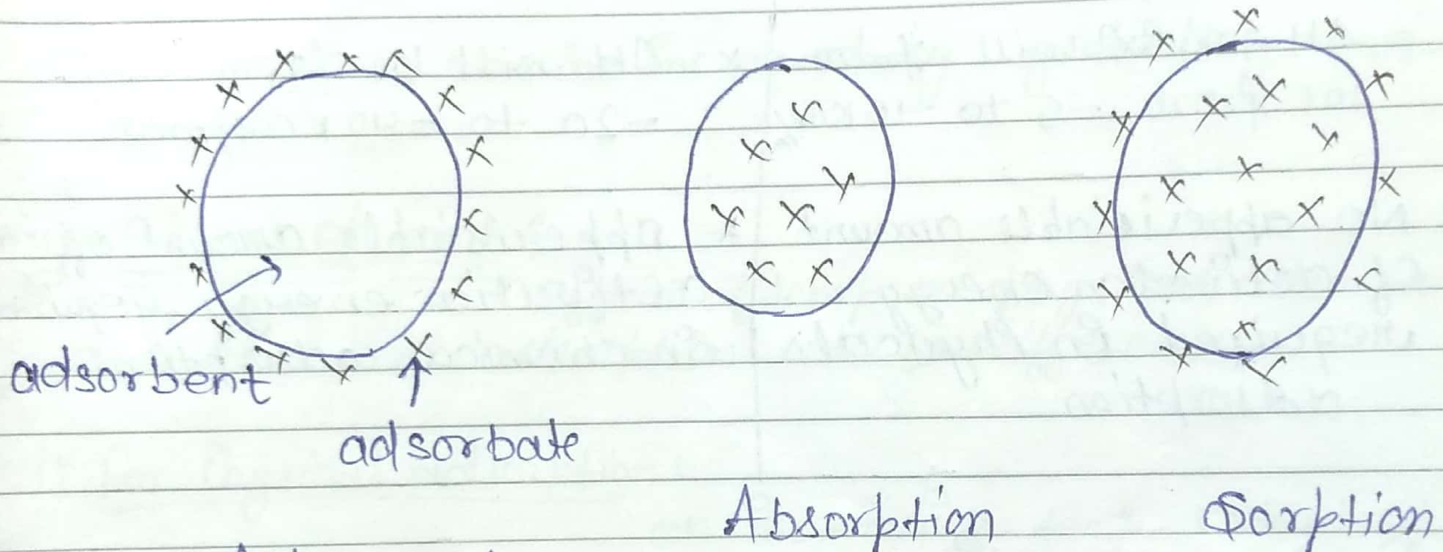
E.C J.A 36 – comp
L.S ⇒ 18 to 30 ⇒ L.S. 07

SBG STUDY

07/10/17

Surface Chemistry

* **Adsorption & absorption:**



⇒ Adsorption

$\Delta H < 0$

$\Delta S < 0$

$\Delta S_{surr.} = \frac{-q_{sys}}{T} > 0$

* Reverse process of Adsorption called desorption

Adsorption can be of two type:

Physical adsorption OR Physisorption	chemical adsorption OR chemisorption.
⇒ weak Waandervall forces will be present in adsorbent adsorbate.	⇒ chemical Rx^n occurs so, chemical bond formed b/w adsorbate and adsorbent.

* Non-specific in Nature	* Specific in nature.
* Reversible in nature	* irreversible in nature
* Multilayer form in Physical adsorption	* Single layer form in chemical adsorption.
* ΔH ~~for~~ ~~R_x^n~~ will ~~form~~ be from -5 to -10 Kcal/mol	* ΔH will be from -20 to -40 Kcal/mol.
* No apperisiable amount of activation energy required in Physical adsorption	* apperisiable amount of activation energy required in chemical adsorption

* factors affecting Extent of adsorption :-

Extent of adsorption $= \frac{x}{M}$

Here x – mass of adsorbate
M – Mass of adsorbent.

1) Nature of gases :-

Easily liquificable gases will have more value of Extant of adsorption because they have high tendency of bond formation.

If $\overset{\text{critical temp.}}{T_c} \uparrow$ & $a \uparrow$ then gas will be easily liquificable.

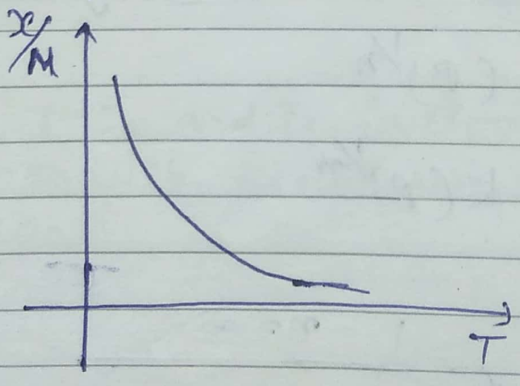
2) Nature of adsorbent: More porous adsorbent have high tendency of adsorption.

