

Unit-3

Physical Pharmaceutics

Surface and interfacial phenomenon:

Liquid interface, surface & interfacial tensions, surface free energy, measurement of surface & interfacial tensions, spreading coefficient, adsorption at liquid interfaces, surface active agents, HLB Scale, solubilisation, detergency, adsorption at solid interface.

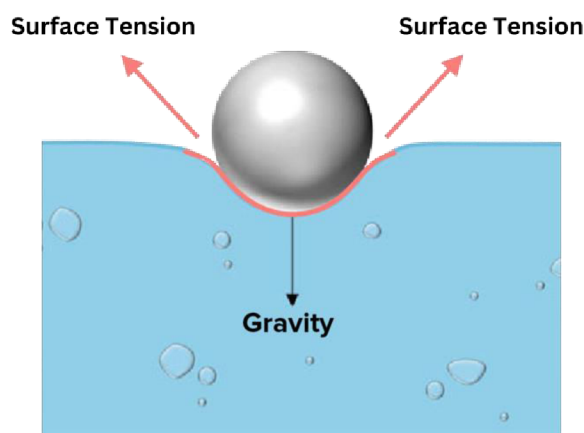


Surface and interfacial phenomena:

Introduction:

Surface and interfacial phenomena are the physical and chemical phenomena that occur at the surfaces and interfaces between two phases. These phases can be solids, liquids, or gases. Surface and interfacial phenomena are important in many different fields, including chemistry, physics, biology, and engineering.

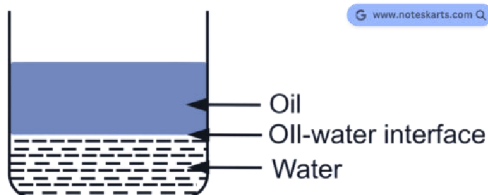
Surface tension is a force that acts at the surface of a liquid. It is caused by the cohesive forces between the liquid molecules. Surface tension is responsible for many phenomena, such as the formation of water droplets, the ability of insects to walk on water, and the capillary effect.



Interfacial tension is a force that acts at the interface between two immiscible liquids. It is caused by the different cohesive forces between the two types of liquid molecules. Interfacial tension is responsible for many phenomena, such as the formation of emulsions and the spreading of liquids on surfaces.

Liquid interface:

- The term surface is used to represent the boundary between solid-gas and liquid-gas phases.
- The two words surface and interface often used synonymously, although interface is preferred for the boundary between two condensed phases i.e. liquid-liquid (Oil in water) etc.



Liquid/Liquid Interface, for example, Oil on Water Surface

Surface & Interfacial Tensions:

Surface Tensions:

The tension that exists between solid-gas phase and liquid-gas phase is known as surface tension.

Or

The tension of the surface film of a liquid caused by the attraction of the particles in the surface layer by the bulk of the liquid, which tends to minimize surface area is known as surface tension.

$$\gamma = \frac{F}{L}$$

Where,

$\gamma = \text{Gama}$ (Surface Tension)

F = Force

L = Length

Unit of Surface Tension:

- The CGS unit of surface tension is dyne/cm and SI unit is N/m.
- The relation between these units is as N/m is equal to 1×10^3 dyne/cm or dyne/cm is equal to m N/m.

Interfacial Tension:

- Interfacial tension is defined as the force per unit length acting at right angle over the interface between two immiscible liquids. Interfacial tension represents the strength of adhesive forces at the boundary between two immiscible liquids.
- Interfacial tension is useful in analyzing fluid reforming, spreading, emulsification, washability and other liquid characteristics.
- When two miscible liquids combined together no interface exist between them for example, ethyl alcohol and water mixture. Wherever, if two immiscible liquids combined there exists an interface between them.

