

Adsorption

Q. Define Adsorption and Absorption.

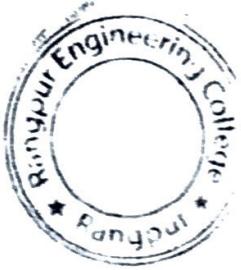
Adsorption:- A process in which the concentration of a chemical species is greater on the surface than in the ^{bulk} resulting from inelastic ^{inelastic} collision suffered by molecules on the surface. The species that is adsorbed is called adsorbed adsorbate and the material of the surface on which adsorption takes place is called adsorbent.

Example:- Adsorption of ethanoic acid by charcoal.

Absorption: Absorption refers to the ^{? WBUT} accumulation and penetration of the particle through the ^{grain, w/ or w/o} surface inside the bulk of the absorbent.

Example:- The uptake of water by a sponge in which water is found throughout the sample of sponge.

metabolic \rightarrow excretory:



Q. What are physical adsorption and chemical adsorption.

physical adsorption: When particles are held on the solid surface by purely physical forces like Van der Waals forces.

chemical adsorption or chemisorption: —

Chemisorption refers to a phenomenon in which there is chemical interaction between adsorbent and adsorbate. In this case the binding force between adsorbent and adsorbate is relatively strong and it can be considered that a true covalent chemical bond is formed.

Q. What are the characteristics of physical and chemical adsorptions.

Characteristics of physical adsorptions:

1. Caused by intermolecular van der Waal's forces.
2. Depends on nature of gas. Easily liquefiable gases are adsorbed readily.
3. Heat of adsorption is small.

~~V~~ Physical adsorption is reversible.

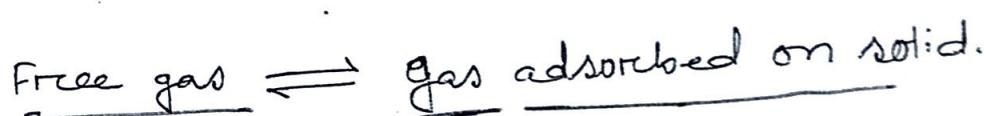
5. It occurs rapidly at low temperature.
6. Increases of pressure increases adsorption.
7. Forms multimolecular layers on adsorbent surface.

Characteristic of chemical adsorption:

1. It caused by chemical bond formation.
2. Much more specific than physical adsorption.
3. Heat of adsorption is large.
4. It is irreversible.
5. It increases with increase of temperature.
6. change of pressure has no effect
7. It forms unimolecular layer.

Q. Explain adsorption isotherm, Freundlich adsorption isotherm, Langmuir adsorption isotherm, and Gibb's adsorption isotherm.

Ans Adsorption isotherm: The adsorption of a gas on a solid adsorbent in a closed vessel is a reversible process.



The amount of the gas adsorbed depends on equilibrium pressure (P) and temperature. The relationship between the equilibrium pressure of a gas and its amount adsorbed on the solid adsorbent at any constant temperature is called an adsorption isotherm. It may be given in the form of an equation or graphical curve.

Ans Freundlich Adsorption Isotherm: Freundlich proposed an empirical relation in the form of a mathematical equation

$$\frac{W}{m} = K P^{1/n}$$

where W is the mass of the gas adsorbed on a mass m of adsorbent at a pressure

P. K and n are constants depending on the nature of the gas and the adsorbent and on temperature. This relation is generally represented in the form of a curve obtained by plotting the mass of the gas adsorbed per unit mass of adsorbent (W/m) against equilibrium pressure.