3) Specific Area: Area of unit mass adsorbent called its specific Area. if specific Area increase then extent of adsorption will also increase

Surface Area can be increased by greinding and creashing.

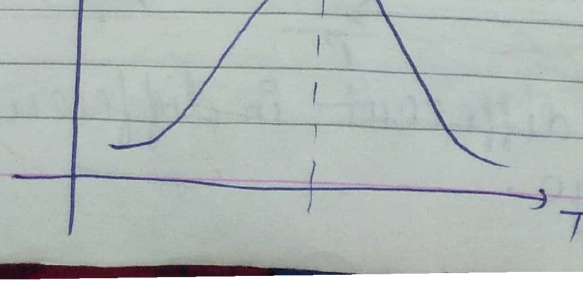
4) effect of temp: Effect of temp. on physical adsorption and chemical adsorption will be different

i) for Physical adsorption: on increasing temp. extent of Physical adsorption decrease.



T↑
- phy. ads ↓
- Chem. ads ↑

ii) for chemical adsorption: on increasing temp. extent of chemical adsorption increase.



* On increasing temp. Physical adsorption can convert in chemical adsorption.

for Ex: at 73 K N_2 Physically adsorbe on iron surface But at 873 K N_2 chemically adsorbe on iron surface

* Physical and chemical adsorption Can occur simitaneously

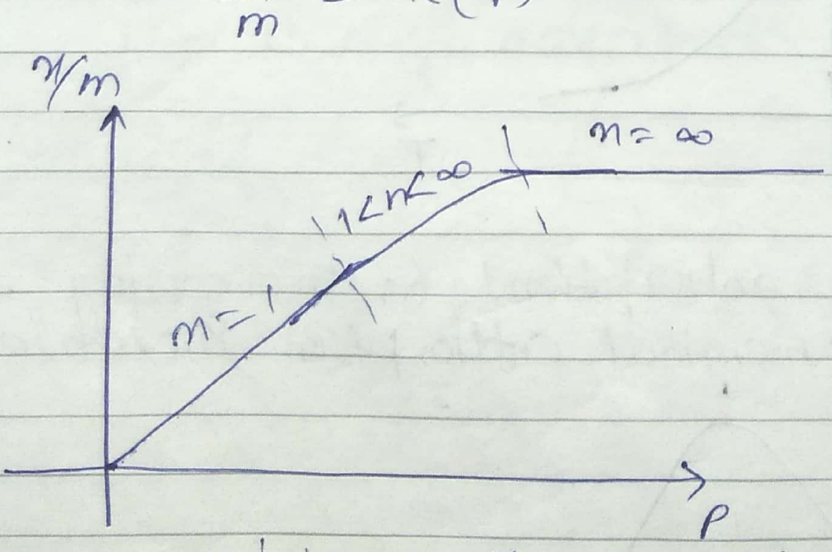
5] effect of Pressure:

On increasing pressure contact b/w adsorbate and adsorbent increase So extent of adsorption also increase.

* Freundlich isotherm for physical adsorption:

$$\frac{x}{m} \propto (P)^{1/n}$$

$$\frac{x}{m} = k(P)^{1/n}$$

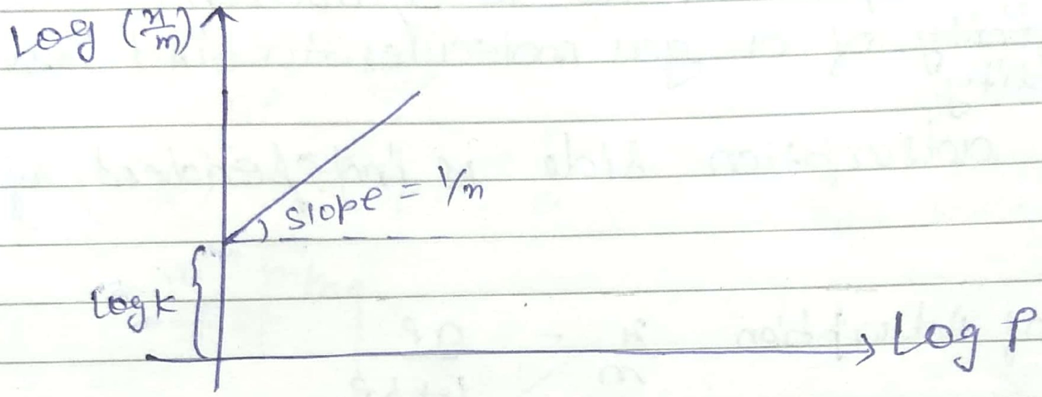


Value of n will be different in different pressure range.

