

## Module 8 : Surface Chemistry

### Lecture 36 : Adsorption

#### Objectives

After studying this lecture, you will be able to

- Distinguish between physisorption and chemisorption.
- Distinguish between monolayer adsorption and multilayer adsorption.
- Outline the main ingredients of the major isotherms.
- Distinguish quantitatively between the adsorption isotherms of Gibbs, Freundlich and Langmuir.
- Characterize a multilayer adsorption through the BET isotherm.
- Determine the heat of reaction using an adsorption isotherm.
- Distinguish between the characteristics of bulk reactions and reactions at surfaces.
- Outline the mechanisms of unimolecular and bimolecular reactions at surfaces.
- List the applications of adsorption.

#### 36.1 Adsorption

The molecules at a surface of a material experience imbalanced forces of intermolecular interaction which contribute to the surface energy. It causes accumulation of molecules of a solute or gas in contact with the substance. This preferential accumulation of substrate molecules at the surface is called adsorption which is purely a surface phenomenon.

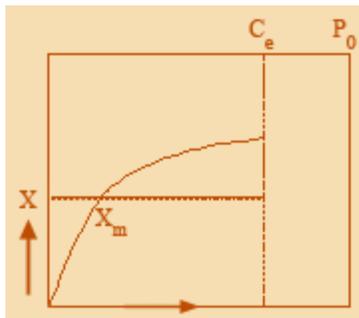
The surface active material is referred to as the adsorbent and the molecules which are accumulated on the adsorbent called adsorbate molecules. The strength by which adsorbate molecules are attached with the adsorbents determines the nature of adsorption. Normally, release of energy in the range of 8 to 25 kJ/mole due to adsorption is termed as physisorption whereas a much larger energy comparable to chemical bonding energy leads to chemisorption. There are always some exceptions to these values. The prescribed value of energy differentiating physisorption and chemisorption are based on general experience.

When an adsorbed molecule receives energy equal to or greater than the energy of adsorption, it will leave the surface. This phenomenon is the reverse of adsorption and is called as desorption. When the number of molecules striking the surface and staying there is equal to the number of molecules that are leaving (evaporating) the surface the system is said to be in equilibrium.

All the atoms or molecules adsorbed on the surface do not have identical environment since distribution of free energy on the surface is not always smooth because of the differences in the energy of the molecular orbitals of the adsorbent and also due to other internal interactions.

#### 36.2 Adsorption Isotherms

A relation between the amount of adsorbate adsorbed on a given surface at constant temperature and the equilibrium concentration of the substrate in contact with the adsorbent is known as Adsorption Isotherm. Two types of typical adsorption isotherms are shown in the following Figures A & B. Figure A shows adsorption with monolayer formation at saturation point. Figure B shows a situation when several layers of adsorbate molecules are formed on the surface of the adsorbent (multilayer adsorption).

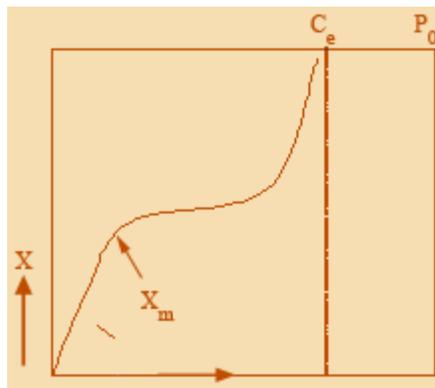


### A. Monolayer adsorption

Fig 36.1 Monolayer vs multilayer adsorption.

$X_m$  is the amount of the substrate required to make a monolayer whereas  $P_0$  is the saturation equilibrium concentration of the substrate.

Arrangement of adsorbed molecules on the surface of the adsorbent could normally be monolayer in nature. Normally, chemisorption leads to monolayer adsorption whereas multilayer arrangement of substrate molecules is observed due to physisorption only. Multilayer formation is also possible due to chemisorption followed by physisorption.



### B. Multilayer adsorption

## 36.2 Adsorption Isotherms

### 36.2.1 Gibb's Adsorption Isotherm

This isotherm normally considers the case when adsorbents are liquids and adsorbates are soluble or partially soluble in it e.g., surfactants / water or organic liquid / water system.

Considering a system having a plane interface between them, the Gibb's free energy of a system containing two components could be written as follows:

$$G = n_1\mu_1 + n_2\mu_2 \quad (36.2.1)$$

Where  $n_1$  and  $n_2$  are the number of moles and  $\mu_1$  and  $\mu_2$  are the chemical potentials of the two components respectively. While dealing with the adsorption of one of the components on the surface of another, an additional term of surface energy has to be introduced, and hence, equation (36.2.1) modifies to

$$G = n_1\mu_1 + n_2\mu_2 + \gamma\sigma \quad (36.2.2)$$

where  $\gamma$  is the surface energy per unit area and  $\sigma$  is the surface area. It is now clear that equation (36.2.1) is for bulk while equation (36.2.2) will be applicable for the surface of the adsorbent liquid. The complete differential of (36.2.2) may be written as

$$dG = n_1d\mu_1 + \mu_1dn_1 + n_2d\mu_2 + \mu_2dn_2 + \gamma d\sigma + \sigma d\gamma \quad (36.2.3)$$

