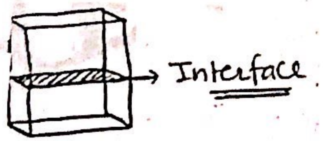
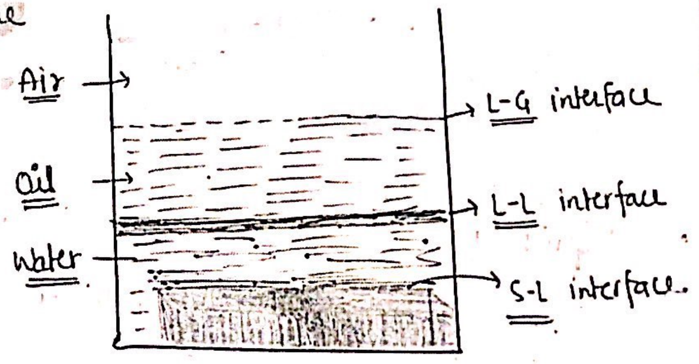
PHYSICAL PHARMACEUTICS || UNIT - 3rd

SURFACE & INTERFACIAL PHENOMENA

- **Interface** :- It forms when two or more immiscible substance contact with each other.

eg:-





- **Surface** :- The outside part of something, but here, surface is the liquid-gas interface or any interface in which Gas is on opposite site.

- **Interfaces :-**
  - Solid-liquid interface :- It forms b/w solid and Liquid.
  - liquid-liquid interface :- It forms b/w liquid and liquid, but liquids does not miscible with each other.
  - liquid-Gas interface :- (surface) It form b/w liquid and gas (air) and it is called as Surface
  - Solid-Gas interface :- (surface) It form b/w solid and gas and it is also called surface

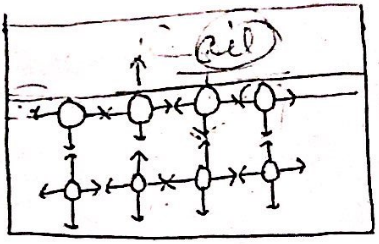
- **Liquid interface :-** It form when liquid is contact or mix with other states of matter (solid and gas) or itself (liquid).

  eg :- Oil in water (liquid-liquid interface) etc

- **Importance :-**
  - Emulsion formation and stability
  - Adsorptions of drugs onto solid adjuncts in dosage forms. etc

Surface and Interfacial tensions :-

S.T.



In Liquid, state, liquid molecules are attached or attracted with each other through cohesive force. (vandarwall forces)

It is a intermolecular force which attract each other from any side. & make them Stable at equlibrium

- Surface tension → It is the force per unit length that must be applied parallel to the surface.

$$\boxed{\gamma = \frac{force}{length}}$$

Gamma

γ(Gama) = surface tension , $\boxed{\text{unit, N/m}}$

- Interfacial tension → Same as surface tension, but it is happened between two immiscible Liquid.

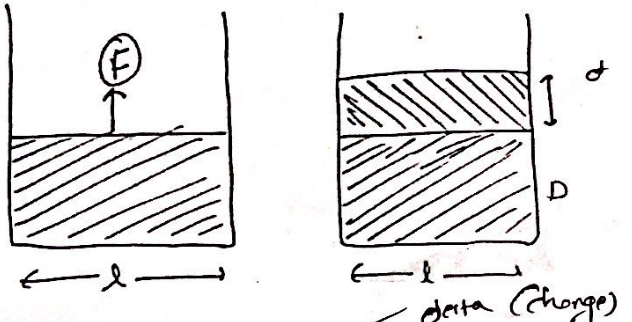
• SURFACE & INTERFACIAL PHENOMENON

- SURFACE FREE ENERGY
- Measurement of surface and Interfacial tensions
    - i) Capillary Rise method
    - ii) Drop count method
    - iii) Drop weight method
    - iv) Wilhelmy plate method
    - v) Ring detachment method

① Surface free energy ⇒

Those energy which want to increase our surface.

The molecules near the surface of liquid have more potential energy as compared to the molecules in the bulk of the liquid, this means that as surface area of liquid increase, the more molecules have this excessive potential energy. This energy is proportional to the size of the free surface, it is called a surface free energy.



delta (change)

$W = f \times \Delta d$

$W = S \times l \times \Delta d$ $[f = S \times l]$ ↓ surface tension.