*A

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log P$$

$$y = c + mx$$

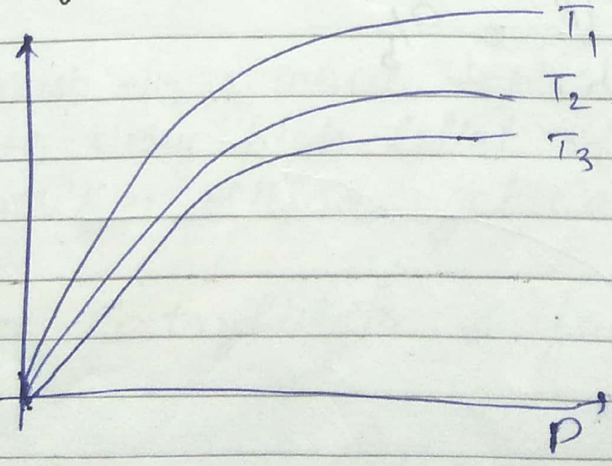


* for Physical adsorption of liquid solution

$$\frac{x}{m} = k(c)^{1/n}$$

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log c$$

Que: Arange T_1, T_2 and T_3 in decreasing order for given frendlich Isotherms of a gas on Solid Surface



$$T_3 > T_2 > T_1$$

* Langmuir Isotherm:

Acc. to Langmor isotherm

1] Each adsorption side is equivalent

2] The ~~affinity~~ ability of a gas molecules to bind itself at an adsorption side is independent of near by sides.

3] Extent of Adsorption $\frac{x}{m} = \frac{aP}{1+bP}$

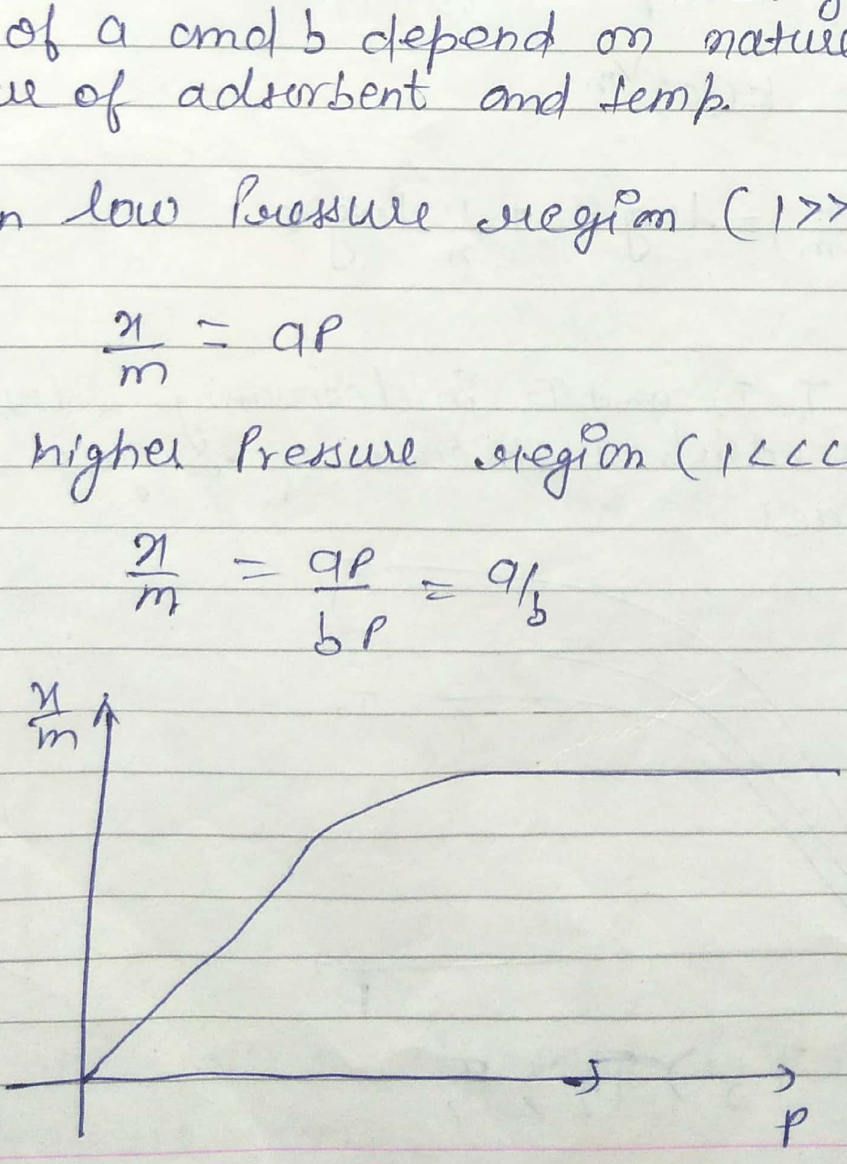
Here a and b are called Langmoor constant
Value of a and b depend on nature of adsorbate, Nature of adsorbent and temp.

