

15/10/2022

Unit - III

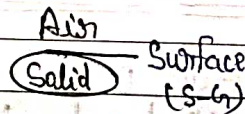
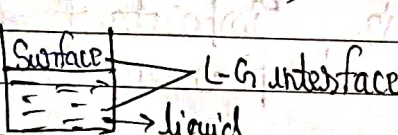
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Surface and Interfacial Phenomenon :-

* ~~the~~ Surface is used to represent the boundary b/w solid-gas and liquid-gas phases.

* The word surface & interface are similar but interface represent the boundary b/w two phases.

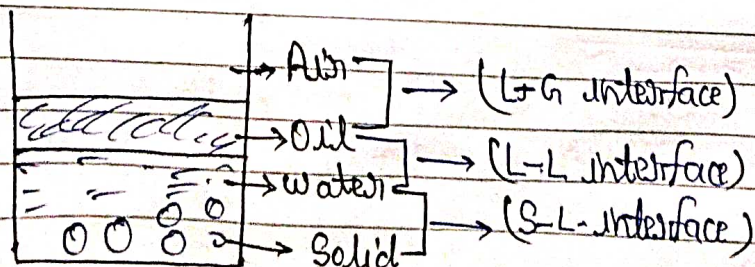
⇒ Types of Surface :-

1. Solid Surface → 
2. Liquid Surface → 

* The Boundary that exist b/w two immiscible phases is known as Interface.

Solid Interface :- It is associated with solid and gas, solid & liquid face or solid & solid.

Liquid Interface :- It is associated with liquid-gas face, liquid-liquid face and liquid-solid face.



Classification of Surface / Interface of System :-

Phases	Type	Examples
Liquid-Liquid	Liquid-Liquid interface	(Oil in water) Emulsion
Liquid-Solid	L-S interface	Suspension
Solid-Solid	S-S interface	Powder
Gas-Solid	Solid Surface	Table, Bench
Gas-Liquid	Liquid Surface	Aerosols
Gas-Gas	No interface	Air

Application of Surface Tension :-

- Interfacial tension concept is utilize in understanding the molecular interaction by phases.
- A few process such as wetting of powder & detergency are based on the principle of interfacial phenomenon.
- Disintegration & adsorption of drug from tablet and spreading of ointment are resultant from interfacial energy.

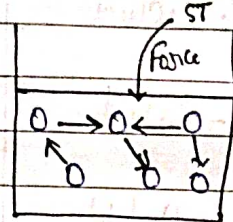
Surface Tension :-

It is defined as the force in Newton acting on the surface of the liquid at right angle to any line of length of surface.

Unit \rightarrow Newton/meter (N/m).

or

dyne/cm



Cohesive Force :-

These are the forces which act between molecules of same phases.

or

Intermolecular attraction between like molecule.

Adhesive Force :-

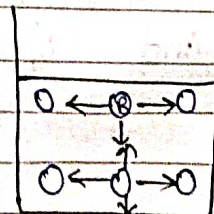
These are the forces which act between molecule of different phases.

or

Intermolecular attraction between unlike molecule.

\Rightarrow Concept of Surface Tension :-

Consider an example of water in a beaker, a molecule present in bulk phase of water (A) is attracted equally from all side.



Hence, the net force acting on molecule is zero (0). (A=0)

Now, Consider a molecule (B) that lie surface of the liquid which is partially surrounded by other molecule.

There are no molecule above this & it experience downward force.

The Adhesive force between molecules B & the air above it are weaker than the cohesive force.

These unbalance molecule acting downwards tends to draw the surface molecule into the bulk of the liquid, therefore the force acting on the surface of liquid is known as Surface tension.

→ Examples of Surface Tension of some solvent at 28°C.

Methanol	—	21.93	N/m
Toluene	—	27.45	N/m
Benzene	—	27.83	N/m
CCl ₄	—	25.77	N/m

Surface Free Energy :-

* It is define as the work required to increase the area of a liquid.

* This energy increases when the surface of the same mass of liquid increases & is therefore known as Surface free energy.

$$w = f \times d$$

$$f = \gamma \times 2L$$

$$w = \gamma \times 2L \times D$$

$$w = \gamma \times \Delta A$$

or

$$\Delta G = \gamma \times \Delta A$$

where, w = work done or surface free energy that increases & it is expressed in mJm^{-2} .
 γ = Surface tension.

