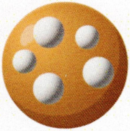
SURFACE CHEMISTRY

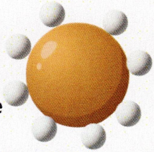
General Terms



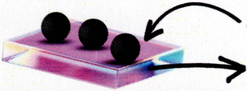
Molecules Drawn into bulk phase

Absorption

Molecules Adhere to the surface



Adsorption



Adsorbent

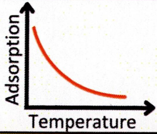
Adsorbate

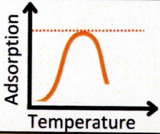
e.g. : H_2 as absorbent on Pt (Adsorbate) for hydrogenation

Important points about Adsorption

- Adsorption is an exothermic process. ΔH = -ve.
- Adsorption ∝ 1/Temperature
- ΔS = -ve (entropy decreases) for an adsorption.
- Adsorption increases with increase in surface area.
- Easily liquefiable gas is more easily adsorbed.
  - e.g. CO_2 is adsorbed more readily than H_2

Physiosorption	Chemiosorption
• Due to Van der Waals	• Due to Chemical Bonding
• Reversible	• Irreversible
• Enthalpy	• Enthalpy High
• $\propto$ Temperature	• $\propto$ 1/Temperature
• No Ea Required	• High Ea required
• Multi-molecular layer	• Uni-Molecular Layer





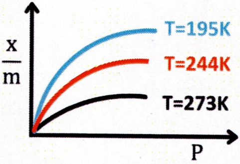
Freundlich Adsorption Isotherms

The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature

$$\frac{x}{m} = KP^{1/n} \ (n > 1)$$

$\frac{x}{m}$ = Extent of Adsorption

Curves Achieve saturation at high P

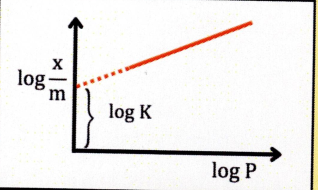


Adsorption from solution phase

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

Calculation of K and n Constants of isotherm

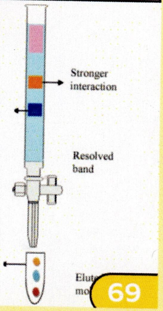
Logarithm form : $$\log\frac{x}{m} = \log K + \frac{1}{n}\log P$$

Plot : log(x/m) vs log P	
Slope : 1/n **Intercept : log K**	
Values of 1/n 0< 1/n < 1	

At low P (1/n = 1)	**Intermediate P**	**At High P** (1/n = 0)
$\frac{x}{m} = KP$	$\frac{x}{m} = KP^{1/n}$	$\frac{x}{m} = K$
First order	--	Zero Order

Applications of Adsorption

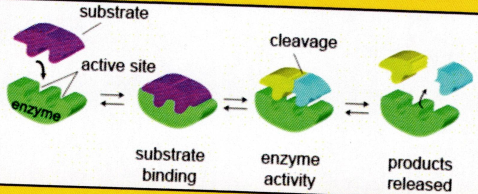
Activated Charcoal in Gas masks	Animal Charcoal as decolouriser
Silica gel in removing moisture	Chromatography
Surfactants	Noble gases sep.
Ion Exchange resin for removing hardness of water	



Enzyme Catalysis

Enzyme	Source	Reaction
Invertase	Yeast	Sucrose to Glucose and Fructose
Zymase	Yeast	Glucose to Ethyl alcohol + CO_2
Diastase	Malt	Starch to maltose
Maltase	Yeast	Maltose to Glucose
Urease	Soya	Urea to NH_3 and CO_2
Pepsin	Stomach	Proteins to Amino Acids

Mechanism of Enzyme Catalysis



Other Important Points for Enzymes

- Highly Efficient & Specific in nature
- Temperature Dependent, Optimum Temp : 298-310K
- pH Dependent range : 5-7
- Co-enzymes activates the Enzymes. e.g. Amylase in presence of NaCl

Mixtures		
True Solutions	**Colloids**	Suspensions
< 1 nm	**1-1000 nm**	> 1000 nm

Type of Colloids (Disperesed phase and medium)

D.P.	D.M.	Type	Example
Solid	Solid	**Solid Sol**	Coloured glass, Gems
Solid	Liquid	**Sold**	Paints, Cell Fluids
Solid	Gas	**Aerosol**	Smoke, dust
Liquid	Solid	**Gel**	Cheese, Butter, Jellies
Liquid	Liquid	**Emulsion**	Milk, hair Cream
Liquid	Gas	**Aerosol**	Fog, Mist, Clouds
Gas	Solid	**Solid Foam**	Pumice stone, Foam
Gas	Liquid	**Foam**	Froth, Whipped cream

Interaction between D.P. & D.M.

Lyophilic Sol	Lyophobic Sol
Natural Attraction of DP-DM	No Natural Attraction
Just mix DP-DM	Special Methods used
Naturally Stable	Stabilising agent Req

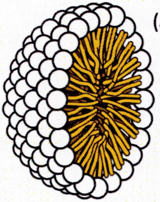
Reversible in Nature	Irreversible in Nature
Organic Sols	Inorganic Sols
e.g. Starch, Cellulose, Gelatin	e.g. Metal Oxide, sulphates

Associated Colloids

This is a surfactant.