We find that the total free energy  $G$  of the whole system depends on independent variables, namely,  $T, P, n_1, n_2$  and  $\sigma$ , thus,

$$G = f(T, P, n_1, n_2, \sigma)$$

and complete differential of  $G$  will be,

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_1, n_2, \sigma} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2, \sigma} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T, P, n_2, \sigma} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T, P, n_1, \sigma} dn_2 + \left(\frac{\partial G}{\partial \sigma}\right)_{T, P, n_1, n_2} d\sigma$$

$$\text{or } dG = -SdT + VdP + \mu_1dn_1 + \mu_2dn_2 + \gamma d\sigma \quad (36.2.4)$$

## 36.2 Adsorption Isotherms

### 36.2.1 Gibb's Adsorption Isotherm (contd..)

When solution is very dilute, the activity  $a_2$  of solute could be replaced by its concentration.

$$\therefore \Gamma_2 = -\frac{c_2}{RT} \left( \frac{d\gamma}{dc_2} \right)_T$$

or, in general for any solute and liquid adsorbent,

$$\Gamma = -\frac{c}{RT} \left( \frac{\partial \gamma}{\partial c} \right)_T \quad (36.2.9)$$

In the above equation  $\gamma$  is essentially surface energy per unit area, which may easily be replaced by surface tension (force/length).

The application of the above equation is as follows. If the detergent (solute or adsorbate) tends to accumulate at the interface its surface excess is positive, and so  $\frac{d\gamma}{dc}$  is negative. This means surface tension decreases when a solute accumulates at the surface.

**Example 36.1:** The surface tensions of the dilute solutions of phenol in water at  $27^\circ\text{C}$  are the following:

Mass % phenol	0.024	0.05	0.125	0.25	0.40
$\gamma \times 10^3 (\text{Nm}^{-1})$	72.7	72.2	71.3	70.3	69.3

Calculate surface excess concentration ( $\Gamma$ ) at a concentration of 0.15 mass of phenol. Comment on the significance of the observed value of  $\Gamma$ .

**Solution :** A plot of  $\gamma$  vs mole of phenol gives a curvature with negative slope for 0.15 mol of phenol slope is  $-\frac{1.7}{0.1875}$ , putting values in equation,

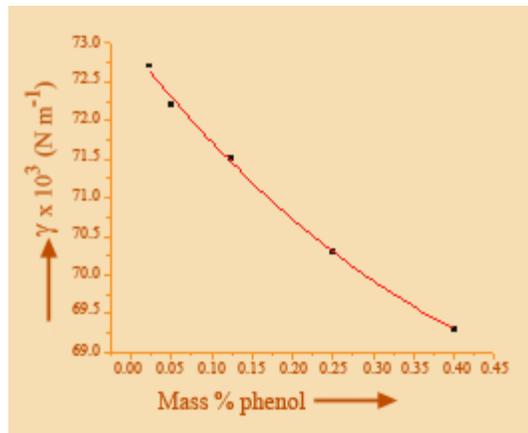


Fig 36.2 Surface tension of phenol vs mass %.

$$\Gamma = -\frac{c}{RT} \left( \frac{\partial \gamma}{\partial c} \right)_T$$

$$\text{We get, } \Gamma = -\frac{0.15}{8.31 \times 300^0 \text{ k}} \left( -\frac{1.7}{0.1875} \right)$$

$$= 5.45 \times 10^{-4} \text{ mol m}^{-2}$$

The positive value of  $\Gamma$  signifies that phenol is surface active and accumulates at the interface.

## 36.2 Adsorption Isotherms

### 36.2.1 Gibb's Adsorption Isotherm (contd..)

At constant temperature and pressure, above equation reduces to,

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + \gamma d\sigma \quad (36.2.5)$$

Comparing equation (36.2.3) and (36.2.5), we get

$$n_1 d\mu_1 + n_2 d\mu_2 + \sigma d\gamma = 0 \quad (36.2.6)$$

A corresponding equation for the bulk of the system may be,

$$n_1^0 d\mu_1 + n_2^0 d\mu_2 = 0 \quad (36.2.7)$$

Where  $n_1^0$  and  $n_2^0$  are the number of moles of adsorbent liquid and solute in the bulk. From the equation (36.2.6) and (36.2.7), we get

$$-\frac{d\gamma}{d\mu_2} = \frac{(n_2 - n_1 n_2^0 / n_1^0)}{\sigma} \quad (36.2.8)$$

Here, the term  $\frac{(n_2 - n_1 n / n_1^0)}{\sigma}$  represents the corresponding excess moles of solute per unit area on the surface of the adsorbent and now be represented by  $\Gamma_2$

$$\therefore -\frac{d\gamma}{d\mu_2} = \Gamma_2$$

The chemical potential of solute  $\mu_2 = \mu_2^0 + RT \ln a_2$

$$\text{or } d\mu_2 = RT d \ln a_2$$

## 36.2 Adsorption Isotherms

### 36.2.2 Freundlich Adsorption Isotherm

It is an empirical relation between the amount of an adsorbate adsorbed per unit weight ( $x/m$ ,  $\text{mg g}^{-1}$ ) of adsorbent and the adsorbate equilibrium concentration ( $C_e$ ,  $\text{moles L}^{-1}$ ) in the fluid. The relation is given below

$$x/m = K C_e^n \quad (36.2.10)$$

where, K and n are Freundlich coefficients. Here,

x = weight of adsorbate adsorbed on m unit weight of adsorbent and  
 $C_e$  = equilibrium concentration of adsorbate.