Measurement of Surface Tension :-

- | | | |
|---------------------------|---|--|
| 1. Capillary rise method | } | for Surface Tension |
| 2. Drop Count method | | |
| 3. Drop weight method | | |
| 4. Wilhelmy Plate method | } | for Surface Tension & Interfacial tension. |
| 5. Ring detachment method | | |

1. Drop Count Method :-

(i) This method is use to determine surface tension through comparing.

(ii) In this system firstly we take the known liquid in stalagmometer at point A.



(iii) Then close the Stalagometer with fingers.

After that the liquid was allowed to flow slowly from capillary until liquid reaches point B & count the number of drops that falls from point A to point B.

(iv) After that same procedure was followed for unknown sample.

(v) Then both the liquids were compare to find out surface tension.

$$\text{Surface Tension } (\gamma_2) = \frac{\rho_2 n_1}{\rho_1 n_2} \times \gamma_1$$

where,

ρ_2 = Density of unknown liquid (gm/ml).

ρ_1 = Density of known liquid (gm/ml)

γ_1 = Surface tension of known liquid (Dyne/cm) / N/m.

γ_2 = Surface tension of unknown liquid (Dyne/cm) / N/m.

n_1 = No. of drops of known liquid from A-B

n_2 = No. of drops of unknown liquid from A-B.

2. Drop Weight Method :-

(i) This method is same as drop count method.

(ii) In this method number of drops that falls b/w point A-B are weight.

(iii) The unknown liquid is filled in stalagometer upto point A then the liquid is allowed to drop slowly from the point A-B & 20-30 drops of liquid is collected in R.D. Bottle & then

The weight of drop of liquid is determine.

$$Y_1 = \frac{W_1}{W_2} \times Y_2$$

where,

Y_1 = Surface tension of unknown liquid

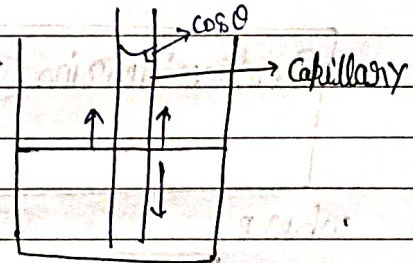
Y_2 = Surface tension of water

W_1 = weight of one drop of water

W_2 = weight of one drop of unknown liquid.

3. Capillary Rise Method:-

(i) When a capillary tube is placed in a liquid contain in a beaker.



(ii) The liquid rise up in the tube to a certain distance this is because the adhesive force b/w the liquid molecules & glass are stronger than the cohesive force b/w liquid.

(iii) The rise in the tube continue untill the upward movement is just balance by the downward force of gravity due to the weight of liquid.

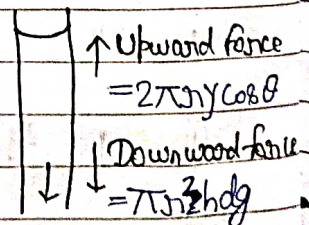
Derivation:-

Upward force = downward force

$$2\pi r_1 y \cos \theta = \pi r_2^2 h \rho g$$

$$y = \frac{\pi r_2^2 h \rho g}{2\pi r_1} \quad \left\{ \begin{array}{l} \cos \theta = 0 \\ \cos \theta = 1 \end{array} \right.$$

$$y = \frac{r_2 h \rho g}{2}$$

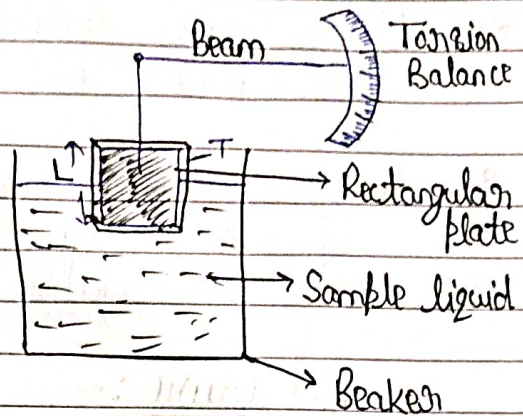


for liquid - $\theta = 0$

$$\therefore \cos \theta = 1$$

4. Wilhelmy Plate Method :-

- Sample / Test liquid is taken in container.
- The plate is immersed into it.
- Container gradually lower till plate detached from the surface of liquid.
- Reading on the Torsion Balance noted just prior to the detachment.