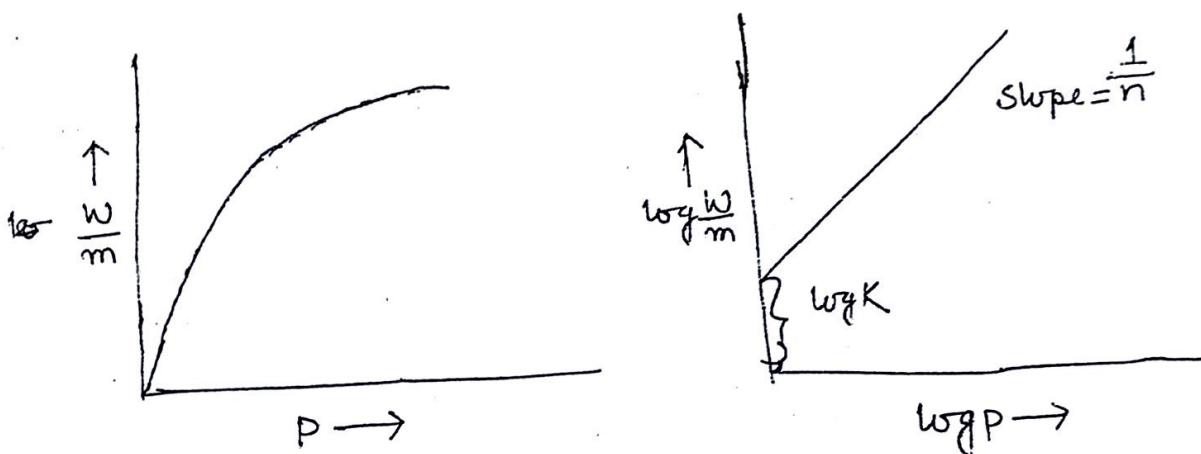


Fig: Freundlich isotherm.

Freundlich isotherm is not applicable at high pressures. Taking logarithms on both sides of Freundlich equation, we have

$$\log \frac{W}{m} = \log K + \frac{1}{n} \log P$$

This is equation for straight line. Thus a plot of $\log \frac{W}{m}$ against $\log P$ should be a straight line with slope $1/n$ and intercept $\log K$. However, it is actually found that the plots were straight lines at low pressures, while at higher pressure

they showed a slight curvature, especially at low temperature. This indicated that Freundlich equation is approximate and does not apply to adsorption of gases by solids at higher pressures.

* * Langmuir adsorption isotherm:

Langmuir derived a simple adsorption isotherm based on theoretical considerations. It was named after him.

Assumptions

Langmuir made the following assumptions.

- ① The layer of the gas adsorbed on the solid adsorbent is one molecule thick.
- ② The adsorbed layer is uniform all over the adsorbent.
- ③ There is no interaction between the adjacent adsorbed molecules.

Derivation of Langmuir Isotherm:

Langmuir considered that the gas molecules $\xrightarrow{\text{adsorb}}$ strike a solid surface and are thus ~~not~~ adsorbed. Some of these molecules then evaporate or are desorbed fairly rapidly. A ~~dynamic~~ dynamic equilibrium is eventually established between

the two opposing processes, adsorption and desorption

If θ is the fraction of the total surface covered by the adsorbed molecules, the fraction of the naked area is $(1-\theta)$. The rate of desorption (R_d) is proportional to the covered surface θ . Therefore,

$$R_d = K_d \theta$$

where K_d is the rate constant for the desorption process.

The rate of adsorption (R_a) is proportional to the available naked surface $(1-\theta)$ and the pressure (P) of the gas.

$$R_a = K_a (1-\theta) P$$

where K_a is rate constant for the adsorption process.

At equilibrium the rate of desorption is equal to the rate of adsorption, that is

$$K_d \theta = K_a (1-\theta) P$$

or, ~~$K_d \theta = K_a (1-\theta) P$~~

$$K_d \theta = K_a P - K_a \theta P$$

or, ~~$K_d \theta + K_a \theta P = K_a P$~~

$$\theta (K_d + K_a P) = K_a P$$

or, $\theta = \frac{K_a P}{K_d + K_a P}$

$$\text{or, } \theta = \frac{(K_a/K_d)P}{1 + (K_a/K_d)P}$$

$$= \frac{KP}{1 + KP}$$

where K is the equilibrium constant and is referred to as the adsorption coefficient.

The amount of gas the gas adsorbed per gram of the adsorbent, x is proportional to θ .

Hence,

$$x \propto \frac{KP}{1 + KP}$$

$$\text{or, } x = K' \frac{KP}{1 + KP} \quad \dots \quad (1)$$

where K' is a new constant. Equation (1) gives the relation between the amount of gas adsorbed to the pressure of the gas at constant temperature and is known as Langmuir Adsorption isotherm.