* In low Pressure region $(1 >>>> bP)$

$$\frac{x}{m} = aP$$

* In higher Pressure region $(1 <<<< bP)$

$$\frac{x}{m} = \frac{aP}{bP} = a/b$$

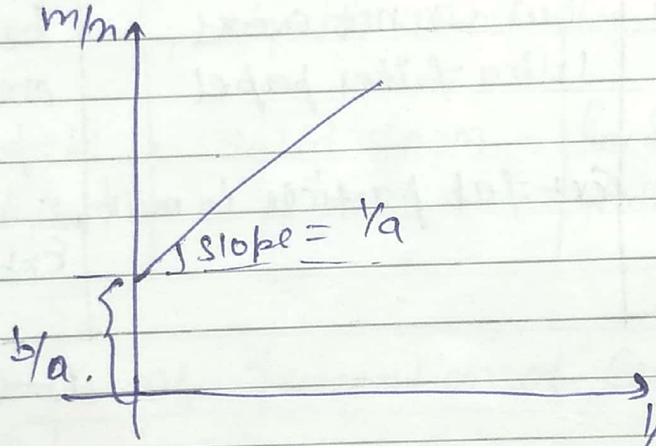


Langmuir Isotherm are Briefly valid for chemical adsorption.

Calculation of Langmuir Const. a and b :

$$\frac{1+bP}{aP} = \frac{m}{x}$$

$$\left(\frac{m}{x}\right) = \frac{1}{a}\left(\frac{1}{P}\right) + \frac{b}{a}$$



* for adsorption of liquid on solid surface

$$\frac{x}{m} = \frac{ac}{1+bc}.$$

* Application of Adsorption :

1) In gas mask to remove ~~toxics~~ toxic gases
2) to create very high level of vaccum
3) In dehumdifier. silica gel can adsorbe humidity

In anziened Cataylist or surface catalyst

* Colloidal Solution :-

On the basis of size of Solute Particle mixture can be of three type.

Solution < 1 nm	1 nm < Colloidal < 1000 nm Solution	Suspension > 1000 nm
* Homogenious * Can cross filter and ultra filter paper	* Hetrogenous * Can cross filter paper but can not cross ultra filter paper	* Hetrogenous * Can not cross both filter paper and ultra filter paper
Ex: aq. sol^n of NaCl	Ex:- fat particle in milk	Ex:- sand particles in water

~~In Collo~~

In Colloidal Solution

Solute ⇒ disperse Phase (d.P)

Solvent ⇒ dispersen medium (d.m).

* Classification of Colloidal Solution :

1) on the basis of physical state of disperse phase (dP) and dm (dispersen medium)

On This basis Colloidal sol^n can be of eight type because gas + gas can never form a colloidal solution

D.P	D.M	Name of Colloidal Sol^n	Example
1) Solid	Solid	Solid sol	dome coloured glases and gem stone
2) Solid	liquid	Sol	Paints, cell fluids
3) Solid	gas	Aerosol	Smoke, Dust
4) Liquid	Solid	Gel	cheese, butter, jellies
5) Liquid	Liquid	Emulsion	Milk, hair cream
6) liquid	gas	liquid aerosol	fog, mist, cloud, insecticide spray
7) gas	Solid	Solid foam	Pumic stone, foam rubber
8) gas	liquid	foam.	froth, whipped cream, Soap lather

2) on the Basis of formation of ~~Cotted~~ colloidial solution :

(1) Mecromolecular Colloide :-
Size of disperse phase Particles will be already equal to Size of collidial particles

for ex: Collidial Sol^n of organic Substances like Protein sol, starch sol,, etc

2) Multimolecular Colloide :
In these type of Colloidal Sol^n before mixing Size of disperse phase particles will be quite less than Size of Colloidal Particles. but after mixing disperse phase Particles associate/ agreegate them selfe to form a Colloidal Sol^n.

