligned} \quad (6.42)$$

As $k = k_r b$ and if we put this value of k in equation (6.42), then E_a become $(E_a)_{w.a}$

$$\begin{aligned} (E_a)_{w.a} &= -R \frac{d(\ln k_r b)}{d \frac{1}{T}} \\ (E_a)_{w.a} &= -R \frac{d}{d \frac{1}{T}} (\ln k_r b) \\ (E_a)_{w.a} &= -R \frac{d}{d \frac{1}{T}} (\ln k_r + \ln b) \end{aligned} \quad (6.43)$$

According to Arrhenius equation, $k_r = A_r e^{-\frac{E_r}{RT}}$

$$\text{So, } (E_a)_{w.a} = -R \frac{d}{d \frac{1}{T}} \left[\ln A_r e^{-\frac{E_r}{RT}} + \ln \left(\frac{b_1}{b_2} \right) e^{-\frac{\Delta H_{rxn}}{RT}} \right]$$

$$\begin{aligned}
 (E_a)_{w.a} &= -R \frac{d}{dT} \left\{ \ln A_r - \frac{E_r}{RT} + \ln \left(\frac{b_1}{b_2} \right) - \frac{\Delta H_{Ads}}{RT} \right\} \\
 (E_a)_{w.a} &= -R \left\{ \frac{d}{dT} \ln A_r - \frac{E_r}{R} \left(\frac{d}{dT} \frac{1}{T} \right) + \frac{d}{dT} \ln \frac{b_1}{b_2} - \frac{\Delta H_{Ads}}{R} - \frac{d}{dT} \frac{1}{T} \right\} \\
 (E_a)_{w.a} &= -R \left\{ 0 - \frac{E_r}{R} + 0 - \frac{\Delta H_{Ads}}{R} \right\} \\
 (E_a)_{w.a} &= R \left\{ \frac{E_r + \Delta H_{Ads}}{R} \right\} \\
 (E_a)_{w.a} &= E_r + \Delta H_{Ads} \tag{6.44}
 \end{aligned}$$

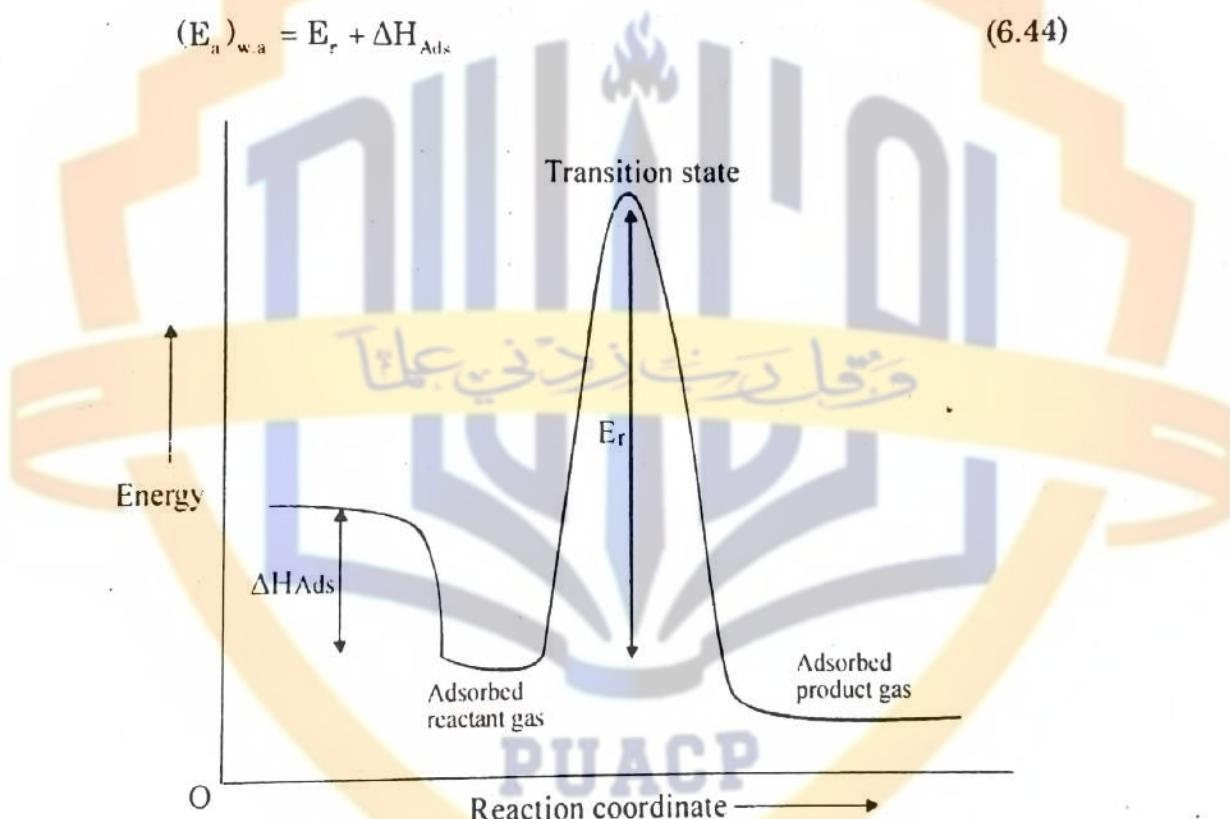


Fig. 6.19 Energy profile showing relative energy of weakly adsorbed gas

(ii) When Gas is Strongly Adsorbed

If gas is strongly adsorbed it means that b is very large so,

$$1 + bP_A \approx bP_A \tag{6.45}$$

As we know,

$$\text{Rate} = k \cdot \frac{bP_A}{1 + bP_A} \tag{6.46}$$

Applying approximation to equation (6.46) from equation (6.45), we get

$$\text{Rate} = k_r \quad (6.47)$$

It means that order of reaction is zero.

Rate can be expressed in terms of rate of decrease in pressure of gas A as

$$-\frac{dP_A}{dt} = k_r \quad (6.48)$$

Equation (6.48) is differential equation which can be solved by separating variables as

$$\begin{aligned} -\int dP_A &= k_r \cdot \int dt \\ -P_A &= k_r t + c \end{aligned} \quad (6.49)$$

Applying boundary conditions, when $t = 0$ then $P_A = P_i$

Put these values in equation (6.49), we get

$$-P_i = k_r(0) + c$$

$$c = -P_i$$

By putting the value of c in equation 6.49, we get

$$-P_A = k_r t - P_i$$

$$P_i - P_A = k_r t \quad (6.50)$$

Equation (6.50) is rate equation for heterogeneous reaction when gas is strongly adsorbed.

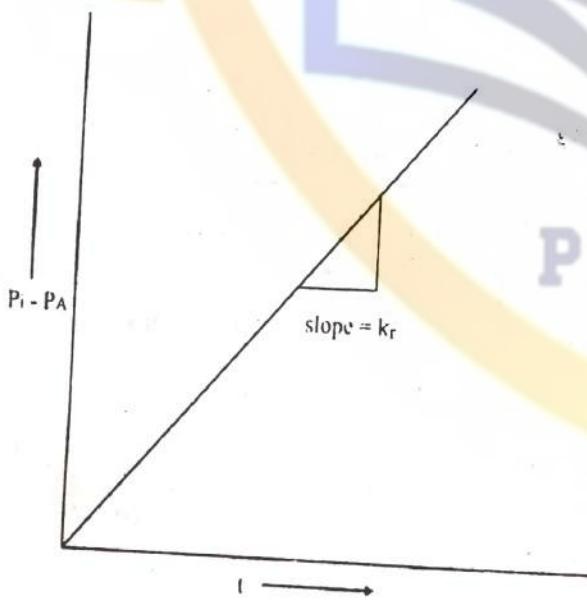


Fig. 6.20 Plot of $P_i - P_A$ as a function of time

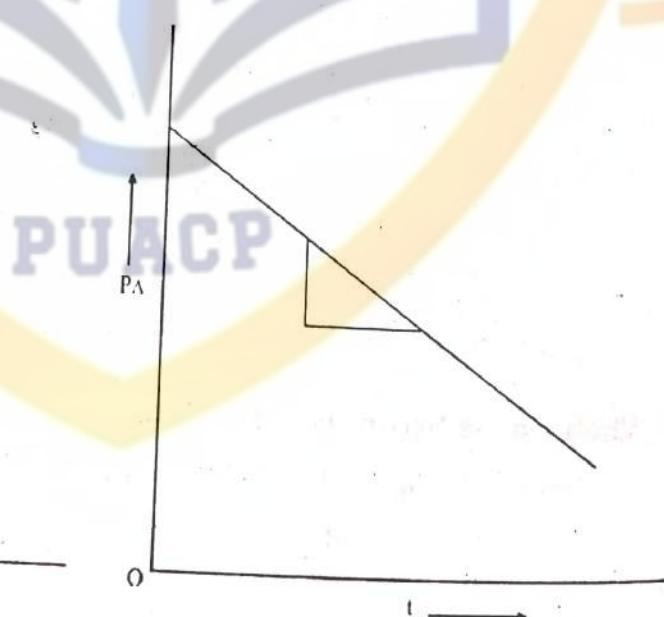


Fig. 6.21 Plot of P_A versus t with intercept and negative slope value

Results concluded from equation (6.50) are as follows

- (i) Equation 6.50 is straight line equation passing through origin.
- (ii) Plot of $\ln(P_i - P_A)$ versus t as shown in Fig. 6.20.
- (iii) The value of k_r can be determined from the slope of the plot as shown in Fig. 6.20.

$$\text{slope} = k_r$$

- (iv) The half life period of gas A can be expressed as:

$$t = t_{1/2} \text{ at } P_A = P_i/2$$

Applying this condition to equation (6.50)

$$P_i - \frac{P_i}{2} = k_r t_{1/2}$$

$$\frac{P_i}{2} = k_r t_{1/2}$$

$$t_{1/2} = \frac{P_i}{2k_r} \quad (6.51)$$

Results can be drawn from equation (6.51) as follows: $t_{1/2}$ is not a function of b , $t_{1/2}$ is a function of P_i and $t_{1/2}$ is a function of temperature because k_r is a function of temperature.

- (v) Rearranging equation (6.50), we get

$$P_A - P_i = -k_r t$$

$$P_A = P_i - k_r t \quad (6.52)$$

Equation (6.52) is an equation of straight line in intercept form with slope equal to $-k_r$ and intercept equal to P_i as shown in Fig. 6.21.

Relation between Homogeneous and Heterogeneous Rate Constants

The kinetic rate equation for homogeneous zero order reaction is given as

$$P_i - P_A = kt \quad (6.53)$$

The kinetic rate equation for heterogeneous zero order reaction is

$$P_i - P_A = k_r t \quad (6.54)$$

By comparing equations (6.53) and (6.54) we get,

$$k = k_r \quad (6.55)$$

Relation between $(E_a)_{s.a}$ and E_r

According to Arrhenius equation,

$$k = Ae^{-\frac{E_a}{RT}}$$

Taking natural logarithm of above equation,

$$\ln k = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln(A)$$

Differentiating above equation with respect to $1/T$

$$\frac{d \ln k}{d \frac{1}{T}} = -\frac{E_a}{R} \frac{d}{d \frac{1}{T}} \left(\frac{1}{T} \right) + 0$$

$$\frac{d \ln k}{d \frac{1}{T}} = -\frac{E_a}{R}$$

$$E_a = -R \frac{d}{d \frac{1}{T}} (\ln k) \quad (6.56)$$

As $k = k_r$ and if we put this value of k in equation (6.56), then E_a become $(E_a)_{s.a}$

$$(E_a)_{s.a} = -R \frac{d}{d \frac{1}{T}} (\ln k_r) \quad (6.57)$$

According to Arrhenius equation, $k_r = A_r e^{-\frac{E_r}{RT}}$

By putting value of k_r in equation (6.57), we get

$$(E_a)_{s.a} = -R \frac{d}{d \frac{1}{T}} \left(\ln A_r e^{-\frac{E_r}{RT}} \right)$$

$$(E_a)_{s.a} = -R \frac{d}{d \frac{1}{T}} \left(\ln A_r - \frac{E_r}{RT} \right)$$

$$(E_a)_{s.a} = -R \left\{ \frac{d}{d \frac{1}{T}} \ln A_r - \frac{E_r}{R} \left(\frac{d}{d \frac{1}{T}} \frac{1}{T} \right) \right\}$$

$$(E_a)_{s.a} = -R \left\{ 0 - \frac{E_r}{R} \right\}$$

$$(E_a)_{s.a} = -R \left(-\frac{E_r}{R} \right)$$

$$(E_a)_{s.a} = E_r \quad (6.58)$$

(iii) When Gas is Moderately Adsorbed

When gas is moderately adsorbed the order of reaction will be in between of zero and 1st order of reaction. It can be 0.1, 0.2, 0.3 ... 0.9.

6.7 LANGMUIR ADSORPTION ISOTHERM FOR DOUBLE SYSTEM

Some adsorbents have an ability to adsorb more than one gas. Langmuir adsorption isotherm for simultaneous adsorption of two gases on an adsorbent can be derived on the basis of same postulates as given in section 6.5.2. in such system, extent of adsorption of a gas is affected by the presence of another gas. For example we have two gases A and B in a container which are going to be adsorbed on a single adsorbent as shown in Fig. 6.22. At any stage of adsorption,

$$\theta_A = \text{Fractional surface covered by gas A}$$

$$\theta_B = \text{Fractional surface covered by gas B}$$

$$(1 - \theta_A - \theta_B) = \text{Fraction of available sites}$$

Rate of adsorption of gas A is proportional to P_A and $1 - \theta_A - \theta_B$

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

$$R_{\text{Ad}} \propto (1 - \theta_A - \theta_B)$$

Combining above relations,

$$R_A \propto P_A (1 - \theta_A - \theta_B)$$

$$R_A \propto k_1 P_A (1 - \theta_A - \theta_B) \quad (6.59)$$

R_{Des} of gas A is proportional to fractional surface coverage of gas A.

$$R_{\text{Des}} \propto \theta_A$$

$$R_{\text{Des}} = k_2 \theta_A \quad (6.60)$$

At equilibrium, rate of adsorption becomes equal to rate of desorption of gas A as given below

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

$$k_1 P_A (1 - \theta_A - \theta_B) = k_2 \theta_A \quad (6.61)$$

The rate of adsorption of gas B is directly proportional to pressure of gas B and fraction of available sites.

$$R_{\text{Ad}} \propto P_B$$

$$R_{\text{Ad}} \propto (1 - \theta_A - \theta_B)$$

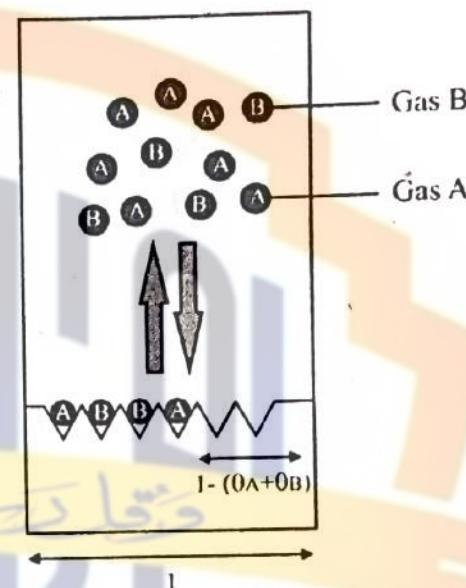


Fig. 6.22 Pictorial diagram of adsorption of two gases on solid surface

(6.59)

Combining above relations,

$$\text{Rate} \propto P_A (1 - \theta_A - \theta_B)$$

$$R_{\text{Ads}} = k_3 P_B (1 - \theta_A - \theta_B) \quad (6.62)$$

The rate of desorption of gas B is proportional to fractional surface coverage of gas B.

$$R_{\text{Des}} \propto \theta_B$$

$$R_{\text{Des}} = k_4 \theta_B \quad (6.63)$$

At equilibrium,

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

$$k_3 P_B (1 - \theta_A - \theta_B) = k_4 \theta_B \quad (6.64)$$

$$k_4 \theta_B = k_3 P_B - k_3 P_B \theta_A - k_3 P_B \theta_B$$

$$k_4 \theta_B + k_3 P_B \theta_B = k_3 P_B - k_3 P_B \theta_A$$

$$\theta_B (k_4 + k_3 P_B) = k_3 P_B - k_3 P_B \theta_A$$

$$\theta_B = \frac{k_3 P_B (1 - \theta_A)}{k_4 + k_3 P_B} \quad (6.65)$$

By putting value of θ_B from equation (6.65) into equation (6.61), we get

$$k_2 \theta_A = k_1 P_A \left[1 - \theta_A - \frac{k_3 P_B (1 - \theta_A)}{k_4 + k_3 P_B} \right]$$

$$k_2 \theta_A = k_1 P_A \left[\frac{k_4 + k_3 P_B (1) - (k_4 + k_3 P_B) \theta_A - k_3 P_B (1) + k_3 P_B (\theta_A)}{k_4 + k_3 P_B} \right]$$

$$k_2 \theta_A = k_1 P_A \left[\frac{\cancel{k_4 + k_3 P_B} - \cancel{k_4 \theta_A} + \cancel{k_3 P_B \theta_A} - \cancel{k_3 P_B} - \cancel{k_3 P_B \theta_A}}{\cancel{k_4 + k_3 P_B}} \right]$$

$$k_2 \theta_A = k_1 P_A \left[\frac{k_4 - k_4 \theta_A}{k_4 + k_3 P_B} \right]$$

$$k_2 \theta_A = k_1 P_A \left[\frac{k_4 (1 - \theta_A)}{k_4 + k_3 P_B} \right]$$

$$k_2 \theta_A (k_4 + k_3 P_B) = k_1 k_4 P_A (1 - \theta_A)$$

$$k_2 \theta_A (k_4 + k_3 P_B) = k_1 k_4 P_A - k_1 k_4 P_A \theta_A$$

$$k_2 \theta_A (k_4 + k_3 P_B) + k_1 k_4 P_A \theta_A = k_1 k_4 P_A$$

$$\theta_A \{k_2(k_4 + k_3 P_B) + k_1 k_4 P_A\} = k_1 k_4 P_A$$

$$\theta_A = \frac{k_1 k_4 P_A}{k_2(k_4 + k_3 P_B) + k_1 k_4 P_A}$$

$$\theta_A = \frac{k_1 k_4 P_A}{k_2 k_4 + k_2 k_3 P_B + k_1 k_4 P_A} \quad (6.66)$$

Divide numerator and denominator by $k_2 k_4$, we get

$$\theta_A = \frac{\frac{k_1}{k_2} P_A}{1 + \frac{k_3}{k_4} P_B + \frac{k_1}{k_2} P_A} \quad (6.67)$$

$\frac{k_1}{k_2} = a$ = Adsorption coefficient for gas A

$\frac{k_3}{k_4} = b$ = Adsorption coefficient for gas B

So, equation (6.67) becomes

$$\theta_A = \frac{a P_A}{1 + a P_A + b P_B} \quad (6.68)$$

By putting value of θ_A in equation (6.65) from equation (6.68), we get

$$\begin{aligned} \theta_B &= \frac{k_3 P_B}{k_4 + k_3 P_B} \left[1 - \frac{a P_A}{1 + a P_A + b P_B} \right] \\ \theta_B &= \frac{k_3 P_B}{k_4 + k_3 P_B} \left[\frac{1 + a P_A + b P_B - a P_A}{1 + a P_A + b P_B} \right] \\ \theta_B &= \frac{k_3 P_B}{k_4 + k_3 P_B} \left[\frac{1 + b P_B}{1 + a P_A + b P_B} \right] \end{aligned} \quad (6.69)$$

Divide numerator and denominator of equation (6.69) by k_4

$$\theta_B = \frac{\frac{k_3 P_B}{k_4}}{\frac{k_4}{k_4} + \frac{k_3 P_B}{k_4}} \left[\frac{1 + b P_B}{1 + a P_A + b P_B} \right]$$

$$\theta_B = \frac{\frac{k_3}{k_4} P_B}{1 + \frac{k_3}{k_4} P_B} \left[\frac{1 + b P_B}{1 + a P_A + b P_B} \right]$$

As we know, $\frac{k_3}{k_4} = b$. So

$$\theta_B = \frac{bP_B}{1+bP_B} \left[\frac{1+bP_B}{1+aP_A + bP_B} \right]$$

$$\theta_B = \frac{bP_B}{1+aP_A + bP_B} \quad (6.70)$$

Equation (6.68) and (6.70) can be used to find θ_A and θ_B .