From the equation, we get

$$\log(x/m) = \log K + n \log C_e \quad (36.2.11)$$

The coefficients K and n can be determined from the intercept and slope of a plot of  $\log(x/m)$  versus  $\log C_e$ .

From the appearance of the type I isotherm (Figure 36.1 A), it is seen that for low values of concentration, the amount adsorbed ( $x/m$ ) is nearly proportional to  $C_e$ , whereas for large values it is nearly constant (or proportional to  $C_e^0$ ). So, it is reasonable that for intermediate values of  $C_e$ ,  $x/m$  should be proportional to some power of  $C_e$  lying between 0 and 1. This is the motivation behind the empirical Freundlich adsorption isotherm.

Freundlich adsorption isotherm may be verified by performing a simple experiment for the adsorption of oxalic acid on charcoal. Supposing m gram of charcoal is added in 50 mL solution of oxalic acid of concentration  $C_i$ . After adsorption is established, the equilibrium concentration of oxalic acid was determined as  $C_f$ . Hence, amount of oxalic acid adsorbed per unit weight of charcoal,

$$x/m (\text{mg g}^{-1}) = (C_i - C_f) \times 63 \times 50 \quad (36.2.12)$$

In a series of such experiments with different initial concentrations of oxalic acid, values of  $x/m$  ( $\text{mg g}^{-1}$ ) are determined. A plot of  $\log x/m$  versus  $C_f$  is made and Freundlich coefficients K and n are determined.

## 36.2 Adsorption Isotherms

### 36.2.3 Langmuir Adsorption Isotherm

In the Langmuir model, the adsorbent surface is considered to possess a number of active interaction sites for adsorption. Langmuir derived a relation between adsorbed material and its equilibrium concentration. His assumption are:

1. There are fixed adsorption sites on the surface of the adsorbent. At a given temperature and pressure, some fraction of these sites are occupied by adsorbate molecules. Let this fraction be  $\theta$ .
2. Each site on the surface of the adsorbent can hold one adsorbate molecule.
3. The heat of adsorption is the same for each site and is independent of  $\theta$ .
4. There is no interaction between molecules on different sites.

Considering the processes of adsorption and desorption of the molecules on the surface, the Langmuir adsorption isotherm may be obtained as follows:

$$\text{Rate of adsorption of molecules on the surface of the adsorbent} = k_a C_e (1 - \theta)$$

$$\text{Rate of desorption} = k_d \theta$$

At equilibrium

$$k_d \theta = k_a C_e (1 - \theta) \quad (36.2.13)$$

$$\theta = \frac{k_a C_e}{k_d + k_a C_e} = \frac{K_L C_e}{1 + K_L C_e}, \text{ where } K_L = \frac{k_a}{k_d} \text{ is the adsorption coefficient}$$

$$\text{Since, } \theta = \frac{x}{x_m}$$

$$\therefore \frac{x}{x_m} = \frac{K_L C_e}{1 + K_L C_e} \quad (36.2.14)$$

where  $x$  and  $x_m$  are the amount of the adsorbent adsorbed at equilibrium concentration  $C_e$  and maximum amount of adsorbate for the formation of monolayer, respectively.

rearranging equation (36.2.2), we get

$$\frac{C_e}{x} = \frac{1}{K_L x_m} + \frac{C_e}{x_m} \quad (36.2.15)$$

If we plot  $\frac{C_e}{x}$  vs  $C_e$ , we will get a straight line. Slope of which will be  $\frac{1}{x_m}$  and intercept as  $\frac{1}{K_L x_m}$ .

Therefore, from values of intercept and slope of the plot values of  $x_m$  and  $K_L$  could be calculated. In the case for the adsorption of gaseous substrate,  $C_e$ ,  $x$ , and  $x_m$  will be replaced by  $p \cdot V$ , and  $V_m$ , respectively.

For chemisorption too, Langmuir's equation works very well but fails for the cases where multilayer formation takes place.

## 36.2 Adsorption Isotherms

### 36.2.3 Langmuir Adsorption Isotherm (contd..)

**Example 36.2:** the volume of  $\text{CH}_4$  (corrected to STP) adsorbed per gram of charcoal at 240 K various pressures of  $\text{CH}_4$  is:

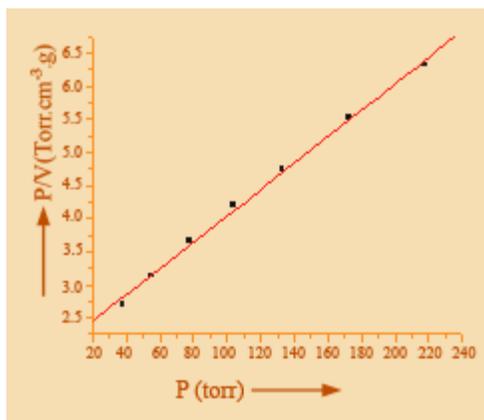
P/(Torr)	38	55	78	104	133	173	218
V/( $\text{cm}^3 \cdot \text{g}^{-1}$ )	14.14	17.52	21.38	24.72	28.00	31.35	34.50

Verify that the data obey Langmuir adsorption isotherm. Also determine Langmuir constant  $K_L$  and the volume corresponding to complete surface coverage. Calculate the fraction of charcoal surface which is covered by

$\text{CH}_4$  molecules at  $P = 150$  torr.