for Ex: Sulphur sol, Ausol, As_2S_3 sol, $Fe(OH)_3$ sol

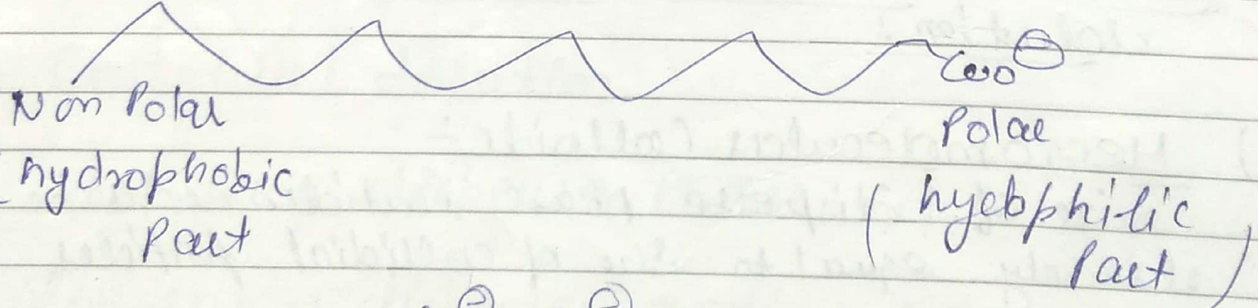
(3) Associated colloides (miscelles):

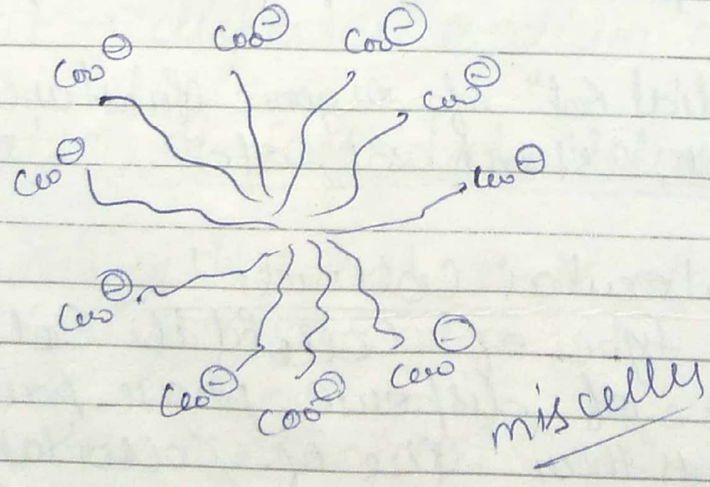
~~Ao~~ solution which behave like true normal electrolyte solⁿ at lower concⁿ and becomes colloidal solution at higher concⁿ. Called associated colloids or miscelles ✓

for Ex: ~~Stro~~ Soap or detergent

$C_{17}H_{35}COONa$

$$C_{17}H_{35}COONa \rightleftharpoons C_{17}H_{35}COO^{\ominus}_{(aq)} + Na^{+}_{(aq)} \quad \Delta h = +ve$$





L.S => 18 to 35 OH
J.A - Comp

Miscells can form above a certain temp. and Conc^n. this temp. is called Craft temp. and this Conc^n is called critical miscell ~~tem~~ Conc^n. (CCMC).

$\boxed{R \uparrow \quad C.M.C \downarrow}$ — Imp.

(3) On the Basis of attraction b/w dP and dM :-

lyophilic Colloidal	lyophobic colloidal Size
i) These will be attraction force b/w DP and DM Particles	i) There will be no attraction b/w DP and DM Particles.
ii) Generally colloidal sol^n of organic substances will be lyophilic in nature for ex: Sol of Protien, Starch, Hemoglobin etc.	ii) Generally Colloidal sol^n of Inorganic substances will be lyophobic in nature for ex: Sol of Au, S, As_2S_3, $Fe(OH)_3$ etc
iii) Highly stable It is defecult to Coagulate lyophilic Sol^n.	iii) unstabl in nature required Stabilizer for stabilisation. it is eassy to Coagulate lyophobic sol^n.
iv) Reversible in nature	iv) Ireversible in nature
v) Can Carry charge but it is Considerable as compared to lyophobic colloidal sol^n.	v) Colloidal Particle carry Considerable amount of similar charge.