In order to test the Langmuir isotherm, equation (1) is rearranged so that

$$x = \frac{K'KP}{1 + KP}$$

$$\text{or, } \frac{1}{x} = \frac{1 + KP}{K'KP}$$

$$\text{or, } \frac{1}{x} = \frac{1}{K'KP} + \frac{1}{K'}$$

$$\text{or, } \frac{P}{x} = \frac{1}{KK'} + \frac{P}{K'} \quad \dots \quad (2)$$

The equation ② is similar to an equation for a straight line. Thus $\frac{P}{n}$ is plotted against P , we should get a straight line with slope $\frac{1}{K}$ and the intercept $\frac{1}{KK}$. It was found in most cases that the actual curves were straight lines. Thus Langmuir isotherm stood verified.

(ii) Gibb's Adsorption Isotherm: when alcohols, phenol, glycerol, fatty acids etc. are dissolved in water, the surface tension of water is reduced, the extent of reduction depending on the concentration of the solute. In such cases it is noticed that the concentration of the solute is more on the surface layer than in the bulk and the solute is said to be positively adsorbed on the surface. Ionic ~~solids~~ dissolved in a liquid cause the surface tension of the liquid to rise and the concentration of the solute is found to be less on the surface. In such cases the solute is said to be negatively adsorbed. Gibbs treated these phenomena from thermodynamic principles.

and derived the following relation:

$$\Gamma = - \frac{d\gamma}{dc} \frac{c}{RT} \quad \text{--- } ①$$

~~where γ is the surface tension of the solution,~~

where,

γ = the surface tension of the solution.

Γ = the excess concentration of the solute on the surface.

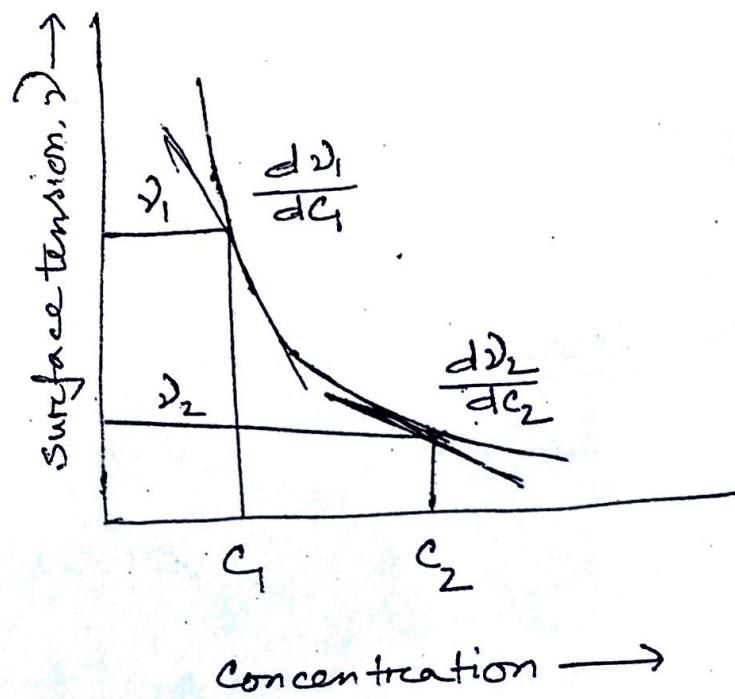
c = the concentration of the solute in solution.

R = the gas constant.

T = the temperature in K.

Excess surface concentration (Γ) means the concentration of the solute on the surface in excess of that in the bulk. Consequently all substances that reduce surface tension must have a higher molecular concentration on the surface than in the bulk. As mentioned, ~~the~~ electrolytes often have a lower concentration on the surface and they increase the surface tension of water. From a measurement of γ , the surface tension of a series of solutions of different concentrations, c , of a solute, a plot of γ vs c is drawn. The gradient of the graph, $d\gamma/dc$ is evaluated

at various values of C as shown in Figure.
Using the values of the gradient Γ may be —
calculated with the help of equation ①. The
equation



The equation has been experimentally verified by determining Γ by actual chemical analysis of very thin sections of the surfaces of solutions.