Plot of  $p/V$  vs  $p$  as shown below is linear which shows that the data verify the Langmuir monolayer adsorption isotherm.

$$\frac{p}{V} = \frac{p}{V_m} + \frac{1}{K_L V_m}$$



Slope of the curve =  $0.02 \text{ cm}^3 \cdot \text{g}^{-1}$

$$\therefore V_m = \frac{1}{\text{slope}} = \frac{1}{0.02 \text{ cm}^3 \cdot \text{g}^{-1}} = 50.0 \text{ cm}^3 \cdot \text{g}^{-1}$$

$$\text{intercept} = 2.05 \text{ torr cm}^3 \cdot \text{g}^{-1} = \frac{1}{K_L V_m}$$

$$\therefore K_L = \frac{1}{V_m \times \text{intercept}}$$

$$K_L = \frac{1}{(50.0 \text{ cm}^3 \cdot \text{g}^{-1})(2.05 \text{ torr cm}^3 \cdot \text{g}^{-1})}$$

$$= 9.75 \times 10^{-3} \text{ torr}^{-1}$$

Fig 36.3 Langmuir adsorption isotherm for  $\text{CH}_4$  adsorbed on charcoal.

Fraction of the surface covered ( $\theta$ )

at P = 150 torr,

$$\theta = \frac{K_L P}{1 + K_L P}$$

$$= \frac{(9.75 \times 10^{-3} \text{ torr}^{-1})(150 \text{ torr})}{1 + (9.75 \times 10^{-3} \text{ torr}^{-1})(150 \text{ torr})}$$

$\theta = 0.593 \Rightarrow$  59.3% of the surface is covered by CH<sub>4</sub> molecules.

### 36.2 Adsorption Isotherms

#### 36.2.4 Langmuir adsorption isotherm for several non-dissociatively adsorbed species

If two species A and B are adsorbed on the surface. Then applying Langmuir hypothesis for species A, we have,

$$v_{a(A)} = k_{a(A)} p_A (1 - \theta_A - \theta_B) \quad (36.2.16)$$

$$v_{d(A)} = k_{d(A)} (\theta)_A \quad (36.2.17)$$

$$\therefore k_{d(A)} \theta_A = k_{a(A)} p_A (1 - \theta_A - \theta_B)$$

$$\theta_A = \left( \frac{k_{a(A)}}{k_{d(A)}} \right) p_A (1 - \theta_A - \theta_B)$$

$$\theta_A = K_A p_A (1 - \theta_A - \theta_B) \left( \because k_A = \frac{k_{a(A)}}{k_{d(A)}} \right) \quad (36.2.18)^W$$

Similarly for species B,

$$\theta_B = K_B p_B (1 - \theta_A - \theta_B) \quad (36.2.19)$$

$$\text{or, } \theta_B = K_B p_B - K_B p_B \theta_A - K_B p_B \theta_B$$

$$\theta_B (1 + K_B p_B) = K_B p_B - K_B p_B \theta_A$$

$$\theta_B = \frac{K_B p_B - K_B p_B \theta_A}{1 + K_B p_B} \quad (36.2.20)$$

Now, putting the value  $\theta_B$  from (36.2.20) into equation (36.2.18), we get

$$\therefore \theta_A = K_A p_A \left( 1 - \theta_A - \frac{K_B p_B - K_B p_B \theta_A}{1 + K_B p_B} \right)$$

$$\theta_A = K_A p_A - K_A p_A \theta_A - \frac{K_B p_B - K_B p_B \theta_A}{1 + K_B p_B}$$

$$\theta_A = \frac{K_A p_A - K_A p_A \theta_A}{1 + K_B p_B} \quad (36.2.21)$$

$$\therefore \theta_A = \frac{K_A p_A}{1 + K_A p_A + K_B p_B} \quad (36.2.22)$$

Similarly, we can obtain

$$\therefore \theta_B = \frac{K_B p_B}{1 + K_A p_A + K_B p_B} \quad (36.2.23)$$

In general, Langmuir adsorption isotherm for species A under conditions of several non-dissociatively adsorbed species could be derived as,

$$\frac{x_A}{x_{m(A)}} = \frac{K_{(A)} p_A}{1 + \sum_i K_i p_i} \quad (36.2.24)$$

where the sum runs over all species.

## 36.2 Adsorption Isotherms

### 36.2.5 Multilayer Adsorption

An important assumption of Langmuir theory is the formation of a monolayer. Because of monolayer formation a saturation in adsorption would reach at higher equilibrium concentration of the adsorbate. This type of adsorption occurs due to short range chemical forces which do not allow penetration through the primary adsorbed molecules. Multilayer formation has been observed when molecules are adsorbed through weak forces (long range forces, normally under physical adsorption) due to cohesive forces exerted by the molecules of the adsorbate.

At high pressure multilayer adsorption takes place. The theory of multimolecular (multilayer) adsorption was developed by Stephen Brunauer, Paul Emmet and Edward Teller and is called BET isotherm. This isotherm derived by them successfully accounts for all types of adsorption.

### 36.2.6 BET Isotherm

It assumes that the surface possess uniform, localised sites and that adsorption on one site does not affect the adsorption on neighbouring sites just as in the Langmuir theory. Also, molecules can be adsorbed in second, third,... and  $n^{\text{th}}$  layers with the surface available for layer equal to the coverage of the next lower layer.