* Considerable amount of dP Can be mixed in dM	* Less amount of dP Can be mixed is dM as compared to Lyphilic Colloidal solution.
* Viscocity of sol^n > viscocity of D.M.	* Viscocity of Colloidal sol^n ≈ ≈ Viscosity of DM. Size

* Properties of Collidial sol^n :-

1) Colligative Property :-

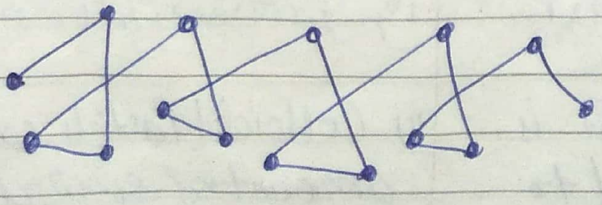
~~depend on no. of solute particle~~

Colloidal solution sol can represent Colligative Properties but value of Colligative Properties of ~~Collidal~~ Colloidal sol^n will be less as compared to Colligative Properties of sol^n.

2) Mechinical Property :-

Brownian motion :-

Colloidal Particles are in a Const. rapid Motion in all Possible directions this motion is called Brownian motion. It is beleved that Brownian motion is due to Collasion of disperse phase Particles with the Particles of dm.

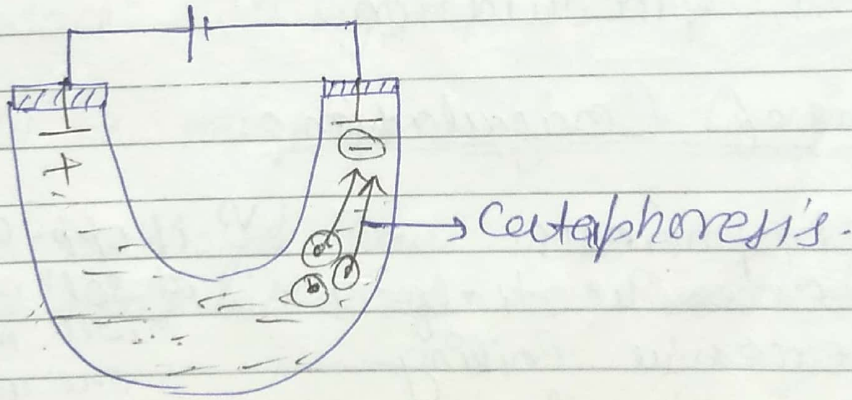


If difference in size of particles of dP and DM is more then Brownian motion will be more emident

* If difference in refractive index b/w dP and dM particles is more then Brownian motion will be more emident.

* **Electrical Property : (Electrophoresis) :**

moment of Colloidal Particles in Electrostatic field called Electrophoresis. If Colloidal Particles are Positively charge then they moves towards cathode and this time it is also called cataphoresis



* **Optical Property : (Tyndall effect) :**

when a beam of light is Passed through a Colloidal solution then colloidal solution disperse this light in all directions. this scattering Phenomina of light by Colloidal Particles called tyndall effect.

Pericbidtical Coagulation

* Tyndall effect can explain ~~buta~~ blue colour of sky.
(ii) blue colour of seawater
(iii) Colour of smoke
(iv) tails of Comets

* **Coagulation or flocculation of colloidal particles:-**

Separation of DP particle from DM called Coagulation or flocculation

If colloidal particles accumulate in bottom after separation then it is called Coagulation and if after separation colloidal particles accumulate on surface of DM then it is called flocculation.

* **Regions of Coagulation:**

i) Electrophoresis
ii) By excessive dialysis
(iii) on excessive Boiling
iv) on excessive freezing
(V) If opp. charge colloidal sol^n are mixed they will mutually coagulate one another.

Imp° (V) 5) ↳ ~~a~~ **By Mixing Electrolyte in colloidal sol^n:**

* **Hardy – Schulze Rule:** for Coagulation of Colloidal solution on mixing Electrolyte:

Rule:-1 ion which have charge opposite to that of colloidal Particles are Responsible for Coagulation of colloidal solution.

Rule:-2 Coagulation power of an electrolyte ion is directly propotional to charge on electrolyte ion causing coagulation raised to power 4.

$$\text{Coagulation Power of ion} \propto \left(\text{charge on ion causing coagulation}\right)^4$$

Que:- For As_2H_3 sol (-ve) coagulation power of which electrolyte will be maximum

~~(i)~~ $FeCl_2$ (iii) $MgCl_2$

(ii) ~~$MgCl_2$~~ $NaCl$ (iv) $MgSO_4$

Cation will be ~~tes~~ Responsible for Coagulation

Que:- for which electrolyte have maximum coagulation power for coagulation of $Fe(OH)_3$ sol (+ve) charg