So,

$$w_L - w = 2(L+T)y$$

$$\boxed{\frac{w_L - w}{2(L+T)} = y}$$

where,

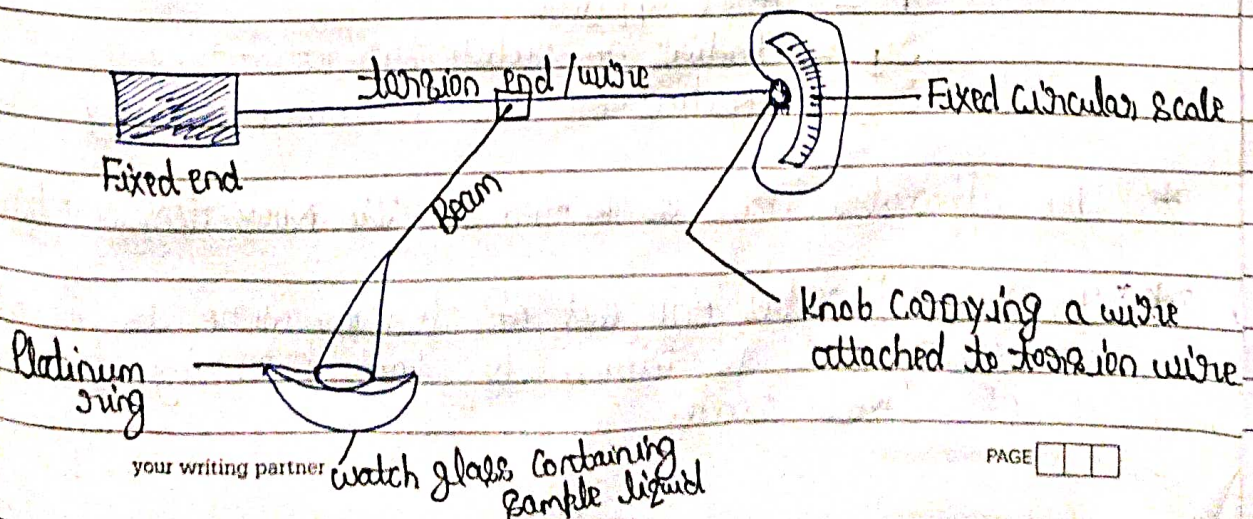
w_L = weight on balance prior to detachment

w = weight of plate in air

L = length of plate

T = Thickness of plate

5. Ring detachment method / Du Nouy tensiometer :-



* It is most widely used method for the determination of interfacial and surface tension.

* This is most convenient method for the determination specially when the quantity of liquid sample is available in small quantity.

Procedure :-

- The liquid sample whose surface tension to be determine is placed watch glass.
- ↓
- Platinum ring just touches the surface of sample liquid.
- ↓
- Knob of torsion wire slowly turned till ring detached.
- ↓
- Reading on scale is noted as F (force).
- ↓
- Surface tension is then calculated by using formula -

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

where,

γ = Surface tension

F = Force applied

r_1 = Radius of outer surface of ring

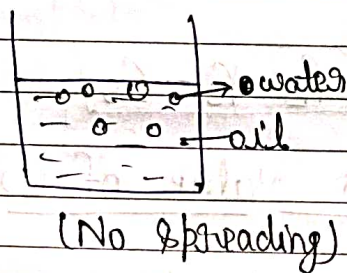
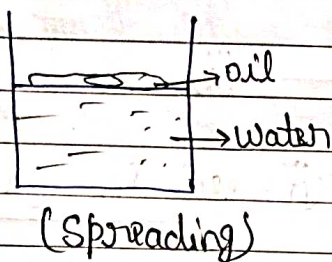
r_2 = Radius of inner surface of ring

* The apparatus used is known as Du Nouy tensiometer.

* In this apparatus one end of torsion wire is fixed & other end is attach to knob carrying pointer of fixed scale.