The rate constants for adsorption and desorption of the primary layer are  $k_a$  and  $k_d$  and those of the subsequent layers are all  $k'_a$  and  $k'_d$ . The number of sites corresponding to zero, monolayer, bilayer, ... coverage at any stage are  $N_0, N_1, N_2$ , etc. and  $N_i$  in general. The condition for equilibrium of the initial layer is the equality of the rates of its formation and desorption,

$$k_a p N_0 = k_d N_1 \quad (36.2.25)$$

The condition for equilibrium of the next layer is

$$k'_a p N_1 = k'_d N_2 \text{ and in general } k'_a p N_{i-1} = k'_d N_i, \quad i = 2, 3, \dots$$

This condition may be expressed in terms of  $N_0$  as follows:

$$\begin{aligned} N_i &= \left( \frac{k'_a}{k'_d} \right) p N_{i-1} \\ &= \left( \frac{k'_a}{k'_d} \right)^2 p^2 N_{i-2} = \left( \frac{k'_a}{k'_d} \right)^{2-1} p^{i-1} N_1 = \left( \frac{k'_a}{k'_d} \right)^{i-1} \left( \frac{k_a}{k_d} \right) p^i N_0 \\ N_i &= \left( \frac{k'_a}{k'_d} \right)^{i-1} \left( \frac{k_a}{k_d} \right) p^i N_0 \end{aligned} \quad (36.2.26)$$

writing  $\frac{k'_a}{k'_d} = x$  and  $\frac{k_a}{k_d} = cx$ , then

$$\begin{aligned} N_i &= x^{i-1} c x p^i N_0 \\ N_i &= c (xp)^i N_0 \end{aligned} \quad (36.2.27)$$

## 36.2 Adsorption Isotherms

### 36.2.6 BET Isotherm (contd..)

Now, we calculate the total volume,  $V$ , of adsorbed material.  $V$  is proportional to the total number of particles adsorbed, and so

$$V = N_1 + 2N_2 + 3N_3 + \dots = \sum_{i=1}^{\infty} i N_i \quad (36.2.28)$$

Because each layer contributes number of particles according to its thickness, i.e., a monolayer one particle, a bilayer site two particles etc.

If there were complete monolayer coverage the volume adsorbed would be  $V_{\text{mono}}$ , with

$$V_{\text{mono}} = N_0 + N_1 + N_2 + \dots = \sum_{i=1}^{\infty} N_i \quad (36.2.29)$$

Because each site contributes only one particle to the total, it follows that

$$\begin{aligned} V &= \sum_{i=0}^{\infty} iN_i = \sum_{i=1}^{\infty} ic(xp)^i N_0 \\ &= cN_0 \sum_{i=1}^{\infty} i(xp)^i \\ &= cN_0 xp \sum_{i=1}^{\infty} i(xp)^{i-1} \\ &= cN_0 xp \frac{1}{(1-xp)^2} \\ V &= cN_0 xp(1-xp)^{-2} \end{aligned} \quad (36.2.30)$$

From equation (36.2.29),

$$\begin{aligned} V_{\text{mono}} &= \sum_{i=0}^{\infty} N_i = N_0 + N_1 + N_2 + \dots \\ &= N_0 + \sum_{i=1}^{\infty} N_i \\ &= N_0 + \sum_{i=1}^{\infty} c(xp)^i N_0 \\ &= N_0 + \frac{cN_0 xp}{1-xp} \\ &= N_0 + cN_0 xp(1+xp+(xp)^2+\dots) \\ \therefore (1-xp)^{-1} &= 1+xp+(xp)^2+\dots \end{aligned} \quad (36.2.31)$$

## 36.2 Adsorption Isotherms

### 36.2.6 BET Isotherm (contd..)

From equation (36.2.30) and 36.2.31), we have

$$\begin{aligned} \frac{V}{V_{\text{mono}}} &= \frac{cN_0 xp(1-xp)^{-2}}{N_0 + cN_0 xp(1-xp)^{-1}} \\ &= \frac{cxp}{1+(c-2)xp+(1-c)(xp)^2} \\ &= \frac{c(p/p^*)}{1+(c-2)p/p^*+(1-c)p^2/p^{*2}} \\ &= \frac{cz}{1+(c-2)z+(1-c)z^2} \end{aligned} \quad (36.2.33)$$

$$x = \left( \frac{K'_a}{k'_d} \right) = \frac{1}{p^*},$$

$p^*$  = equilibrium pressure, (ads)  $\Leftrightarrow$  vapour putting  $z = p/p^*$

$$\begin{aligned} \frac{V}{V_{\text{mono}}} &= \frac{cz}{1+cz-2z+z^2-cz^2} = \frac{cz}{(1-z)\{1-(1-c)z\}} \\ &= \frac{c p / p^*}{(1-p/p^*)\{(1-1+c)p/p^*\}} \end{aligned} \quad (36.2.34)$$

$$\begin{aligned}
&= \frac{c.p/p^*}{(1-p/p^*)[1+(c-1)p/p^*]} \\
\frac{V}{(z/(1-z))} &= \frac{V_{\text{mono}}c}{1(1-c)z} \\
\frac{V}{(z/(1-z))} &= \frac{V_{\text{mono}}c}{1(1-c)z} \\
\frac{z}{(1-z)} \cdot \frac{1}{V} &= \frac{1}{cV_{\text{mono}}} + \frac{(c-1)z}{cV_{\text{mono}}} \quad (36.2.35)
\end{aligned}$$

$\frac{(c-1)}{cV_{\text{mono}}}$  can therefore be obtained from the slope of a plot of  $\frac{z}{(1-z)V}$  against  $z$ , and  $cV_{\text{mono}}$  can be found from the intercept at  $z = 0$ , the result combined to give  $c$  and  $V_{\text{mono}}$  from the corresponding value of  $V_{\text{mono}}$  at 273 K and 1 atm, number of molecules present in  $V_{\text{mono}}$  could be calculated. By knowing the contact area of a molecule, surface area of the adsorbent per unit mass could be determined.