According to equation (6.68) and (6.70) adsorption of gas A and B depends upon the adsorption coefficients of gas A and B, and on the pressure of gas A and B.

- (i) When both gases are weakly adsorbed then, $1 + bP_B + aP_A \approx 1$. By putting this in equation (6.68)

$$\theta_A = aP_A$$

$$\theta_A \propto P_A$$

By putting above approximation in equation (6.70), we get

$$\theta_B = bP_B$$

$$\theta_B \propto P_B$$

It means that when both gases are weakly adsorbed then adsorption of one gas is not affected by the other.

- (ii) When gas A is strongly adsorbed then, $1 + bP_B + aP_A \approx aP_A$. By putting this approximation in equation (6.68), we get

$$\theta_A = \frac{aP_A}{aP_A}$$

$$\theta_A = 1 = \text{Constant}$$

Similarly by putting this approximation in equation (6.70), we get

$$\theta_B = \frac{bP_B}{aP_A}$$

$$\theta_B \propto \frac{P_B}{P_A}$$

So, when gas is strongly adsorbed than the other gas, then all surface which is covered by strongly adsorbed gas which will retard the adsorption of the other gas.

- (iii) If both gases are strongly adsorbed then, $1 + bP_B + aP_A \approx aP_A + bP_B$. By putting in equation (6.68)

$$\theta_A = \frac{aP_A}{aP_A + bP_B}$$

By putting above approximation in equation (6.70), we get

$$\theta_B \approx \frac{bP_B}{aP_A + bP_B}$$

So, when both gases are strongly adsorbed then extent of adsorption of gas is strongly affected by the presence of the other.

6.8 CATALYTIC REACTION OF TWO GASES ON SOLID SURFACE

Generally following steps are involved in catalytic reaction of two gases on solid surface.

- (i) Diffusion of reactant towards solid surface
- (ii) Adsorption of reactant on solid surface
- (iii) Product formation after interaction of reactants
- (iv) Desorption of product
- (v) Diffusion of product towards gas phase

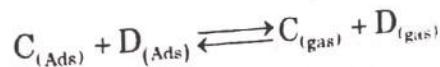
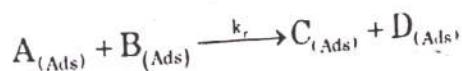
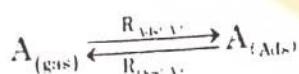
Catalytic reaction of two gases on a solid surface can take place by one of the following mechanisms: Langmuir Hinshelwood mechanism or Eiley-Rideal mechanism

6.8.1 Langmuir-Hinshelwood Mechanism

Langmuir Hinshelwood mechanism involves the following steps

- (i) Diffusion of reactant gases towards solid surface of catalyst.
- (ii) Interaction of adsorbed reactant gases on catalyst surface.
- (iii) Product formed after interaction of reactants.
- (iv) Desorption of product occurs, which is followed by diffusion of product towards gas phase.

Steps of Langmuir Hinshelwood Mechanism in the Form of Chemical Equations



According to Langmuir Hinshelwood mechanism, the rate of reaction is proportional to fraction of surface covered by A and B i.e.

$$\text{Rate of reaction} \propto \theta_A$$

(6.71)

$$\text{Rate of reaction} \propto \theta_B \quad (6.72)$$

Combining equation (6.71) and (6.72), we get

$$\text{Rate of reaction} = k_r \theta_A \theta_B \quad (6.73)$$

From equation (6.68) and (6.70) by putting values of θ_A and θ_B in equation (6.73)

$$R_{\text{rex}} = k_r \frac{(aP_A)(bP_B)}{(1 + aP_A + bP_B)^2}$$

$$R_{\text{rex}} = k_r \frac{abP_A P_B}{(1 + aP_A + bP_B)^2} \quad (6.74)$$

Equation (6.74) is the rate expression for the catalytic reaction of two gases on solid following Langmuir-Hinshelwood mechanism.

Depending upon value of adsorption coefficients of gas A and B, following approximations are concluded

- (i) When both gases are weakly adsorbed then, $1 + aP_A + bP_B \approx 1$ by putting this approximation in equation (6.74), we get

$$R_{\text{rex}} = k_r abP_A P_B$$

$$R_{\text{rex}} \propto P_A P_B$$

It is the equation for second order reaction.

- (ii) When gas A is strongly adsorbed then, $1 + aP_A + bP_B \approx aP_A$. Putting this approximation in equation (6.74), we get

$$R_{\text{rex}} = k_r (ab) \frac{P_A P_B}{(aP_A)^2}$$

$$R_{\text{rex}} = k_r \frac{(ab)}{a^2} \frac{P_A P_B}{P_A^2}$$

$$R_{\text{rex}} = k_r \frac{b}{a} \frac{P_B}{P_A}$$

So, overall order of reaction is zero because order of reaction with respect to A is -1 while order of reaction with respect to B is 1.

The increase in pressure of gas A will decrease the rate of reaction when A is strongly adsorbed. This reduction in rate of reaction is known as "retardation by reactants". Retardation is not only caused by strong adsorption of one reactant gas, high pressure of one of the reactant gases can also cause retardation. For example at constant value of P_B , rate of reaction increases with the increase of P_A upto a certain value. But further increase in pressure of gas A causes reduction in rate of reaction i.e.

If $P_B = \text{constant}$ and $P_A = \text{variable}$ then

(i) When P_A is very low then, $1 + aP_A + bP_B \approx 1 + bP_B$ equation (6.74) will be

$$R_{\text{rea}} = k_r \frac{abP_A P_B}{(1 + bP_B)^2}$$

So, rate of reaction increases with P_A within low range value of P_A

(ii) When P_A is very high then, $1 + aP_A + bP_B \approx aP_A$ the equation (6.74) will be

$$R_{\text{rea}} = k_r (ab) \frac{P_A P_B}{(aP_A)^2}$$

$$R_{\text{rea}} = k_r \frac{b}{a} \frac{P_B}{P_A} \quad (\text{Retardation by reactants})$$

So, rate of reaction decreases with high value of P_A .

The value of P_A for which rate of reaction is maximum is called $P_{A(\text{max})}$. After $P_{A(\text{max})}$, retardation by reactant starts as shown in Fig. 6.23.

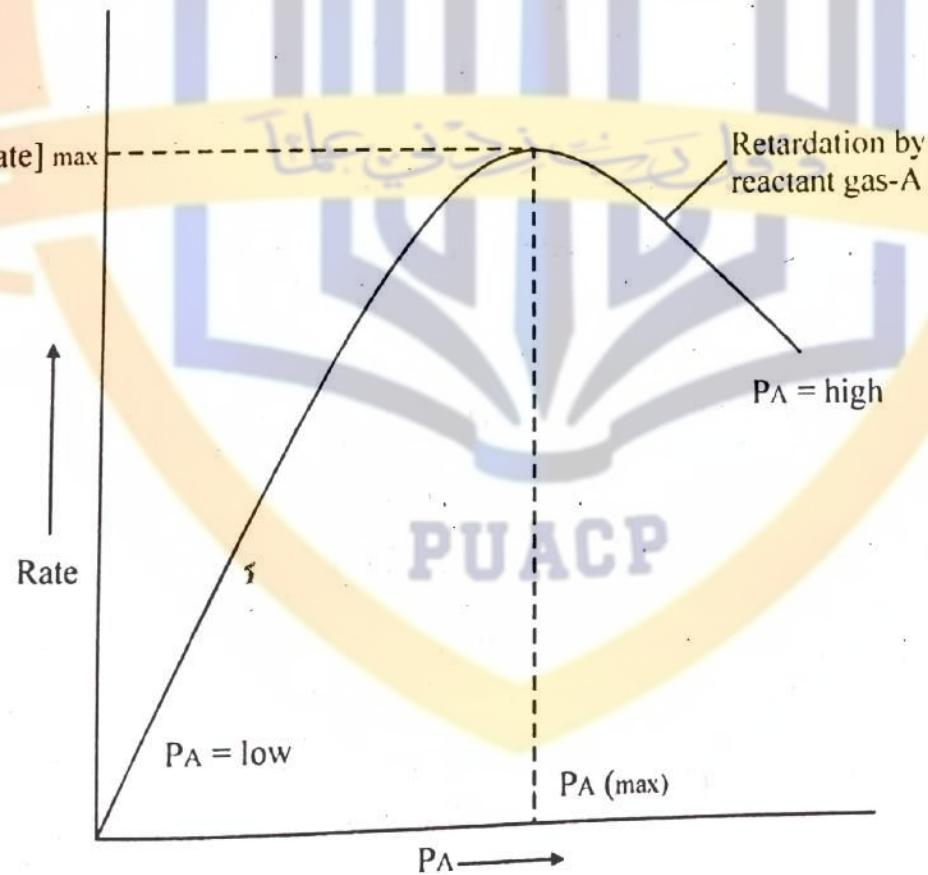


Fig. 6.23 Plot of rate of reaction versus pressure of gas A

Differentiating equation (6.74) with respect to "P_A"

$$\frac{d[\text{Rate}]}{dP_A} = k_r abP_B \frac{d}{dP_A} \left[\frac{P_A}{(1 + aP_A + bP_B)^2} \right]$$

$$\frac{d[\text{Rate}]}{dP_A} = k_r ab P_B \frac{d}{dP_A} [P_A (1 + aP_A + bP_B)^{-2}]$$

By applying product rule,

$$\frac{d[\text{Rate}]}{dP_A} = k_r ab P_B \left[P_A \cdot \frac{d(1 + aP_A + bP_B)^{-2}}{dP_A} + (1 + aP_A + bP_B)^{-2} \frac{dP_A}{dP_A} \right]$$

$$\frac{d[\text{Rate}]}{dP_A} = k_r ab P_B \left[P_A (-2)(1 + aP_A + bP_B)^{-3} \frac{d}{dP_A} (1 + aP_A + bP_B) + (1 + aP_A + bP_B)^{-2} (1) \right]$$

$$\frac{d[\text{Rate}]}{dP_A} = k_r ab P_B \left[\frac{-2P_A}{(1 + aP_A + bP_B)^3} \left(\frac{d}{dP_A} (1) + a \frac{dP_A}{dP_A} + b \frac{dP_B}{dP_A} \right) + (1 + aP_A + bP_B)^{-2} (1) \right]$$

The derivative of constant is zero. Hence, above equation become,

$$\frac{d[\text{Rate}]}{dP_A} = k_r ab P_B \left[\frac{-2aP_A}{(1 + aP_A + bP_B)^3} + \frac{1}{(1 + aP_A + bP_B)^2} \right]$$

At $[\text{Rate}]_{\text{max}}$, the slope of graph is zero and $P_A = P_{A(\text{max})}$

$$0 = k_r ab P_B \left[\frac{-2aP_{A(\text{max})}}{(1 + aP_{A(\text{max})} + bP_B)^3} + \frac{1}{(1 + aP_{A(\text{max})} + bP_B)^2} \right] \quad (6.75)$$

Equation (6.75) is a product of two quantities which is equal to zero. One quantity on L.H.S must be zero, constant $k_r ab P_B$ can't be zero. So,

$$0 = \left[\frac{1}{(1 + aP_{A(\text{max})} + bP_B)^2} - \frac{2aP_{A(\text{max})}}{(1 + aP_{A(\text{max})} + bP_B)^3} \right]$$

$$\frac{2aP_{A(\text{max})}}{(1 + aP_{A(\text{max})} + bP_B)^3} = \frac{1}{(1 + aP_{A(\text{max})} + bP_B)^2}$$

$$2aP_{A(\text{max})} = \frac{(1 + aP_{A(\text{max})} + bP_B)^3}{(1 + aP_{A(\text{max})} + bP_B)^2}$$

$$2aP_{A(\text{max})} = (1 + aP_{A(\text{max})} + bP_B)$$

$$2aP_{A(\text{max})} - aP_{A(\text{max})} = 1 + bP_B$$

$$aP_{A(\text{max})} = 1 + bP_B$$

$$P_{A(\text{max})} = \frac{1 + bP_B}{a} \quad (6.76)$$

Using equation (6.76), we can calculate the value of pressure of gas A at which rate of reaction is maximum. The retardation caused by high pressure of gas A is not much significant, %age decline in rate of reaction from $P_{A(\max)}$ to $2P_{A(\max)}$ is only 11.1%. It can be proved mathematically as

Rate of Reaction at $P_A = P_{A(\max)}$

$$[\text{Rate}]_{P_A = P_{A(\max)}} = k_r ab \left[\frac{P_{A(\max)} P_B}{(1 + aP_{A(\max)} + bP_B)^2} \right] \quad (6.77)$$

Putting value of $P_{A(\max)}$ from equation (6.76) into equation (6.77), we get

$$[\text{Rate}]_{P_A = P_{A(\max)}} = k_r ab \left[\frac{\left(\frac{1 + bP_B}{a} \right) P_B}{\left(1 + a \left(\frac{1 + bP_B}{a} \right) + bP_B \right)^2} \right]$$

$$[\text{Rate}]_{P_A = P_{A(\max)}} = k_r \frac{ab}{a} \left[\frac{(1 + bP_B) P_B}{(1 + (1 + bP_B) + bP_B)^2} \right]$$

$$[\text{Rate}]_{P_A = P_{A(\max)}} = k_r b \left[\frac{(1 + bP_B) P_B}{(2 + 2bP_B)^2} \right]$$

$$[\text{Rate}]_{P_A = P_{A(\max)}} = \frac{k_r b}{4} \left[\frac{(1 + bP_B) P_B}{(1 + bP_B)^2} \right]$$

$$[\text{Rate}]_{P_A = P_{A(\max)}} = \frac{k_r b}{4} \left[\frac{P_B}{(1 + bP_B)} \right] \quad (6.78)$$

Rate of Reaction at $P_A = 2P_{A(\max)}$

$$[\text{Rate}]_{P_A = 2P_{A(\max)}} = k_r ab \left[\frac{2P_{A(\max)} P_B}{(1 + a2P_{A(\max)} + bP_B)^2} \right] \quad (6.79)$$

Putting value of $P_{A(\max)}$ from equation (6.76) into equation (6.79), we get

$$[\text{Rate}]_{P_A = 2P_{A(\max)}} = k_r ab \left[\frac{2 \left(\frac{1 + bP_B}{a} \right) P_B}{\left(1 + 2a \left(\frac{1 + bP_B}{a} \right) + bP_B \right)^2} \right]$$

$$[\text{Rate}]_{P_A = 2P_{A(\max)}} = 2k_r b \left[\frac{(1 + bP_B) P_B}{(1 + 2(1 + bP_B) + bP_B)^2} \right]$$

$$[\text{Rate}]_{P_A = 2P_{A(\max)}} = 2k_r b \left[\frac{(1+bP_B)P_B}{(1+2+2bP_B+bP_B)^2} \right]$$

$$[\text{Rate}]_{P_A = 2P_{A(\max)}} = 2k_r b \left[\frac{(1+bP_B)P_B}{(3+3bP_B)^2} \right]$$

$$[\text{Rate}]_{P_A = 2P_{A(\max)}} = \frac{2}{9} k_r b \frac{(1+bP_B)P_B}{(1+bP_B)^2}$$

$$[\text{Rate}]_{P_A = 2P_{A(\max)}} = \frac{2k_r b}{9} \frac{P_B}{(1+bP_B)} \quad (6.80)$$

Percentage of rate at $P_A = 2P_{A(\max)}$

$$\% \text{age Rate} = \frac{[\text{Rate}]_{P_A = 2P_{A(\max)}}}{[\text{Rate}]_{P_A = P_{A(\max)}}} \times 100 \quad (6.81)$$

Substituting values of $[\text{Rate}]_{P_A = 2P_{A(\max)}}$ and $[\text{Rate}]_{P_A = P_{A(\max)}}$

$$\% \text{age Rate} = \frac{\frac{2}{9} k_r b (P_B)}{\frac{k_r b}{4} \left(\frac{P_B}{1+bP_B} \right)} \times 100$$

$$\% \text{age Rate} = \frac{\frac{2}{9}}{\frac{1}{4}} \times 100$$

$$\% \text{age Rate} = \frac{2 \times 4}{9} \times 100$$

$$\% \text{age Rate} = \frac{8}{9} \times 100$$

$$\% \text{age Rate} = 88.9\%$$

$$\% \text{age decline in rate} = 100 - 88.9 = 11.1\% \text{ of maximum rate}$$

"The decline in rate is difference or reduction in rate when pressure changes from $P_A = P_{A(\max)}$ to $P_A = 2P_{A(\max)}$ " as shown in Fig. 6.24.