* In this method force required to detach a platinum ring from liquid surface is equals to the downward pull due to surface tension acting along the circumference of ring therefore the length of circumference is taken.

Spreading Coefficient :-



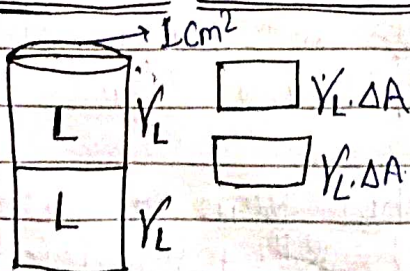
* If a small quantity of immiscible liquid is placed on the surface of another liquid it will either spread as a film on the surface of other liquid and remains as a drop.

* Spreading Coefficient is a ability of a liquid to spread over another liquid is calculated as spreading coefficient:

⇒ It is difference between the work of adhesive & work of Cohesive.

$$S = W_A - W_C \quad \text{--- (i)}$$

Work of Cohesive :-

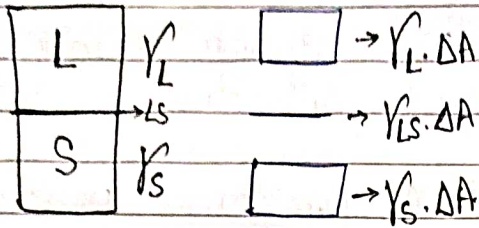


$$W_C = \gamma_L \cdot \Delta A + \gamma_L \cdot \Delta A$$

IF $\Delta A = 1 \text{ cm}^2$

$$W_C = \gamma_L + \gamma_L$$

$$W_C = 2\gamma_L \quad \text{--- (ii)}$$

Work of Adhesive :-

$$W_A = \gamma_L \cdot \Delta A + \gamma_S \cdot \Delta A - \gamma_{LS} \cdot \Delta A$$

$$\text{If } \Delta A = 1 \text{ cm}^2$$

$$\boxed{W_A = \gamma_L + \gamma_S - \gamma_{LS}} \quad \text{--- (iii)}$$

Putting the value of (i) & (ii) equ. in equ. (i)

$$S = W_A - W_C$$

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

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

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

Where,

S = Spreading co-efficient.

γ_L = Spreading liquid

γ_S = Sublayer

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

* Spreading occurs when surface tension of sub-layer is greater than the sum of surface tension of spreading liquid and interfacial tension b/w sub-layer and spreading liquid.

* Spreading does not occur when sum of surface tension of spreading liquid & the interfacial tension b/w sub-layer & spreading liquid.

is greater than surface tension of sub-layer.

* In this case, spreading liquid forms a globules or drop.

⇒ Pharmaceutical Application of Spreading Coefficient :-

- (i) Stabilization of dispersed system such as Emulsion
- (ii) Adsorption from topical doses form such as -
Cream, lotion etc.
- (iii) Coating of the tablets.

Adsorption at liquid interfaces :-

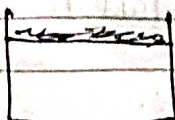
* The phenomenon of adsorption is the adhesion of ions, atoms and molecule from a gas or liquid to the dissolved solids to the surface or interface of gas-liquid & liquid-liquid.

⇒ Adsorption is 2 types :-

1. Positive Adsorption
2. Negative Adsorption

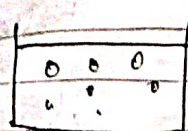
Positive Adsorption

(i) Certain solute molecules or ions when dispersed in a liquid get partition in favour of surface or interface.



Negative Adsorption

(ii) Some other molecules or ions are partition in favour of bulk of the liquid.



~~Negative~~ Positive Adsorption

(ii) Resulted in ~~it~~ increase in conc. of such molecules & Tens of surface or interface on bulk.

(iii) When the conc. of Adsorbate is more on ~~the~~ the adsorbent surface of relative to its conc. of bulk is known as positive

Negative Adsorption

(ii) Resulted in decreases in conc. of such molecule at the surface or interface than bulk.

(iii) When the conc. of Adsorbate is less on the surface of adsorbent relative to its conc. of bulk is known as Negative.