$W = S \times \Delta A$

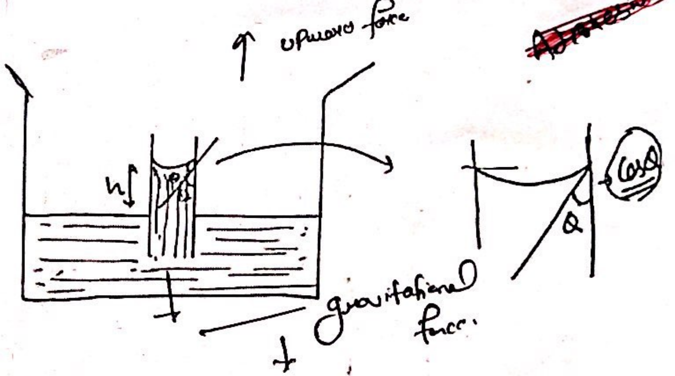
$\boxed{W = \gamma \times \Delta A}$ $\left[\Delta A = \frac{\text{Area of change of}}{\text{surface}}\right]$

where, W = Surface free energy (work done)
γ = Surface tension, ΔA = Increase in area

- Measurement of Surface and Interfacial tension.

1) **Capillary rise method** :-

It is used to measure surface tension.



<u>Principle</u> :- When a thin glass tube (capillary) Is placed in b/w liquid, liquid rises up in the capillary tube upto certain height.

- It is because adhesive force between capillary and liquid is more than the cohesive force b/w intermolecular molecules of liquid.

- Due to surface tension liquid rises but some gravitational force is also apply on liquid which pull downward liquid.
- when both forces are equal liquid is an equilibrium and stable in that sitution.

- **Derivation :-**

— **Upward force** →

capillary is circular that's why $2\pi r$

Gamma

$$f = 2\pi r . \gamma\cos\theta \quad \text{—— (i)}$$

$$\boxed{f = 2\pi r . \gamma}$$

where,

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

$\gamma\cos\theta$ = Surface tension & angle of contact

— **Downward force** →

$$f = mgh + \omega \quad \text{—— (ii)}$$

where,

mgh = potential energy with respect to gravitational force

ω = weight of liquid.

we know that,

density ← rho

$= \frac{mass}{volume}$

$$\rho = \frac{M}{V} \Rightarrow \frac{m}{\pi r^2} \qquad [V = \pi r^2]$$

where,

ρ = density of liquid

M = mass

V = volume

rho

$$\boxed{M = \rho . \pi r^2} \quad \text{—— (iii)}$$

ρ

Put. eq^n (iii) value in eq^n (ii)

$$f = \rho\pi r^2 gh + \omega$$

Now,

liquid is in equilibrium. means both forces are equal.

So,

Upward force = Downward force

$$2\pi r \gamma \cos\theta = \rho \pi r^2 g h + \omega$$

$$\therefore 2\cancel{\pi}\cancel{r} \gamma \cos\theta = \rho \cancel{\pi} r^2 g h + \omega$$

for water,

$$\boxed{\gamma = \frac{1}{2}\left[\rho g h r + \omega\right]}$$

where,

γ = surface tension

ρ = density

g = gravitation

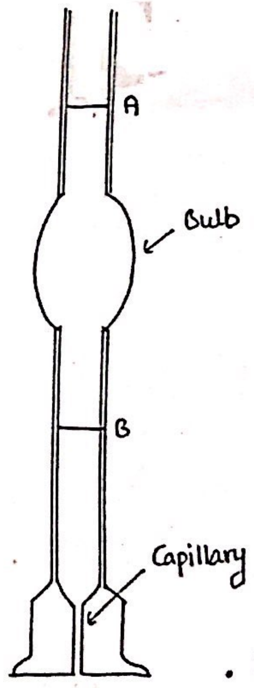
h = height of rising liquid

r = radius of that liquid

ω = weight of

11) Drop count method :-

It is used to measure the surface tension of liquid.



- **Stalagmometer**

In this method, we find out surface tension through comparing.

i) firstly take known liquid, which we know the surface tension.

ii) then fill stalagmometer with that liquid at point A. then stalagmometer closed from buttom from or with the help of finger.

iii) Now, Release liquid slowly-slowly dropwise from capillary untill liquid reached at point B. and continously count no. of drop, then note it.

iv) Now, Do same with other liquid, which we have to find surface tension.

v) So, on comparing both, by using formula we find out surface tension (γ).

Let's see how??