### 36.3 Determination of Heat of adsorption

The temperature dependence of  $K$  can be used to determine the isoseric enthalpy of adsorption ( $\Delta H^\theta$ , the enthalpy of adsorption at a fixed surface coverage).

From Langmuir adsorption isotherm, fraction of covered surface,  $\theta = \frac{Kp}{1+Kp}$  (36.3.1)

or  $Kp = \frac{\theta}{1-\theta}$ , where  $\theta$  is constant

$\ln K + \ln p = \text{constant}$  so, from the So from free equation  $\left(\frac{d \ln K}{dT}\right)_\theta = \frac{\Delta H^\theta}{RT^2}$ ,

$$\therefore \left(\frac{\partial \ln P}{\partial T}\right)_\theta = -\left(\frac{d \ln K}{dT}\right)_\theta = -\frac{\Delta H^\theta}{RT^2} \quad (36.3.2)$$

using  $d\left(\frac{1}{T}\right) = -\frac{1}{T^2}$ , this rearranges to,

$$\left(\frac{\partial \ln P}{\partial T}\right)_\theta = +\frac{\Delta H^\theta}{R} \times \left(\frac{d\left(\frac{1}{T}\right)}{dT}\right)$$

$$\left(\frac{\partial \ln P}{\partial T}\right)_\theta \left(\frac{dT}{d\frac{1}{T}}\right)_\theta = \frac{\Delta H^\theta}{R}$$

$$\left(\frac{d \ln P}{d\frac{1}{T}}\right)_\theta = \frac{\Delta H^\theta}{R} \quad (36.3.3)$$

Thus, a plot of  $\ln P$  against  $1/T$  should be a straight line with slope  $\frac{\Delta H^\theta}{R}$ . Therefore  $\Delta H^\theta$  could be determined from the slope.

### 36.4 Reaction on surfaces

In the case of a solid immersed in a solution, the reactants in the solution must diffuse to the interface, get adsorbed there and participate in a given reaction mechanism on the solid surface. The product on the surface must then desorb and diffuse into the solution.

### 36.4.1 Unimolecular reactions on surfaces

Consider the surface catalysis of isomerisation or dissociation of a substance A on surface S as follows. The substance S gets adsorbed on the surface forming AS and then dissociates into products.



$$\text{Reaction velocity, } v = k_2 C_{AS} \quad (36.4.3)$$

Where,  $C_{AS}$  = concentration  $\left(\frac{\text{moles}}{\text{cm}^2}\right)$  of A on the surface

If,  $C_s$  = total of surface sites/cm<sup>2</sup> and represents the surface sites covered by A, then

$$C_{AS} = C_s \theta$$

or, reaction velocity,

$$v = k_2 C_s \theta$$

Let  $C_a$  = concentration of A either in gas or solution

Since  $C_s$  is constant, it can be incorporated into the rate constant

$$v = k_2 \theta$$

Applying the steady state approximation to AS,

$$\frac{dC_{AS}}{dt} = 0 = k_1 C_a (1 - \theta) - k_{-1} \theta - k_2 \theta$$

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

$$\therefore v = \frac{k_1 k_2 C_a}{k_1 C_a + k_{-1} + k_2} \quad (36.4.4)$$

$$\frac{1}{v} = \frac{1}{k_2} + \frac{k_{-1} + k_2}{k_1 k_2 C_a} \quad (36.4.5)$$

A plot of  $\frac{1}{v}$  vs  $\frac{1}{C_a}$  yields  $\frac{1}{k_2}$  as the intercept and  $\frac{k_{-1} + k_2}{k_1 k_2}$  as the slope.

## 36.4 Reaction on surfaces

### 36.4.1 Unimolecular reactions on surfaces (contd..)

Usually it is more convenient to use limiting cases as follows:

#### Case I

$k_2$ , the rate of decomposition is very large compared with the rate of adsorption and desorption. In this case,  $k_2 \gg (k_1 C_a + k_{-1})$  and hence equation (36.4.4) reduces to,

$$\therefore v = k_1 C_a$$

Physically, the assumption that  $k_2$  is large implies that an adsorbed molecule decomposes immediately after coming in contact with the surface. This situation is found for the decomposition of HI on Pt and N<sub>2</sub>O on gold.

#### Case II

$k_2$  is very small (negligible) in comparison to  $(k_1 C_a + k_{-1})$  and hence equation (36.4.4) reduces to :

$$\therefore v = \frac{k_1 k_2 C_a}{k_1 C_a + k_{-1}}$$

$$= \frac{k_2 K C_a}{K C_a + 1}, \quad K = \frac{k_1}{k_{-1}}$$

at low concentration of the species A,  $K C_a \ll 1$

$$\therefore v = k_2 K C_a$$

Where as at high concentration  $K C_a \gg 1$  or  $\theta \simeq 1$

$$\therefore v = k_2$$

#### Sub-Case of I

A diatomic molecule  $A_2$  dissociates upon adsorption to the surface.