Surface Active Agents :- / Surfactants :-

↓ Surface tension
↓ Interfacial tension

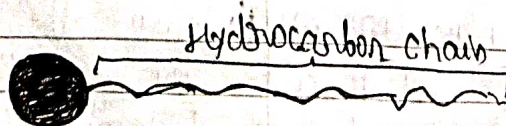
*

Surface active agents is a surfactants which are used to prevent surface tension and interfacial tension.

* Surfactant have dual characteristics of Hydrophilicity and Lipophilicity.

* The polar portion of surfactant exhibit a strong affinity towards polar solvent and non-polar part is exhibit affinity towards oil.

* Surfactants ^{are} also known as Amphiphiles.



Hydrophilic
(Head)

Lipophilic
(Tail)

Structure of Surfactant :-

⇒ Classification of Surfactant :-

Surfactants are classified into 4 category :-

	Hydrophilic	Hydrophobic
(i) Cationic Surfactant	⊕	~
(ii) Anionic Surfactant	⊖	~
(iii) Non-Ionic Surfactant	○	~
(iv) Amphoteric Surfactant	⊕	~

(i) 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 bactericides & antiseptic.

E.g.:-

- Quaternary ammonium salts.
- Benzal ~~Chloride~~ Konium Chloride
- Cetyl ~~Tri~~-methyl ammonium bromide (CTAB)

(ii) Anionic Surfactants :-

- * They give rise to a negatively charge surfactant ions upon ~~resol~~ dissolution in water.
- * This is the most widely used types of surfactant for dishwashing liquid Shampoo & Laundry because of its excellent cleaning property.
- * Most of the anionic ~~properties~~ ^{surfactant} are, Carboxylate Sulphate and Sulphonate ion.

E.g.:-

- Alkyl Sulphate
- Alkyl Ethoxylate Sulphate & Soaps

* Anion surfactants are relatively non-toxic.

(iii) Non-Ionic Surfactants:-

* Surfactants that do not ionise in aqueous solution due to their hydrophilic group are of non-dissociable type. Such as - Phenol, ether, ester, alcohol or amide.

* These surfactant do not have an electrical charge which makes them resistant to water hardness deactivation.

E.g.-

→ Tween

→ Span

→ Poloxamers or Pluronic

→ Poly oxy ethylene ester (PEG)

↳ Poly ethylene glycol.

* The most commonly used non-ionic surfactants are ether of fatty alcohol.

(iv) Amphoteric Surfactants:-

* It is also known as Zwitter-Ionic Surfactant.

* These surfactant have both cationic & Anionic centre attached to the same molecule.

* These surfactant are less common than Anionic, Cationic & Non-ionic.

* These surfactant are very mild making them particularly suited for used in personal care & household cleaning product.

E.g.-

→ Alkyl Betaine

→ Amphocetates

→ Lecithin.

Micelle :-

* Fundamental property of Surface Active agent is that monomers ~~in~~ ^{that} solution tends to form aggregates which is known as micelle.

or in other words in aqueous solution molecules having both polar & non-polar regions form aggregate which is known as micelle.

* In a micelle polar head form an outer cell in contact with water while non-polar tail are arranged in the interior.

⇒ Critical Micelle Concentration :-

* It is defined as the conc. of surfactant above which micelles form & all additional surfactant added to the system will form micelle.

⇒ Krafft Temperature :-

* It is defined as the minimum temp. from ~~with~~ which the micelle formation takes place.

HLB Scale (Hydrophilic Lipophilic Balance)

	19	
	18	
	17	→ Solubilizing agent (16-19)
	16	} → Detergent (13-16)
	15	
	14	
	13	
Hydrophilic	12	→ O/w emulsifying agent (0-16)
	11	
	10	
	9	} → Wetting agent & Spreading agent (7-9)
	8	
	7	
	6	→ w/o emulsifying agent (3-8)
	5	
Lipophilic	4	
	3	} → Antifoaming agent (0-3)
	2	
	1	
	0	

* HLB scale was developed by Griffin in 1949.

* HLB is an arbitrary scale on no. system that indicate the extend of polar & non-polar nature of the surface active agent.

* It is the relative efficiency of the hydrophilic portion of the surfactant molecule to ~~the~~ its lipophilic portion of the same molecules.

* Emulsifiers or surfactant are categorised 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 an emulsifier that is hydrophilic in nature is assigned a high HLB number.

