B.Sc-IV sem

Physical Chemistry

Chapter: Distribution Law

Distribution Law: Statement: Nernst distribution law When two immiscible solvents A and B taken in a beaker, they form separate layers. ... “ if a solute X distributes itself between two immiscible solvents A and B at constant temperature and X is in the same molecular condition in both solvents.

When two immiscible solvents A and B taken in a beaker, they form separate layers. Now a solute X which is soluble in both solvents is added, it gets distributed or partitioned between them. Molecules of X pass from solvent A to B and from B to A. finally a dynamic equilibrium is set up. At equilibrium, the rate, at which molecules of X pass from one solvent to the other is balanced.

$$\frac{Concenetration\ \ of\ x\ in\ A}{Concenetration\ \ of\ x\ in\ B} = \text{a Constant}$$

Nernst (1891) studied the distribution of several solutes between different appropriate pairs of solvents. He gave a generalization which governs the distribution of a solute between two non-miscible solvents. This is called Nernst’s Distribution law or Nernst’s Partition law or simply Distribution law or Partition law.
It states that,

> “ if a solute X distributes itself between two immiscible solvents A and B at constant temperature and X is in the same molecular condition in both solvents.”

$$\frac{Concenetration\ \ of\ x\ in\ A}{Concenetration\ \ of\ x\ in\ B} = K_D$$

If C_1 denotes the concentration of the solute in solvent A and C_2 the concentration in solvent B, Nernst's Distribution law can be expressed as

$$\frac{C_1}{C_2} = K_D$$

The constant K_D (or simply K) is called the distribution coefficient or Partition coefficient or Distribution ratio.

When a solute is shaken with two non-miscible solvents, at equilibrium both the solvents are saturated with the solute. Since the solubility also represents concentration,

the Distribution Law is also written as,

$$\frac{C_1}{C_2} = \frac{S_1}{S_2} = K_D$$

Where S_1 and S_2 are the solubilities of the solute in the two solvents.

Limitations of the Nernst Distribution Law:

The law is valid when the molecular state of the solute is same in both the solvents. If the solute undergoes dissociation or association in any one of the solvents, then in such cases the distribution law no longer holds good.

The distribution law can be applied in such cases with some modifications.

Modification in case of association, dissociation and chemical changes

1. Association of the solute in one of the solvents.

Let X represents the molecular formula of the solute. Let it remain as such in the first phase marked I, in which its concentration is C_1 Suppose it is largely associated to give the molecules $(X)_n$ in the second phase marked II. The associated molecules will exist in equilibrium with single molecules as shown.

Let C_2 be the total concentration of the solute in this phase.

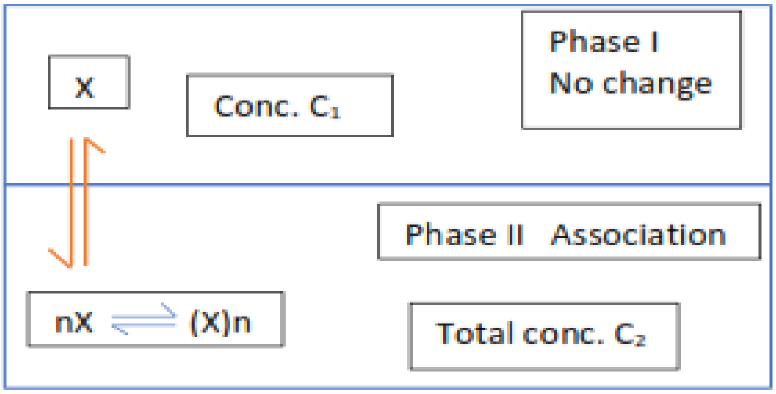


Fig. 1. Association in one of the phases.

Applying the law of chemical equilibrium to the equilibrium between the associated and single molecules, in the second phase, we have

$$(X)_n \leftrightharpoons nX$$

$$K = [X]^n/[(X)_n] \qquad \text{……….(1)}$$

$$\text{Or, } [X] = \sqrt[n]{K \times [(X)_n]} = constant \times \sqrt[n]{[(X)_n]} \text{ ……….(2)}$$

If the solute exists largely as associated molecules, which is generally true except at large dilutions, the concentration of the associated molecules, $[(X)_n]$ may be taken as equal to c_2, the total concentration.

$$[(X)_n] = c_2 \qquad \text{……….(3)}$$

From equation (2) and (3), $[X] = constant \times \sqrt[n]{c_2}$ ………..(4)

Since the distribution law is valid only for concentration of similar molecular species in the two phases, hence, $\frac{c_1}{[X]} = constant$ ……….(5)

From equation (4) and (5) we have, $\frac{c_1}{\sqrt[n]{c_2}} = constant = K_D$ …….(6)

Equation (6) has been checked by studying the distribution benzoic acid between water and benzene. The acid exists almost entirely as $(C_6H_5COOH)_2$ in benzene but in normal state in water.

