Surface Phenomena

Adsorption –

The phenomenon of higher concentration of any molecular species at the surface than in the bulk of a solid is known as adsorption.

The process that involves accumulation of a substance in molecular species in higher concentrations on the surface is called adsorption.
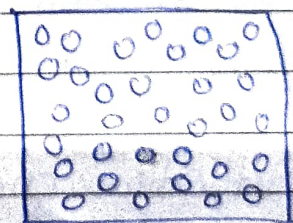
Adsorbate –

Substance that is deposited on the surface of another substance is known as adsorbate.
ex. H_2, N_2 and O_2 gases.

Adsorbent –

Surface of a substance on which adsorbate adsorbs is called adsorbent.
ex. charcoal, silica gel, alumina gel, clay.

adsorbate →   ← adsorbent
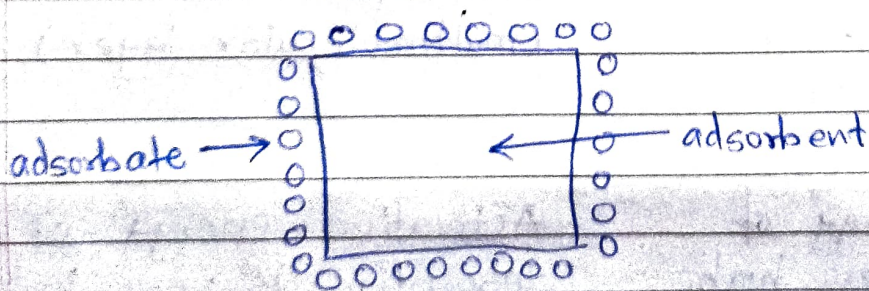
Adsorption   Absorption.
                          ↳ penetration into the body of solid.

* Adsorption is classified as
  1. Chemical adsorption (chemisorption)
  2. Physical adsorption (physisorption)

Chemical Adsorption	Physical Adsorption
Can occur at all temperatures.	Occurs only at very low temperatures below the boiling point of adsorbate.
Increases with rise in temperature	Decreases with rise in temperature.
Heat evolved is very high. $40 - 400$ KJ mol^{-1}	Heat evolved is quite low $4 - 40$ KJ mol^{-1}.
Irreversible	Reversible
Does not extend beyond a monolayer of gas molecules or atoms on the surface of solid.	May extend beyond a monolayer. (multimolecular layer)
Activation energy of desorption is very high.	Activation energy of desorption is very low.
Caused by chemical bond formation.	Caused by intermolecular van der Waal's forces.
Change of pressure has no effect.	Increase of pressure increases adsorption, ↓ in pressure → desorption

⭐ Adsorption isotherm -

An adsorption isotherm is a graph that represents the variation in the amount of adsorbate adsorbed on the surface of the adsorbent with the change in pressure at constant temperature.

Variation of adsorption with pressure at a given constant temperature which is expressed graphically.

⭐ Freundlich Adsorption Isotherm -
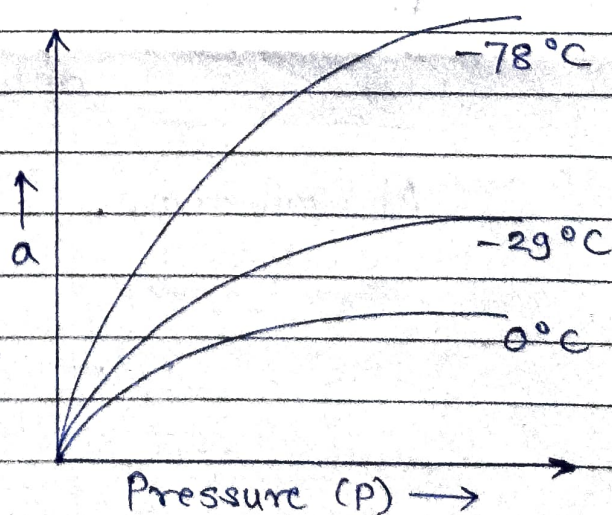
Mathematical expression

$$a = k \cdot p^n$$

a - amount of gas adsorbed per unit mass of adsorbent
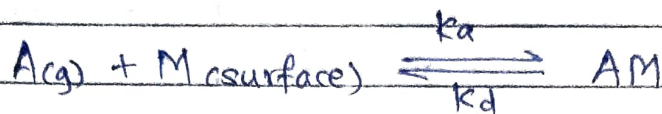
p - pressure

k and n - constants depending upon nature of gas and nature of adsorbent

$$n < 1$$

Freundlich adsorption isotherm gives the variation in the quantity of gas adsorbed by a unit mass of solid adsorbent with the change in pressure of the system for a given temperature

$$A_{(g)} + M_{(surface)} \underset{k_d}{\overset{k_a}{\rightleftharpoons}} AM$$

... dynamic equilibrium between adsorbed molecules and the free molecules of gas (A).