Unit of Surface and Interfacial Tension:

Interfacial tension has units that of surface tension, that is dyne/cm or N/m



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Surface Free Energy:

- The Molecules near the surface of liquid have more potential energy as compare to the molecules in the bulk of the liquid (Due to surface tension).
- This means that as surface of the liquid increase the more molecules have potential energy.
- Surface of the liquid increase, Energy of the liquid also increase.
- Energy is proportional to the size of the free surface called **Surface Free Energy**.

$$W = \gamma \times \Delta A$$

Where,

W = Surface Free Energy

Γ = Surface Tension

ΔA = Area of Surface Area

Measurement of Surface & Interfacial Tensions:

- Capillary rise method
- Drop weight method
- Drop count method
- Wilhelmy plate methods
- Ring detachment method

Capillary rise method:

- Capillary rise method is a simple and common method for determining the surface tension of a liquid.
- It is based on the principle of capillary rise, which is the phenomenon of a liquid rising in a narrow tube due to the combined effect of surface tension and adhesive forces.

Derivation:

Upward Force:

$$F = (2\pi r\gamma) \cos \theta \text{ -----} 1$$

Where,

$2\pi r$ = Circumference of that capillary.

$\gamma \cos \theta$ = Surface tension and angle of contact.



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Downward force:

$$F = w \text{ -----2}$$

Where,

w/mg = weight of liquid

We know that,

$$P = \frac{M}{V} = \frac{M}{\pi r^2 h} \quad [V = \pi r^2 h]$$

Where,

P = density of liquid

M = Mass

V = Volume

$$M = \rho \cdot \pi r^2 h \text{ -----3}$$

Put equation -3 value in equation-2

$$F = \rho \cdot \pi r^2 gh$$

Now,

Liquid is in equilibrium means both force are equal.

Upward force = Downward force

$$(2\pi r\gamma) \cos \theta = \rho \pi r^2 gh$$

$$\text{Finally - } \gamma = \frac{1}{2\cos \theta} [\rho ghr]$$

Where,

γ = Surface tension

ρ = density

g = gravitation

h = Height of rising liquid

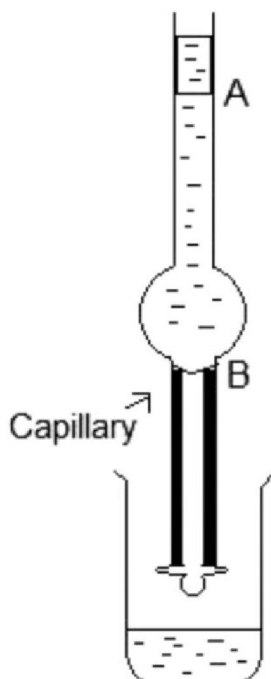
r = radius of that liquid



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Drop weight method:

This is determine by using an apparatus “**stalagmometer**” When the sample liquid is fill up to mark A in stalagmometer and allow to fall liquid dropwise then by using weight of the drop surface tension can be calculated.



$$W = 2\pi r\gamma$$

$$\gamma_1 = \frac{W_1}{2\pi r}$$

$$\gamma_2 = \frac{W_2}{2\pi r}$$

$$\frac{\gamma_1}{\gamma_2} = \frac{W_1}{2\pi r} \frac{W_2}{2\pi r}$$

$$\frac{\gamma_1}{\gamma_2} = \frac{W_1}{W_2}$$

Where,

- γ_1 = Surface tension of water
- γ_2 = Surface tension of sample
- W_1 = Weight of water
- W_2 = Weight of Sample



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Drop count method:

In this method surface tension is determined by using a stalagmometer. The same volume of water and sample is filled up to the mark and allowed to fall by counting the number of drops of sample and water. Surface tension is calculated.

$$W = 2\pi r \gamma$$

$$\gamma = \frac{W}{2\pi r n} = mg$$

$$\gamma = \frac{M}{V}$$

$$m = \rho V$$

$$\gamma_1 = \frac{\rho_1 v g}{2\pi r n_1}$$

$$\gamma_2 = \frac{\rho_2 v g}{2\pi r n_2}$$

$$\frac{\gamma_1}{\gamma_2} = \frac{\rho_1}{\rho_2} \times \frac{n_2}{n_1}$$

Where,

- γ_1 = Surface tension of water
- γ_2 = surface tension of sample
- ρ_1 = Density of water
- ρ_2 = Density of sample
- n_1 = No of drop of water
- n_2 = No of drop of sample

Wilhelmy plate methods:

In the Wilhelmy plate method the liquid is raised until the contact between the surface and the plate is observed. The maximum tension acts on the balance at this instance; this means that the sample does not need to be moved again during the measurement.

$$\gamma = \frac{F}{[L \cos \theta]}$$

where,

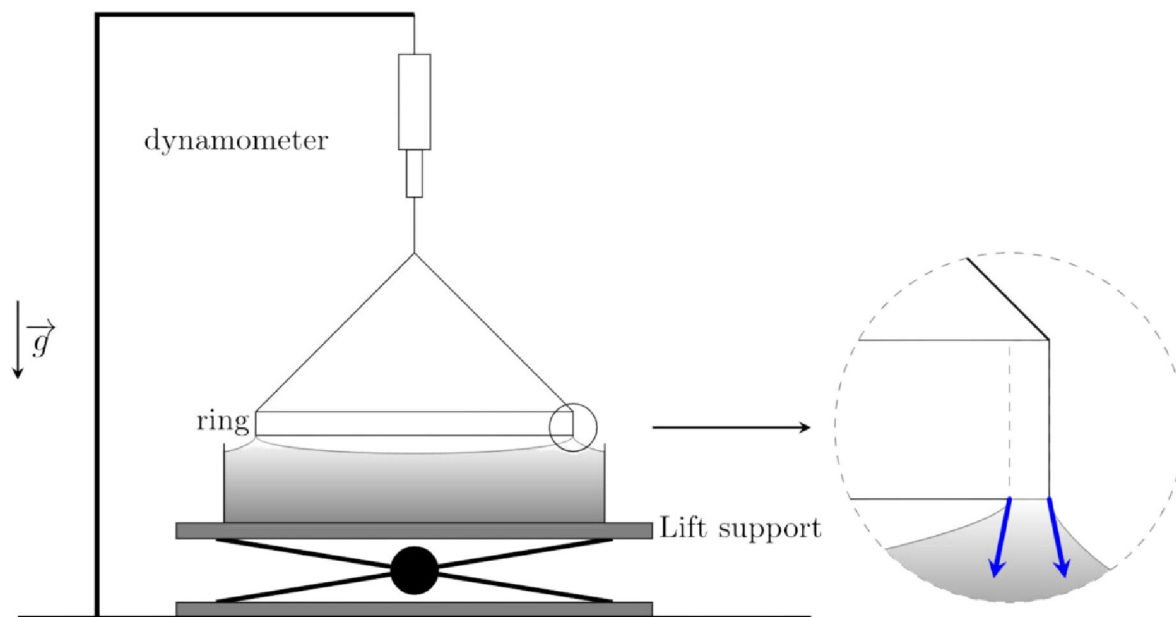
- γ is surface or interfacial tension,
- F is force acting on the balance,
- L is the wetted length
- θ is contact angle



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Ring detachment method:

- It is also known as du nouy method.
- It is used for measure both surface and interfacial tension.
- In this method, A slowly lifting ring often made up of platinum it attached from the surface of liquid.
- The force (f) required to raise the ring the liquid's surface is measured and related to the liquid's surface tension.



$$\gamma = \frac{mg}{4\pi r}$$

$$\gamma = \frac{f}{2\pi(r_1 + r_2)}$$

Where,

- γ = Surface Tension
- f = Force Applied
- r_1 = Radius of outer surface
- r_2 = Radius of inner surface



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Spreading Coefficient:

- If a small quantity of immiscible liquid is placed on the surface of another liquid it will either spread as a film on the surface of other liquid and remains as a drop.
- Spreading Coefficient is a ability of a liquid to spread over another liquid is calculated as spreading Coefficient.

Work of adhesion (W_a)-

- Consider a liquid drop with surface tension γ_{LV} and a solid surface with surface tension γ_{SV} . When the liquid drop adheres to the solid surface, it forms a surface tension γ_{SL} .
- The work of adhesion is simply the difference between the surface tensions of the liquid/vapour and solid/vapour and that of the solid/liquid. The work of adhesion is given by the following equation:

$$W_a = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}$$

Work of cohesion (W_c)-

- The work of cohesion is the work of adhesion when the two phases are the same. Consider a liquid cylinder with unit cross-sectional area.
- When this liquid is subdivided into two cylinders, two new surfaces are formed.
- The two new areas will have a surface tension of $2\gamma_{LV}$ and the work of cohesion is expressed by the following equation:

$$W_c = 2\gamma_{LV}$$

- The spreading coefficient (S) is the difference between the work of adhesion and the work of cohesion ($W_a - W_c$). This implies that if the work of adhesion is more than the work of cohesion, spreading will occur.