2. Dissociation of the solute in one of the solvents.

Let X, as before, represent the normal formula of the solute. Suppose, it does not dissociate in the solvent marked I, but dissociates into A and B in the solvent marked II

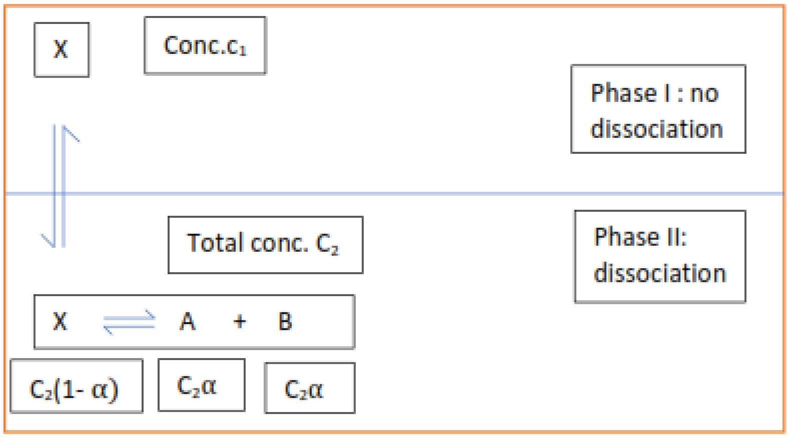


Fig. 2. Dissociation in one of the phases.

Let c_1 be its concentration in the first solvent and c_2, the total concentration in the second solvent. The distribution law is valid only for the ratio of concentrations of similar molecular species in the two solvents.

Suppose, α is the degree of dissociation of the solute X in phase II. Then, the concentrations of the various species would be as shown below:

$$\begin{array}{ccccc} X & \leftrightharpoons & A & + & B \\ C_2(1-\alpha) & & C_2\alpha & & C_2\alpha \end{array}$$

Therefore, according to the distribution law,

$$\frac{c_1}{c_2(1-\alpha)} = K_D \qquad \ldots\ldots\ldots..(7)$$

Limitations of Distribution law

The two essential prerequisites for the validity of the distribution law are:

1. Constant temperature and
2. Existence of similar molecular species in the two phases in contact with each other.

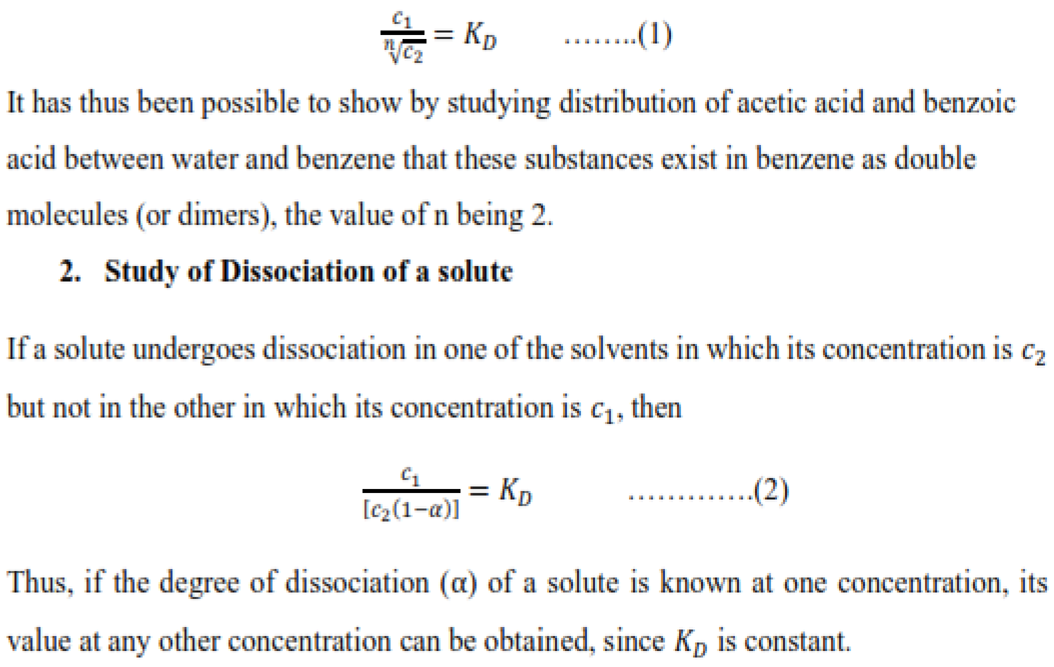
In addition, the following conditions are also necessary:

3. The solutions are dilute.
4. The two liquids are mutually insoluble or only very sparingly soluble (e.g., benzene and water) and their mutual solubility is not altered by the presence of the solute.

Applications of the Nernst Distribution law:

1. Study of Association of a solute

If a solute associates in one of the solvents in which its concentration is C_1 but not in the other in which its concentration is C_2 then n being the number of simple molecules which combine to form one associated molecule.



$$\frac{c_1}{\sqrt[n]{c_2}} = K_D \qquad \text{........(1)}$$

It has thus been possible to show by studying distribution of acetic acid and benzoic acid between water and benzene that these substances exist in benzene as double molecules (or dimers), the value of n being 2.