Rate of adsorption is proportional to pressure of A, i.e. P_A and the number of vacant sites on the surface i.e. $N(1-\theta)$.

$N \rightarrow$ total no. of sites

$\theta \rightarrow$ fraction of surface sites occupied by gas molecules.

$$\theta = \frac{\text{No. of adsorption sites occupied}}{\text{No. of adsorption sites available.}}$$

∴ Rate of adsorption $= k_a \, P_A \, N \,(1-\theta)$.

Rate of desorption is proportional to number of adsorbed molecules i.e. $N\theta$.

∴ Rate of desorption $= k_d \cdot N \theta$.

k_a and k_d - rate constants for adsorption and desorption resp.

At equilibrium,

Rate of adsorption = Rate of desorption

∴ $k_a \cdot P_A \cdot \cancel{N} \,(1-\theta) = k_d \cdot \cancel{N} \cdot \theta$

$$\frac{ka}{kd} \cdot P_A \cdot (1-\theta) = \theta$$

$$K \cdot P_A (1-\theta) = \theta \qquad \dots \text{where } K = \frac{ka}{kd}$$

$$\frac{1-\theta}{\theta} = \frac{1}{K P_A}$$

$$\frac{1}{\theta} - 1 = \frac{1}{K \cdot P_A}$$

$$\frac{1}{\theta} = \frac{1}{K \cdot P_A} + 1 = \frac{1 + K \cdot P_A}{K \cdot P_A}$$

Hence,

$$\boxed{\theta = \frac{K P_A}{1 + K \cdot P_A}}$$
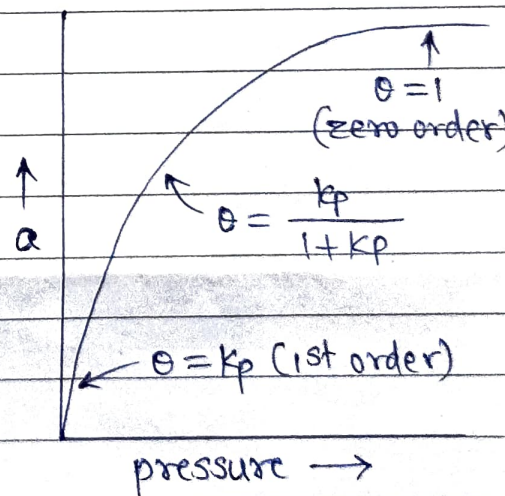
This is called Langmuir adsorption isotherm

Case -1
At low pressure, $K \cdot P_A \ll 1$
$$\therefore \theta = K \cdot P_A$$
i.e. fraction of surface covered
is directly prop. to partial press.
of the gas molecule.

$\theta = 1$
(zero order)

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

$\theta = kp$ (1st order)

pressure →

Case - 2
At high pressure, $K P_A \gg 1$
$$\therefore \theta = 1$$
θ tends to become unity, makes the reaction rate
independent of pressure

BET Theory of Multilayer Adsorption

The Langmuir theory of adsorption is restricted to the formation of a monomolecular layer of the gas molecules on the solid surface and disregards the possibility that multilayer adsorption may also take place. The theory of adsorption proposed in 1938 by Brunauer, Emmett and Teller (known as the BET theory, after the initials of these scientists) assumes that physical adsorption resulting in the formation of multilayers, is the true picture of adsorption. In the BET theory, it is assumed that the solid surface possesses uniform, localized sites and that adsorption at one site does not affect adsorption at neighbouring sites, as was assumed in the Langmuir theory. It is further assumed that molecules can be adsorbed in second, third,...... and nth layers, the surface area available for the nth layer being equal to the coverage of the $(n - 1)$th layer. The energy of adsorption in the first layer, E_1, is assumed to be constant and the energy of adsorption in succeeding layers is assumed to be the same as E_L, the energy of liquefacation of the gas. Based on the above assumptions, Brunauer, Emmett and Teller derived the following equation, known after them as the **BET equation :**