Then,

$$W_a - W_c = \gamma_L + \gamma_S - \gamma_{LS} - 2\gamma_L$$

$$S = \gamma_L + \gamma_S - \gamma_{LS}$$

$$S = \gamma_S - (\gamma_L + \gamma_{LS})$$

Where,

S = Spreading Co-efficient

γ_L = Spreading liquid

γ_S = Sublayer

γ_{LS} = Interfacial tension b/w two liquids



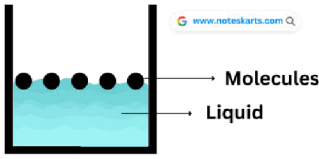
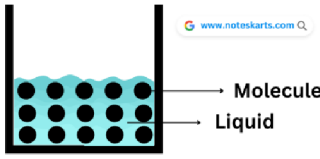
Application of Spreading Coefficient:

- Stabilization of Dispersed system such as Emulsion.
- Adsorption from topical dose form such as: Cream, Lotion, etc.
- Coating of the Tablets.

Adsorption at Liquid Interfaces:

The Phenomena of adsorption is the adhesion of Ions, atoms and molecule from a gas surface or interface of gas-liquid and liquid-liquid.

1. Positive Adsorption
2. Negative Adsorption

S.No.	Positive Adsorption	Negative Adsorption
1.	<p>Certain solute molecules or Ions when dispersed in a liquid get partition in favour of surface or interface.</p>  <p>Molecules settle down on surface</p>	<p>Some other molecules or ions are partition in favour of bulk of the liquid.</p>  <p>Molecules Mixed with liquid</p>
2.	Increase in concentration of such molecules and Ions of Surface or Interface or bulk.	Decrease in concentration of such molecules at the surface or interface than bulk..
3.	When the con. of adsorbate is more or the surface of adsorbent relative to its concentration of bulk is known as positive.	When the concentration of adsorbate is less on the surface of adsorbent relative to its concentration of bulk is known as negative.

Surface Active Agents (Surfactants):

- Surface active agent is surfactants which are used to prevent surface tension and interfacial tension.
- These agents are detergents, soaps, emulsifier which help in mixing of immiscible liquid (Oil into water)
- Surfactants have dual characteristics of hydrophilicity and lipophilicity.

Types of Surfactants:

- Anionic Surfactants



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- Non-ionic Surfactants
- Cationic Surfactants
- Polymeric Surfactants

Anionic Surfactants:

- Anionic Surfactants are dissociated in water in an amphiphilic anion, and a cation, which is in general an alkaline metal (Na^+ , K^+) or a quaternary ammonium.
- They are the most commonly used surfactants.
- They include alkylbenzene sulfonates (detergents), (fatty acid) soaps, lauryl sulfate (foaming agent), di-alkyl sulfosuccinate (wetting agent), lignosulfonates (dispersants) etc.

Non-ionic Surfactants:

- Nonionic Surfactants do not ionize in aqueous solution, because their hydrophilic group is of a non-dissociable type, such as alcohol, phenol, ether, ester, or amide.
- A large proportion of these nonionic surfactants are made of hydrophilic portion (by the presence of a polyethylene glycol chain) and lipophilic portion (alkyl or alkylbenzene)

Cationic Surfactants:

- The head of the cationic surfactants is positively charge.
- Cationic surfactants have good emulsifying property.
- These surfactants have also being found to be good Bacteroides and antiseptic.

Eg:

- Sulfobetaines, and natural substances such as amino acids and phospholipids

Polymeric Surfactants:

- Polymeric surfactants are often not accounted as surfactants.
- Their importance is growing however; because they enter in many formulated products as dispersants, emulsifiers, foam boosters, viscosity modifiers, etc.
- Some of them commonly used are polyEO-PolyPO block copolymers, ethoxylated or sulfonated resins, carboxymethyl cellulose and other polysaccharide derivatives, polyacrylates, xanthane etc.

