Unit III

Surface and interfacial phenomenon

Adsorption at solid interface:

The substance in adsorbed state is called adsorbate, while that present in one or other (or both) of the bulk phases and capable of being adsorbed may be distinguished as adsorptive.

When adsorption occurs at the interface between liquid and solid, the solid is usually called the adsorbent; for gas-liquid interfaces sometimes the liquid is called adsorbent.

The adsorption process is generally classified as

- ✓ physisorption
- ✓ chemisorption.

Adsorption of gases has wide applications as removal of objectionable odors from food, rooms, characterization of powders, adsorption chromatography, prevention of obnoxious gases entering body by gas masks, production of high vacuum, moisture removal etc.

Adsorption of gas on solid is like that of adsorption at liquid surfaces, where the surface free energy is reduced.

While comparing solids and liquids with respect to adsorption the surface tension determinations are easier for liquids as they are more mobile than the solids.

The average lifetime of molecule at liquid surface is very low i.e. 1 sec compared to atoms at the surface of non-volatile metallic surface.

Solid-Gas Adsorption:

It is probable that all solids adsorb gases to certain extent, but the phenomenon is not prominent unless adsorbent possess large surface area.

The adsorption of gas on to a solid surface is of mainly of two types.

➢ Physisorption

➢ Chemisorption

Physisorption:

Physisorption is adsorption in which the forces involved are intermolecular forces (van der Waals forces) of the same kind as those responsible for imperfection of real gases, condensation of vapors and which do not cause a significant change in electronic orbital patterns of species involved.

The term van der Waals adsorption is synonymous with physical adsorption but its use is not recommended.

Characteristics of Physisorption:

1. It is a general phenomenon and occurs in any solid/ fluid systems.

2. Minimum change in electronic state of adsorbate and adsorbent is observed.

3. Adsorbed species are chemically identical with those in the chemical adsorbent, so the chemical nature of the adsorbent is not changed by adsorption and subsequent desorption.

4. Energy of interaction between the molecules of adsorbate and adsorbent is of same order of magnitude.

5. Elementary step in adsorption of gas does not involve activation energy.

6. Equilibrium is established with increase in pressure and usually decreases with temperature.

7. Under appropriate condition of temperature and pressure, molecules of gas can be adsorbed more than those in direct contact with surface.
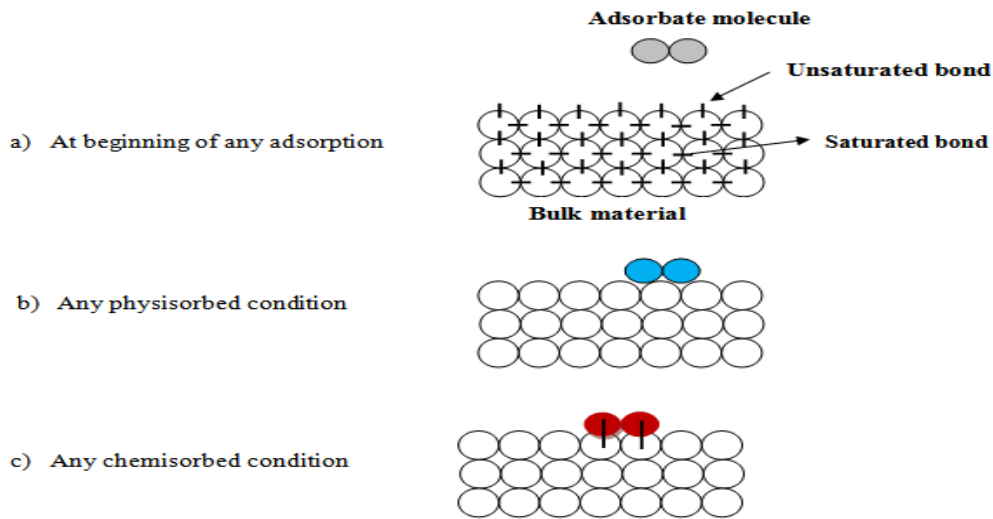

Figure: Schematic representation of different adsorption processes

Chemisorption:

Chemical adsorption or chemisorption is a process in which valance forces of some kind, operating in the formation of chemical compounds are involved. The difference between chemisorption and physisorption is same as that of difference between physical and chemical interaction in general.

Characteristics of Chemisorption:

1. The phenomenon is characterized by chemical specificity.

2. Change in electronic state may be detectable by suitable physical means (e.g. UV, IR, microwave spectroscopy, conductivity etc.)