$$\frac{p}{v_{total}(p_0 - p)} = \frac{1}{v_{mono}c} + \frac{c-1}{v_{mono}c}\left(\frac{p}{p_0}\right)$$ ...(20)

where v_{total} is the volume of the gas adsorbed at the pressure p, v_{mono} is the volume adsorbed when the surface of the solid is covered completely with a monolayer of the adsorbed molecules of the gas and c is a constant depending upon the nature of the gas. Its numerical value is given approximately by the expression $c = \exp(E_1 - E_L)/RT$ in which E_1 is the heat of adsorption in the first layer and E_L is

the heat of liquefacation of the gas. Since c is a constant for a given gas and v_{mono} is a constant for a given gas-solid system, the plot of $p/v_{total}(p_0 - p)$ against p/p_0 should give a straight line. This has been checked in the case of adsorption of a number of gases on various solid adsorbents. The results obtained in the case of adsorption of nitrogen on silica gel at $-183°C$ are shown in Fig. 5. As can be seen, the plot obtained is a good straight line. Fairly satisfactory straight lines are obtained in most cases as long as pressure p does not exceed one–third of the saturation pressure p_0, *i.e.*, the pressure required to condense the gas into the liquid state at the prevailing temperature. At higher pressures, however, deviations set in.

Fig. 5. BET plot for the adsorption of N_2 on silica gel at $-183°C$.

The slope of the linear plot, evidently, gives the value of $(c - 1)/(v_{mono}c)$ while the intercept yields the value of $1/(v_{mono}c)$. Thus, from the slope and the intercept, both v_{mono} and c can be evaluated.

Determination of Surface Area. Knowing v_{mono}, the surface area of the adsorbent can be easily calculated, as shown in the following example. The assumption is that the molecules of the gas adsorbed in the first layer are closely packed on the surface.
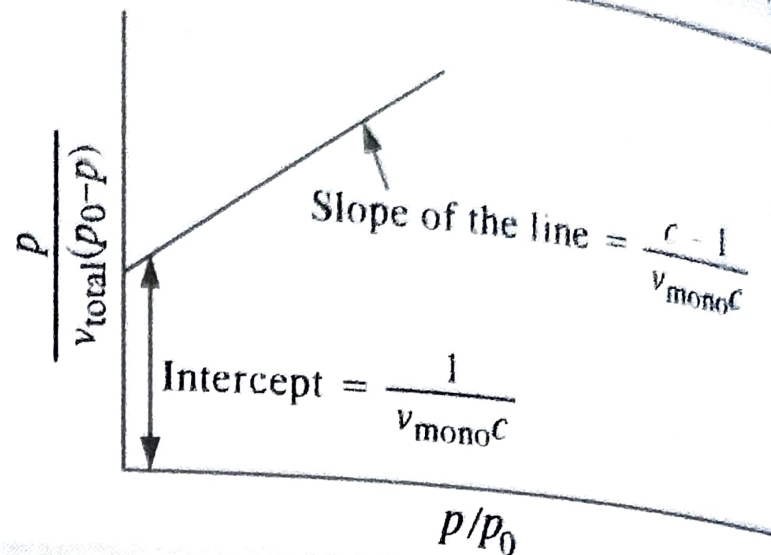
Adsorption of a solute from a solution onto a solid adsorbent is more difficult to treat theoretically than the corresponding adsorption of gases on solids. It appears, however, that in this case, too, like the gas—solid adsorption, a monomolecular layer is formed. The solvating power of the solvent inhibits the formation of a multilayer.

For adsorption from solutions, a commonly used isotherm is the Freundlich adsorption isotherm. If x is the mass of the solute adsorbed on mass m of adsorbent and c is the concentration of the solute in the solution, then the Freundlich adsorption isotherm is expressed as

$$x/m = a = kc^n \qquad \qquad ...(44)$$

where k and n are empirical constants. Taking logs,

$$\ln a = \ln k + n \ln c \qquad \qquad ...(45)$$

This logarithmic form is convenient to use. If we plot $\ln a$ versus $\ln c$, the plot would be a straight line with slope equal to n and intercept equal to $\ln k$.