This reaction can be written as



$$K_C = \frac{k_a}{k_d} = \frac{[AS]^2}{[A_2][S]^2}$$

Because two surface sites are involved in the adsorption and desorption process, the rates of adsorption,  $v_a$ , and desorption  $v_d$ , are

$$v_a = k_a p_{A_2} (1 - \theta)^2 C_s^2 \quad (36.4.7)$$

$$v_d = k_d \theta^2 C_s^2 \quad (36.4.8)$$

Where,  $C_s$  = total surface sites/cm<sup>2</sup>,  $\theta$  = fraction of the surface covered and  $p$  represents the pressure of the molecules  $A_2$ .

At equilibrium, these rates are equal, and so

$$k_a p_{A_2} (1 - \theta)^2 = k_d \theta^2$$

$$K p_{A_2} (1 - \theta)^2 = \theta^2$$

$$\theta = \frac{K^{1/2} p_{A_2}^{1/2}}{1 + K^{1/2} p_{A_2}^{1/2}} \quad (36.4.9)$$

$$\frac{1}{\theta} = 1 + \frac{1}{K^{1/2} p_{A_2}^{1/2}} \quad (36.4.10)$$

A plot of  $\frac{1}{\theta}$  vs  $\frac{1}{p_{A_2}^{1/2}}$  will yield a straight line with slope  $\frac{1}{K^{1/2}}$  and intercept 1.

### 36.4 Reaction on surfaces

#### 36.4.2 Bimolecular reactions on surfaces

A bimolecular reaction between two molecules A and B on a surface may occur through different alternative steps out of which following two are important

##### (i) Langmuir – Hinshelwood mechanism

The two reacting molecules A and B react after being adsorbed on neighbouring sites on the surface of the catalyst. This mechanism is called as Langmuir - Hinshelwood mechanism. Reaction rate  $v$ , for such reaction may be written as follows:

$$v = k \theta_A \theta_B \quad (36.4.11)$$

Putting the values of  $\theta_A$  and  $\theta_B$  from equations (36.2.15) and (36.2.16), we get

$$v = \frac{k K_A K_B p_A p_B}{(1 + K_A p_A + K_B p_B)^2} \quad (36.4.12)$$

Above equation could be subjected to two special cases as follows:

1. If the pressures of A and B species,  $p_A$  and  $p_B$  are both sufficiently low so that  $K_A p_A$  and  $K_B p_B$  may be

neglected in comparison with unity, the rate equation becomes,

$$v = kK_A K_B [A][B] \quad (36.4.13)$$

This would mean reaction to be second order. This is a frequently observed behaviour in Langmuir – Hinshelwood mechanism.

2. If a reactant A is very weakly adsorbed,  $k_A p_A$  in the denominator of equation (36.4.11) may be neglected, and the rate equation become,

$$v = \frac{kK_A K_B p_A p_B}{(1 + K_B p_B)^2} \quad (36.4.14)$$

Reaction of hydrogen with ethylene on copper follows a nearly similar rate law as follows:

$$v = \frac{K[H_2][C_2H_4]}{(1 + K[C_2H_4])^2}$$

If reactant B is adsorbed very strongly such that  $K_B p_B \gg 1$ , equation (36.4.13) becomes

$$v = \frac{kK_A p_A}{K_B p_B} \quad (36.4.15)$$

The rate is now inversely proportional to  $P_B$ . Such behaviour is observed in reaction between carbon monoxide and oxygen on quartz and on platinum. In these cases, rate is inversely proportional to the pressure of carbon monoxide, which must be strongly adsorbed.

#### (ii) Langmuir - Rideal mechanism

If reaction is due to collision of gaseous molecules A with adsorbed B molecules, the mechanism is known as Langmuir – Rideal mechanism and the rate law in this case will be,

$$v = k\theta_B p_A \quad (36.4.16)$$

$$\text{or, } v = \frac{kK_A p_A p_B}{1 + K_A p_A + K_B p_B} \quad (36.4.17)$$

The reaction of ethylene and  $H_2$  on copper surface presents a case of Langmuir – Rideal mechanism.  $C_2H_4$  gets adsorbed much strongly on the surface. Rate equation for the reaction of  $C_2H_4$  and  $H_2$  on copper surface follows as below:

$$v = \frac{k[H_2][C_2H_4]}{(1 + c[C_2H_4])^2} \quad (36.3.18)$$

### 36.5 Surface Catalysis

Many industrial chemical reactions are carried out in the presence of solid catalyst e.g., Fe-catalyzed synthesis of  $NH_3$  from  $N_2$  and  $H_2$ ,  $SiO_2/Al_2O_3$  catalyzed cracking of high molecular weight hydrocarbons to gasoline. Reactions involving catalysts of a phase different from reactants are known as heterogeneous catalysis. Besides other usual applications, heterogeneous catalysis is extremely important and will be discussed in detail.