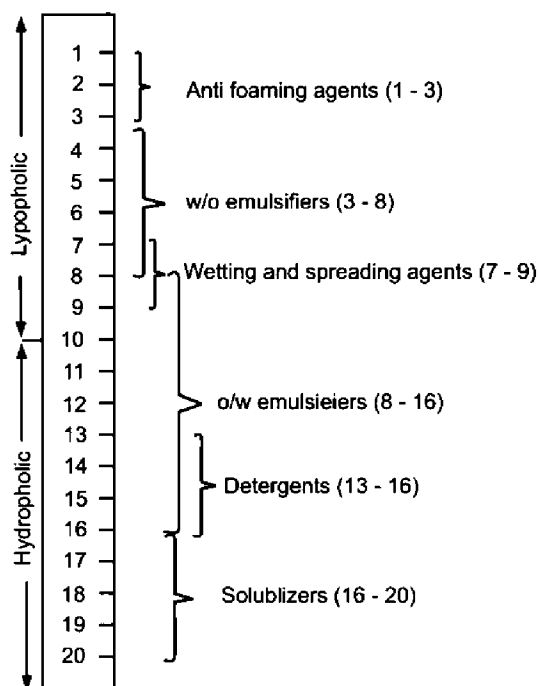
HLB Scale (Hydrophilic Lipophilic Balance (HLB) System):

- The hydrophilic lipophilic balance (HLB) system is based on the concept that some molecules of surfactants are having hydrophilic groups.
- HLB is an arbitrary scale no. system that indicate the extend of polar and non-polar nature of the surface active agent.



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- HLB scale was developed by Griffin in 1949.
- Emulsifier or surfactant are categorized according to the balance b/w the Hydrophilic and lipophilic portion of these molecules.
- An emulsifier that is lipophilic in nature is assigned a low HLB number and or emulsifies that is Hydrophilic in nature is assigned a high HLB number.
- A common system, which is used to express the amphiphilic nature as a balance between hydrophilic and lipophilic portion of the molecule is called as HLB system.
- The Hydrophilic lipophilic balance that indicate the polarity of the molecules and most commonly used emulsifier having the value b/w 1-19.
- Eg: Spans with low HLB value are lipophilic in nature.
- Tween with High HLB are Hydrophilic.



Method used for determining HLB Value:

Method-1:

For Polyhydric alcohol, fatty acid, esters, such as glycerol monostearate.

$$HLB = 20 \left(1 - \frac{S}{A} \right)$$

Where,

S = Saponification no of ester

A = Acid number of Ester



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Method-2:

For Those fatty acids, ester where sharp saponification data is not easily determine and which have poly oxy ethylene unit.

$$HLB = \frac{E + P}{5}$$

Where,

E = % weight of oxyethylene chain

P = % weight of polyhydric alcohol group

Method-3:

When hydrophilic components of surfactants is composed of polyoxy ethylene group.

$$HLB = \frac{E}{5}$$

Where,

E= % weight of oxyethylene chain

Method-4 (Griffins Method):

Griffins method for non-ionic surfactants was describe in 1954 works as follow.

$$HLB = \frac{20 \times Mh}{M}$$

Where,

Mh= molecular mass of the hydrophilic partion of the molecule.

M = Molecular mass of the whole molecule giving a result on a scale of HLB.

And HLB value of 0 corresponds to completely lipophilic molecules and the value of 20 carrespond to completely hydrophilic molecules.

Solubilisation:

- It is the process in which, solubility of organic compound is increased in aqueous medium with the help of surface active agents (surfactants), This phenomena is known as solubilization.
- It is used in many industries for the mixing of two immiscible liquid and help in making of drugs.