The Gibbs Adsorption Isotherm for Adsorption From Solutions

The concentration of a solute at the surface of a solution is, in general, markedly different from that in the bulk. If the surface tension of the solute is lower than that of the liquid, it tends to accumulate at the surface of the liquid thereby decreasing the surface tension (or the surface free energy per unit area) of the liquid. A quantitative treatment of the thermodynamics of adsorption of a solute at the surface of a liquid was given in 1878 by J.W. Gibbs (1839-1903), the greatest 19th century American mathematical physicist.

For a system containing two components, the Gibbs free energy can be written as

$$G = n_1\mu_1 + n_2\mu_2 \qquad \qquad ...(46)$$

where n_1 and n_2 are the amounts (number of moles) and μ_1 and μ_2 are the chemical potentials (i.e., partial molar Gibbs free energies) of the two components, respectively. Since we are dealing with the adsorption of one of the components on the surface which results in changing the surface free energy, Eq. 46 is modified to

$$G = n_1\mu_1 + n_2\mu_2 + \gamma\sigma \qquad \qquad ...(47)$$

... γ is the surface energy which is numerically the same as the surface tension and σ is the ... area.

The complete differential of Eq. 47 is written as

$$dG = n_1 d\mu_1 + \mu_1 dn_1 + n_2 d\mu_2 + \mu_2 dn_2 + \gamma d\sigma + \sigma d\gamma \qquad ...(48)$$

... see that free energy G now depends upon five independent variables, viz., T, P, n_1, n_2 and σ.

$$G = f(T, P, n_1, n_2, \sigma) \qquad ...(49)$$

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

$$+ \left(\frac{\partial G}{\partial \sigma}\right)_{T,P,n_1,n_2} d\sigma \qquad ...(50)$$

According to thermodynamics, the partial derivatives

$$-\left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2,\sigma}, \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2,\sigma}, \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,\sigma}, \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,\sigma} \text{ and } \left(\frac{\partial G}{\partial \sigma}\right)_{T,P,n_1,n_2} \text{ in Eq. 50 are,}$$

respectively, equal to S, V, μ_1, μ_2 and γ.

Hence,
$$dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2 + \gamma d\sigma \qquad ...(51)$$

At constant temperature, $dT=0$ and at constant pressure, $dP=0$. Hence, Eq. 51 reduces to

$$(dG)_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 + \gamma d\sigma \qquad ...(52)$$

From Eqs. 48 and 49,

$$n_1 d\mu_1 + n_2 d\mu_2 + \sigma d\gamma = 0 \qquad ...(53)$$

The corresponding expression for the bulk of the liquid is

$$n_1^\circ d\mu_1 + n_2^\circ d\mu_2 = 0 \qquad ...(54)$$

where n_1° and n_2° are the amounts (number of moles) of the liquid and the solute, respectively, in the bulk phase.

Since the system is in equilibrium, the chemical potential of each component in the bulk and the surface phase must be the same. The system, on being disturbed, attains a new equilibrium so that the changes in the chemical potentials must be identical in both the phases, i.e., $d\mu_1$ and $d\mu_2$ in Eqs. 53 and 54 must be identical. Elimination of $d\mu_2$ from these equations gives

$$n_1[-(n_2^\circ/n_1^\circ)d\mu_2] + n_2 d\mu_2 + \sigma d\gamma = 0 \qquad ...(55)$$

or
$$(n_2 - n_1 n_2^\circ/n_1^\circ)d\mu_2 + \sigma d\gamma = 0$$

or
$$-\frac{d\gamma}{d\mu_2} = \frac{n_2 - (n_1 n_2^\circ/n_1^\circ)}{\sigma} \qquad ...(56)$$

The quantity within parenthesis of Eq. 56 gives the amount n_2° of solute 2 associated with the amount n_1° of liquid 1 in the bulk phase. On the other hand, n_2 is the amount of the solute associated with the amount n_1 of the liquid at the surface. Thus, the numerator on the right hand side of Eq. 56 gives the excess amount of the solute present in the surface of the liquid. Evidently, the right hand

side of Eq. 56 gives the **surface excess**, i.e., the excess concentration of the solute per unit area of the surface, designated as Γ_2, i.e., $[n_2 - (n_1 n_2^o / n_1^o)]/\sigma = \Gamma_2$.