* The Hydrophilic lipophilic Balance that indicate the polarity of the molecules and most commonly used emulsifiers having the value b/w 1-19.

E.g.: - → Spans with low HLB value are lipophilic in nature.

→ Tween - with high HLB are Hydrophilic.

⇒ Methods Used for determining HLB value:-

Method-1:- For polyhydric alcohol, fatty acid, ~~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

Method-2:-

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

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

Where,

E = Percentage (%) weight of oxyethylene chain.

P = Percentage (%) weight of polyhydric alcohol group.

Method-3:-

When hydrophilic components of surfactants is composed of poly oxy ethylene group.

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

Where,

E = (%) Percentage weight of oxyethylene chain.

Method-4:- (Griffins Method):-

Griffins method for non-ionic surfactants was described in 1954 works as follow:-

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

Where,

M_h = Molecular mass of the hydrophilic portion of the molecule

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

→ And HLB value of 0 correspond to completely lipophilic molecules & the value of 20 correspond to completely hydrophilic molecules.

Method-5 :- (Davie's Method):-

In 1957, Davie's suggested a method based on calculating a value which is based on the chemical group of the molecule.

$$HLB = 7 + \sum_{i=1}^m H_i - n \times 0.475$$

Where, m = no. of hydrophilic groups in the molecules

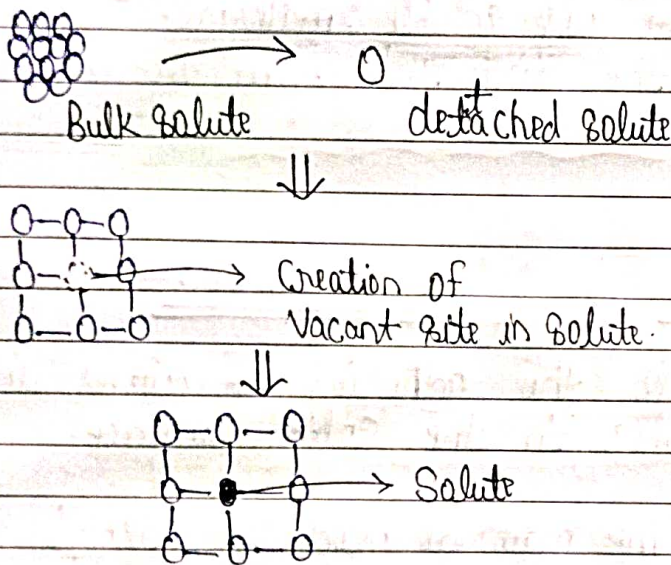
H_i = Value of i is given in table

n = no. of lipophilic group in the molecule

Solubilization :-

Solubilization is defined as the spontaneous passage of poorly water soluble solute molecules into an aqueous solution of soap or detergent in which a thermodynamically stable solution is formed.

⇒ Process of Solubilization :-



1. Breaking of Inter-ionic or Intermolecular bond in solute.
2. Separation of solute molecule from bulk solute.
3. Interaction b/w the solute & the solvent which result in the solubilization of solute in solvent.

Detergency :-

* Detergents are the surfactants used for removal of dirt or foreign material/substance such as glass, fabric wall, utensils etc.

* Effective detergent are required for clarity of production equipment containers, for packaging and also used to maintain proper hygiene in the organisation.

⇒ Phenomenon of Detergency :-

Detergency is a complex process which consist a several steps :-

1. Initial wetting of dirt from the surface.
2. Solubilizing of the dirt.
3. Removing the Insoluble dirt.
4. Suspending the particles in the detergent solution.
5. Removing the oil soluble material.
6. Converting the dirt into foam so as wash easily.

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 b/w Adsorption & Absorption :-

Adsorption	Absorption
* It is a process in which a substance takes another surface on its surface i.e. they remain on the surface.	* It is the surface process in which one substance absorb or penetrate into another substance i.e. the molecule penetrate into the body of solid.