2. Study of Dissociation of a solute

If a solute undergoes dissociation in one of the solvents in which its concentration is c_2 but not in the other in which its concentration is c_1, then

$$\frac{c_1}{[c_2(1-\alpha)]} = K_D \qquad \text{............(2)}$$

Thus, if the degree of dissociation (α) of a solute is known at one concentration, its value at any other concentration can be obtained, since K_D is constant.

3. Distribution indicators

It is a common experience that iodine distributes itself considerably more in carbon disulphide than in water when both the solvents are in contact with each other. Therefore, an extremely dilute solution of iodine in water can be successfully titrated by adding a drop or two of carbon disulphide. The concentration in the carbon disulphide layer becomes large enough to give a distinct violet colour.

4. Study of complex ions

The Nernst Distribution law has been successfully applied in determining the formula of the complex ions formed between bromine and bromide ion as well as between iodine and iodide ion.

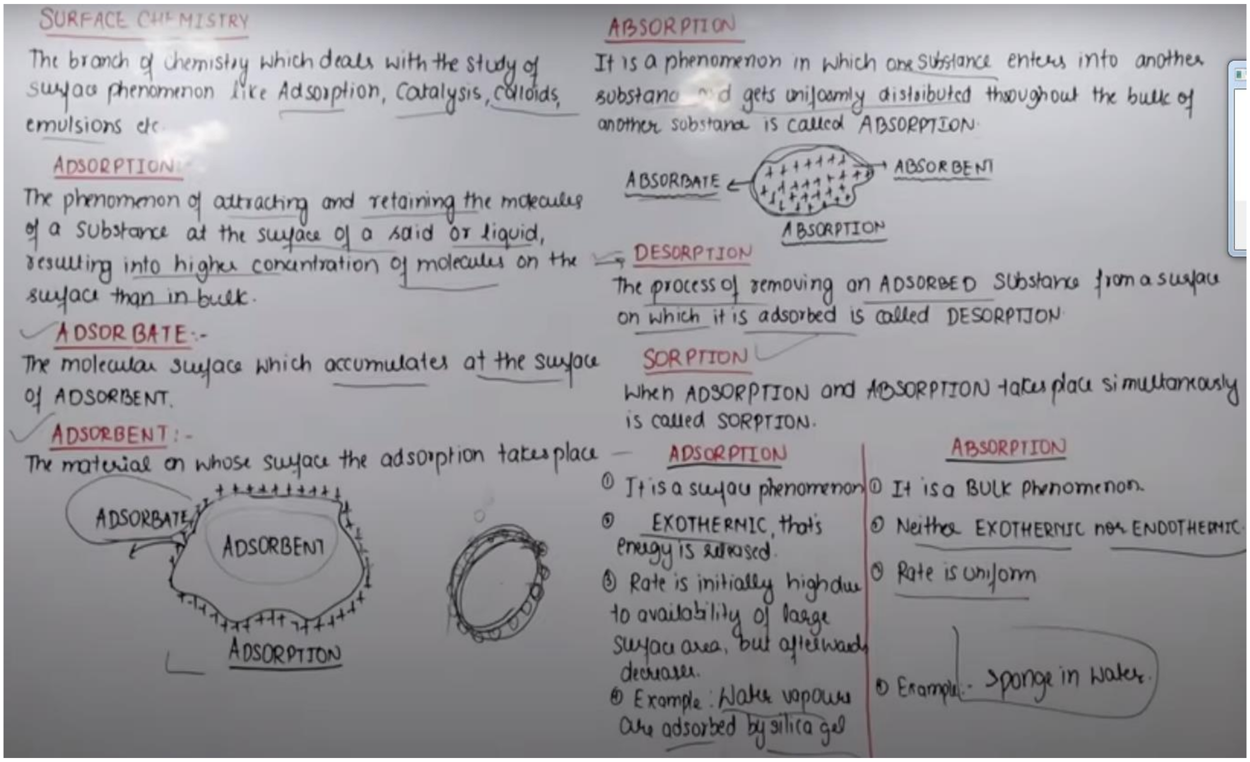
5. Solvent extraction

The most important application of the distribution law is in the process of extraction, in the laboratory as well as in industry. In the laboratory, it is frequently used for the removal of a dissolved organic substance from aqueous solution with solvents such as benzene, ether, chloroform, carbon tetrachloride, etc. the advantage is taken of the fact that the partition coefficient of most of the organic compounds is very largely in favour of organic solvents.

--------------END------------

ADSORPTION

Langmuir's adsorption isotherm their significance, BET equation (no derivation). Application of BET equation in the determination of surface area of adsorbent. 3Hrs



SURFACE CHEMISTRY

The branch of chemistry which deals with the study of surface phenomenon like Adsorption, Catalysis, Colloids, emulsions etc.

ADSORPTION:

The phenomenon of attracting and retaining the molecules of a substance at the surface of a solid or liquid, resulting into higher concentration of molecules on the surface than in bulk.

ADSORBATE:-

The molecular surface which accumulates at the surface of ADSORBENT.