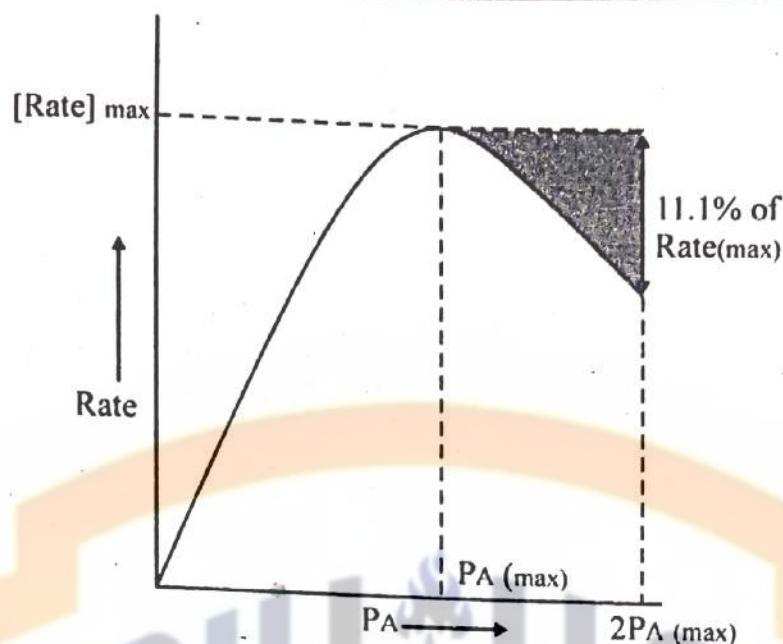


Fig. 6.24 Rate of reaction as a function of P_A showing decline rate at $2P_{A(\max)}$

Example 6.4

A catalytic reaction following Langmuir Hinshelwood mechanism was carried out in a container containing solid catalyst at a constant pressure of gas B equal to 200 Pa. The values of adsorption coefficients of gas A and B are 0.2 and 0.35 Pa^{-1} respectively. Calculate the value of P_A , at which the rate of reaction is maximum.

Solution

The value of P_A at which the rate of reaction is maximum i.e. $P_{A(\max)}$, can be calculated using equation (6.76), according to which

$$P_{A(\max)} = \frac{1 + bP_B}{a}$$

$$P_{A(\max)} = \frac{1 + (0.35)(200)}{0.2} = 355 \text{ Pa}$$

6.8.2 Eiley-Rideal Mechanism

Eiley-Rideal mechanism involves the following steps

- (i) One reactant get adsorb on surface of catalyst.
- (ii) Second reactant doesn't adsorb on catalyst surface. Instead it interact with adsorb reactant. In E-R mechanism, both reactants adsorb on catalyst surface. This is different from Langmuir-Hinshelwood mechanism. In L-H mechanism both reactants adsorb on catalyst surface.
- (iii) After interaction products are formed. Later adsorbed product diffuses into reaction vessel after desorption.

However, product can remain in gaseous state and doesn't adsorb on catalyst surface in E-R mechanism.

Scheme of Eiley-Rideal (E-R) Mechanism

Reactant gases A and B are going to be converted into products C and D by following mechanism according to E-R mechanism.



According to E-R mechanism, rate of reaction is directly proportional to fraction of the surface covered by gas A and pressure of gas B, because adsorbed molecules of gas A interact with gaseous B to form product i.e.

$$\text{Rate of reaction} \propto \theta_A$$

$$\text{Rate of reaction} \propto P_B$$

Hence,

$$\text{Rate of reaction} = k_r \theta_A P_B \quad (6.82)$$

Rate of reaction is independent of P_A , as θ_A depends upon P_A . For double system, we have

$$\theta_A = \frac{aP_A}{1 + aP_A + bP_B}$$

Then equation (6.82) will be

$$\text{Rate} = k_r \frac{aP_A P_B}{1 + aP_A + bP_B} \quad (6.83)$$

This is a rate law expression for the catalytic reaction of two gases on solid surface following E-R mechanism. Since, B is not an adsorbing specie so, $b \approx 0$ then,

$$1 + aP_A + bP_B \approx 1 + aP_A$$

So, equation (6.83) will be,

$$\text{Rate} = k_r \frac{aP_A P_B}{1 + aP_A}$$

$$\text{Rate} = k_r \left(\frac{aP_A}{1 + aP_A} \right) P_B \quad (6.84)$$

Terms in bracket is related to gas A, it has factor aP_A which can increase or decrease rate of reaction. We reach at following results

- (i) When the partial pressure of gas A is very low then, $1 + aP_A \approx 1$. So, equation (6.84) will be,

$$\text{Rate} = k_r aP_A P_B$$

If partial pressure of gas A is low, then reaction will be 2nd order reaction.

(ii) When pressure of gas A is very high then, $1 + aP_A \approx aP_A$. So, equation (6.84) will be,

$$\text{Rate} = k_r \frac{aP_A P_B}{aP_A}$$

$$\text{Rate} = k_r P_B$$

Above equation shows, when P_A is very high, then reaction will be 1st order. It also shows that, when P_A is very high then rate of reaction is independent of extent of adsorption of gas A.

6.9 CATALYTIC INORGANIC REACTIONS

6.9.1 Catalytic Oxidation of Carbon Monoxide (CO)

Carbon monoxide can be converted into carbon dioxide by heterogeneous catalysis i.e.



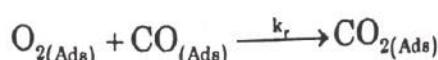
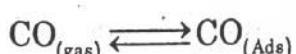
Important features of reaction are as follows

It is a heterogenous catalytic reaction because catalyst is in solid form and reactants are in gaseous phase. It is a simple reaction and can be considered as an example of double system. In this case both reactants are diatomic molecules. One reactant is a homonuclear i.e. O_2 having non polar nature while, CO is heteronuclear as having two different atoms having slightly polar nature. CO is strongly adsorbed on platinum surface because it is π acceptor ligand and has polar nature. O_2 is weakly adsorbed as it is non polar and has no π acceptor ligand ability. So, it can't easily form strong bond with catalyst, e.g. Pt, Pd etc.

The experimental rate law computed by earlier studies is

$$\text{Rate} \propto \frac{P_{\text{O}_2}}{P_{\text{CO}}}$$

According to Langmuir Hinshelwood mechanism, the reaction scheme can be written as



(6.85)

$$R_{\text{rex}} \propto \theta_{\text{O}_2}$$

(6.86)

$$R_{\text{rex}} \propto \theta_{\text{CO}}$$

By combining equations (6.85) and (6.86)

$$\begin{aligned} R_{\text{rea}} &\propto \theta_{O_2} \theta_{CO} \\ R_{\text{rea}} &= k_r \theta_{O_2} \theta_{CO} \end{aligned} \quad (6.87)$$

Putting values of θ_{O_2} and θ_{CO} in equation (6.87),

$$R_{\text{rea}} = k_r \frac{(aP_{O_2})(bP_{CO})}{(1 + aP_{O_2} + bP_{CO})^2} \quad (6.88)$$

As CO is strongly adsorbed, so $b \ggg a$. Then $1 + aP_{O_2} + bP_{CO} \approx bP_{CO}$. By putting this approximation in equation (6.88), we get

$$R_{\text{rea}} = k_r \frac{abP_{O_2} P_{CO}}{(bP_{CO})^2}$$

$$R_{\text{rea}} = k_r \frac{a}{b} \left(\frac{P_{O_2}}{P_{CO}} \right)$$

As k_r and a/b are constants. So,

$$\text{Rate} \propto \frac{P_{O_2}}{P_{CO}}$$

Hence rate of formation of CO_2 is first order with respect to P_{O_2} and negative first order with respect to P_{CO} . So it is a zero order reaction.

6.9.2 Catalytic Decomposition of Ammonia (NH_3)

Ammonia is commercially produced by Haber's process which is a catalytic process. Its synthesis reaction is reversible. Nitrogen gas (N_2) and hydrogen gas (H_2) are produced on decomposition of ammonia.



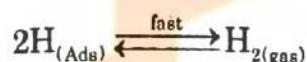
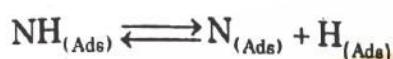
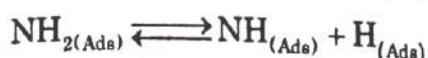
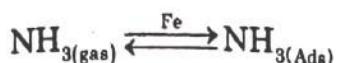
Important features of reaction are as follows

It is a catalytic reaction which is an example of heterogeneous catalysis because catalyst is in solid state and reactant is in gaseous state. Catalyst used in this reaction may be Pt, Pd, and Fe. But Pt and Pd are expensive, so Fe is used on industrial scale. It is a reversible process, so catalyst increases rate of formation as well as rate of decomposition of NH_3 .

It is experimentally proved that the rate of decomposition of ammonia is directly related to pressure of ammonia and inversely proportional to pressure of hydrogen by the expression given below.

$$\text{Rate of decomposition of } NH_3 \propto \frac{P_{NH_3}^m}{P_{H_2}^n} \quad (6.89)$$

One of the suggested mechanisms for catalytic decomposition of NH_3 on the iron (Fe) surface is stepwise removal of hydrogen atom from NH_3 molecule. The scheme of the reaction is given below.



Desorption of nitrogen is rate determining step. So, rate of decomposition of ammonia depends upon this step.

Tempkin Adsorption Isotherm for Decomposition of NH_3

Tempkin gave an adsorption isotherm to explain the adsorption-desorption of nitrogen on iron surface. According to this isotherm, rate of adsorption and desorption are exponentially related to fractional surface coverage.

$$R_{\text{Ads}} \propto P_{\text{N}_2}$$

$$R_{\text{Ads}} \propto \frac{1}{e^{g\theta_N}}$$

Where, "g" is a roughness factor which indicates heterogeneity of surface of adsorbent and related to activation energy of adsorption. θ_N is fractional surface coverage of nitrogen gas.

$$R_{\text{Ads}} = k_a \frac{P_{\text{N}_2}}{e^{g\theta_N}}$$

$$R_{\text{Ads}} = k_a P_{\text{N}_2} e^{-g\theta_N} \quad (6.90)$$

By increasing P_{N_2} , R_{Ads} increases. But by increasing θ_N , R_{Ads} decreases exponentially.

Rate of desorption of nitrogen is

$$R_{\text{Des}} \propto e^{h\theta_N}$$

$$R_{\text{Des}} = k_d e^{h\theta_N} \quad (6.91)$$

Rate of desorption of nitrogen is exponentially related to fractional surface coverage of nitrogen (θ_N).

At equilibrium stage, rate of adsorption becomes equal to rate of desorption of nitrogen as

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

$$k_a P_{N_2} e^{-g\theta_N} = k_d e^{h\theta_N}$$

$$\frac{k_a}{k_d} P_{N_2} = \frac{e^{h\theta_N}}{e^{-g\theta_N}}$$

As, $a = \frac{k_a}{k_d}$ so, above equation becomes

$$aP_{N_2} = e^{h\theta_N} e^{g\theta_N}$$

$$aP_{N_2} = e^{\theta_N(h+g)}$$

$$\text{Let, } h + g = f$$

$$aP_{N_2} = e^{\theta_N f}$$

Taking natural logarithm of above equation

$$\ln(aP_{N_2}) = \ln(e^{\theta_N f})$$

$$\ln(aP_{N_2}) = f\theta_N$$

$$\theta_N = \frac{\ln(aP_{N_2})}{f} \quad (6.92)$$

From equation (6.92) putting the value of θ_N into equation (6.91), we get

$$R_{\text{Des}} = k_d e^{h \left(\frac{1}{f} \ln(aP_{N_2}) \right)}$$

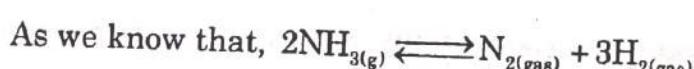
$$R_{\text{Des}} = k_d e^{\ln(aP_{N_2}) \frac{h}{f}}$$

$$R_{\text{Des}} = k_d \left(aP_{N_2} \right)^{\frac{h}{f}} \quad (6.93)$$

$$\text{As, } (R_{\text{Des}})_{N_2} = (R_{\text{Decomposition}})_{NH_3}$$

Then, equation (6.93) will be,

$$(R_{\text{Decomposition}})_{NH_3} = k_d \left(aP_{N_2} \right)^{\frac{h}{f}} \quad (6.94)$$



$$K = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3}$$

Where, K is the equilibrium constant.

$$P_{N_2} = \frac{P_{NH_3}^2}{P_{H_2}^3 \cdot K} \quad (6.95)$$

Putting the value of P_{N_2} from equation (6.95) into equation (6.94)

$$(R_{\text{Decomposition}})_{NH_3} = k_d \left(a \frac{P_{NH_3}^2}{P_{H_2}^3 \cdot K} \right)^{\frac{h}{f}}$$

$$(R_{\text{Decomposition}})_{NH_3} = k_d \left(\frac{a}{K} \right)^{\frac{h}{f}} \left(\frac{P_{NH_3}^2}{P_{H_2}^3} \right)^{\frac{h}{f}} \quad (6.96)$$

a, h and f are constants. The value of h/f may be 0 to 1.

(i) When value of h/f is equal to 0 then, equation (6.96) will be,

$$(R_{\text{Decomposition}})_{NH_3} = k_d$$

Hence, the rate of decomposition of ammonia is independent of pressure of NH_3 and H_2 .

(ii) When the value of h/f is equal to 1 then equation (6.96) will be,

$$(R_{\text{Decomposition}})_{NH_3} = k_d \left(\frac{a}{K} \right) \left(\frac{P_{NH_3}^2}{P_{H_2}^3} \right)$$

$$(R_{\text{Decomposition}})_{NH_3} \propto \left(\frac{P_{NH_3}^2}{P_{H_2}^3} \right)$$

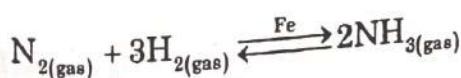
Hence, the rate of decomposition of ammonia is dependent on pressure of NH_3 and H_2 at maximum value of h/f.

6.10 CATALYSIS OR USE OF CATALYST IN INDUSTRY

80% of reactions in world are catalytic reactions. Out of this, more than 90 % reactions in industry are also catalytic reactions.

(1) Fertilizer Industry

The 1st step of urea synthesis in Haber's process is catalytic in which the synthesis of ammonia can be done. The reaction is reversible and catalytic as given below

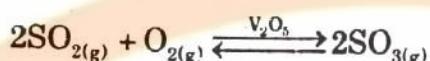


(2) Production of CO₂

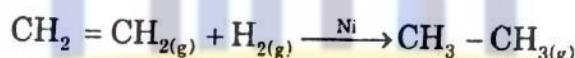
Most of the refreshing drinks in world are carbonated. Hence, on large scale CO₂ is required. One of the methods of preparation of CO₂ is the catalytic oxidation of CO given as

**(3) Production of H₂SO₄**

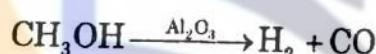
H₂SO₄ is widely used in industry and academic institutes. The basic step of H₂SO₄ synthesis involves catalytic oxidation of SO₂ as follows

**(4) Hydrogenation**

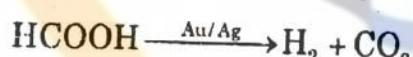
This heterogenous catalytic process is used to convert oils into vegetable ghee. In this reaction, unsaturated hydrocarbons or their derivatives are converted into saturated hydrocarbons or their derivatives. For example, ethene is converted into ethane by hydrogenation.

**(5) Production of Hydrogen Gas**

Hydrogen gas is prepared on industrial scale by the following heterogeneous catalytic processes as given below



Methanol



Formic acid

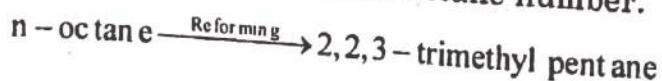
PUACP

(6) Cracking in Petroleum Industry

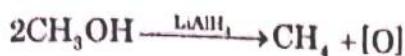
Cracking is the process of breaking long-chain hydrocarbons into lower molecular weight hydrocarbons. The rate of cracking is dependent on the temperature and presence of catalyst. Hence, cracking process in petroleum industry is catalytic in nature.

(7) Petroleum Reforming

Catalytic reforming is the process used to convert the linear chain hydrocarbons into the branched chain hydrocarbons in the presence of catalyst. Petroleum reforming can be done in industry on this basis. Reforming increases the burning capability and thus increases the octane number.



(8) Redox Reaction



It is a reduction process.

6.10.1 Problems in Use of Catalyst in Industry

(1) Sintering

"The retardation in catalytic activity due to aggregation of particles of same size and decrease in surface area called sintering." Promoters perform two functions: avoid sintering and enhance the activity of catalyst. Promoters occupied the space between particles and resist sintering.

U.S nitration fixation laboratory has done work on promoters. Brunaure and Emmet use Fe_2O_3 and Al_2O_3 together as catalyst. Here, Fe_2O_3 is catalyst and Al_2O_3 is promoter.

One or more than one promoter can be used along with catalyst in reactions. e.g. $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ is a singly promoted catalyst having only one promoter.