Detergency:

- Detergency is a complex process involving the removal of foreign matter from surfaces.
- Surfactants are used for the removal of dirt through the detergency effect.
- Initial wetting of the dirt and of the surface to be cleaned is carried out by deflocculation and suspension or emulsification or solubilization of the dirt particles.
- A wetting agent that when dissolved in water, lowers the advancing contact angle, aids in displacing an air phase at the surface and replacing it with a liquid phase.
- Wetting agents are useful in
 1. Displacement of air from sulfur, charcoal and other powders for dispersing these drugs in liquid vehicles
 2. Displacement of air from the matrix of cotton pads and bandages so that medicinal solutions may be absorbed for application to various body areas.
 3. Displacement of dirt and debris using detergents in the washing of wounds.
 4. The application of medicinal lotions and sprays to the surface of the skin and mucous membrane.

Adsorption at Solid Interface:

- Adsorption is the adhesion of atoms, ions or molecules to the Solid surface.
 - **Adsorbent:** The material used to adsorb gases or liquid is term as adsorbent.
 - **Adsorbate:** The substance that is attached to the surface of solid that is adsorbate.

Difference between Adsorption and Absorption:

S.No.	Adsorption	Absorption
1.	The substances like gas, liquids or dissolved solids loosely adhere or stick to the surface of another substance which can be solid or liquid.	It is a process in which any substance (atoms, ions, or molecules) is taken by or absorbed by another substance, especially in the solid or liquid material.
2.	The Process of adsorption is fast in the being and gradually become slower.	The process of absorption occurs at uniform rate.
3.	At the end of the process molecules of the adsorption are found only on the surface.	At the end of process absorption molecule penetrate and found inside the system.

Depending on the nature of Interaction adsorption is classified into:

- Physical Adsorption (Physiosorption)
- Chemical Adsorption (Chemisorption)



S.No.	Physical Adsorption	Chemical Adsorption
1.	It is reversible process.	It is irreversible process.
2.	Weak forces are involved in physical adsorption.	Strong forces are involved in Chemical adsorption.
3.	Non-specific process.	More specific process.
4.	Occurs at low temperature	Occurs at high temperature
5.	It does not require any activation energy.	It requires activation energy.
6.	No electron transfer takes place in physical adsorption.	Electron transfer takes place in chemical adsorption.

Principles of Adsorption:

1. Freundlich's Adsorption Isotherm:

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

$$\frac{W}{M} = kp^{-1/n}$$

Where,

W = mass of gas adsorbed

M = Mass of adsorbent

P = Pressure

k & n = is constant which depends on nature of gas and adsorbent at temp.

Taking log on both sides

$$\log \frac{W}{M} = \log \frac{k+1}{n} \log p$$

2. Langmuir Adsorption Isotherm:

He derived in 1916.

Derivation:

- Langmuir considered that gas molecules strike a solid surface and adsorb while some molecules evaporate and desorb.
- A dynamic equilibrium is established between two opposite processes: adsorption and desorption.
- If θ is the fraction of total surface covered by adsorbed molecules, the fraction of naked surface is $1 - \theta$.
- So the rate of desorption (Rd) is proportional to the covered area (θ).

Then



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$$R_d = k_d \theta \text{ ----- 1}$$

Where,

k_d = rate constant of desorption

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

$$R_a = k_a (1 - \theta)P \text{ ----- 2}$$

Where,

k_a = Rate constant for adsorption.

At equilibrium rate of desorption = rate of adsorption put value in equation.

$$R_d = R_a \text{ ----- 3}$$

$$k_d \theta = k_a (1 - \theta)P$$

$$k_d \theta = k_a P - k_a P \theta$$

$$k_d \theta + k_a P \theta = k_a P$$

$$\theta(k_d + k_a P) = k_a P$$

$$\theta = \frac{k_a P}{k_d + k_a P}$$

Divide right side of equation with k_d

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

Where

k = equilibrium constant which is known as adsorption Co-efficient.

The amount of gas adsorption per gram of adsorbent X is proportional to θ

$$X \propto \frac{kP}{1 + kP}$$

This is known as Langmuir equation

Isotherm: Which gives relation b/w amount of gas adsorbed to pressure of gas at constant temp.



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Application of Adsorption:

- Production of high Vacuum.
- Adsorption of poisonous gases at surface of mass.
- Removal of coloring matter from solution.
- Adsorption of catalyst on reactant in order to increase the rate of reaction.

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