-Derivation of formula ⇒

we know that

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

where, $2\pi r$ = circumference of capillary

1st case → when we take water [known surface tension]

$$W_1 = 2\pi r \gamma_1$$

$$\gamma_1 = \frac{W_1}{2\pi r \cdot n_1}$$ [∵ r = radius is same for both liquid]

2nd case → when we take unknown S.T. liquid.

$$W_2 = 2\pi r \gamma_2$$

$$\gamma_2 = \frac{W_2}{2\pi r \cdot n_2}$$ [where n = no. of drop]

Now,

we know that

$w = m.g$ & $\rho = \frac{M}{v}$ (density) $\Rightarrow \underline{M = \rho.v}$

mass

gravitational force

$\boxed{w = \rho.v.g}$, where, ρ = density of liquid
v = volume of liquid
g = gravitational force

- Put these value in <u>main eqn</u>

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

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

<u>On Comparing both,</u>

$$\frac{\gamma_1}{\gamma_2} = \frac{\frac{\rho_1 v g}{2\pi r n_1}}{\frac{\rho_2 v g}{2\pi r n_2}}$$

So,

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

where, γ = surface tension
ρ = density of liquid
n = no. of drop count

→ So, in this we know ρ_1, ρ_2, n_1, n_2 and γ_1, so we can easily find out the surface tension, by putting these value

iii) **Drop weight method** :-

It is same as drop count method, in which we use same capillary or stalagmometer.

Difference is that,

In which we weight the drop (one drop), firstly those liquid

which we know surface tension,
then weight the other liquid's drop
which we have to find out the surface tension.

1st case → know Liquid.

$W_1 = 2\pi r \gamma_1$

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

2nd case → Unknow

$W_2 = 2\pi r \gamma_2$

$\gamma_2 = \frac{W_2}{2\pi r}$ [r = radius is same due to same capillary]

On Comparing both,

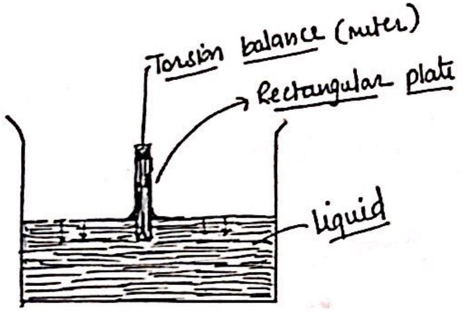
$$\frac{\gamma_1}{\gamma_2} = \frac{\frac{W_1}{\cancel{2\pi r}}}{\frac{W_2}{\cancel{2\pi r}}}.$$

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

where,
γ = surface tension
W = weight of the drop.

iv) **Welhemy plate method** :-

It is used to used to measure surface tension.



- firstly we put the rectangular plate in that Liquid, which we have to find out the surface tension.
- Now, Surface tension is applied on plate which pulled plate downward in the liquid.
- And we pulled rectangular plate upward with some force and surface tencion is also oppose this.
- Now, that condition, when we pulled (detached) out plate from liquid, that time the force we applied is same as the surface tension of liquid.

$$\boxed{\gamma = \frac{f}{L\cos\theta}}$$

where,

γ = surface tension of liquid

f = force applied

L = length of plate (perimeter)

θ = angle of contact,

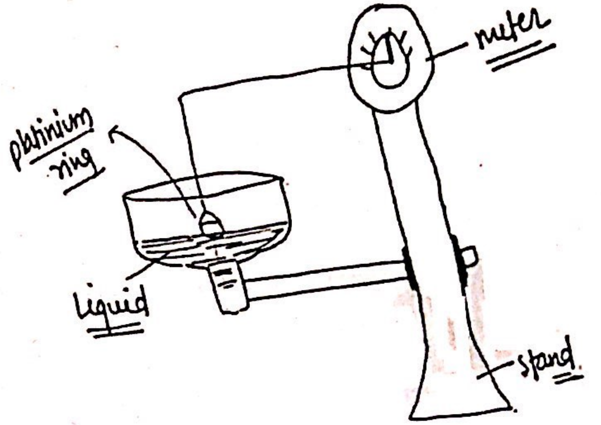
[$\cos\theta = 1$ for water]

v) Ring detachement method :-

It is used for measure both surface and interfacial tension.

→ It is also known as du nuoy method.

- In this method, A slowly lifting ring, often made up of platinium it attached from the surface of liquid
- The force f, required to raise the ring from the liquid's surface is measured and related to the liquid's surface tension.