Doubly promoted catalyst has 2 promoters e.g. Fe_2O_3 acts as a catalyst while Al_2O_3 and K_2O can act as promoters in combination of Fe_2O_3 , Al_2O_3 and K_2O .

(2) Ostwald Ripening

Big particles provide attachment site for small particles, so small particles attach on a big particle and form coagulates. Catalyst in this way loses its activity, because Ostwald ripening results in reduction of surface area.

(3) Catalytic Poisoning

Impurity will cause catalytic poisoning. If adsorbing ability of impurities is greater than the adsorbing ability of reactants, then impurities will adsorb on catalyst and occupy active sites. Reactants do not adsorb and retardation occurs. Catalytic poisoning may be permanent or temporary.

6.11 ADVANCED APPROACH TO HOMOGENEOUS CATALYSIS

"In homogeneous catalysis reactants and catalyst both are in same phase." Some examples of homogeneous catalysis are as follows

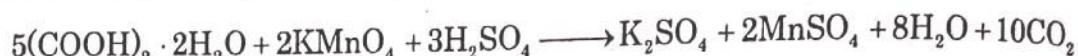
- (1) Autocatalysis
- (2) Enzyme catalysis
- (3) Acid or base catalysis

6.11.1 Autocatalysis

"A type of catalysis in which one of the products formed act as a catalyst is called autocatalysis."

The chemical reaction between acidified potassium permanganate (KMnO_4) and oxalic acid is an example of autocatalysis. The plot of concentration of product as

a function of time is given in the Fig. 6.25. It is clear from the Fig. that the concentration of product increases with time very slowly at initial stages of reaction. After this, rapid increase in concentration of product with time indicates that one of the products act as catalyst which speeds up the reaction. The chemical reaction is



Where, MnSO_4 acts as an autocatalyst.

Kinetics of Autocatalysis

Kinetics of autocatalysis involves following general scheme of reactions.



Where, (i) is a simple reaction and (ii) is an autocatalytic reaction. Kinetics of reaction (ii) can be discussed under following two cases

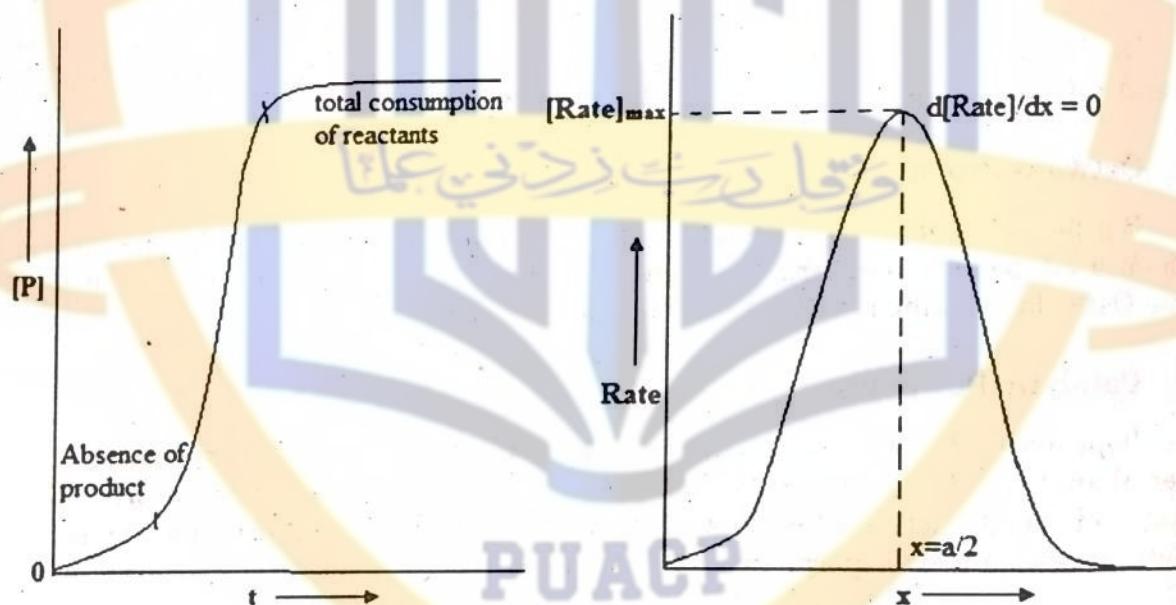


Fig. 6.25 Plot of concentration of product as a function of time for autocatalytic reaction

Fig. 6.26 Plot of rate of reaction versus concentration of autocatalyst

Case 1: When Initial Concentration of Autocatalyst B is Zero

Reaction (ii) is a 2nd order reaction and rate law expression for this reaction is

$$\frac{dx}{dt} \propto [\text{A}][\text{B}]$$

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

$$\frac{dx}{dt} = k_1(a - x)(x) \quad (6.97)$$

Equation (6.97) is the differential form of rate law. Rate of autocatalytic reaction depends upon the concentration of reactant and autocatalyst at time t.

When $x = 0$, equation (6.97) will be,

$$\frac{dx}{dt} = k_1(a - 0)(0) = 0$$

Rate of reaction increases with the increase of x initially and then decreases with increase of x as shown in Fig. 6.26. Using concept of maxima, value of concentration of autocatalyst can be determined at which rate of reaction is maximum. It is depicted from Fig. 6.26 if x is less or greater than $a/2$ then rate is less than $[rate]_{\max}$. Rate is maximum, if $x = a/2$.

From equation (6.97), we have

$$\text{Rate} = k_1(a - x)(x)$$

By differentiating above equation with respect to x, we get

$$\frac{d(\text{Rate})}{dx} = \frac{d}{dx}(k_1ax - k_1x^2)$$

At maxima, $\frac{d(\text{Rate})}{dx}$ will be 0. So,

$$0 = k_1a - 2k_1x$$

$$k_1a = 2k_1x$$

$$x = \frac{a}{2}$$

Case 2: When Initial Concentration of Autocatalyst is not Zero

Rate of reaction is low when reaction is started without catalyst, but rate of reaction can be increased by adding some quantity of catalyst with reactant. Since, catalyst is also generated in autocatalysis therefore concentration of autocatalyst B increases with progress of reaction while, concentration of reactant decreases with reaction progress. If we have a and b as initial concentration of reactant A and autocatalyst B respectively, then



At $t = 0$ a b

At time=t a-x b+x

Rate law expression for the reaction (ii) is

$$\frac{dx}{dt} \propto [A][B]$$

$$\frac{dx}{dt} \propto (a-x)(b+x)$$

$$\frac{dx}{dt} = k_1 (a-x)(b+x) \quad (6.98)$$

By separating variables and integrating equation (6.98), we get

$$\int \frac{dx}{(a-x)(b+x)} = k_1 \int dt \quad (6.99)$$

Equation (6.99) can be solved by partial fractions as

$$\frac{1}{(a-x)(b+x)} = \frac{A}{a-x} + \frac{B}{b+x} \quad (6.100)$$

$$1 = A(b+x) + B(a-x) \quad (6.101)$$

When $b+x = 0$ then $x = -b$, by putting value of x in equation (6.101), we get

$$1 = 0 + B(a+b)$$

$$B = \frac{1}{(a+b)} \quad (6.102)$$

When $a-x = 0$ then $x = a$, by putting value of x in equation (6.101), we get

$$1 = A(a+b)$$

$$A = \frac{1}{(a+b)} \quad (6.103)$$

Putting values of A and B from equation (6.103) and (6.102) in equation (6.100), we get

$$\frac{1}{(a-x)(b+x)} = \frac{1}{(a+b)(a-x)} + \frac{1}{(b+x)(a+b)}$$

By putting the value of $1/(a-x)(b+x)$ in equation (6.99) from above equation we get,

$$\int \frac{dx}{(a-x)(b+x)} = \frac{1}{(a+b)} \left[\int \frac{dx}{(a-x)} + \int \frac{dx}{(b+x)} \right]$$

$$\int \frac{dx}{(a-x)(b+x)} = \frac{1}{(a+b)} \left[-\ln(a-x) + \ln(b+x) \right]$$

$$\int \frac{dx}{(a-x)(b+x)} = \frac{1}{(a+b)} \ln \frac{(b+x)}{(a-x)}$$

Now equation (6.99) becomes,

$$\frac{1}{(a+b)} \ln \frac{(b+x)}{(a-x)} = k_1 t + c \quad (6.104)$$

By applying initial conditions, we can determine the value of integration constant c .

When $t = 0$, then $x = 0$

Then equation (6.104) will be,

$$\frac{1}{(a+b)} \ln \frac{b}{a} = c \quad (6.105)$$

Putting value of constant (c) from equation (6.105) into equation (6.104), we get

$$\begin{aligned} \frac{1}{(a+b)} \ln \frac{(b+x)}{(a-x)} &= k_1 t + \frac{1}{(a+b)} \ln \frac{b}{a} \\ \frac{1}{(a+b)} \ln \frac{a(b+x)}{b(a-x)} &= k_1 t \\ \ln \frac{a(b+x)}{b(a-x)} &= (a+b)k_1 t \end{aligned} \quad (6.106)$$

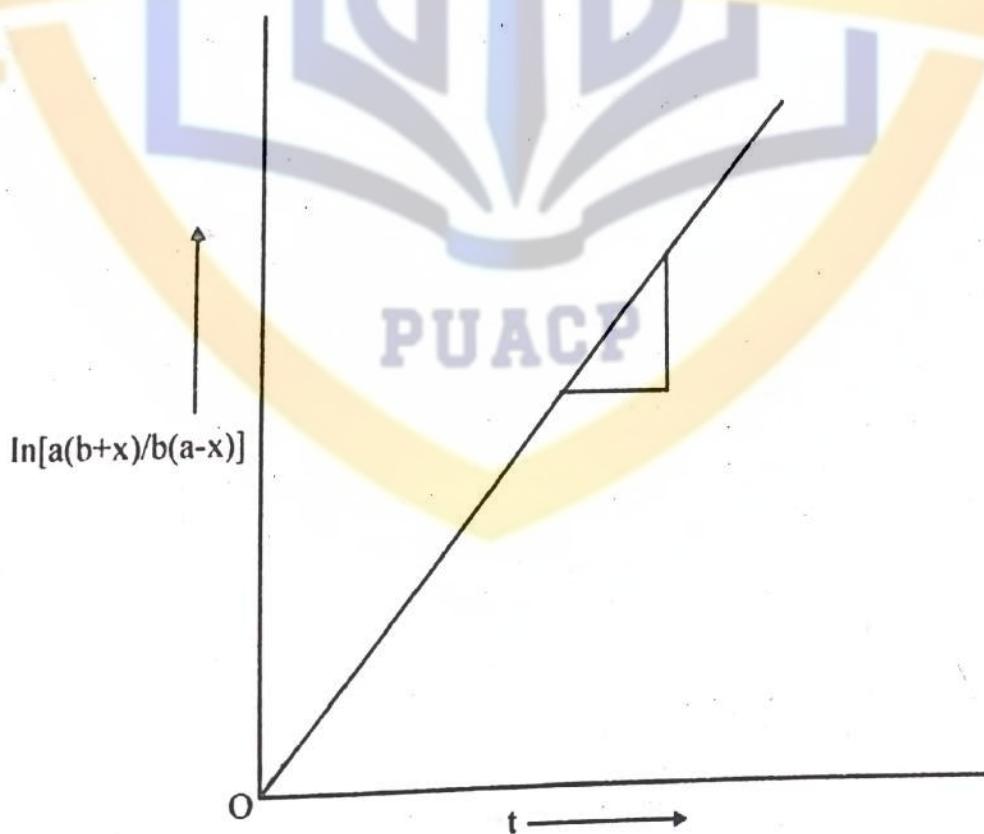


Fig. 6.27 Plot of $\ln[a(b+x)/b(a-x)]$ versus time for autocatalyst

Equation (6.106) is a straight line equation passing through the origin as shown in Fig. 6.27. Units of k_1 are $\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$ and value of k_1 can be determined from the slope of the plot of $\ln [a(b+x)]/[b(a-x)]$ versus t as

$$\text{Slope} = k_1(a + b)$$

$$k_1 = \frac{\text{slope}}{(a + b)}$$

Case 3: Non-Autocatalyzed Reaction and Autocatalyzed Reactions as Parallel Reactions

In case 1 and 2 we considered only autocatalysis step of the reaction scheme. Here, we will discuss both steps of reaction scheme as parallel. Step (i) is simple 1st order reaction with rate constant k_1 and step (ii) is autocatalytic reaction with rate constant k_2 .



Rate expression for the reaction (i) can be written as

$$R_1 \propto [A]$$

$$R_1 = k_1(a - x) \quad (6.107)$$

Rate expression for reaction (ii) can be written as

$$R_2 \propto [A][B]$$

$$R_2 = k_2(a - x)(x) \quad (6.108)$$

Overall rate of reaction is given as

$$\frac{dx}{dt} = R_1 + R_2$$

Putting values of R_1 and R_2 from equation (6.107) and (6.108) in above equation, we get

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

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

By separating variables and integrating above equation we get

$$\int \frac{dx}{(a - x)(k_1 + k_2 x)} = \int dt \quad (6.109)$$

Using partial fractions,

$$\frac{1}{(a-x)(k_1+k_2x)} = \frac{A}{(a-x)} + \frac{B}{(k_1+k_2x)} \quad (6.110)$$

$$1 = A(k_1+k_2x) + B(a-x) \quad (6.111)$$

When $a-x = 0$, then $x = a$. Putting value of x in to equation (6.111), we get

$$1 = A(k_1+k_2a)$$

$$A = \frac{1}{(k_1+k_2a)} \quad (6.112)$$

When $k_1+k_2x = 0$, then $x = -k_1/k_2$. Putting value of x into equation (6.111), we get

$$1 = B\left(a + \frac{k_1}{k_2}\right)$$

$$1 = B\left(\frac{k_2a+k_1}{k_2}\right)$$

$$B = \frac{k_2}{k_2a+k_1} \quad (6.113)$$

From equations (6.112) and (6.113) putting the values of A and B in equation (6.110), we get

$$\begin{aligned} \frac{1}{(a-x)(k_1+k_2x)} &= \frac{1}{(k_1+k_2a)(a-x)} + \frac{k_2}{(k_2a+k_1)(k_1+k_2x)} \\ \frac{dx}{(a-x)(k_1+k_2x)} &= \frac{1}{(k_1+k_2a)} \left\{ \frac{dx}{(a-x)} + \frac{k_2 \cdot dx}{(k_1+k_2x)} \right\} \\ \int \frac{dx}{(a-x)(k_1+k_2x)} &= \frac{1}{(k_1+k_2a)} \left\{ - \int \frac{(-1)dx}{(a-x)} + \int \frac{k_2 \cdot dx}{(k_1+k_2x)} \right\} \end{aligned} \quad (6.114)$$

By comparing equation (6.109) and (6.114), we get

$$\begin{aligned} \frac{1}{(k_1+k_2a)} \left\{ - \int \frac{(-1)dx}{(a-x)} + \int \frac{k_2 \cdot dx}{(k_1+k_2x)} \right\} &= \int dt \\ \frac{1}{(k_1+k_2a)} \left\{ - \ln(a-x) + \ln(k_1+k_2x) \right\} &= t + c \\ \frac{1}{(k_1+k_2a)} \left[\ln \frac{k_1+k_2x}{a-x} \right] &= t + c \end{aligned} \quad (6.115)$$

Applying initial conditions,

When $t = 0$ then $x = 0$. Applying this condition at equation (6.115)

$$\frac{1}{(k_1 + k_2 a)} \ln\left(\frac{k_1}{a}\right) = c \quad (6.116)$$

Putting value of constant (c) from equation (6.116) into equation (6.115), we get

$$\frac{1}{(k_1 + k_2 a)} \left[\ln \frac{k_1 + k_2 x}{a - x} \right] = t + \frac{1}{(k_1 + k_2 a)} \ln\left(\frac{k_1}{a}\right)$$

$$\frac{1}{(k_1 + k_2 a)} \ln \frac{a(k_1 + k_2 x)}{k_1(a - x)} = t$$

$$\ln \frac{a(k_1 + k_2 x)}{k_1(a - x)} = (k_1 + k_2 a)t \quad (6.117)$$

Equation (6.117) is an equation of straight line passing through the origin with slope, $(k_1 + k_2 a)$ as shown in Fig. 6.28.

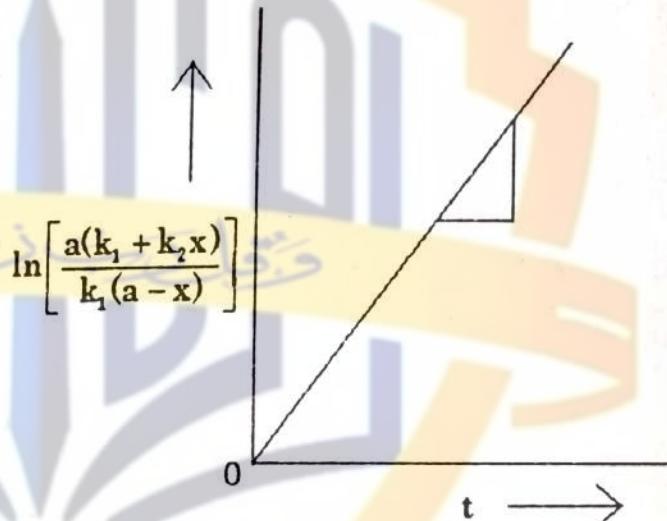
From the slope value of rate constants k_1 and k_2 cannot be found. Hence, it is better to remove product from reaction mixture time to time. So, that no product remains in reaction mixture and process could not be autocatalyzed. So, $k_2 \approx 0$.