3. The chemical nature of the adsorptive may be altered by surface reaction in such a way that on desorption the original surfaces cannot be recovered.

4. Like chemical reactions, chemisorption is either exothermic or endothermic and magnitude of energy changes may vary from small to very large.

5. The elementary step in chemisorption involves activation energy.

6. The rate of chemisorption increases with increase in temperature and when activation energy of adsorption is small, removal of chemisorbed species from the surface may be possible under extreme conditions of temperature and pressure or by some suitable chemical treatment of the surface.

7. Adsorbed molecules are linked to the surface by valence bonds that occupy certain adsorption sites on surface forming monolayer.

Factors Affecting Adsorption:

✓ **Surface area of adsorbent:**

Being surface phenomena extent of adsorption depends on available surface area of adsorbent. Finely divided materials since has large surface area, more adsorption is observed on their surfaces.

✓ **Nature of adsorbate:**

The amount of adsorbate adsorbed on solids depends on its nature; easily liquefiable gases adsorbed to greater extent.

✓ **Temperature:**

As seen under the characteristics of physical adsorption, it decreases with increase in temperature, while chemical adsorption increases with increase in temperature.

✓ **Pressure:**

Applying LeChatelier's principle, dynamic equilibrium exists between adsorbed gas molecules and molecules in contact with adsorbate. In fact, it is observed that increase in pressure increases adsorption.

✓ **Process characteristics:**

As physical adsorption, inversely proportional and chemical adsorption is directly proportional to temperature, reversing this process condition adsorption can be decreased.

✓ **Thickness of adsorbed layer:**

Langmuir from his studies of isotherms showed that at low pressures physically adsorbed gas forms only one layer one molecule thick while at higher pressures forms multilayers with increased extent of adsorption.

Adsorption isotherms:

Adsorption isotherm is the relation between the quantity of adsorbate adsorbed and the partial pressure in the gas phase (or composition of bulk phase, in adsorptions from liquids) under equilibrium conditions at constant temperature.

Freudlich's Adsorption Isotherm:

The scientist Freudlich's studied adsorption of gas on solid and from the experimental data; he gave empirical equation called equation of Freudlich's adsorption isotherm,

$$y = w/m$$
$$= kP^{1/b}$$

where, y is amount (w) of adsorbate adsorbed by m gram of adsorbent at equilibrium pressure P and are determined from the experiment at constant temperature. The constants k and b depends on nature of adsorbate and adsorbent as well as on temperature.

In above equation, $b > 1$ therefore the amount of adsorbed gas increases less rapidly than the pressure. This equation holds good only for medium pressures of gas. If w/m is plotted against pressure, a curve results of which first part is linear and over this range at low pressures $x/m \propto p$. At higher pressures a limiting value

x/m is reduced and curve is parabolic in shape as shown in Fig. Above equation is known as Freudlich's adsorption isotherm.

Taking logarithm on both sides of above equation

$$\log\left(\frac{w}{m}\right) = \left(\frac{1}{b}\right)\log P + \log K$$

This equation is valid at a given temperature. If adsorption is on the surface on solid, then above equation becomes

$$\log\left(\frac{w}{m}\right) = \left(\frac{1}{b}\right)\log C + \log K$$

Extrapolating the line from the any point on line, the intercept on Y-axis is log (w/m) and on X-axis is log C and slope of the line is 1/b.

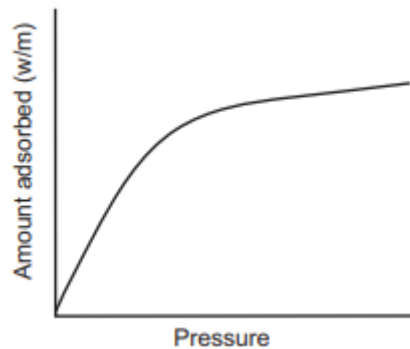**Figure: Adsorption of Gas on a Solid**

Langmuir Adsorption Isotherm:

In 1916, scientist Irving Langmuir (1916) published a new isotherm for gases adsorbed on solids, which retained his name. It is an empirical isotherm derived from assumptions of his extensive study.

1. The surface of a solid is made-up of elementary spaces and each space can adsorb one gas molecule.

2. All the elementary spaces are identical in their capacity for adsorbing a gas molecule.

3. The adsorption of a gas molecule in one element of space does not affect the properties of neighboring spaces.

4. It is possible that the adsorption layers are just of a single molecule thickness because intra-molecular forces fall off rapidly at distance beyond it.