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

where,

γ = Surface tension

f = force applied

r_1 = radius of outer surface

r_2 = radius of inner surface

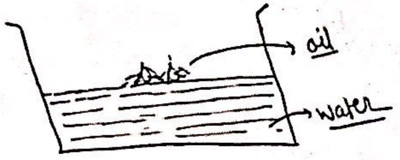
- Spreading Coefficient
- Adsorption of Liquid interface.

1) Spreading Coefficient :-

In two immiscible liquid, when we placed first's liquid drop on the surface of other it will spread as a film.

And the ability of one liquid to spread over another liquid is calculated as spreading coefficient.

Eg:- Emulsion, oil in water etc



And it occurs, when adhesive force is more than cohesive force

i.e. $\boxed{S = W_A - W_c}$ —— ①

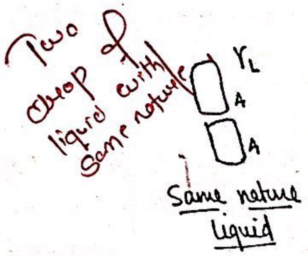
where,

S = spreading coefficient
W_A = Work done of adhesive force
W_c = Work done of cohesive force

- **Adhesive force** :- It applied on the different nature's liquid.
- **Cohesive force** :- It applied on the same nature's liquid.

Derivation,

1st case → for Cohesive force



$W_c = \gamma_L \Delta A + \gamma_L \Delta A$ [∵ γ_L = Surface tension of water
ΔA = Area of drop]

$W_c = 2\gamma_L \Delta A$

If $\Delta A = 1cm^2$, then

$\boxed{W_c = 2\gamma_L}$. —— ⑪

D.
Adsorption - Surface 12.

Absorption - absorb.

2nd Case:- for different nature's liquid.
(Adhesive force).

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

If $\Delta A = 1cm^2$

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

Now, put value of eq^n (ii) & (iii) into (i)

$$S = W_A - W_C$$

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

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

If, $\gamma_S > (\gamma_L + \gamma_{LS})$, then
spreading occurs,

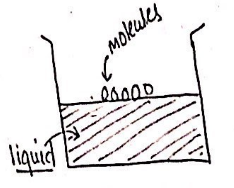
$\gamma_S < (\gamma_L + \gamma_{LS})$, the spreading
does not occurs,

• Adsorption of Liquid surfaces :-

Adsorption is defined as the deposition of some molecules or ions [molecular species] onto the surface of liquid.

Positive Adsorption

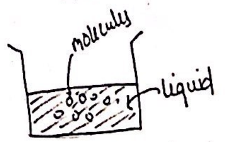
- → molecules deposite on the surface of liquid.
- → Surface free energy & surface tension decreased. ↓



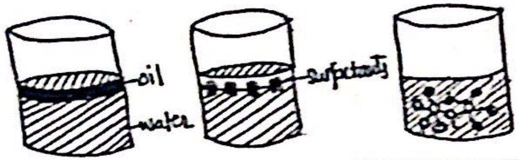
→ molecules settle down on surface.

Negative Adsorption
(Absorption)

- → Molecules does not deposite on surface it mix with the liquid.
- → Surface free energy & surface tension increase. ↑



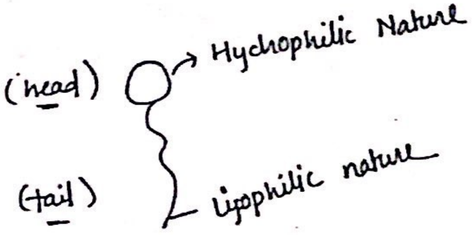
→ molecules mixed with liquid.



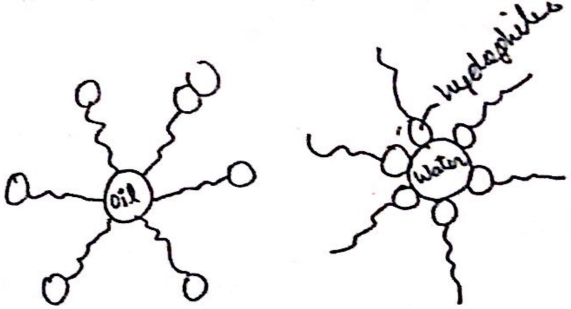
• Surface Active agents (Surfactants)

These are those agents (substances) which reduced the surface tension and interfacial tension b/w two liquids.

eg:- Detergents, soaps, emulsifier etc
It helps in mixing of oil into water..



If we add oil & water in any container, then it is immiscible, so we used surfactants to reduced interfacial tension and helps to mix them.