Thus, from Eq. 56,

$$\Gamma_2 = - \, d\gamma/d\mu_2 \qquad \qquad \cdots(57)$$

The chemical potential of solute 2 is given by

$$\mu_2 = \mu_2^*(l) + RT \ln a_2 \qquad \qquad \cdots(58)$$

where $\mu_2^*(l)$ is the chemical potential of the pure solute in the liquid phase. Hence,

$$d\mu_2 = RT \, d \ln a_2 \qquad \qquad [\because \, d\mu_2^*(l) = 0] \qquad \qquad \cdots(59)$$

Substituting for $d\mu_2$ in Eq. 57, we obtain

$$\Gamma_2 = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial \ln a_2}\right)_T = -\frac{a_2}{RT}\left(\frac{\partial\gamma}{\partial a_2}\right)_T \qquad \qquad \cdots(60)$$

When the solution is very dilute, it behaves ideally so that the activity a_2 of the solute can be replaced by its concentration c_2. Thus,

$$\Gamma_2 = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial \ln c_2}\right)_T = -\frac{c_2}{RT}\left(\frac{\partial\gamma}{\partial c_2}\right)_T \qquad \qquad \cdots(61)$$

Eq. 61 is called the **Gibbs adsorption isotherm.** Knowing the concentration–dependence of γ, Γ_2 can be calculated.

1. Low Energy Electron Diffraction (LEED). When a surface is bombarded with electrons, the electrons may be scattered elastically (*i.e.*, with no loss of energy) or inelastically. The elastically scattered electrons are diffracted if their de Broglie wave length is quite small. Thus, LEED provides a means for studying the atomic geometry of a surface. In the LEED experiment, the electrons are accelerated in an electron gun and strike the surface normally. Some of the electrons are backscattered by the surface. The inelastically scattered electrons are removed by means of the grids in front of the screen while the elastically scattered electrons are accelerated onto the phosphorescent screen for viewing the diffraction pattern. The presence of sharp diffraction spots shows that the surface is ordered on the atomic scale. LEED can also yield information about the structure of an adsorbed layer in chemisorption.

2. Photo Electron Spectroscopy (PES). We have discussed the basic principles of PES in the chapter on Spectroscopy. Suffice it to mention here that the photons with energies in the UV region (the technique is then called UPES) eject electrons from the valence orbitals of an adsorbed molecule or from the valence bands of the solid. UPES experiments are carried out using the He–I radiations (21·22 eV) or the He–II radiations (40·8 eV). The UPES of a molecule physisorbed on a solid is a superposition of the UPES of the valence band of the solid and the gas-phase MOs of the adsorbed molecule. The UPES of the physisorbed molecule is similar to UPES of the corresponding gas molecule because of the weak interaction with the surface. However, in a chemisorbed molecule, chemisorption affects the valence orbitals of the molecule and the valence band of the solid resulting in a complex UPES.

In XPES in which X-ray photons are used for photoelectron spectroscopy, the core electrons are ejected from the metal and from the adsorbed species, the source of X-rays being either the Mg K_α (1253·6 eV) or Al K_α (1486·6 eV). Since the energies of the atomic core levels are characteristic of each element in the Periodic table, XPES is often used to obtain the elemental analysis of the surface.

In Auger Electron Spectroscopy (AES), an electron is ejected by an X-ray photon, as in XPES, but *the emission of secondary electrons is analyzed* rather than the primary electrons. When a core electron is ejected by an X-ray photon, an electron from a higher energy level may jump into the core energy level. The energy liberated in this manner may bring about emission of a second electron called Auger electron (this effect was studied by the French physicist P. Auger). The energies of the Auger electrons are characteristic of the core levels. AES can thus yield information about the bonding of the core electrons of the adsorbed species.

3. Scanning Tunnelling Microscopy (STM). A major breakthrough in experimental physics was achieved in the early 1980s, thanks to the major discovery of scanning tunnelling microscopy (STM) by the German scientists G. Binnig and H. Rohrer (who shared the 1986 Physics Nobel Prize with E. Ruska (1906-1988), the discoverer of the electron microscope). With STM, one can 'see' a single molecule adsorbed on a surface. In a simple, ingeniously designed STM, experiment, a very sharp metal tip is moved over the surface of an electrical conductor at a height of about 500 pm. Since the tip remains close to the surface, the wave functions of the atoms of the tip overlap with those of the surace. **Quantum mechanical tunnelling,** caused by the application of an electric field between the tip and the surface, allows a current to flow through the vacuum gap. The potential of the tip with respect to the surface is held constant and a peizoelectric feedback mechanism regulates the vertical motion of the tip, thereby keeping the tunnelling current constant. This tip traces the surface topography as it is moved over the surface. These traces can be used to produce an image of the surface.