Adsorption	Absorption
* The process of adsorption is fast in the beginning and gradually become slower.	* The process of absorption occurs at uniform rate.
* At the end of the process molecule 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:-

1. Physical Adsorption (Physisorption).
2. Chemical Adsorption (Chemisorption).

Physical Adsorption	Chemical Adsorption
* It is reversible process.	* It is irreversible process.
* Weak forces are involve in physical Adsorption.	* Strong forces are involve in chemical adsorption.
* In physical adsorption H-bonding and weak electronic bond are involves.	* Strong covalent bond are involves.
* Non-specific process.	* More specific process.
* Occurs at low temperature	* Occurs at high temperature.
* Heat of adsorption is low (20-40 kJ/mol).	* Heat of adsorption is high. (40-400 kJ/mol).
* It does not require any activation energy.	* It require activation energy.

* Increase of pressure increases adsorption.

* No electron transfer takes place in physical adsorption.

* No new compound is formed in the process.

* Change of pressure has no effect of adsorption.

* Electron transfer takes place in chemical adsorption.

* New Compound can be formed in the process.

⇒ Principles of Adsorption :-

1. Freundlich Adsorption Isotherm :-

* He proposed a relation in the form of ~~math~~ mathematical equation.

$$\frac{w}{m} = Kp^{-1/n}$$

{ graph plotted against $\frac{w}{m}$ and p .
{ curved graph }

where,

w = mass of gas adsorb

m = mass of adsorbent

p = pressure

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

Taking log on both sides

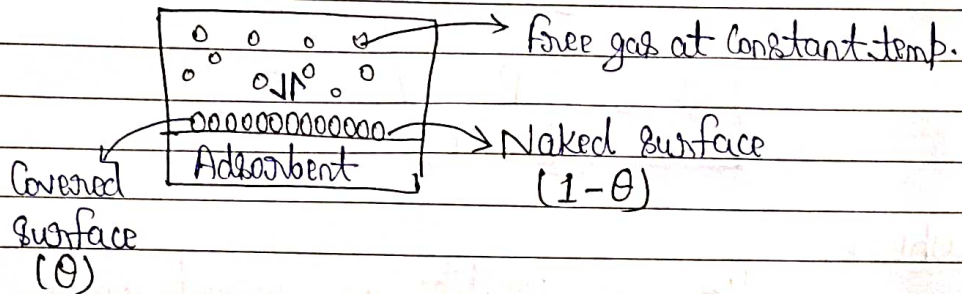
$$\log \frac{w}{m} = \log \frac{K+1}{n} \cdot \log p \quad (\text{straight line graph})$$

2. Langmuir Adsorption Isotherm :-

* He derive in 1916.

Derivation: -

- * Langmuir considered that gas molecules strike a solid surface & absorb while some molecules evaporate and ~~dissolve~~ desorb.



- A dynamic equilibrium is established b/w two opposite ~~process~~ ^{processes} i.e., adsorption & desorption.

- If θ is fraction of total surface covered by adsorb molecules. the fraction of naked surface is $1-\theta$.

- So, rate of desorption (R_d) is proportional to covered area (θ).

Then,

$$R_d = k_d \theta \quad \text{--- (i)}$$

where,

k_d = rate constant of desorption

- The Rate of adsorption (R_a) is proportional to available naked surface & pressure (P) of gas.

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

where,

k_a = Rate constant for adsorption

At equilibrium rate of desorption = rate of adsorption.

Put value in equi (3) → $k_d \theta = k_a (1-\theta) P$

$(R_d = R_a)$ - iii $k_d \theta = k_a P - k_a P \theta$

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

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

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

divide right side of equation with k_d .

$$Q = \frac{k_a P}{k_d} \cdot \frac{1}{1 + \frac{k_a P}{k_d}}$$

$$Q = \frac{K P}{1 + K P}$$

Where,

K_a = equilibrium constant which is known as adsorption co-efficient -

→ The amount of gas adsorbed per gram of adsorbent X is proportional to Q .

$$X \propto \frac{K P}{1 + K P}$$

This is known as Langmuir's equation / Langmuir Adsorption Isotherm.

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

⇒ Application of Adsorption :-

- (i) Production of high vacuum.
- (ii) Adsorption of poisonous gases at surface of mass.
- (iii) Removal of colouring matter from solution.
- (iv) Prevention of adsorption of moisture in medicine by Silica Gel to Control Humidity.
- (v) Adsorption of catalyst on reactant in order to increase the rate of reaction.