ADSORBENT:-

The material on whose surface the adsorption takes place

ABSORPTION

It is a phenomenon in which one substance enters into another substance and gets uniformly distributed throughout the bulk of another substance is called ABSORPTION.

DESORPTION

The process of removing an ADSORBED substance from a surface on which it is adsorbed is called DESORPTION.

SORPTION

When ADSORPTION and ABSORPTION takes place simultaneously is called SORPTION.

ADSORPTION	ABSORPTION
① It is a surface phenomenon	① It is a BULK phenomenon.
② EXOTHERMIC, that's energy is released.	② Neither EXOTHERMIC nor ENDOTHERMIC.
③ Rate is initially high due to availability of large surface area, but afterwards decreases.	③ Rate is uniform
④ Example: Water vapours are adsorbed by silica gel	④ Example:- Sponge in Water.

Adsorption

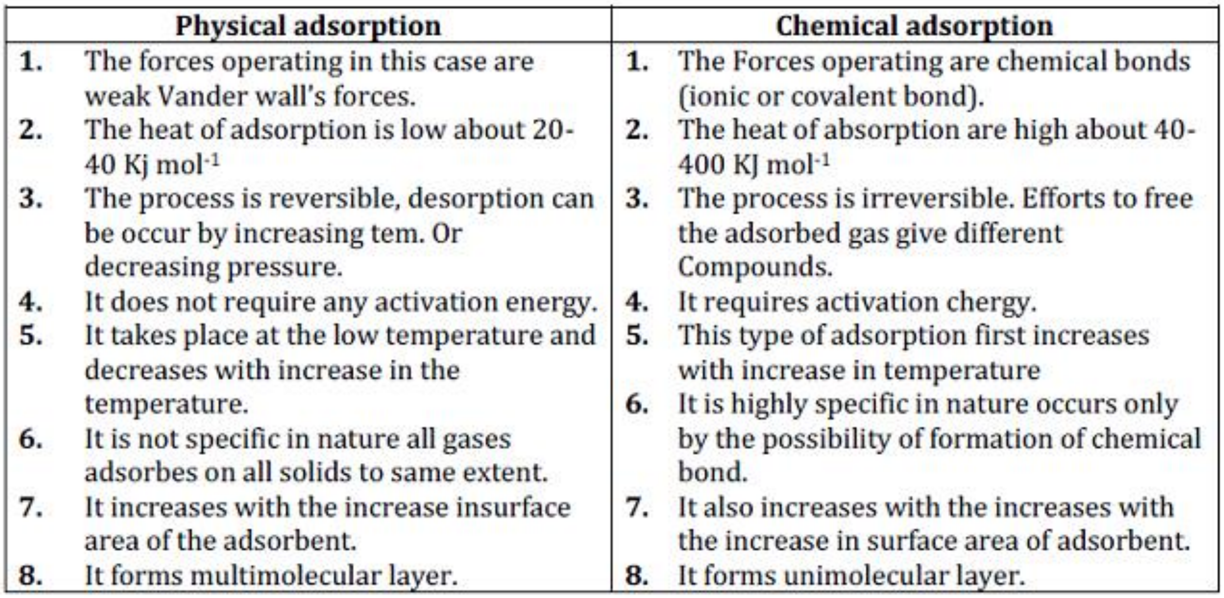
Reversible and irreversible adsorption

The adsorption is **reversible,** if the adsorbent can be easily removed from the surface of the adsorbent by physical methods. It is called **irreversible adsorption**, if the adsorbate can not be removed from the surface of the adsorbent.

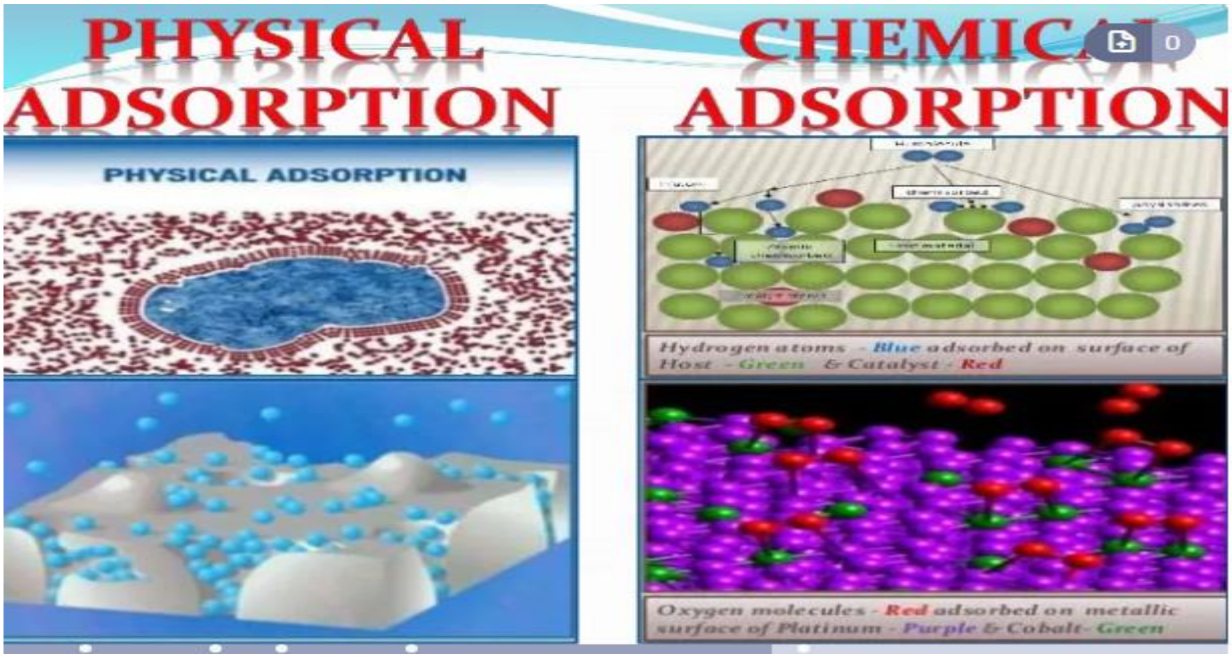
A gas adsorbed on a solid surface can be completely removed in vacuum. It is, therefore, reversible adsorption. Examples of irreversible adsorption are adsorption of oxygen on tungsten adsorbate and adsorption of CO on tungsten surface