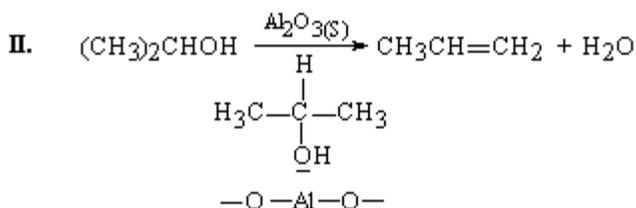
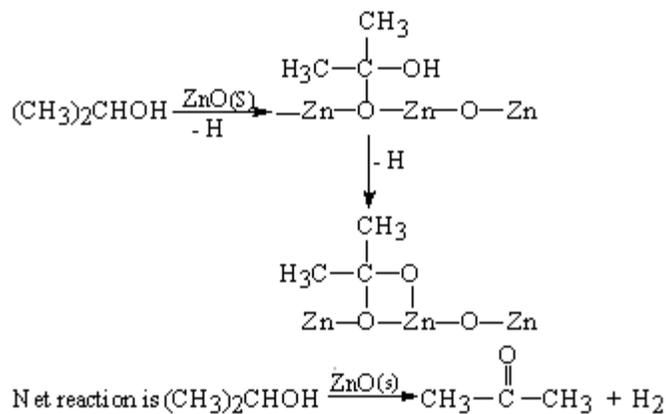
Heterogeneous catalysis, like its homogeneous counterpart, changes the rate of a reaction by providing an alternative reaction mechanism. Solid catalysts lower activation energies by much greater extent than homogeneous catalysts. For the reaction,  $2HI \xrightarrow{\quad} I_2 + H_2$  without catalyst, the activation energy is 44 kcal/mol; 25 kcal/mol when catalyzed by Au, and is only 14 kcal/mol when catalyzed by Pt. Uncatalyzed reaction  $2H_2O(aq) \xrightarrow{\quad} 2H_2 + O_2$  has activation energy 17 kcal/mol, 12 kcal/mol when catalyzed by colloidal Pt and only 2 kcal/mol when catalyzed by enzyme catalase.

Similarly, decomposition of  $N_2O$  in gas phase without a catalyst has an activation energy 250 kJ/mol, and with catalysts Au and Pt, is about 125 kJ/mol.

The substances most often studied and used as heterogeneous catalysts are transition metals, alloys and semiconducting oxides and sulfides. The effectiveness of a catalyst can be measured by the amount of product formed per unit time per unit surface area of the catalyst. Activity of a catalyst depends on the nature

of active sites present on the surface e.g., point defects, lattice distortions of % d-character of the metallic bond within the solid metal. A catalyst with a different surface property may lead to the formation of a different product from the same starting reactant. For example, isopropanol undergoes dehydrogenation on a surface of ZnO while dehydration occurs on  $\text{Al}_2\text{O}_3(\text{s})$ . ZnO is n-type semiconductor whereas  $\text{Al}_2\text{O}_3$  is an ionic insulator and acts as a Lewis acid. The probable mechanism may be given as follows:

I.



In a surface catalyzed reaction, activation energy is normally lowered due to adsorption of reacting molecules on the surface of the catalyst. After adsorption, surface molecules are not allowed to perform translational motion but are able to perform vibrational motion.

### 36.6 Applications of Adsorption

The process of adsorption is very important as it has many applications in domestic as well as in industrial processes. Some of them are as follows:

- In heterogeneous catalysis:** Surface active materials are widely used as catalysts mostly due to adsorption processes. If the surface active materials (adsorbents) have a different phase from that of substrates, then the catalysis is called heterogeneous catalysis. A system where both the catalyst and the substrate are in same phase is called homogeneous (catalysis).
- In removal of colouring material:** Many coloured materials or impurities are removed through adsorption by suitable surface active materials like charcoal. Activated charcoal has been extensively used for this purpose.
- In ion exchange resins:** Several polymeric materials are used for the separation of ionic substances in chromatography through ion-exchange.
- In adsorption indicators:** Several dyes like eosin and fluorescein are used as indicators in the titrations of  $\text{Cl}^-$ ,  $\text{Br}^-$  etc., against  $\text{Ag}^+$  (Fajan's method).
- In gas masks :** Activated charcoal is used to remove toxic gases in gas masks.
- In dyeing of cloth:** Many substances work as mordants for dyeing of cloths. Several metal cyanogen complexes and alums work as efficient mordants in dyeing cloths.
- In de humidizers:** Many substances, when they adsorb water, change their colour. Silica and alumina gels are used as adsorbents for removing moisture. Silica is colourless but after adsorbing water becomes blue.

### Recap

In this lecture you have learnt the following

#### 36.7 : Summary

In the present lecture on surface chemistry, we began by distinguishing between physisorption and chemisorption and also between monolayer adsorption and multilayer adsorption. The binding energies in physisorption are much smaller and in the range of 8 to 25 kJ/mole. A relation between the amount of adsorbate adsorbed on a given surface at constant temperature and the equilibrium concentration of the substrate in contact with the adsorbent is known as Adsorption Isotherm. We have outlined the main ingredients of some important isotherms such as the adsorption isotherms of Gibbs, Freundlich and Langmuir

A multiplayer adsorption was characterized through the BET isotherm.

The heat of a reaction was obtained using an adsorption isotherm. We also outlined the mechanisms of unimolecular and bimolecular reactions at surfaces. The Langmuir – Hinshelwood mechanism and the Langmuir – Rideal mechanism of bimolecular surface reactions were described in detail. Towards the end, the role of adsorption in surface catalysis was highlighted and the other applications of adsorption were listed.