(Micelle)

→ oil (lipophilic), so attached with lyophilic part of surfactants.

→ Water (hydrophilic), so attached with hydrophilic part of surfactants.

→ And on which temperature micelle formed is called craft temperature

Types of Surfactants :-

i) Anionic
ii) Cationic
iii) Ampholytic
iv) Non-ionic

i) Anionic surfactants :- It contain organic tail with negative charge head and small positive molecules like ammonia.

- these are unpleasant taste. so not suitable for internal use

eg:- Alkali metals and ammonium soaps (sodium stearate) (o/w)

ii) Cationic surfactants :-

It contain organic tail with positive charge head and small negative molecules like chloride

- these are sometimes used on the skin for cleansing of wands.

eg:- Benzalkonium chloride ~~And~~ etc

iii) Amphoteric surfactants :- (Ampholytic)

Ampholytic and Amphoteric surfactants sometimes reffered to as zwitter ionic molecules surfactants that possess both cationic and anionic group in the same molecules.

- they depends on the pH of the systems

- they mostly used as co-surfactants that boosts the detergency and the foaming power of anionic surfactants

eg:- Lecithin, Amino acetic acid etc

iv) Non-ionic surfactants :-

they are non-ionic, so they does not ionize in water, because their hydrophilic part consist of non-dissociable molecules.

→ these are mostly used in pharmaceutical industry

→ they are resistant to pH change

eg :- Glycerol

HLB System :- [Hydrophilic - Lipophilic Balance System]

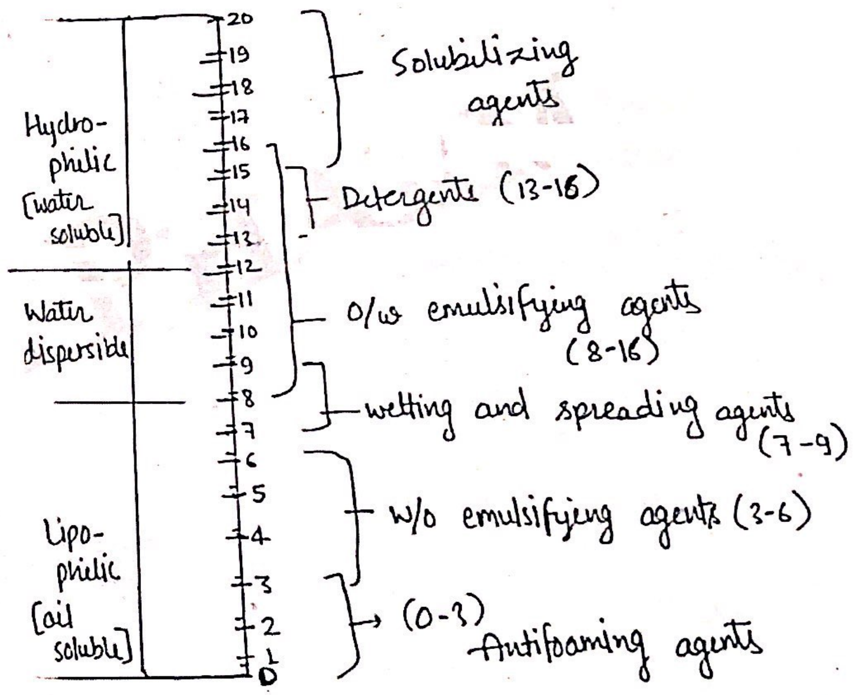
These system consist of arbiratory scale in which values are assigned to different surfactants according to their nature

→ HLB value of 1 indicates → Surfactants is lipophilic & soluble in oil.

→ HLB value of 20 indicates → Surfactants is hydrophilic & soluble in water.

$$\boxed{HLB = \frac{\text{Hydrophilic}}{\text{Lipophilic}}}$$

HLB SCALE



Solubilization :-

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 & help in making of drugs

Detergency :-

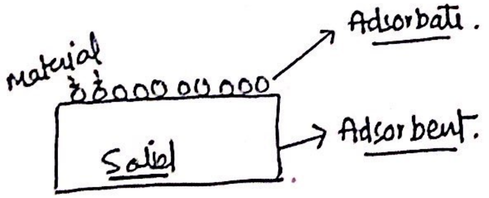
It is the process or phenomenon in which dirt (oil and solid objects) remove from the surface with the help of ~~surface~~ detergent.
And these detergent are basically made up with Surfactants or itself surfactants.