Adsorbent, Adsorbate and Interface

- The substances upon whose surface the change of concentration occurs, is called ***absorbent***.
- The substance taken up on the surface is call ***adsorbate***.
- The common surface between the two phases where the adsorbed molecules concentrate is called the ***interface.***

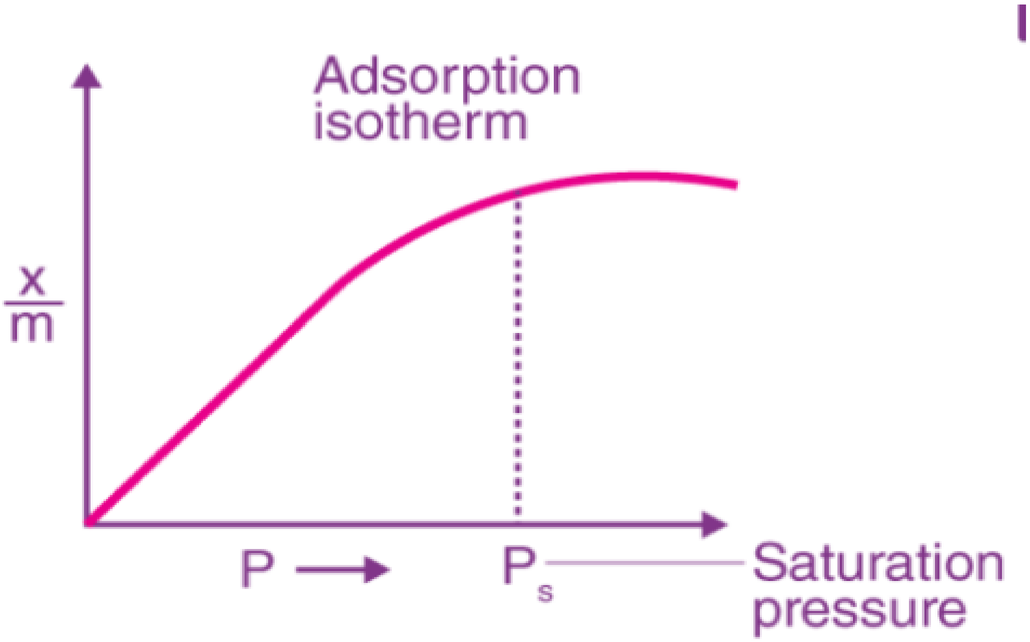


	Physical adsorption		Chemical adsorption
1.	The forces operating in this case are weak Vander wall's forces.	**1.**	The Forces operating are chemical bonds (ionic or covalent bond).
2.	The heat of adsorption is low about 20-40 Kj mol^{-1}	**2.**	The heat of absorption are high about 40-400 KJ mol^{-1}
3.	The process is reversible, desorption can be occur by increasing tem. Or decreasing pressure.	**3.**	The process is irreversible. Efforts to free the adsorbed gas give different Compounds.
4.	It does not require any activation energy.	**4.**	It requires activation chergy.
5.	It takes place at the low temperature and decreases with increase in the temperature.	**5.**	This type of adsorption first increases with increase in temperature
6.	It is not specific in nature all gases adsorbes on all solids to same extent.	**6.**	It is highly specific in nature occurs only by the possibility of formation of chemical bond.
7.	It increases with the increase insurface area of the adsorbent.	**7.**	It also increases with the increases with the increase in surface area of adsorbent.
8.	It forms multimolecular layer.	**8.**	It forms unimolecular layer.



https://youtu.be/s8ChYf7k69o

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



From the graph, we also observe that after attaining a pressure P_s, that is the **saturation pressure**, the variation in the amount of adsorbent adhering to the adsorbate becomes zero. This happens because the surface area available for adsorption is limited and as all the sites are occupied, a further increase in pressure does not cause any difference.