(A) $NaCl$

(B) $MgSO_4$

(C) $AlCl_3$

~~(D)~~ Na_3PO_4

Race Next – 15
and – 16 Race

Important

Positively charge Colloidal Solution	Negatively charge colloidal Solution
1) oxides and hydrooxides colloidal sol^{n} will be generally +ve charge colloidal soln.	(i) oxides sol of sulphide are generally negatively charge colloidal sol^{n}.
for Ex:- TiO_2 sol, $Fe(OH)_3$ sol $Cr(OH)_3$ sol	for Ex:- As_2S_3 sol, Sb_2S_3 sol,
2) generally charge on basic colloidal sol^{n} will be +ve charge	2) Sol of Metals for Au sol, S sol.
for Ex:- Methylene blue —(NH_2)	3) Colloidal sol^{n} of acidic Nature. for Ex:- —(COOH) ↳ Congored.
3) Hemoglobin	

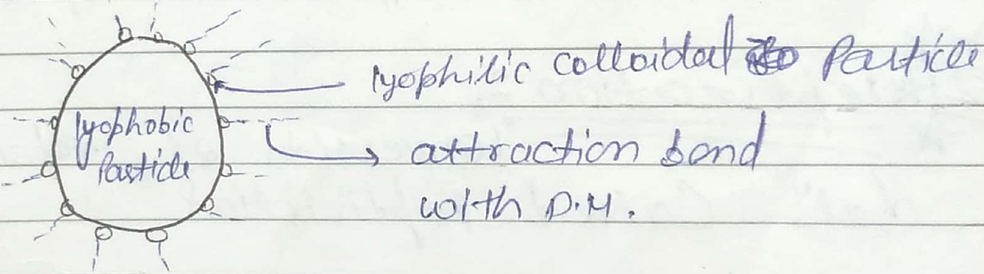
* Coagulation value of an Electrolyte:-

milli moles of an electrolyte required to Coagulate 1 Litre of colloidal Solution called Coagulation value of electrolyte

If Coagulation value ↑ Coagulating power ↓

* <u>Protective Colloid</u> :- if lyophilic Colloidal Sol^n is mixced in lyophobic colloidal Sol^n then Lyophilic colloidal Sol^n can Protect lyophobic Colloidal Sol^n from Coagulation on mixing electrolyte. So, lyophilic Colloidal Sol^n are called Protective Colloidal Sol^n.

Size of lyophilic Colloidal Particles is far as Compared to Size lyophobic Colloidal Particles on mixing lyphilic colloidal Particles in lyophobic colloida ~~Sol~~^{n}. Particles, Lyphilic Particles adsorve on the surface of lyophibic colloidal Particles and Create extra Stability by bonding with D.M Particles.



* <u>Gold number</u> :-
Amount of Proctected Colloids (lyophobic Colloid that must be required in miligram to add in 10 ml Saturated Au Sol. to just Prevent its Coagulation on mixing 1 ml 10% w/w Solution of NaCl

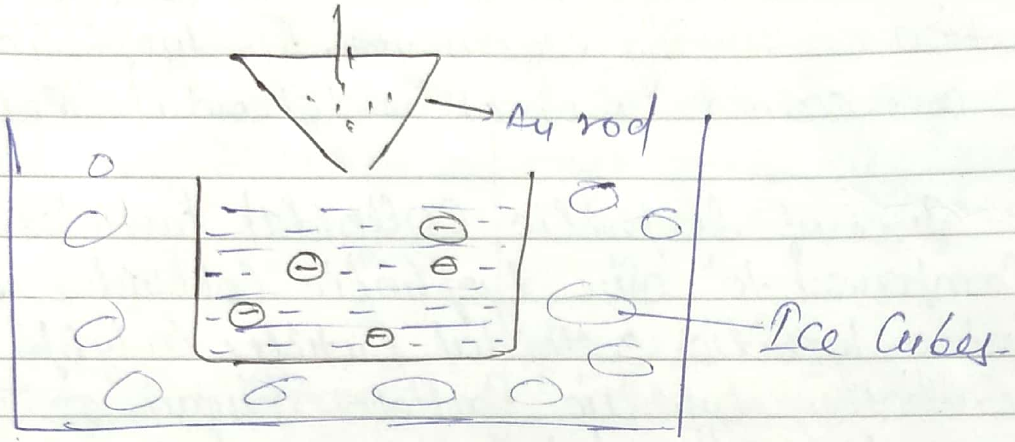
Gold no ↑ Proctecting Power ↓

N.I

* <u>Method of prepration of Colloidal Sol^n</u> :-

Lyophobic

1) Bredig arc Method :- Bredig arc method are used to form colloidal sol^n of metals



Colloidal sol^n of metal will be –ve charge due to $e^{\ominus}$ capture from atmosphere.