5. Due to thermal kinetic energy of some the adsorbed molecule they get detached and pass back into space. Therefore, adsorption can be considered as consisting of two opposing processes in equilibrium (i.e. condensation and evaporation).

6. Initially rate of adsorption is high but as the surface area of adsorbent is covered with adsorbate molecules the rate of removal of adsorbed molecules goes on increasing. (i.e. rate of adsorption and evaporation are equal).

Langmuir had developed an equation based on the theory that the molecules or atoms of gas are adsorbed on active sites of the solid to form a layer one molecule thick. If fraction of active centers occupied on surface of adsorbent by gas molecules at pressure P is expressed as θ then the fraction of sites unoccupied is $1 - \theta$. The rate of adsorption (R_1) is proportional to unoccupied spots and the pressure P and the rate of evaporation (R_2) of molecule bound on surface is proportional to the fraction of surface occupied, θ.

$$R_1 \propto \text{fraction of sites unoccupied} \times \text{Pressure}$$

$$R_1 = k_1 (1 - \theta) P$$

$$R_2 \propto \text{Fraction of sites occupied}$$

$$R_2 = k_2 \, \theta$$

At equilibrium, $R_1 = R_2$

$$k_1(1 - \theta) P = k_2 \, \theta$$

After rearranging the above equation obtains

$$\theta = \frac{k_1 P}{k_2 + k_1 P}$$

$$\theta = \frac{\left(\frac{k1}{k2}\right)P}{1+\left(\frac{k1}{k2}\right)P}$$

Replacing θ by y/y_m and k_1/k_2 by b, where y is mass of gas adsorbed per gram of adsorbent at pressure P and at constant temperature and y_m is mass of gas that adsorbed on 1 gram of adsorbent to form complete monolayer. On substituting the values for θ and k_1/k_2 the following equation is obtained

$$\frac{y}{ym} = \frac{bp}{1+bp}$$

$$y = \frac{ymbp}{1+bp}$$

The above equation is known as Langmuir adsorption isotherm equation and it can also be written in the following form.

$$\frac{p}{y} = \frac{1}{ymb} + \frac{p}{ym}$$

By plotting a graph of P/y against P, Fig, we get a straight line with slope equal to y_m and intercept as b.
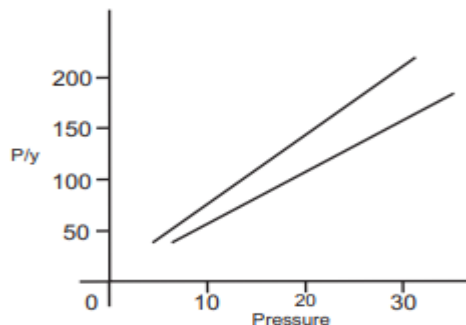

Figure: Langmuir Adsorption Isotherm

Multimolecular adsorption:

Sometimes, gases absorb as multi molecular layers on solids. Braunauer, Emmette and Teller have extended equation as

$$\frac{P}{y(P_0 - P)}) = \frac{1}{ymb} + \frac{b - P}{ymb} \cdot \frac{P}{P_0}$$

Where,   P = Pressure of the adsorbate, mmHg or Pa

Y = mass of the vapour per gram, kg

P_0 = vapour pressure at saturation (monolayer), mmHg or Pa

Y_m = amount of vapour absorbed per unit mass of adsorbent, when the surface is covered with monomolecular layer, kg

b = constant, proportional to heat of adsorption and latent heat of condensation of subsequent layers.

The equation is known as BET equation. It is used to determine 'y_m'. Here 'b' is greater than 2. If only monomolecular layer is formed, this plot reduces to Langmuir adsorption isotherm.