Different adsorption isotherms have been proposed by different scientists namely,

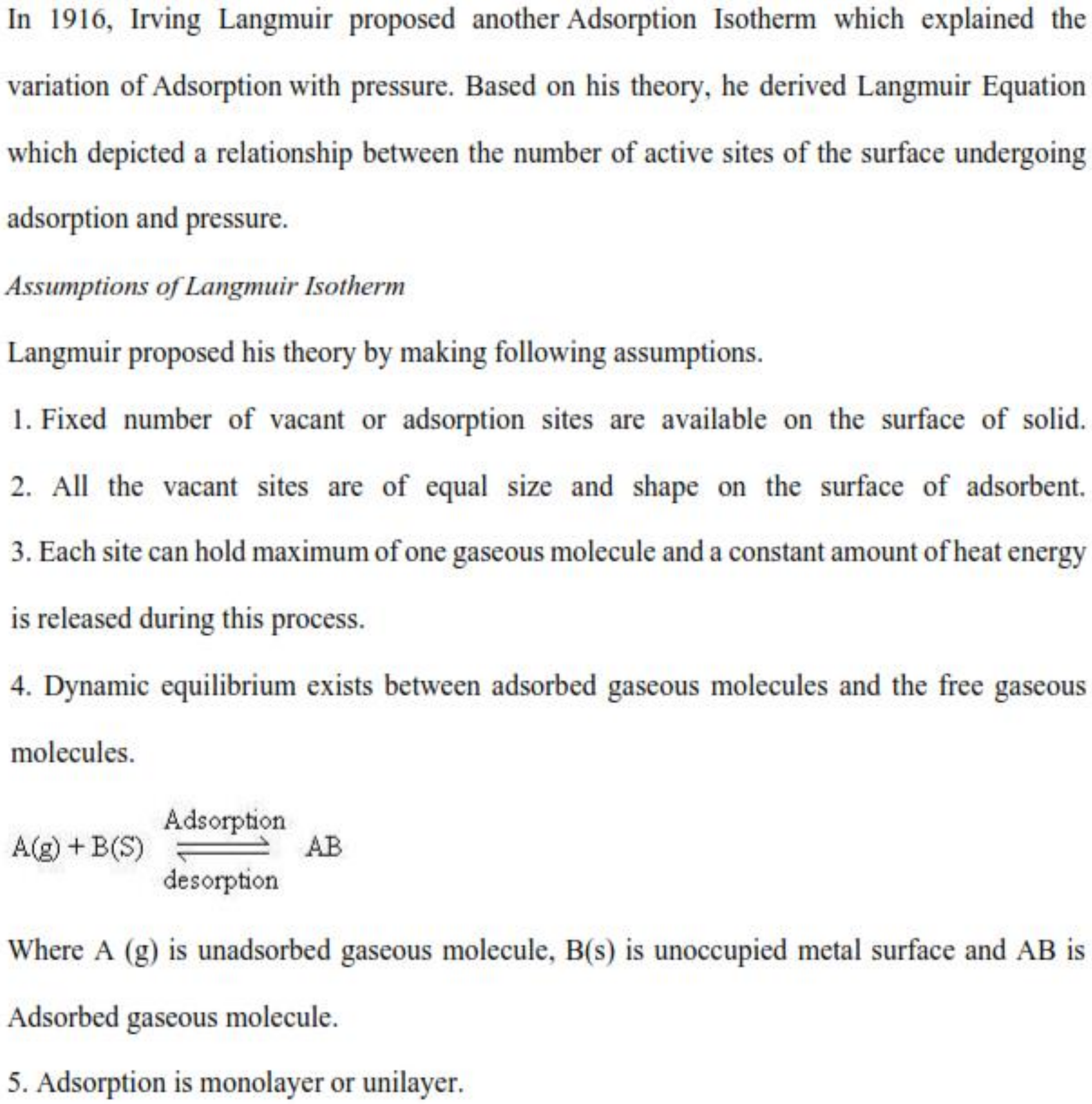
- ***Langmuir isotherm***
- ***Freundlich isotherm***
- ***BET theory***

Langmuir Adsorption Isotherm: (1916)

Assumptions:

1. Surface of solid is made up of elementary sites each of which absorbs gas molecules.
2. Surface of solid is homogeneous(have Same affinity).
3. Absorbed gas behaves Ideally.
4. Only monolayer is formed on the surface.
5. No lateral interaction.
6. Absorbed molecules are localized.

OR



In 1916, Irving Langmuir proposed another Adsorption Isotherm which explained the variation of Adsorption with pressure. Based on his theory, he derived Langmuir Equation which depicted a relationship between the number of active sites of the surface undergoing adsorption and pressure.

Assumptions of Langmuir Isotherm

Langmuir proposed his theory by making following assumptions.