E.g. : $C_{17}H_{35}COONa$

In presence of organic dust, Micelles (aggregates) are formed at higher conc.



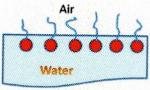
Micelle

Kraft Temperature

The minimum temperature from which the micelle formation takes place.

Critical Micelle Conc. (CMC)

Surfactant concentration at which micelle formation is first seen in the solution



At Low Concentration, these stay at surface of water behaving as normal electrolyte

Multimolecular colloids are formed when Small Molecules join to form colloids e.g. S_8 ; **Macromolecular Colloids** are formed when Big molecules gets dissolved in a solution to form colloidal size. E.g. Polymers like Starch, Cellulose, Gelatin.

Preparation of Colloids

- **Chemical Method**
  - $FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$ **(Hydrolysis)**
  - $SO_2 + 2H_2S \rightarrow 3S + 2H_2O$ **(Oxidation)**
  - $As_2O_3 + H_2S \rightarrow As_2O_3 + 3H_2O$ **(Double Decomp.)**
  - $2AuCl_3 + 3SnCl_2 \rightarrow SnCl_4 + 2Au$ **(Reduction)**

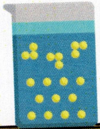
- **Bredig's Arc method:**

Au, Ag, Pt etc., is prepared by this method. Electrical arc stuck b/w two rods of metal and kept in D.M.

- **Peptisation**

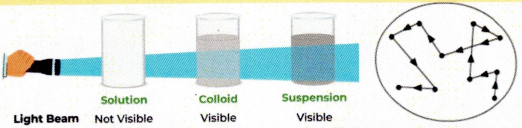
Conversion of a fresh precipitate into colloids by shaking it with the dispersion medium with small amount of suitable electrolyte. e.g.

  - $Fe(OH)_3$ ppt peptised with $FeCl_3$
  - SnO_2 peptised with HCl
  - AgCl peptisd with HCl
  - CdS can be peptised with H_2S



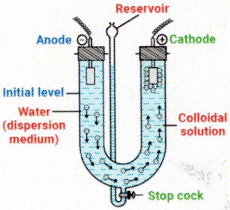
Properties of Colloids

- **Brownian Movement :** Continuous Zig Zag motion of particles. This depends on Size of particles and viscosity of solution.
  - Provides stability to solution (not settle down)
  - Visible proof of Kinetic motion of molecules
  - Not Observed in suspension



- **Tyndall Effect :** When a beam of light strikes the surface of colloidal particles, path of beam get illuminated (scattering of light). Observed only when
  - Diameter of dispersed particles is not much smaller than wavelength of light used
  - Refractive Index of DP and DM must differ high.
  - Colour of solution depends on wavelength of light scattered. Colour also changes on the manner in which observer sees light

- **Electrophoresis :** Under the influence of Electric field, Colloidal particles move towards oppositely charged electrodes. Neutral sols form ppt.
- **Electrosmosis :** In this, Particles of Dispersion medium are under influence of Electric Field and not the colloidal particles.



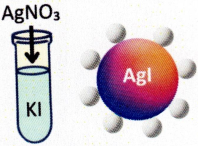
Electrophoresis

Charge of Colloids

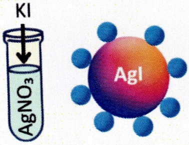
- **Charge of Colloidal Particles**
- **Positively Charged Sols :** Hydrated metal oxides like $Fe_2O_3.xH_2O$, $Al_2O_3.xH_2O$; Methylene Blue; Haemoglobin; Oxides like TiO_2.
- **Negatively Charged Sols** : Metals like Cu, Ag, Au; Metallic Sulphides like As2S3, CdS; Sols of Starch, Gelatin, Clay, Charcoal, gum etc.

Origin of Charges due to

Frictional electrification	Dissociation of Surfactants.	Formation of Double Layer

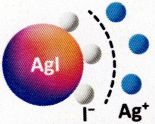


Negative Sol ● = I^-



Positive Sol ● = Ag^+

- Similarly, $FeCl_3$ in hot water gives Positive sol & $FeCl_3$ in NaOH gives Negative Sol.
- The potential difference between fixed later and Diffused layer is **ZETA Potential**



Coagulation of Colloids

- The process of settling of colloidal particles
  - Can be carried out using electrophoresis, mixing two oppositely charged sol, Boiling, persistent dialysis, addition of electrolytes

Hardy-Schulze rule

- Precipitating effect on dispersed phase increases with the valence of the ion.
- For Precipitating As_2S_3 (-ve sol) : $Al^{3+} > Ba^{2+} > Na^+$
- For $Fe(OH)_3$ (+ve sol) : $[Fe(CN)_6]^{3-} > SO_4^{2-} > Cl^-$

- The minimum concentration of electrolyte in milimoles required to precipitate a sol is Flocculation value $\propto$ 1/Coagulating power.

Protection of Colloids

Gold Number : No. of mg of lyophilic colloid that will prevent precipitaion of 10mL of gold sol on addition of 1mL of 10% NaCl Solution.

E.g. Weight of Starch = 0.0250g
Gold number = 0.025x1000 = **25**

Congo Rubin Number : No. of mg of lyophilic colloid that will prevent Colour change of 100mL of 0.01% congo rubin dye to which 0.16 g KCl is added.