The preferred gases are nitrogen and krypton. Nitrogen is used for most samples exhibiting greater surface (1.0 m^2/g), while materials with smaller surface areas are measured using krypton. The low vapour pressure of krypton causes a large amount of gas to be adsorbed on the solid, resulting in more accurate values at low surface area values.
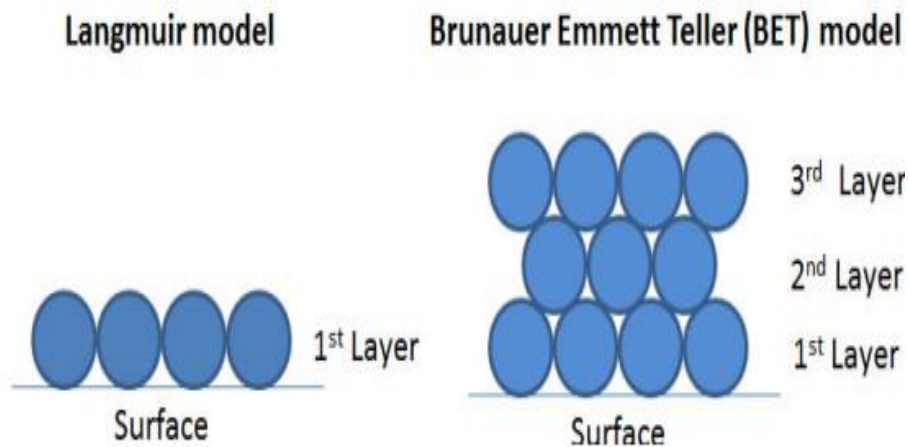

Figure: Difference between Langmuir and BET model

Adsorption Isotherms:

Adsorption isotherms are defined as the plots drawn between the amount of gas adsorbed on a solid (y axis) against the equilibrium pressure (in case of gases) or concentration (in case of solutions) (x axis) at constant temperature.
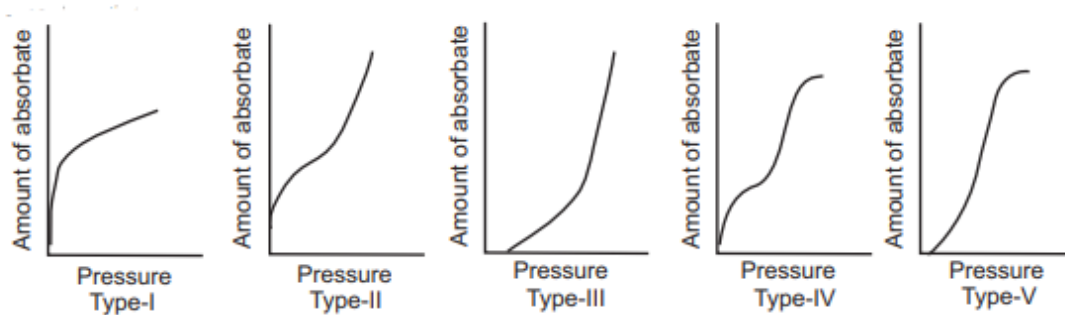
There are 5 different types of adsorption isotherms.

Figure: Types of adsorption isotherms

Type-I:

Langmuir and Freundlich isotherms are of Type-I, Fig, where adsorption takes place on non-porous solids. It represents behaviour of nitrogen or oxygen on charcoal. Total surface area can be determined from this isotherm by multiplying the total number of molecules in the volume of gas adsorbed by the cross-sectional area of the molecule.

Type-II:

In this type of isotherm gases are physically adsorbed on a non-porous solid forming monolayer followed by multilayer formation. The first inflection in the curve represents formation of monolayer and subsequent increase in pressure shows multilayer adsorption. This isotherm is explained by BET (Branauer, Emmett and Teller) equation

$$\frac{P}{y(P_0 - P)}) = \frac{1}{ymb} + \frac{b-P}{ymb} \cdot \frac{P}{P_0}$$

where, P is pressure of the adsorbate

y is mass of vapour per gram of adsorbent

P_0 is vapor pressure at saturation of adsorbent by adsorbate,

Y_m is amount of vapour adsorbed per unit mass of adsorbent when the surface is covered with monomolecular layer

b is constant equal to difference between heat of adsorption in the first layer and latent heat of condensation in the next layers. This isotherm is sigmoid in shape and observed with adsorption of nitrogen on iron catalysts, on silica gel and other surfaces.

Type-III:

This isotherm is rarely observed for example, bromine and iodine on silica gel, where heat of adsorption in the first layer is less than the latent heat of condensation in the next layers. The constant b of the BET equation is less than two.

Type-IV:

This isotherm is typical of adsorption onto porous solids where if the first point is extrapolated to zero pressure represents the amount of gas required in forming monolayer on solid surface. Condensation within the capillaries is responsible for the further adsorption. The example of this type is adsorption of benzene on ferric oxide and silica gel.

Type-V:

It is like type-III adsorption as capillary condensation is observed on the porous solids for example, adsorption of water vapor on charcoal at 100°C.

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