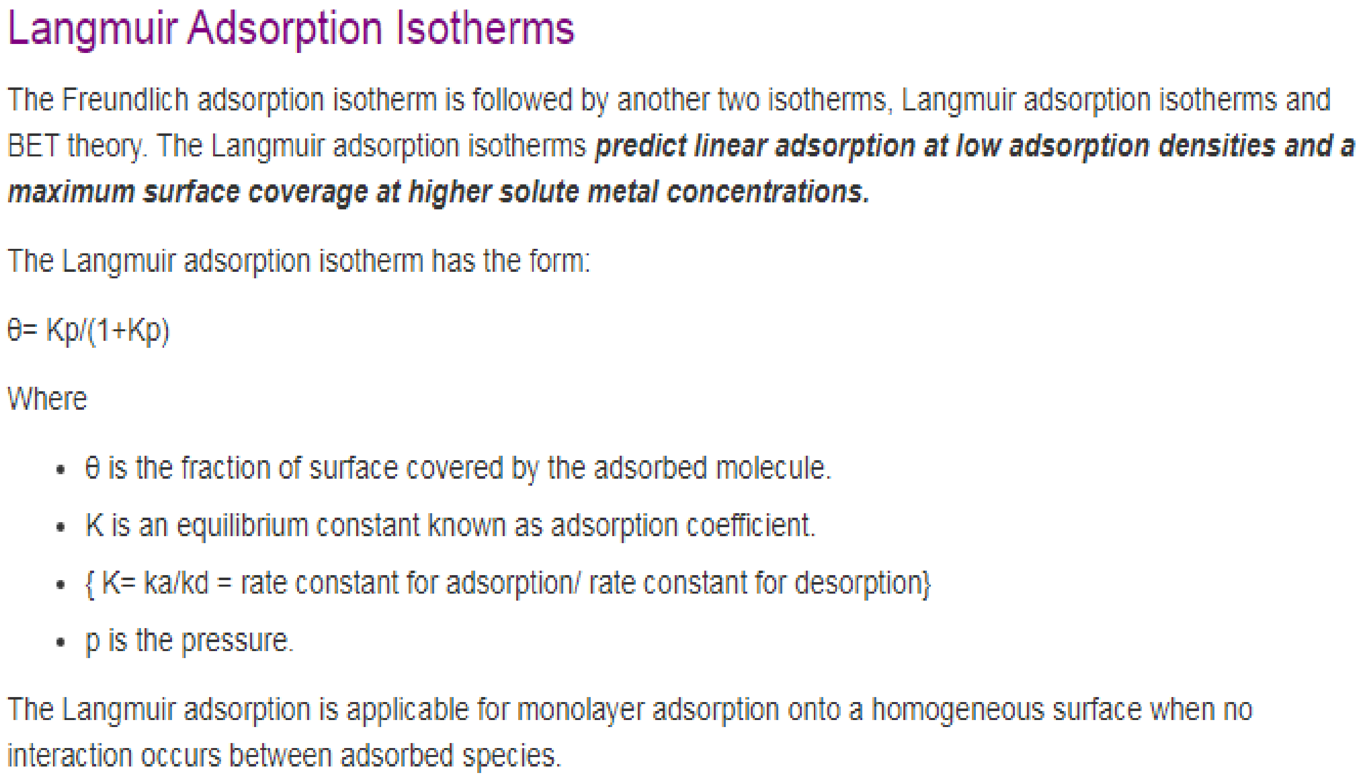
1. Fixed number of vacant or adsorption sites are available on the surface of solid.
2. All the vacant sites are of equal size and shape on the surface of adsorbent.
3. Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is released during this process.
4. Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.

$$A(g) + B(S) \underset{\text{desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} AB$$

Where A (g) is unadsorbed gaseous molecule, B(s) is unoccupied metal surface and AB is Adsorbed gaseous molecule.

5. Adsorption is monolayer or unilayer.

7.



Langmuir Adsorption Isotherms

The Freundlich adsorption isotherm is followed by another two isotherms, Langmuir adsorption isotherms and BET theory. The Langmuir adsorption isotherms ***predict linear adsorption at low adsorption densities and a maximum surface coverage at higher solute metal concentrations.***

The Langmuir adsorption isotherm has the form:

$\theta = Kp/(1+Kp)$

Where

- θ is the fraction of surface covered by the adsorbed molecule.
- K is an equilibrium constant known as adsorption coefficient.
- { K= ka/kd = rate constant for adsorption/ rate constant for desorption}
- p is the pressure.

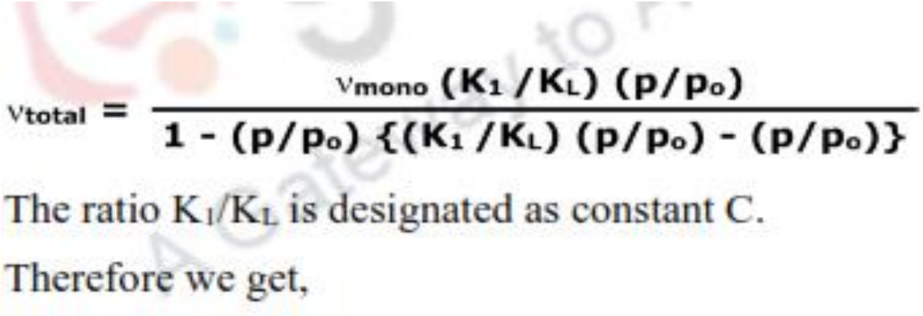
The Langmuir adsorption is applicable for monolayer adsorption onto a homogeneous surface when no interaction occurs between adsorbed species.