Applying this condition to equation (6.117), we get

$$\ln \frac{ak_1}{k_1(a-x)} = k_1 t$$

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

Fig. 6.28 Plot of $\ln \frac{a(k_1 + k_2 x)}{k_1(a - x)}$ versus t for non-autocatalyzed and autocatalyzed parallel reactions



Hence, from above equation k_1 can be found. By putting the value of k_1 in equation (6.117) we can get the value of k_2 :

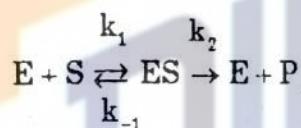
6.11.2 Enzyme Catalysis

Enzymes are bio organic catalysts which catalyze the chemical reactions occurring in the human body. Enzymes are macromolecules and proteins in nature, because they have origin in living organism so they are also called biopolymers. Amino acids are the building blocks of enzymes. Number of amino acids in a single enzyme is large so, 10000-1000000 g/mol is the molecular weight of enzyme. Enzymes act as catalyst in all types of reactions i.e. redox, acid base and decomposition

reactions. Enzymes are specific in nature and functioning. Stereo specificity is basic character of enzymes. They react with stereo specific reactants and also produce stereo specific products. Enzymes only work on specific temperature and specific pH. Optimum pH or temperature is that pH or temperature at which enzyme show maximum activity. "The number of reactant molecules converted into product per unit time by a single enzyme molecule is called turn over number."

Michaelis-Menton Mechanism

Michaelis-Menton mechanism of enzyme catalysis obeys lock and key model of enzyme functioning. An enzyme has specific site for adsorption of a particular substance. According to this model, substrate can form a complex with enzyme by a reversible process, then enzyme-substrate complex is converted into product with regeneration of enzyme by irreversible process. The pictorial diagram is shown in Fig. 6.29. The scheme of Michaelis-Menton mechanism of enzyme catalyzed reaction can be given as



According to above equation, rate of reaction is

$$u = k_2 [ES] \quad (6.118)$$

Net rate of formation of enzyme-substrate complex can be written as

$$\frac{d[ES]}{dt} = k_1 [E][S] - k_{-1}[ES] - k_2[ES] \quad (6.119)$$

Applying steady state approximation, because ES complex is formed and used during reaction and it is an unstable intermediate. So, $d[ES]/dt = 0$, equation (6.119) will be

$$0 = k_1 [E][S] - k_{-1}[ES] - k_2[ES]$$

$$k_{-1}[ES] + k_2[ES] = k_1 [E][S]$$

$$[ES]\{k_{-1} + k_2\} = k_1 [E][S]$$

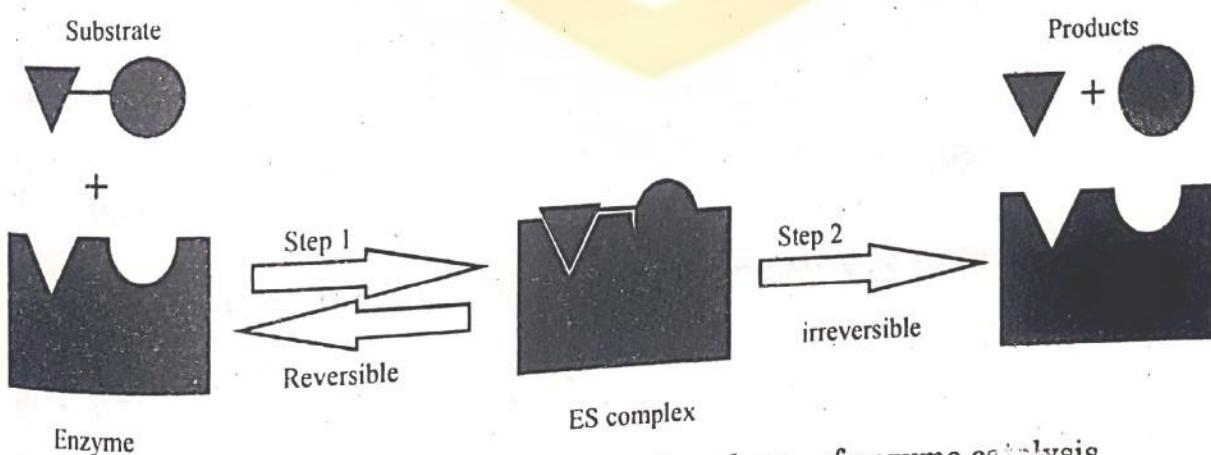


Fig. 6.29 Pictorial diagram showing the scheme of enzyme catalysis

$$[ES] = \frac{k_1 [E][S]}{k_{-1} + k_2} \quad (6.120)$$

Enzyme is present in a vessel in free form as well as in ES complex form. So,

$$[E]_o = [E] + [ES]$$

Where $[E]_o$ is the initial concentration of enzyme, $[E]$ is the available concentration of free enzyme and $[ES]$ is available concentration of enzyme substrate complex.

$$[E] = [E]_o - [ES] \quad (6.121)$$

Putting value of $[E]$ from equation (6.121) into equation (6.120), we get

$$\begin{aligned} [ES] &= \frac{k_1 \{[E]_o - [ES]\}[S]}{k_{-1} + k_2} \\ [ES] &= \frac{\{[E]_o - [ES]\}[S]}{\frac{k_{-1} + k_2}{k_1}} \end{aligned} \quad (6.122)$$

$$k_M = \frac{k_{-1} + k_2}{k_1}$$

Where, k_M is the Michaelis-Menton constant.

So, equation (6.122) will be

$$[ES] = \frac{[E]_o [S] - [ES][S]}{k_M}$$

$$[ES] = \frac{[E]_o [S]}{k_M} - \frac{[ES][S]}{k_M}$$

$$[ES] + \frac{[ES][S]}{k_M} = \frac{[E]_o [S]}{k_M}$$

$$[ES] \left[\frac{k_M + [S]}{k_M} \right] = \frac{[E]_o [S]}{k_M}$$

$$[ES] = \frac{[E]_o [S]}{k_M + [S]} \quad (6.123)$$

Putting value of $[ES]$ from equation (6.123) into (6.118), we get

$$v = k_2 \frac{[E]_o [S]}{k_M + [S]} \quad (6.124)$$

Results deduced from equation (6.124) are as follows

- Rate of reaction is a function of concentration of substrate.
- Rate of reaction is directly proportional to $[S]$ but up to certain limit only.

When $[S]$ is low, then $k_M + [S] \approx k_M$ so, equation (6.124) will be

$$v = k_2 \frac{[E]_o [S]}{k_M}$$

$$v = \text{constant} \times [S]$$

$$v \propto [S]$$

So, rate of reaction is directly proportional to concentration of substrate if concentration of substrate is very low as shown in Fig. 6.30.

- When $[S]$ is very high, then $k_M + [S] \approx [S]$. applying this condition to equation (6.124), we get

$$v = k_2 \frac{[E]_o [S]}{[S]}$$

$$v = k_2 [E]_o = v_{\max}$$

v_{\max} is constant value, because k_2 and $[E]_o$ are constants. v_{\max} is independent of $[S]$. When $v = v_{\max}/2$, then $[S] = k_M$. It means k_M is concentration of substrate when rate of reaction is half of maximum rate. Fig. 6.30 shows that v is directly proportional to substrate concentration if concentration of substrate is low. But for high concentration of substrate v is independent of $[S]$.

This is because all the active sites of enzymes are fully occupied at high concentration of substrate and no more sites are available so, rate of reaction is independent of substrate concentration.

- Physical Significance of k_M :** " k_M is the concentration of substrate for which rate of reaction is half of v_{\max} ." i.e.

Let $[S] = k_M$ applying this condition on equation (6.124), we get

$$v = k_2 \frac{[E]_o k_M}{2k_M}$$

$$v = k_2 \frac{[E]_o}{2}$$

$$v = \frac{v_{\max}}{2}$$

Unit of k_M are mol/dm³. As we know that

$$k_M = \frac{k_{-1} + k_2}{k_1}$$

$$k_M = \frac{k_{-1}}{k_1} + \frac{k_2}{k_1} \quad (6.125)$$

$k_s = \frac{k_{-1}}{k_1}$ is the dissociation constant so, equation (6.125) will be

$$k_M = k_s + \frac{k_2}{k_1}$$

If $k_2/k_1 = 0$ then $k_M = k_s$. The value of k_s normally ranges 10^{-2} to 10^{-5} mol/dm³ which is comparable to ionization constant of carboxylic acids. Generally $k_M \leq k_s$, so k_M can serve as minimum value of k_s .

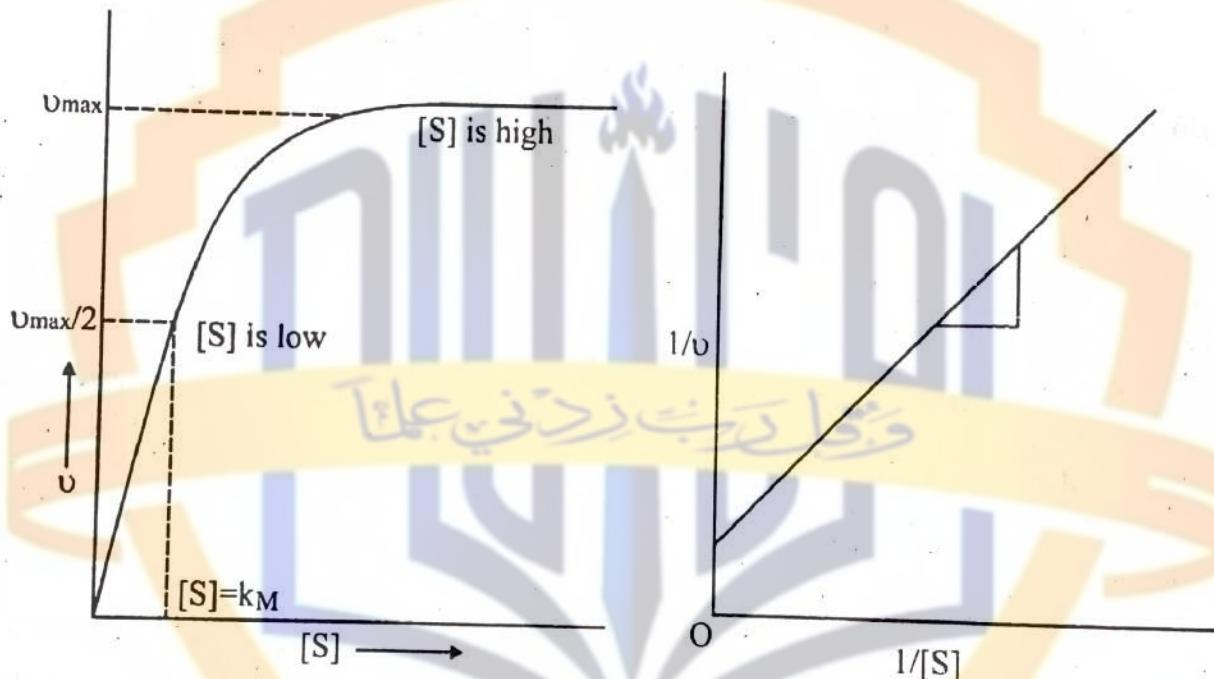


Fig. 6.30 Plot of rate of enzyme catalyzed reaction versus substrate concentration

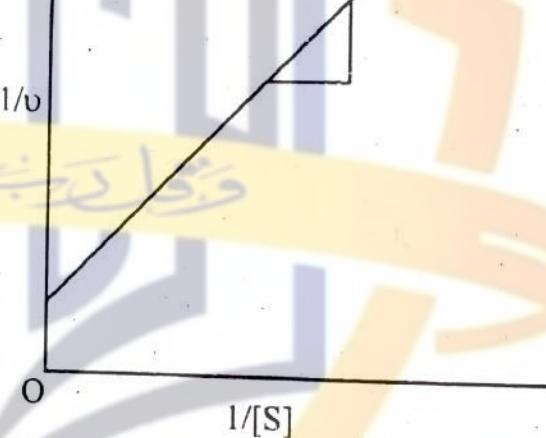


Fig. 6.31 Plot of $1/v$ versus $1/[S]$

- (v) The value of k_M and k_2 can be determined by converting equation (6.124) into equation of straight line i.e.

$$v = \frac{k_2 [E]_o [S]}{k_M + [S]}$$

$$\frac{1}{v} = \frac{k_M + [S]}{k_2 [E]_o [S]}$$

$$\frac{1}{v} = \frac{k_M}{k_2 [E]_o [S]} + \frac{[S]}{k_2 [E]_o [S]}$$

$$\frac{1}{v} = \frac{k_M}{k_2 [E]_o [S]} + \frac{1}{k_2 [E]_o}$$

$$\frac{1}{v} = \frac{k_M}{k_2 [E]_o} \frac{1}{[S]} + \frac{1}{k_2 [E]_o}$$

This is an equation of straight line and named as Lineweaver-Burk plot as shown in Fig. 6.31. The value of k_M can be determined from the slope of $1/v$ versus $1/[S]$ plot and k_2 from the intercept of the same plot as

$$\text{Slope} = \frac{k_M}{k_2 [E]_o}$$

$$\text{Intercept} = \frac{1}{k_2 [E]_o}$$

$$\frac{1}{k_2} = [E]_o \times \text{Intercept}$$

$$k_2 = 1/[E]_o \times \text{Intercept}$$

The rate of slope to intercept also gives the value of k_M .

$$\frac{\text{Slope}}{\text{Intercept}} = \frac{k_M}{k_2 [E]_o}$$

$$\frac{\text{Slope}}{\text{Intercept}} = k_M$$

Second Possible Mechanism of Enzyme Catalysis

The Michaelis-Menton plot doesn't always show that this mechanism is true, because many other possible mechanisms can give this plot. For example stepwise formation of product from ES complex follows the equation almost similar to Michaelis-Menton equation discussed in the previous section. Pictorial diagram of this mechanism is given in Fig. 6.32.

The scheme of this mechanism can be written as

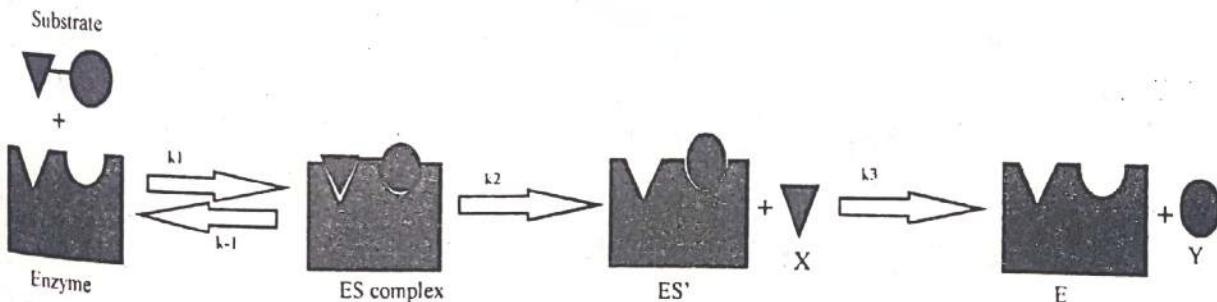
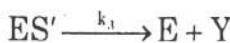
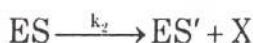
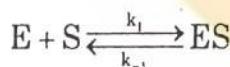


Fig. 6.32 Pictorial diagram of mechanism of enzyme catalyzed reaction

Rate of reaction is directly proportional to concentration of ES complex.

$$v \propto [ES]$$

$$v = k_2[ES] \quad (6.126)$$

k_2 is the rate constant of second step.

Net rate of formation of ES complex is

$$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES]$$

Applying steady state approximation, we get

$$0 = k_1[E][S] - [ES]\{k_{-1} + k_2\}$$

$$[ES]\{k_{-1} + k_2\} = k_1[E][S]$$

$$[ES] = \frac{k_1[E][S]}{k_{-1} + k_2}$$

$$[ES] = \frac{[E][S]}{\frac{k_{-1}}{k_1} + k_2}$$

$$[ES] = \frac{[E][S]}{k_M} \quad (6.127)$$

Enzyme is present in free as well as in enzyme-substrate complex forms in reaction mixture. Thus total concentration of enzyme is equal to sum of concentration of all these three forms as

$$[E]_o = [E] + [ES] + [ES']$$

$$[E] = [E]_o - [ES] - [ES'] \quad (6.128)$$

Putting value of $[E]$ from equation (6.128) into (6.127), we get

$$[ES] = \frac{\{[E]_o - [ES] - [ES']\}[S]}{k_M}$$

$$[ES] + \frac{[ES][S]}{k_M} = \frac{\{[E]_o - [ES']\}[S]}{k_M}$$

$$[ES] + \frac{[ES][S]}{k_M} = \frac{[E]_o[S] - [ES'][S]}{k_M}$$

$$\frac{k_M[ES] + [ES][S]}{k_M} = \frac{[E]_o[S] - [ES'][S]}{k_M}$$

$$[ES](k_M + [S]) = [E]_o[S] - [ES'][S] \quad (6.129)$$

Net rate of formation of ES'

$$\frac{d[ES']}{dt} = k_2[ES] - k_3[ES'] \quad (6.130)$$

As ES' is also an intermediate. So, steady state approximation can also be applied to it.

$$0 = k_2[ES] - k_3[ES']$$

$$k_2[ES] = k_3[ES']$$

$$[ES'] = \frac{k_2[ES]}{k_3} \quad (6.131)$$

Putting value of [ES'] from equation (6.131) into equation (6.129), we get

$$\begin{aligned} [ES](k_M + [S]) &= [E]_o[S] - \frac{k_2[ES]}{k_3}[S] \\ [ES](k_M + [S]) + \frac{k_2[ES][S]}{k_3} &= [E]_o[S] \\ [ES] \left\{ k_M + [S] + \frac{k_2[S]}{k_3} \right\} &= [E]_o[S] \\ [ES] \left\{ k_M + \left(1 + \frac{k_2}{k_3} \right)[S] \right\} &= [E]_o[S] \end{aligned} \quad (6.132)$$

$$[ES] \left\{ k_M + \left(\frac{k_3 + k_2}{k_3} \right)[S] \right\} = [E]_o[S] \quad (6.133)$$

$$[ES] = \frac{[E]_o[S]}{k_M + \left(\frac{k_3 + k_2}{k_3} \right)[S]} \quad (6.133)$$

Putting value of [ES] from equation (6.133) into (6.126), we get

$$\begin{aligned} u &= \frac{k_2[E]_o[S]}{k_M + \left(\frac{k_3 + k_2}{k_3} \right)[S]} \\ u &= \frac{k_2 \left(\frac{k_3}{k_2 + k_3} \right) [E]_o[S]}{\left(\frac{k_3}{k_2 + k_3} \right) k_M + \left(\frac{k_3 + k_2}{k_3} \right) \left(\frac{k_3}{k_2 + k_3} \right) [S]} \end{aligned}$$

$$v = \frac{k_2 \left(\frac{k_3}{k_2 + k_3} \right) [E]_o [S]}{\left(\frac{k_3}{k_2 + k_3} \right) k_M + [S]} \quad (6.134)$$

And $k = \left(\frac{k_3}{k_2 + k_3} \right)$

So, equation (6.134) will be,

$$v = \frac{k_2 k [E]_o [S]}{k_M k + [S]} \quad (6.135)$$

$k_3 \gg k_2$ then $k = 1$. This is a maximum value of k .