- It work that, it reduce the adhesive force, so dirt particles easily remove from the surface

Adsorption at Solid interface :-

- When substance (material) deposite on the surface of solid is called the adsorption at solid interfaces.

- The material (substance) which deposite on the surface of solid is called adsorbate.
- The material (substance) on whose surface the process takes place is called adsorbent.



Now, adsorbent and adsorbate are attached with each other with some attraction forces

- On the basis of attraction forces adsorption divided into two.

i) Physisorption (Physical adsorption)
ii) Chemisorption (chemical adsorption)

i) **Physisorption** :- When adsorbent and adsorbate is attached with each other with some weak bonds as like as,
Vandarwall forces, and

- these are reversible
- And these have weak force of attraction as compared to chemisorption
- It is less energy consuming

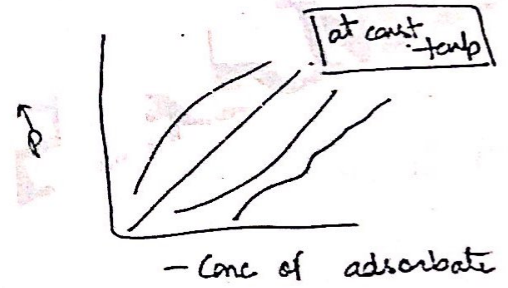
ii) Chemisorption :-

When adsorbate and adsorbent are attached with each other with some strong chemical bond, as like as, covalent bond, Ionic bond.

- they are irreversible
- they have strong force of attraction b/w adsorbent and ~~ab~~ adsorbate.
- It is more energy consuming as compared to physisorption.

Adsorption Isotherm

→ At constant temperature, graph b/w pressure & concn of adsorbate.



Freundlich theorem

Langmuir theorem

i) freundlich theorem →

let, When adsorbate is attached on the adsorbent

that time, (let)

x = mass of adsorbate

M = mass of adsorbent

and then

$$\boxed{\text{fraction of adsorption} = \frac{x}{m}}$$

and on increasing amount of adsorbate, fraction of adsorption increase and on increasing pressure, fraction of adsorption increased.

So, Acc. to freundlich

$$\frac{x}{m} \propto p^{1/n}$$

$$\boxed{\frac{x}{m} = Kp^{1/n}}$$

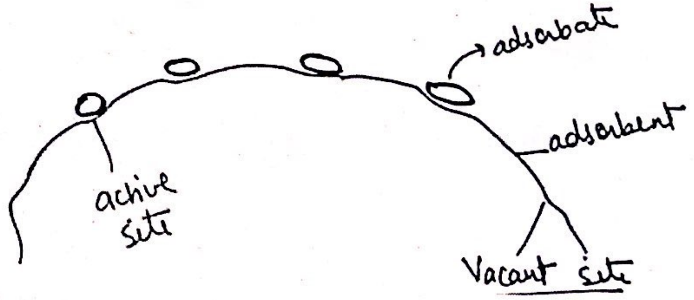
→ It is based on Chemisorption.

ii) Langmuir theorem :-

→ It is based on physisorption.

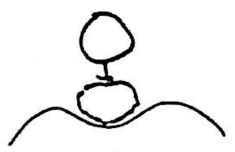
In this case,

we let their are some vacant site on which particles attached,



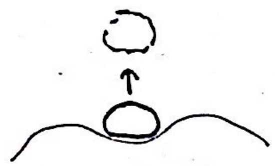
Active site, on which particles attached

Vacant site, when particles detached from active site after adsorption



adsorption

[attachement of particles on surfa]



desorption

[detachement of particles from surface]

let,

r_1 = rate of adsorption

r_2 = rate of desorption

let,

θ = filled site

$(1-\theta)$ = Vacant site

→ Rate of adsorption is depend on **vacant site**, because the more vacant site, the more particles attached.

So,

$r_1 \propto (1-\theta) \times P$

$r_1 = k_1(1-\theta) \times P$

[where,
r_1 = rate of adsorption
k_1 = constant
P = pressure which help in adsorptio

→ Rate of desorption is depend on active site. because the more particle attached get more detached.

So,

$r_2 \propto \theta$ [pressure is not required for detachement]

$r_2 = k_2\theta$

At equilibrium, $\underline{r_1 = r_2}$

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

$k_1P - k_1\theta P = k_2\theta$

$k_1P = k_2\theta + k_1\theta P$

$\boxed{k_1P = \theta[k_2 + k_1P]}$ — this is Langmuir **equation**.