BET (*Brunauer, Emmett and Teller*)Adsorption Isotherm:

The theory of ***multilayer adsorption proposed by Brunauer, Emmett and Teller in 1938*** (BET Theory) assumes that physisorption results in the formation of multilayer adsorption. The theory also assumes that the solid surface has uniform sites of adsorption and that adsorption at one site does not affect adsorption at neighbouring sites.

After the formation of the monolayer, the adsorption process can continue with the formation of multilayer involving the second layer, third layer and so on.

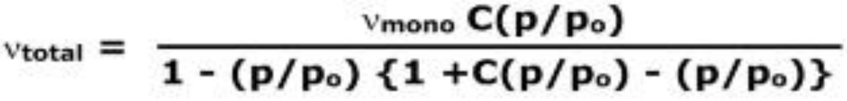
The equation for BET is



$$V_{total} = \frac{V_{mono}\,(K_1/K_L)\,(p/p_o)}{1 - (p/p_o)\,\{(K_1/K_L)\,(p/p_o) - (p/p_o)\}}$$

The ratio K_1/K_L is designated as constant C.

Therefore we get,



$$V_{total} = \frac{V_{mono}\,C(p/p_o)}{1 - (p/p_o)\,\{1 + C(p/p_o) - (p/p_o)\}}$$

$$\mathbf{V_{total}} = \frac{\mathbf{V_{mono}\,C\,\frac{P}{P_0}}}{\mathbf{1 - \frac{P}{P_0}\left\{1 + C\left(\frac{P}{P_0}\right) - \left(\frac{P}{P_0}\right)\right\}}}$$

This is the required BET equation for multilayer adsorption of gaseous molecules on adsorbent surface.

Where V = Volume of the gas (reduced to STP) adsorbed at given pressure P and constant temperature.

Vm = Volume of the gas (reduced to STP) adsorbed when the surface is completely covered bya unimolecular layer.

P = equilibrium pressure of adsorbate.

$\mathbf{P_0}$ **=** saturation pressure of adsorbate

c = BET constant = exp ($E1-EL/\ R$T).

$E1$ = heat of adsorption for the first layer .

EL = heat of vaporization or heat of liquefaction of the gas.

Above Equation can be written as

BET equation can be plotted to determine monolayer adsorbed gas quantity and the BET constant

$$\frac{p}{v_{total}(p/p_o)} = \frac{1}{v_{mono}C} + \frac{C-1}{v_{mono}C}\,\frac{p}{p_o} \qquad (28)$$

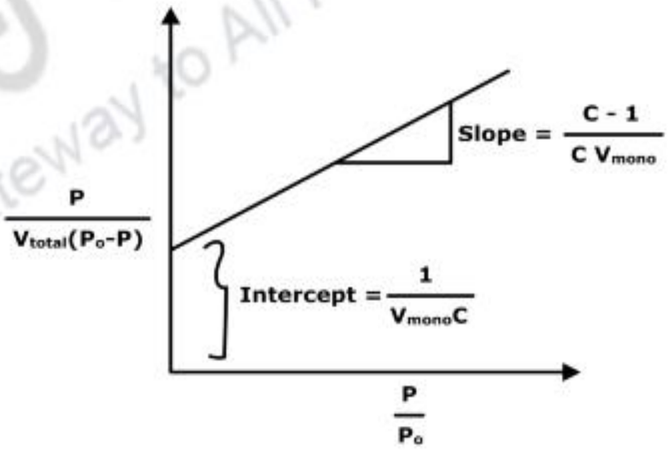
where,

V_{total} = Volume of gas adsorbed under given conditions of temperature and pressure, reduced to standard conditions

V_{mono} = Volume of gas required to form a monolayer on the adsorbent surface, reduced to standard conditions

C = Characteristic constant for a particular adsorbate-adsorbent system

The validity of BET adsorption isotherm can be proved by plotting a graph between $\frac{P}{V_{total}\ (P_o - P)}$ and $\frac{P}{P_o}$ (Fig. 1)



Take numerical values for slope and intercept to solve for v_m and c

$$slope = \frac{c - 1}{v_m c}$$

$$\text{intercept} = \frac{1}{v_m c}$$

$$v_m = \frac{1}{slope + intercept}$$

$$c = 1 + \frac{slope}{intercept}$$

From the monolayer absorbed gas volume (vm), we can determine total and specific surface area.

$$S_t = \frac{v_m N s}{V}$$

S_t = total surface area of sample material
v_m= monolayer absorbed gas volume
N = Avogadro's number = 6.02×10^{23} molecules/mol
s = cross-sectional area of adsorbed gas molecule
V = molar volume of adsorbed gas

$$S_{BET} = \frac{S_t}{a} \text{ [=] } m^2/g$$

S_{BET} = specific surface area
a = mass of sample

$$S_{BET} = \frac{6.023x10^{23}}{a\ x\ 22400} V_m \text{ x } S.$$