Results deduced from equation (6.135) are as follows

- (i) Rate of enzyme catalyzed reaction is directly proportional to substrate concentration for small values of $[S]$. i.e.
- (a) If $[S]$ is low, then $k_M k + [S] \approx k_M k$

Applying this condition to equation (6.135), we get

$$v = \frac{k_2 k [E]_o [S]}{k_M k}$$

Hence, $v \propto [S]$

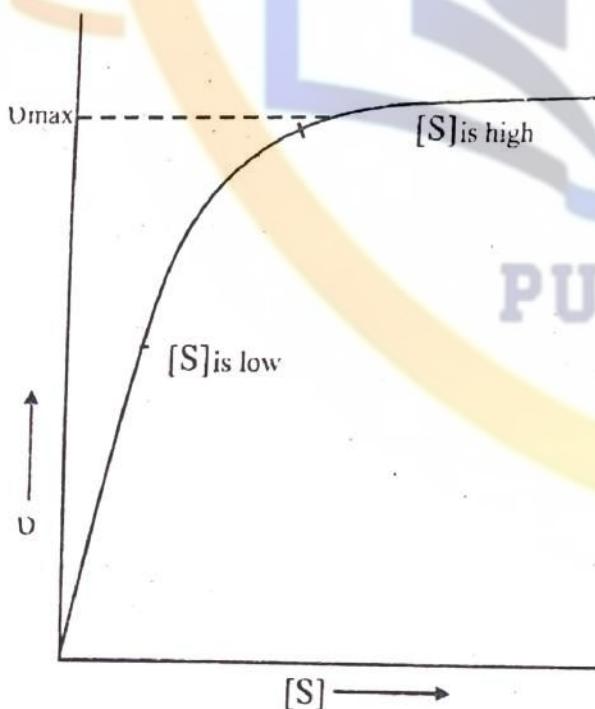


Fig. 6.33 Plot of rate of enzyme catalyzed reaction versus substrate concentration

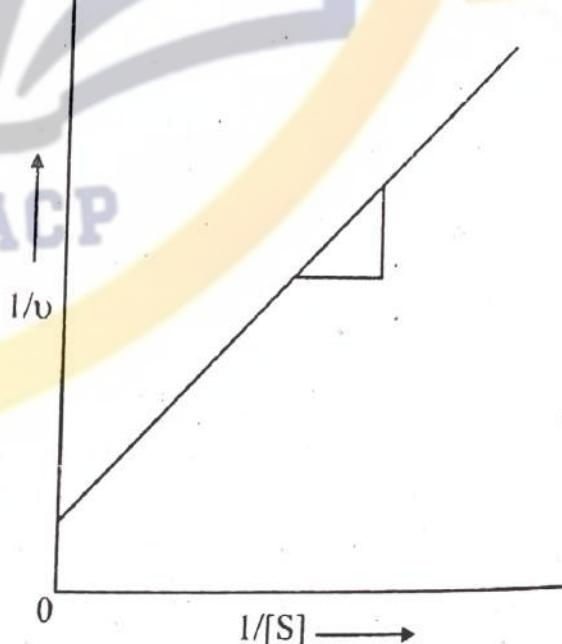


Fig. 6.34 Plot of 1/v versus 1/[S]

- (b) When value of $[S]$ is high then u is independent of $[S]$ i.e. if $[S]$ is large, then $k_M \cdot k + [S] \approx [S]$ so, equation (6.135) will be

$$u = k_2 k [E]_0$$

Fig. 6.33 depicts that rate of enzyme catalyzed reaction depends upon substrate at low concentration but at high substrate concentration rate becomes independent of substrate concentration.

- (ii) The value of k_M can be determined by converting equation (6.135) into equation of straight line i.e.

Taking inverse of equation (6.135), we get

$$\frac{1}{u} = \frac{k_M k + [S]}{k_2 k [E]_0 [S]}$$

$$\frac{1}{u} = \frac{k_M}{k_2 [E]_0 [S]} + \frac{1}{k_2 k [E]_0}$$

This is equation of straight line with intercept as shown in Fig. 6.34. The ratio of slope to intercept of the plot of $1/u$ as a function of $1/[S]$ can be used for the determination of k_M .

6.12 ENZYME INHIBITION

"The decrease in rate of enzyme catalyzed reaction as a result of complex formation of a foreign substance with enzyme is called enzyme inhibition and foreign specie is called inhibitor."

Types of Enzyme Inhibition

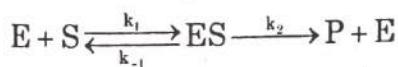
Reversible and irreversible are two types of enzyme inhibition. Reversible inhibition is further classified into three types.

- (i) Competitive inhibition
- (ii) Un competitive inhibition
- (iii) Non-competitive inhibition

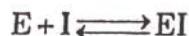
6.12.1 Competitive Inhibition

In this inhibition, there are complexations between substrate and enzyme and between enzyme and foreign specie. In competitive inhibition enzyme has ability to bind with substrate as well as with inhibitor because size and shape of inhibitor and substrate are not only same and but also similar to active site.

The scheme of competitive inhibition can be written as



The complexation of enzyme with inhibitor is a reversible process and can be written as



From above equilibrium, dissociation constant of the complex is

$$K_1 = \frac{[E][I]}{[EI]}$$

By rearranging above equation, we get

$$[EI] = \frac{[E][I]}{K_1} \quad (6.136)$$

Rate of reaction is directly proportional to available concentration of enzyme substrate complex.

$$v \propto [ES]$$

$$v = k_2 [ES] \quad (6.137)$$

Net rate of formation of $[ES] = R_{\text{formation}} - R_{\text{consumption}}$

$$\frac{d[ES]}{dt} = k_1 [E][S] - k_{-1} [ES] - k_2 [ES]$$

Applying steady state approximation to it

$$0 = k_1 [E][S] - k_{-1} [ES] - k_2 [ES]$$

$$k_1 [E][S] = k_{-1} [ES] + k_2 [ES]$$

$$k_1 [E][S] = (k_2 + k_{-1}) [ES]$$

$$[ES] = \frac{k_1 [E][S]}{k_2 + k_{-1}}$$

$$[ES] = \frac{[E][S]}{\frac{k_2 + k_{-1}}{k_1}}$$

$$[ES] = \frac{[E][S]}{k_M}$$

$$[E] = \frac{[ES]k_M}{[S]} \quad (6.138)$$

The concentration of enzyme is as follows

$$[E]_o = [E] + [ES] + [EI] \quad (6.139)$$

Putting value of $[EI]$ from equation (6.136) into (6.139), we get

$$[E]_o = [E] + [ES] + \frac{[E][I]}{K_1}$$

$$[E]_o = [ES] + [E] \left\{ 1 + \frac{[I]}{K_i} \right\} \quad (6.140)$$

Putting value of $[E]$ from equation (6.138) into equation (6.140), we get

$$[E]_o = [ES] + \frac{[ES]k_M}{[S]} \left\{ 1 + \frac{[I]}{K_i} \right\}$$

$$[E]_o = [ES] \left(1 + \frac{k_M}{[S]} \left\{ 1 + \frac{[I]}{K_i} \right\} \right)$$

$$[ES] = \frac{[E]_o}{\left(1 + \frac{k_M}{[S]} \left\{ 1 + \frac{[I]}{K_i} \right\} \right)} \quad (6.141)$$

Putting value of $[ES]$ from equation (6.141) into (6.137), we get

$$u = k_2 \frac{[E]_o}{\left(1 + \frac{k_M}{[S]} \left\{ 1 + \frac{[I]}{K_i} \right\} \right)}$$

This is the rate of enzyme catalyzed reaction in the presence of inhibitor.

$$u = \frac{k_2 [E]_o [S]}{\left([S] + k_M \left\{ 1 + \frac{[I]}{K_i} \right\} \right)} \quad (6.142)$$

Equation (6.142) proves that u decreases with increase in $[I]$ and increases with increase in $[S]$ i.e.

(i) If $[I] = 0$, then equation (6.142) will be

$$u = \frac{k_2 [E]_o [S]}{[S] + k_M}$$

This is rate of enzyme catalyzed reaction in the absence of inhibitor.

(ii) If $[I]/K_i = 1$ and $k_M = [S]$, then

$$u = \frac{k_2 [E]_o}{3}$$

$$u = \frac{U_{max}}{3}$$

(iii) If $[I]/K_i = 0$ and $k_M = [S]$, then equation (6.142) will be

$$u = \frac{k_2 [E]_o}{2}$$

$$v = \frac{v_{\max}}{2}$$

This is in the absence of inhibitor as shown in Fig. 6.35.

- (iv) If $[S] \ggg k_M$, then equation (6.142) is

$$v = \frac{k_2 [E]_o [S]}{[S]}$$

$$v = k_2 [E]_o$$

$$v = v_{\max}$$

By taking inverse of equation (6.142), we get

$$\begin{aligned} \frac{1}{v} &= \frac{[S] + k_M \left\{ 1 + \frac{[I]}{K_I} \right\}}{k_2 [E]_o [S]} \\ \frac{1}{v} &= \frac{1}{k_2 [E]_o} + \frac{k_M \left\{ 1 + \frac{[I]}{K_I} \right\}}{k_2 [E]_o [S]} \\ \frac{1}{v} &= \frac{k_M}{k_2 [E]_o} \left(1 + \frac{[I]}{K_I} \right) \frac{1}{[S]} + \frac{1}{k_2 [E]_o} \end{aligned} \quad (6.143)$$

Plot of equation (6.143) is shown in Fig. 6.36.

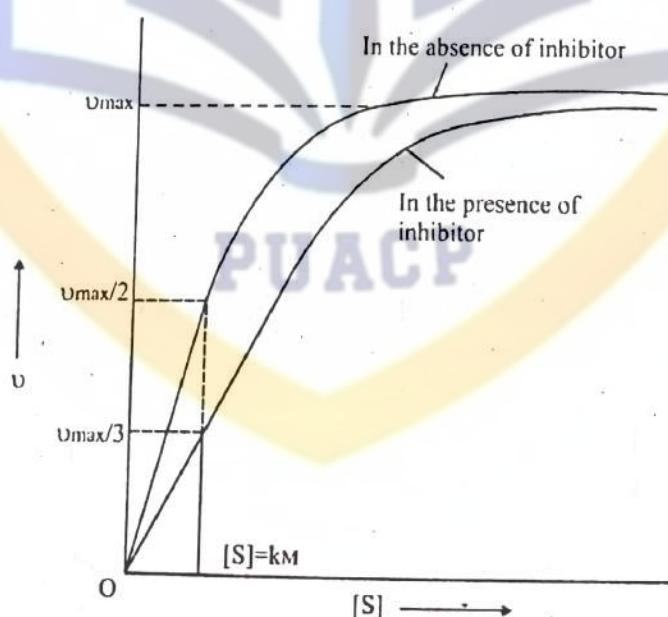


Fig. 6.35 The rate of enzyme catalyzed reaction as a function of substrate concentration in the presence and absence of inhibitor

With the increase in $[I]$ the curve will shift anti clockwise with increasing slope and intercept will remain constant.

$$\text{Intercept} = \frac{1}{k_2 [E]_o}$$

$$k_2 = \frac{1}{\text{Intercept} [E]_o}$$

$$\text{Slope} = \frac{k_M}{k_2 [E]_o} \left(1 + \frac{[I]}{K_I} \right)$$

Then, we can find K_I from slope.

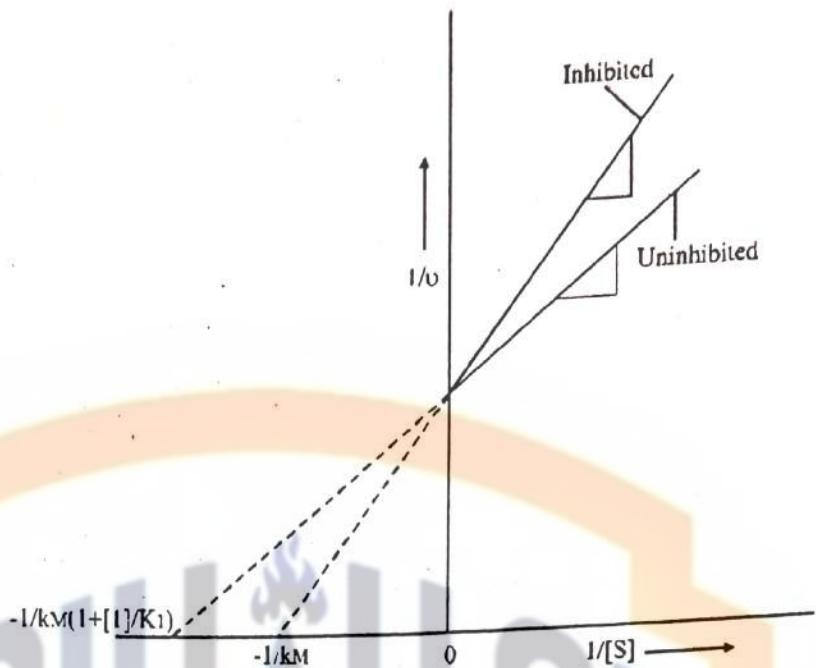


Fig. 6.36 Plot of $1/u$ as a function of $1/[S]$ in the presence (competitive inhibition) and absence of inhibitor

Example 6.5

Prove that the value of x-intercept of the plot $1/u$ versus $1/[S]$ is equal to

$$-\frac{1}{k_M \left(1 + \frac{[I]}{K_I} \right)}$$

Solution

x- Intercept of $1/u$ versus $1/[S]$ plot is the value of $1/[S]$ for which $1/u$ is equal to zero. Hence, from equation (6.143) we have

$$0 = \frac{k_M}{k_2 [E]_o} \left(1 + \frac{[I]}{K_I} \right) \frac{1}{[S]} + \frac{1}{k_2 [E]_o}$$

$$-\frac{k_M}{k_2 [E]_o} \left(1 + \frac{[I]}{K_I} \right) \frac{1}{[S]} = \frac{1}{k_2 [E]_o}$$

$$\frac{1}{[S]} = -\frac{1}{k_M \left(1 + \frac{[I]}{K_I} \right)}$$

As required.

Example 6.6

An enzyme catalyzed reaction was inhibited competitively. The intercept to slope ratio of plot $1/u$ versus $1/[S]$ was found to be $1.5 \text{ mol}/\text{dm}^3$ in the presence of 0.01 M inhibitor. The value of k_M is $1.2 \times 10^{-4} \text{ mol}/\text{dm}^3$. Calculate the value of K_I .

Solution

$$\text{As we know that, } \frac{\text{Intercept}}{\text{Slope}} = \frac{k_M}{k_2 [E]_o} \left(1 + \frac{[I]}{K_I} \right) \times k_2 [E]_o$$

$$\frac{\text{Intercept}}{\text{Slope}} = k_M \left(1 + \frac{[I]}{K_I} \right)$$

By putting values in above equation from the given data we can determine value of K_I as follows

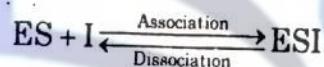
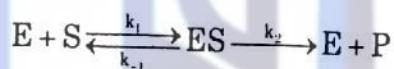
$$1.5 = 1.2 \times 10^{-4} \left(1 + \frac{0.01}{K_I} \right)$$

$$1.25 \times 10^4 = 1 + \frac{0.01}{K_I}$$

$$K_I = 7.999 \text{ mol dm}^{-3}$$

6.12.2 Uncompetitive Inhibition

In such type of inhibition, enzyme doesn't make a complex with inhibitor directly but enzyme-substrate form a complex with inhibitor and stabilize it. As a result of this process product formation is inhibited. The scheme of uncompetitive inhibition is given below



Dissociation constant of $[ESI]$ will be

$$K_I = \frac{[ES][I]}{[ESI]}$$

$$[ESI] = \frac{[ES][I]}{K_I} \quad (6.144)$$

$$u \propto [ES]$$

$$u = k_2 [ES] \quad (6.145)$$

Net rate of formation of $[ES]$ complex

$$\frac{d[ES]}{dt} = k_1 [E][S] - k_{-1} [ES] - k_2 [ES]$$

Applying steady state approximation to it

$$0 = k_1 [E][S] - k_{-1} [ES] - k_2 [ES]$$

$$k_1[E][S] = k_{-1}[ES] + k_2[ES]$$

$$k_1[E][S] = (k_2 + k_{-1})[ES]$$

$$[ES] = \frac{k_1[E][S]}{k_2 + k_{-1}}$$

$$[ES] = \frac{[E][S]}{\frac{k_2 + k_{-1}}{k_1}}$$

$$[ES] = \frac{[E][S]}{k_M} \quad (6.146)$$

$$[E]_o = [E] + [ES] + [ESI]$$

$$[E] = [E]_o - [ES] - [ESI] \quad (6.147)$$

By putting value of [ESI] from equation (6.144) into equation (6.147), we get

$$[E] = [E]_o - [ES] - \frac{[ES][I]}{K_I}$$

Putting value of [E] into equation (6.146), we get

$$[ES] = \frac{\left([E]_o - [ES] - \frac{[ES][I]}{K_I} \right) [S]}{k_M}$$

$$[ES]k_M = \left([E]_o - [ES] - \frac{[ES][I]}{K_I} \right) [S]$$

$$[ES]k_M = \left([E]_o - [ES] \left\{ 1 + \frac{[I]}{K_I} \right\} \right) [S]$$

$$[ES]k_M = [E]_o[S] - [ES][S] \left\{ 1 + \frac{[I]}{K_I} \right\}$$

$$[ES]k_M + [ES][S] \left\{ 1 + \frac{[I]}{K_I} \right\} = [E]_o[S]$$

$$[ES] \left(k_M + [S] \left\{ 1 + \frac{[I]}{K_I} \right\} \right) = [E]_o[S]$$

$$[ES] = \frac{[E]_o[S]}{k_M + [S] \left\{ 1 + \frac{[I]}{K_I} \right\}} \quad (6.148)$$

Putting value of $[ES]$ from equation (6.145) into equation (6.148), we get

$$u = k_2 \frac{[E]_o [S]}{k_M + [S] \left\{ 1 + \frac{[I]}{K_I} \right\}} \quad (6.149)$$

It is the rate law expression of enzyme catalyzed reaction in the presence of inhibitor due to uncompetitive inhibition.