Imp

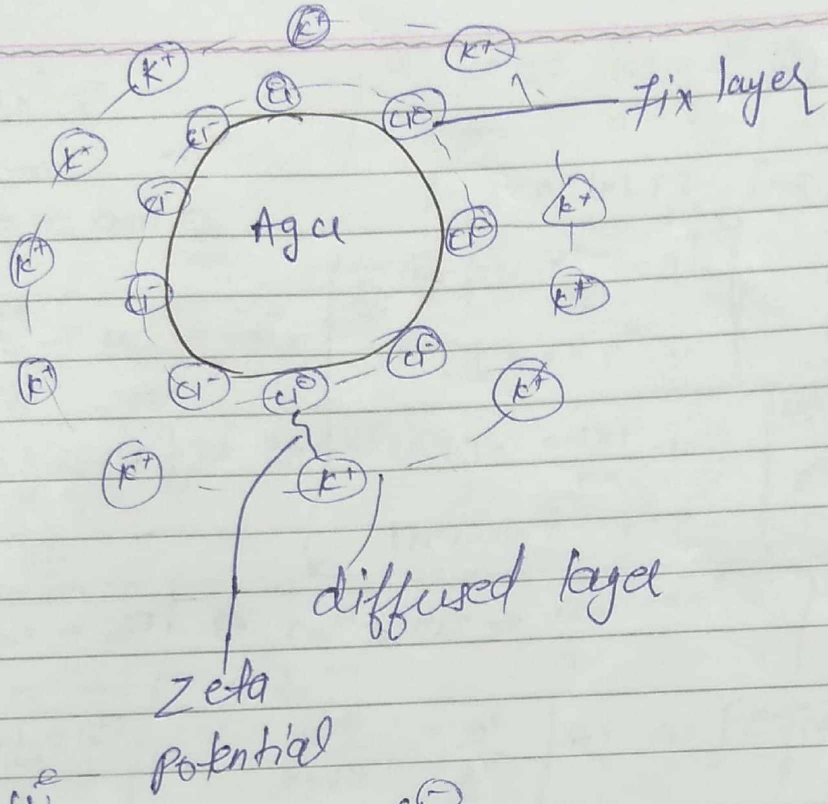
2) ☆ Peptization :- Conversion of Precipitation into Colloidal sol^n Called peptization

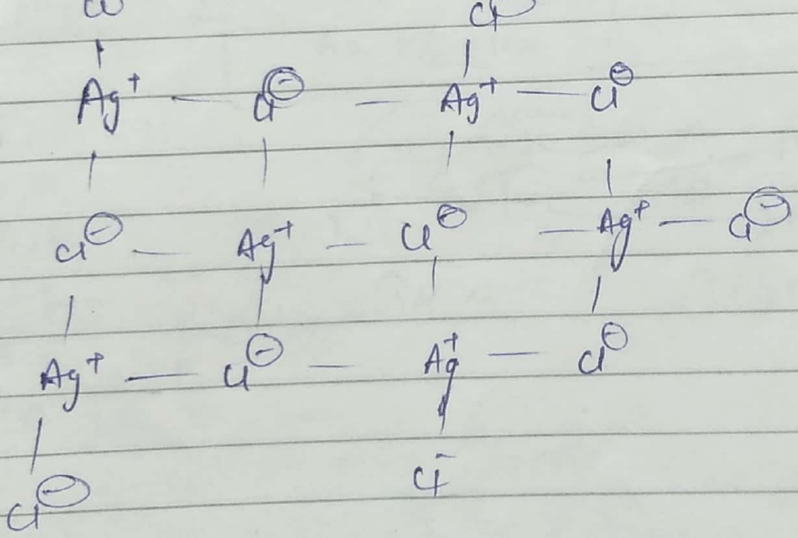
Reason of Peptization is Preferential adsorption of similar type of ion by p.p.t

$$\underset{P.P.t}{AgCl} + AgNO_{3(aq)} \longrightarrow \underset{+ve}{AgCl/Ag^{+}} \underbrace{\;+ NO_3^{\ominus}}_{\text{zeta Potential}}$$

$$\underset{P.P.t}{AgCl} + KCl \longrightarrow \underset{-ve}{AgCl/Cl^{\ominus}} \underbrace{\;+ K^{\oplus}}_{\text{zeta potential}}$$

Liquid sol


K+
Cl−
AgCl
fix layer
diffused layer
Zeta potential


Cl⊖
Ag+
Cl⊖
Ag+
Cl⊖
Cl⊖
Ag+
Cl⊖
Ag+
Cl⊖
Ag+
Cl⊖
Ag+
Cl⊖
Ag+
Cl⊖
Cl−
Cl⊖