

(iii) When Gas is Moderately Adsorbed

When gas is moderately adsorbed the order of reaction will be in between of zero and 1<sup>st</sup> 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,

$\theta_A$  = Fractional surface covered by gas A

$\theta_B$  = Fractional surface covered by gas B

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

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

$$R_{Ads} \propto P_A$$

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

Combining above relations,

$$R_{Ads} \propto P_A (1 - \theta_A - \theta_B)$$

$$R_{Ads} = k_1 P_A (1 - \theta_A - \theta_B)$$

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

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

$$R_{Des} = k_2 \theta_A$$

(6.60)

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

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

(6.61)

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

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

$$R_{Ads} \propto P_B$$

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

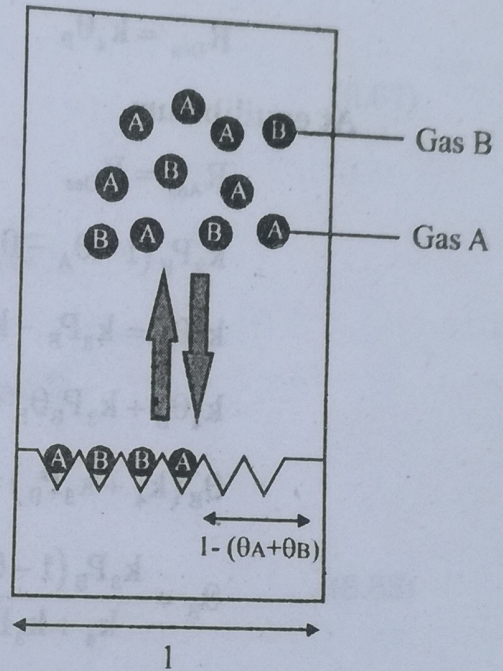


Fig. 6.22 Pictorial diagram of adsorption of two gases on solid surface (6.59)



Combining above relations,

$$\begin{aligned} \text{Rate} &\propto P_A (1 - \theta_A - \theta_B) \\ R_{\text{Ads}} &= k_3 P_B (1 - \theta_A - \theta_B) \end{aligned} \quad (6.62)$$

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

$$\begin{aligned} R_{\text{Des}} &\propto \theta_B \\ R_{\text{Des}} &= k_4 \theta_B \end{aligned} \quad (6.63)$$

At equilibrium,

$$R_{\text{Ads}} = R_{\text{Des}} \quad (6.64)$$

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

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

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

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

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

By putting value of  $\theta_B$  from equation (6.65) into equation (6.61), we get

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

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

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

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

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

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

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

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



$$\theta_A \{k_2(k_4 + k_3P_B) + k_1k_4P_A\} = k_1k_4P_A$$

$$\theta_A = \frac{k_1k_4P_A}{k_2(k_4 + k_3P_B) + k_1k_4P_A}$$

$$\theta_A = \frac{k_1k_4P_A}{k_2k_4 + k_2k_3P_B + k_1k_4P_A} \quad (6.66)$$

Divide numerator and denominator by  $k_2k_4$ , we get

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

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

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

So, equation (6.67) becomes

$$\theta_A = \frac{aP_A}{1 + aP_A + bP_B} \quad (6.68)$$

By putting value of  $\theta_A$  in equation (6.65) from equation (6.68), we get

$$\theta_B = \frac{k_3P_B}{k_4 + k_3P_B} \left[ 1 - \frac{aP_A}{1 + aP_A + bP_B} \right]$$

$$\theta_B = \frac{k_3P_B}{k_4 + k_3P_B} \left[ \frac{1 + aP_A + bP_B - aP_A}{1 + aP_A + bP_B} \right]$$

$$\theta_B = \frac{k_3P_B}{k_4 + k_3P_B} \left[ \frac{1 + bP_B}{1 + aP_A + bP_B} \right] \quad (6.69)$$

Divide numerator and denominator of equation (6.69) by  $k_4$

$$\theta_B = \frac{\frac{k_3P_B}{k_4}}{\frac{k_4}{k_4} + \frac{k_3P_B}{k_4}} \left[ \frac{1 + bP_B}{1 + aP_A + bP_B} \right]$$

$$\theta_B = \frac{\frac{k_3}{k_4}P_B}{1 + \frac{k_3}{k_4}P_B} \left[ \frac{1 + bP_B}{1 + aP_A + bP_B} \right]$$



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  $\theta_A$  and  $\theta_B$ .

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

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

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

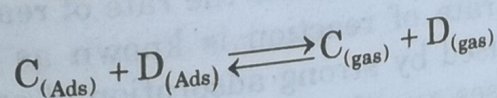
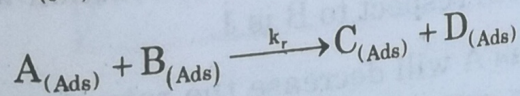
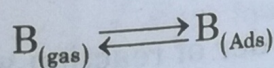
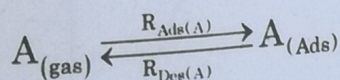
Catalytic reaction of two gases on a solid surface can take place by one of the following mechanisms: Langmuir Hinshelwood mechanism or Eiley-Rideal mechanism

#### 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)