Taking inverse of equation (6.149)

$$\begin{aligned} \frac{1}{u} &= \frac{k_M + [S] \left\{ 1 + \frac{[I]}{K_I} \right\}}{k_2 [E]_o [S]} \\ \frac{1}{u} &= \frac{k_M}{k_2 [E]_o [S]} + \frac{1}{k_2 [E]_o} \left\{ 1 + \frac{[I]}{K_I} \right\} \end{aligned} \quad (6.150)$$

This is the rate law expression for enzyme catalyzed reaction suffering uncompetitive inhibition. We can know that the inhibition is competitive or uncompetitive by Line weaver Burk Plot. If intercept is same but slope is different in Line weaver Burk plot then this will be competitive inhibition. If intercept is different and slope will be same in Line weaver Burk plot then this will be uncompetitive inhibition as shown in Fig. 6.37.

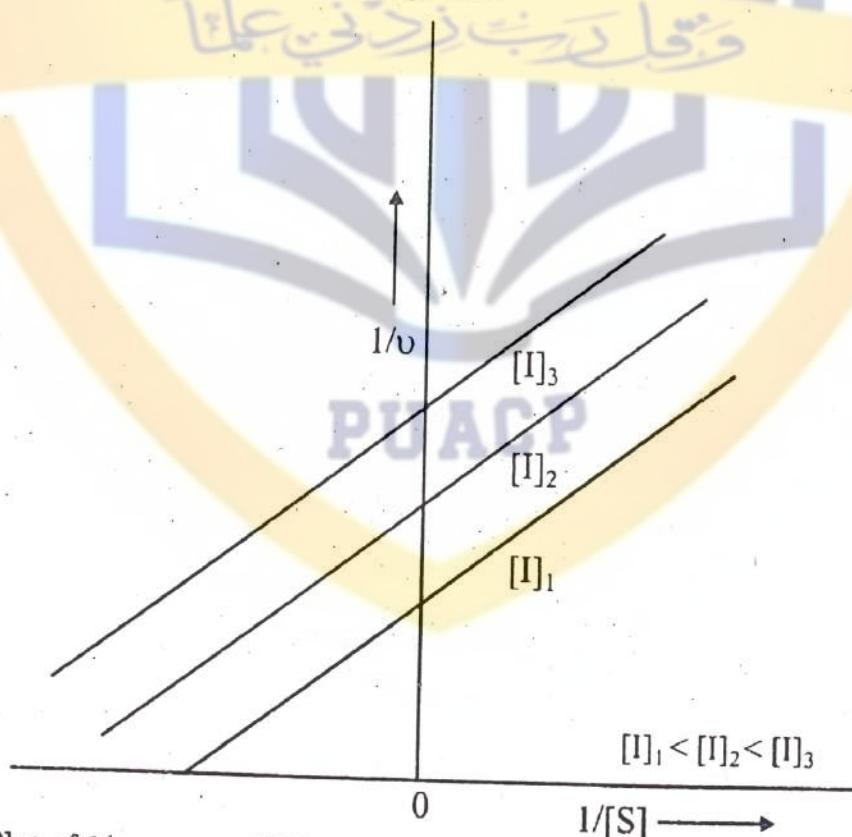
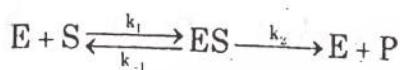


Fig. 6.37 Plot of $1/u$ versus $1/[S]$ showing uncompetitive inhibition with different intercept values

6.12.3 Non-Competitive Inhibition

In this type of enzyme inhibition, inhibitor is not attached with enzyme through active site. Inhibitor forms complex with enzyme by attaching active site available for substrate. Because shape and size of inhibitor and of substrate are different from each other. The reaction scheme of non-competitive inhibition is given below



Dissociation constant of possibility 1 is

$$K_1 = \frac{[E][I]}{[EI]}$$

$$[EI] = \frac{[E][I]}{K_1} \quad (6.151)$$

Dissociation constant of possibility 2 is

$$K_1 = \frac{[ES][I]}{[ESI]}$$

$$[ESI] = \frac{[ES][I]}{K_1} \quad (6.152)$$

$$u = k_2 [ES] \quad (6.153)$$

Net rate of formation of [ES] complex

$$\frac{d[ES]}{dt} = k_1 [E][S] - k_{-1} [ES] - k_2 [ES]$$

Applying steady state approximation to it

$$0 = k_1 [E][S] - k_{-1} [ES] - k_2 [ES]$$

$$k_1 [E][S] = k_{-1} [ES] + k_2 [ES]$$

$$k_1 [E][S] = (k_2 + k_{-1}) [ES]$$

$$[ES] = \frac{k_1 [E][S]}{k_2 + k_{-1}}$$

$$[ES] = \frac{[E][S]}{\frac{k_2 + k_{-1}}{k_1}}$$

$$[ES] = \frac{[E][S]}{k_M} \quad (6.154)$$

Initial concentration of enzyme should be equal to the sum of various forms of enzyme concentration.

$$[E]_o = [E] + [ES] + [EI] + [ESI] \quad (6.155)$$

Putting value of [ES] from equation (6.154) into equation (6.155)

$$[E]_o = [E] + \frac{[E][S]}{k_M} + [EI] + [ESI] \quad (6.156)$$

Putting values of [EI] and [ESI] from equation (6.151) and (6.152) into equation (6.156), we get

$$[E]_o = [E] + \frac{[E][S]}{k_M} + \frac{[E][I]}{K_I} + \frac{[ES][I]}{K_I}$$

$$[E]_o = [E] + \frac{[E][S]}{k_M} + \frac{[E][I]}{K_I} + \frac{[E][S][I]}{k_M K_I}$$

$$[E]_o = [E] \left(1 + \frac{[S]}{k_M} + \frac{[I]}{K_I} + \frac{[S][I]}{k_M K_I} \right)$$

$$[E] = \frac{[E]_o}{\left(1 + \frac{[S]}{k_M} + \frac{[I]}{K_I} + \frac{[S][I]}{k_M K_I} \right)}$$

Now putting value of [E] from above equation into equation (6.154)

$$[ES] = \frac{[S]}{k_M} \frac{[E]_o}{\left(1 + \frac{[S]}{k_M} + \frac{[I]}{K_I} + \frac{[S][I]}{k_M K_I} \right)}$$

Putting value of [ES] into equation (6.153), we get

$$v = \frac{k_2 [E]_o [S]}{k_M \left(1 + \frac{[S]}{k_M} + \frac{[I]}{K_I} + \frac{[S][I]}{k_M K_I} \right)}$$

$$v = \frac{k_2 [E]_o [S]}{\left(k_M + k_M \frac{[I]}{K_I} + [S] + \frac{[S][I]}{K_I} \right)}$$

$$v = \frac{k_2 [E]_o [S]}{k_M \left(1 + \frac{[I]}{K_I} \right) + [S] \left(1 + \frac{[I]}{K_I} \right)} \quad (6.157)$$

Taking inverse of equation (6.157), we get

$$\frac{1}{u} = \frac{k_M}{k_2 [E]_o} \left(1 + \frac{[I]}{K_I} \right) \frac{1}{[S]} + \frac{1}{k_2 [E]_o} \left(1 + \frac{[I]}{K_I} \right) \quad (6.158)$$

Equation (6.158) is an equation of straight line with intercept form.

$$\text{Slope} = \frac{k_M}{k_2 [E]_o} \left(1 + \frac{[I]}{K_I} \right)$$

$$\text{Intercept} = \frac{1}{k_2 [E]_o} \left(1 + \frac{[I]}{K_I} \right)$$

$[I]$ is present in slope and intercept so, by changing $[I]$ the y-intercept and slope will change, but x-intercept remains constant. The plot will be different from competitive and uncompetitive inhibition in which one thing remains constant either slope or intercept but in this case both are variable as shown in Fig. 6.38.

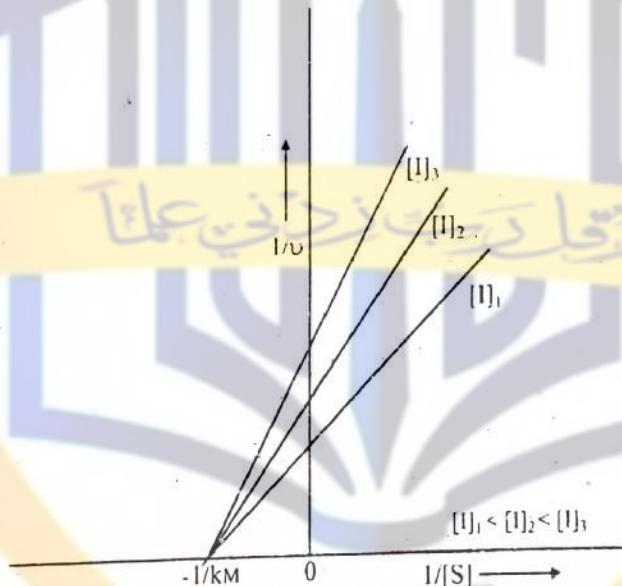


Fig. 6.38 Plot of $1/u$ versus $1/[S]$ in case of non-competitive inhibition

Example 6.7

Prove that the value of x-intercept of the plot of $1/u$ vs. $1/[S]$ is equal to $-\frac{1}{k_M}$.

Solution

x-intercept of $1/u$ versus $1/[S]$ plot is the value of $1/[S]$ for which $1/u$ is equal to zero so, from equation (6.158) we have,

$$0 = \frac{k_M}{k_2 [E]_o} \left(1 + \frac{[I]}{K_I} \right) \frac{1}{[S]} + \frac{1}{k_2 [E]_o} \left(1 + \frac{[I]}{K_I} \right)$$

$$-\frac{k_M}{k_2[E]_o} \left(1 + \frac{[I]}{K_1}\right) \frac{1}{[S]} = \frac{1}{k_2[E]_o} \left(1 + \frac{[I]}{K_1}\right)$$

$$-k_M \left(1 + \frac{[I]}{K_1}\right) \frac{1}{[S]} = \left(1 + \frac{[I]}{K_1}\right)$$

$$\frac{1}{[S]} = -\frac{1}{k_M}$$

Hence, it has been proved that $1/[S]$ is equal to $-1/k_M$.

6.13 B.E.T EQUATION

The various types of adsorption isotherms could not be explained by monomolecular layer adsorption theory of Langmuir, Brunauer, Emett and Teller developed a theory of multi-molecular layer adsorption of gases and vapours. This theory is known as B.E.T theory. These workers extended Langmuir theory to multi-layer adsorption and derived a mathematical equation called B.E.T equation or B.E.T isotherm, which explained satisfactorily all the five types of experimental adsorption isotherms.

Postulates of B.E.T Theory

This theory is based upon the following assumptions

- (i) Adsorption involves the formation of multi-molecular layer, rather than mono-molecular layer. This is represented as follows
 - Vapour + Free surface \rightleftharpoons Single complexes
 - Vapour + Single complexes \rightleftharpoons Double complexes
 - Vapour + Double complexes \rightleftharpoons Triple complexes, etc.
- (ii) Langmuir's idea of fixed (localized) adsorption sites was retained.
- (iii) The interactions between the adsorbate molecules in the adsorption layer were neglected.
- (iv) For the formation of single complexes, the assumption made in Langmuir's theory is adopted.
- (v) There is dynamic equilibrium between the successive layers. The rate of evaporation (desorption) from the first layer is equal to the rate of condensation on the preceding layer.
- (vi) The forces that produce consideration are responsible for binding energy in successive multilayers.
- (vii) Heat of adsorption of first layer is different from that of subsequent layers.
- (viii) After the first layer, the heat of adsorption is equal to heat of condensation of vapours.
- (ix) Adsorption and desorption occur on surface only.

Statement of B.E.T Equation

On the basis of above postulates, Brunauer, Emmett and Teller derived the following equation

$$\frac{p}{V(p^o - p)} = \frac{1}{V_m C} + \left(\frac{C-1}{V_m C} \right) \frac{p}{p^o} \quad (6.159)$$

This equation is called B.E.T equation. In this equation

Here V is volume, reduced to standard conditions of the gas adsorbed at pressure p and temperature T , p^o is saturated vapour pressure of adsorbate (gas or vapour) at temperature T and V_m is volume of gas, reduced to standard conditions (i.e. at NTP), adsorbed to form a saturated monolayer per gram of the adsorbent. While C is a constant equal to $e^{(E_1 - E_L)/RT}$ at any given temperature. Here E_1 is heat of adsorption of first layer, E_L is heat of condensation of the gas and $E_1 - E_L$ is net heat of adsorption.

Derivation of B.E.T Equation

If at any time θ_1, θ_2 and $\theta_3 \dots$ are the fractions of the surface covered by single, double and triple complexes respectively, then the extent of adsorption is given by the volume of the gas adsorbed on the surface. Then

$$V = V_m (\theta_1 + 2\theta_2 + 3\theta_3 + \dots) \quad (6.160)$$

Where V_m is the volume of the adsorbed gas to form unimolecular layer or it is the capacity for one dense layer.

Since equilibrium exists between different phases, hence expressions for the equilibrium constants of the reactions are

Fraction of surface covered \propto Naked surface \times Number of molecules striking per unit area

Fraction of surface covered $\propto (1 - \theta) \times P$

Fraction of surface covered $\propto \theta_o \times P$

So

$$\theta_1 = K_1 P \theta_o$$

$$K_1 = \frac{\theta_1}{P \theta_o} \quad (6.161)$$

Similarly

$$K_2 = \frac{\theta_2}{P \theta_1} \quad (6.162)$$

$$K_3 = \frac{\theta_3}{P \theta_2} \quad (6.163)$$

Where θ_0 is the fraction of free surface at equilibrium. The difference between K_1 and K_2 is usually large because K_1 is very greater than K_2 . This is due to sharp reduction in adsorbate-adsorbent interaction with increase in distance. The difference between K_2 and K_3 or K_3 and K_4 are very small, hence it is assumed that

$$K_2 = K_3 = K_L \quad (6.164)$$

Where K_L is the equilibrium constant for saturated vapour-liquid transition and is given by

$$K_L = \frac{1}{P_0} \quad (6.165)$$

Thus from equations (6.161) to (6.164), we have

$$\begin{aligned} \theta_2 &= K_2 P \theta_1 = K_L P \theta_1 = \left(\frac{P}{P_0} \right) \theta_1 \\ \theta_3 &= K_3 P \theta_2 = K_L P \theta_2 = \left(\frac{P}{P_0} \right) \left(\frac{P}{P_0} \right) \theta_1 = \left(\frac{P}{P_0} \right)^2 \theta_1 \\ &\dots \\ &\dots \\ \theta_i &= K_i P \theta_{i-1} = K_L P \theta_{i-1} = \left(\frac{P}{P_0} \right)^{i-1} \theta_1 \end{aligned} \quad (6.166)$$

Using equation (6.166), equation (6.160) is modified as

$$\begin{aligned} V &= V_m \left(\theta_1 + \left(\frac{P}{P_0} \right)^2 \theta_1 + \left(\frac{P}{P_0} \right)^3 \theta_1 + \dots \right) \\ V &= V_m \theta_1 \left(1 + \left(\frac{P}{P_0} \right)^2 + \left(\frac{P}{P_0} \right)^3 + \dots \right) \\ V &= V_m K_L P \theta_0 \left(1 + \left(\frac{P}{P_0} \right)^2 + \left(\frac{P}{P_0} \right)^3 + \dots \right) \end{aligned} \quad (6.167)$$

Using binomial theorem, for values $P \leq P_0$ we have

$$\left(1 + \left(\frac{P}{P_0} \right)^2 + \left(\frac{P}{P_0} \right)^3 + \dots \right) = \frac{1}{\left(1 - \frac{P}{P_0} \right)^2}$$

Putting this value in equation (6.167) we have

$$V = V_m \left(\frac{K_L P \theta_0}{\left(1 - \frac{P}{P_0} \right)^2} \right) \quad (6.168)$$

The total coverage of the surface

$$\theta_0 + \theta_1 + \theta_2 + \theta_3 + \dots = 1$$

Putting values of $\theta_1, \theta_2, \theta_3, \dots$ into above equation

$$\theta_0 + K_1 P \theta_0 + \left(\frac{P}{P^0} \right) K_1 P \theta_0 + \left(\frac{P}{P^0} \right)^2 K_1 P \theta_0 + \dots = 1$$

$$\theta_0 \left(1 + K_1 P + \left(\frac{P}{P^0} \right) K_1 P + \left(\frac{P}{P^0} \right)^2 K_1 P + \dots \right) = 1$$

$$\theta_0 \left(1 + K_1 P \left(1 + \left(\frac{P}{P^0} \right) + \left(\frac{P}{P^0} \right)^2 + \dots \right) \right) = 1$$

As $1 + r + r^2 + \dots + \infty = \frac{1}{1-r}$, so above equation is modified as

$$\theta_0 \left(1 + \frac{K_1 P}{\left(1 - \frac{P}{P^0} \right)} \right) = 1 \quad (6.169)$$

$$\theta_0 \left(\frac{1 - \frac{P}{P^0} + K_1 P}{1 - \frac{P}{P^0}} \right) = 1$$

$$\theta_0 = \left(\frac{1 - \frac{P}{P^0}}{1 - \frac{P}{P^0} + K_1 P} \right) \quad (6.170)$$

Substituting the value of θ_0 from equation (6.170) into (6.168)

$$V = V_m \left(\frac{K_1 P \left(\frac{1 - \frac{P}{P^0}}{1 - \frac{P}{P^0} + K_1 P} \right)}{\left(1 - \frac{P}{P^0} \right)^2} \right)$$

$$V = V_m \left(\frac{K_1 P}{\left(1 - \frac{P}{P^o}\right) \left(1 - \frac{P}{P^o} + K_1 P\right)} \right)$$

$$V = V_m \left(\frac{K_1 P}{\left(1 - \frac{P}{P^o}\right) \left(1 + \frac{K_1 P P^o - P}{P^o}\right)} \right)$$

$$V = V_m \left(\frac{K_1 P}{\left(1 - \frac{P}{P^o}\right) \left(1 + (K_1 P^o - 1) \frac{P}{P^o}\right)} \right) \quad (6.171)$$

As $K_1 P = (K_1 P^o) \frac{P^o}{P} = \frac{K_1}{K_L} \left(\frac{P}{P^o} \right) = c \left(\frac{P}{P^o} \right)$

and $K_1 P^o = \frac{K_1}{K_L} = c$

Putting value of $K_1 P$ and $K_1 P^o$ into equation (6.171)

$$V = V_m \left(\frac{c \left(\frac{P}{P^o} \right)}{\left(1 - \frac{P}{P^o}\right) \left(1 + (c - 1) \frac{P}{P^o}\right)} \right)$$

This is the B.E.T equation for adsorption. It involves vapour pressure (P), saturated vapour pressure (P^o) at the temperature of the experiment, and two constants V_m and c . This equation can be rearranged as

$$V \left(1 - \frac{P}{P^o}\right) = \frac{V_m c \left(\frac{P}{P^o} \right)}{\left(1 + (c - 1) \frac{P}{P^o}\right)}$$

$$\frac{1}{V \left(1 - \frac{P}{P^o}\right)} = \frac{1 + (c - 1) \frac{P}{P^o}}{V_m c \left(\frac{P}{P^o} \right)}$$

$$\frac{\frac{P}{P^o}}{V \left(1 - \frac{P}{P^o}\right)} = \frac{1 + (c - 1) \frac{P}{P^o}}{V_m c}$$

$$\frac{P}{V\left(1 - \frac{P}{P^o}\right)} = \frac{1}{V_m c} + \frac{(c-1)\frac{P}{P^o}}{V_m c}$$

$$\frac{P}{V\left(1 - \frac{P}{P^o}\right)} = \frac{1}{V_m c} + \frac{(c-1)P}{V_m c P^o}$$

$$\frac{P}{V\left(\frac{P^o - P}{P^o}\right)} = \frac{1}{V_m c} + \frac{(c-1)P}{V_m c P^o}$$

$$\frac{P}{(P^o - P)V} = \frac{1}{V_m c} + \frac{(c-1)P}{V_m c P^o}$$

Interpretation of B.E.T Equation

1. B.E.T equation suggests that the plot of $\frac{P}{(P^o - P)V}$ versus $\frac{P}{P^o}$ should give a straight line. This has been found to be so experimentally (Fig. 6.39) which confirms the correctness (validity) of BET equation.

$$\text{Slope} = \frac{(c-1)}{V_m c}$$

$$\text{Intercept} = \frac{1}{V_m c}, c = \frac{1}{V_m \times \text{Intercept}}$$

By adding slope and intercept, we get

$$\text{Slope} + \text{Intercept} = \frac{c-1}{V_m c} + \frac{1}{V_m c}$$

$$\text{Slope} + \text{Intercept} = \frac{c-1+1}{V_m c}$$

$$\text{Slope} + \text{Intercept} = \frac{1}{V_m}$$

From above two equations, the value of V_m and c (volume of gas to form monomolecular layer) can be calculated.

2. It is easy to see that when only unimolecular layer is formed on the surface, the BET equation would reduce to Langmuir equation.
3. The scheme of multilayered adsorption followed in BET theory can be represented as shown in Fig. 6.40.

4. BET equation is better to obey by process involving high value of $(E_1 - E_L)$ as under such condition only the adsorbate-adsorbent interaction is predominant.

For adsorption process, the variation of equilibrium constant with temperature is given by Vont Hoff's equation

$$\Delta G = -RT \ln K$$

$$K = e^{-\frac{\Delta G}{RT}}$$

So

$$K_1 = g_1 e^{\frac{E_1}{RT}}$$

$$K_L = g_L e^{\frac{E_L}{RT}}$$

Here E_1 is heat of adsorption of first layer, E_L is heat of condensation and g_1 and g_2 are various distinguishable states of adsorption.

$$c = \frac{K_1}{K_L} = \frac{g_1 e^{\frac{E_1}{RT}}}{g_L e^{\frac{E_L}{RT}}} = \frac{g_1 e^{\frac{E_1 - E_L}{RT}}}{g_L} = g e^{\left(\frac{E_1 - E_L}{RT}\right)}$$

If we ignore the energy states then

$$c = e^{\left(\frac{E_1 - E_L}{RT}\right)} = e^{\left(\frac{E_1 - E_L}{KN_A T}\right)}$$

Where K is Boltzmann's constant while N_A is Avogadro's number. $E_1 - E_L$ represents the difference between the heat of adsorption of first layer and heat of condensation. $E_1 - E_L$ is net heat of adsorption. The B.E.T equation is better obeyed by processes involving high values of $E_1 - E_L$, as under such conditions only adsorbate-adsorbent interaction is predominant.

Limitations of BET Theory

1. The assumption that adsorbate has liquid properties is not occurred.
2. When the net heat of adsorption ($E_1 - E_L$) is low, the constant C in BET equation is small. At $C < 2$, the BET equation gives a concave isotherm.
3. BET equation holds good when p/p° values lie between 0.05 and 0.35. This equation fails if p/p° is below 0.05 and above 0.35.
4. Coordination number of molecules is the higher layers also add to the criticism of the BET equation in another way.
5. Low adsorbate-adsorbent energies, however the adsorbate-adsorbent interactions cannot be neglected. In the cases the isotherm (i.e. curves) are more complicated in shape.

Thus BET equation is approximate and needs modification.

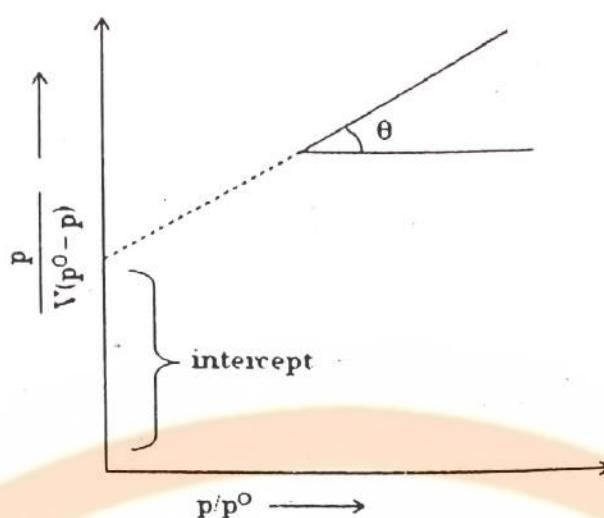


Fig. 6.39 Testing of BET equation

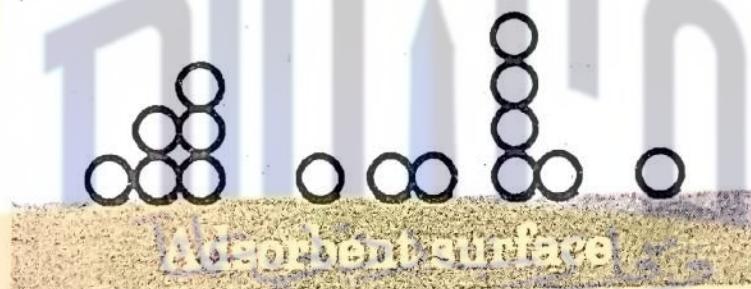


Fig. 6.40 Scheme of multi-layer adsorption

6.14 SURFACE AREA DETERMINATION OF SOLID ADSORBENTS

Generally the solid adsorbents which are used in adsorption are porous and used in powder form. So surface area of adsorbents gets increased. This enhances the magnitude of adsorption. The question of the surface area possessed by finely divided solid is not only important in adsorption, but also in contact catalysis and many other fields. BET isotherm showed that it is possible to use adsorption of gases by such materials for determination of their surface areas and thus finished a very powerful tool being widely used at present.

The porous solid adsorbents possess two types of surface areas: (A) external or outer surface area of porous particles and (B) inner surface area which is due to inner walls of capillaries and cracks in the porous particles.

The roughness factor of the catalyst is defined as

$$\text{Roughness factor} = \frac{\text{Total surface area}}{\text{Outer surface area}}$$

Hence (i) for smooth surface, roughness factor is unity and (ii) for rough surface, it is very high.

$$\text{Specific surface area} = \frac{\text{Surface area}}{\text{Mass of adsorbent}}$$

The following methods are employed to determine the surface area of solid adsorbents.

- (i) BET method
- (ii) Point B method
- (iii) Radioactive tracer method
- (iv) Electron micrograph method

(i) BET Method

This method is extensively used for determination of surface area. The BET equation is

$$\frac{P}{(P^o - P)V} = \frac{1}{V_m c} + \frac{(c-1)P}{V_m c P^o}$$

The plot of $\frac{P}{(P^o - P)V}$ versus $\frac{P}{P^o}$ should give a straight line. This has been found to be so experimentally (Fig. 6.39) which confirms the correctness (validity) of BET equation.

$$\text{Slope} = \frac{(c-1)}{V_m c}$$

$$\text{Intercept} = \frac{1}{V_m c}$$

By adding slope and intercept, we get

$$\text{Slope} + \text{Intercept} = \frac{1}{V_m}$$

$$V_m = \frac{1}{\text{Slope} + \text{Intercept}}$$

By calculating value of slope and intercept from graph and putting in above equation, V_m is calculated.

As

22400 mL of gas at NTP contains = N_A molecules

1 mL of gas at NTP contains = $N_A / 22400$ molecules

V_m mL of gas at NTP contains = $V_m N_A / 22400$ molecules

If A is the area of cross-section of each adsorbent molecule, i.e. the area of surface covered by each molecule and m is the mass of adsorbent, then surface area of solid adsorbent will be

$$\text{Surface area of solid adsorbent} = \frac{N_A V_m A}{22400}$$

Specific surface area = Surface area per gram of adsorbent

$$\text{Specific surface area} = \frac{N_A V_m A}{22400 \times m}$$

In BET method, nitrogen gas is commonly used at its boiling point (-195.8 °C). At this temperature $16.2 \times 10^{-20} \text{ m}^2$ is the area of nitrogen molecule.

Table 6.1 Estimates surface area of clean Nickel films from the physical adsorption of various gases

Gas	Area per molecule ($\times 10^{-20} \text{ m}^2$)	Amount adsorbed to give monolayer on 1 g Ni film	Surface area of 1 g Ni film (m^2)
Kr	14.6	6.15×10^{19}	9.0
Kr	14.6	5.85×10^{19}	8.6
CH ₄	15.7	5.40×10^{19}	8.5
n-C ₄ H ₁₀	24.5	3.48×10^{19}	8.5

Table 6.2 Volumes of adsorbed nitrogen to form a monolayer and surface area of a number of catalysts

Material	Monolayer volume (liter at STP g ⁻¹)	Surface area (m^2/g)
Fused Cu catalyst	0.09×10^{-3}	0.39
Fe, K ₂ O catalyst 930	0.14	0.61
Fe, Al ₂ O ₃ , K ₂ O catalyst 931	0.81	3.5
Cr ₂ O ₃ gel	53.3	230
Silica gel	116.2	500

(ii) Point B Method

In this method relative pressure P/P_0 is plotted against volume of gas adsorbed. The curve is shown in Fig. 6.41 is obtained.

Point B is the first inflection point in the curve and it corresponds to the condition when unimolecular layer is formed.

If V_B is the volume of the gas corresponding to point B, reduced to standard conditions ($P_0 = 1 \text{ atm}$ and $T_0 = 273 \text{ K}$)

$$\text{Then } P_0 V_B = nRT_0$$

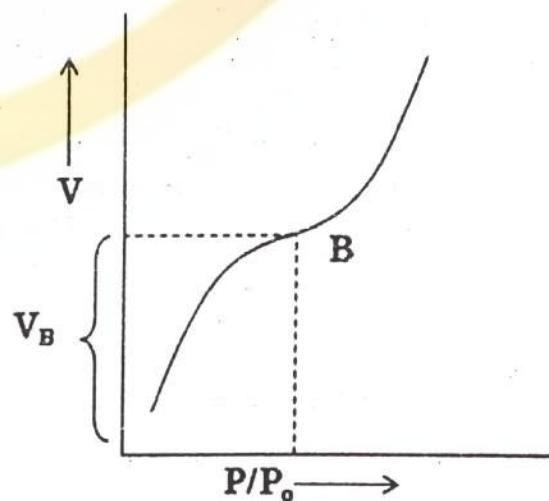


Fig. 6.41 Plot of V versus P/P_0

$$n = \frac{P_o V_B}{RT_o}$$

Where n is the number of moles.

$$\text{Number of molecules adsorbed} = n N_A$$

$$\text{Number of molecules adsorbed} = \frac{P_o V_B N_A}{RT_o}$$

If A is area of cross-section of each adsorbed molecules, then total surface area is

$$\text{Total surface area} = \frac{AN_A P_o V_B}{RT_o}$$

$$\text{Specific surface area} = \frac{AN_A P_o V_B}{mRT_o}$$

This method cannot be applied to all types of solid adsorbents and gas adsorbates. Generally nitrogen is used in this method. The value of A for nitrogen is measured by using following formula

$$A = \left(\frac{M}{\rho N_A} \right)^{2/3}$$

Where ρ is density of nitrogen and M is its molecular weight.

QUESTIONS

Q.1. The rate of catalytic reaction of two gases on solid surface is

$$\text{Rate} = \frac{aP_A bP_B}{(1 + aP_A + bP_B)^2}$$

- (i) Discuss the effect of pressure of gas A on rate of reaction at constant P_B under various conditions.
- (ii) Prove that the rate of reaction is maximum at $P_A = (1+bP_B)/a$

Q.2. Langmuir adsorption isotherm for single system is

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

- (i) Rearrange above expression in the form of equation of straight line. Draw a plot according to this equation.
- (ii) Explain the effect of equilibrium pressure on fractional surface coverage.
- (iii) Derive kinetic rate equation for catalytic decomposition of a gas on metal surface when reactant gas is weakly adsorbed.

Q.3. Derive the relation for rate of decomposition of ammonia using Tempkin's Isotherm.

Q.4. The rate of enzyme catalyzed reaction is

$$v = \frac{k_2 [E]_o [S]}{k_M + [S]}$$

- (i) Explain the parameters present in this relation.
- (ii) Give plot of v as a function of $[S]$.
- (iii) Discuss the effect of substrate concentration on rate of reaction.
- (iv) Define k_M in term of substrate concentration and give its units.
- (v) How can you evaluate k_2 and k_M from above expression.
- (vi) Give condition for maximum rate of enzyme catalyzed reaction.
- (vii) How can you find the value of k_M graphically.

Q.5. The rate of catalytic reaction of two gases on solid surface is

$$\text{Rate} = \frac{aP_A bP_B}{(1 + aP_A + bP_B)^2}$$

- (i) Derive the relation for P_A in term of a and b at which rate of reaction is maximum.
- (ii) Prove that the %age rate fall is only 11 % when P_A is twice the optimum value.
- (iii) Discuss the effect of P_A and P_B on rate of reaction on following conditions.
 - (a) When A and B both gases are weakly adsorbed.
 - (b) When gas A is strongly adsorbed.

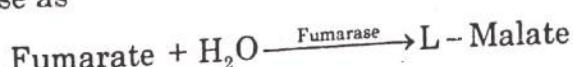
Q.6. Differentiate the followings

- (i) Langmuir Hinshelwood mechanism and Eiley Rideal mechanism
- (ii) Adsorption and desorption
- (iii) Physical adsorption and chemical adsorption

Q.7. Calculate the pressure of a gas using Langmuir adsorption isotherm at which fractional surface coverage is

- (i) 0.2
- (ii) 0.8

Q.8. The hydrolysis of fumarate is carried out in the presence of enzyme, the fumarase as



The value of k_2 for this enzyme is $3 \times 10^3 \text{ s}^{-1}$ and k_M is $4 \times 10^{-5} \text{ M}$. Calculate the rate of fumarate conversion if the initial concentration of fumarate is $1 \times 10^{-6} \text{ M}$ and fumarate concentration is $4 \times 10^{-4} \text{ M}$.

- Q.9. At 300 K, when the pressure of gas is 40 kPa the sample adsorbs 0.72 mg of CO. At same temperature, the mass of gas adsorbed is 0.24 mg at 8 kPa. By using Langmuir adsorption isotherm find the fractional surface coverage of surface at two pressures. ($\theta_A = 0.75, \theta_B = 0.375$)
- Q.10. Adsorption of a gas on solid obeys Langmuir adsorption isotherm. At 6.71 kPa and 20°C gas adsorbs 2.56 mg. The enthalpy change is 10.9 J when 1 mmol of the adsorbed gas is desorbed. What is the pressure for adsorption of same gas at 40°C. ($P_2 = 14.5 \text{ kPa}$)
- Q.11. Explain the kinetics of reaction of two gases on solid surface.
- Q.12. Discuss heterogeneous kinetics of single system reactions. Explain the phenomenon of retardation by reactants and products.
- Q.13. Discuss the kinetics of heterogeneous reactions. Explain retardation of rate of reactions by products and reactants.
- Q.14. What do you understand about heterogeneous kinetics? Explain the kinetics of a single reacting gas on solid surface.

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