Adsorption: The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed as adsorption.

Adsorbate: The substance which is being adsorbed on the surface of another substance is called adsorbate.

Adsorbent: The substance present in bulk, on the surface of which adsorption is taking place is called adsorbent.

Desorption: The process of removing an adsorbed substance from a surface on which it is adsorbed is called desorption.

Absorption: It is the phenomenon in which a substance is uniformly distributed all over the surface.

Sorption: When adsorption and absorption take place simultaneously, it is called sorption.

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Dept. of Science & Mathematics
IIITG, Guwahati

Surface

The three-dimensional region of contact between two phases α and β where molecules interact with molecules of both phases is called the **interfacial layer, surface layer, or interphase region**. **Interface** *refers to the apparent two-dimensional geometrical boundary surface separating the two phases.*

Due to differences in intermolecular interactions, molecules in the interphase region have a different average intermolecular interaction energy than molecules in either of the bulk phases. Thus an adiabatic change in the area of the interface between **α** *and* **β** *will change the system's internal energy U.*

Molecules at the surface of a phase are in a different environment than those in the interior of the phase. Many reactions occur most readily on the surfaces of catalysts (heterogeneous catalysis). Lubrication, corrosion, adhesion, detergency, and electrochemical-cell reactions, biological cell membranes function involving surface effects.

Properties of liquid surface

At liquid-air interfaces, surface tension results from the greater attraction of liquid molecules to each other (due to cohesion) than to the molecules in the air (due to adhesion). The increase in the number of molecules in the interphase region is proportional to increase in the area of the interface dA , and thus work needed to increase the interfacial area is proportional to dA. The proportionality constant is symbolized by $\gamma^{\alpha\beta}$.

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Dept. of Science & Mathematics
IIITG, Guwahati

*The term **surface tension of liquid α** refers to the **interfacial tension $\gamma^{\alpha\beta}$** for the system of liquid α in equilibrium with its vapour β. It is the elastic tendency of liquids that makes them acquire the least surface area possible.*

Thus the work done on the closed system of bulk phases α and β is $dw_{rev} = -P\,dV + \gamma^{\alpha\beta}\,dA$ plane interface

Surface tension γ has units of work / energy divided by area: erg/cm² dyn/cm, SI units of γ are J/m² N/m.

1 erg/cm² = 1 dyn/cm = 10^{-3} J/m² 10^{-3} N/m 1 mN/m 1 mJ/m².

As the temperature of a liquid-vapour equilibrium is raised, the two phases become increasingly similar until a the critical temperature Tc when the liquid–vapour interface disappears and only one phase is present. At Tc, the value of γ must therefore become 0, and γ of a liquid decreases as T is raised to T_c. The Katayama-Guggenheim empirical equation of liquids is:
$$\gamma = \gamma_0\left(1 - T/T_c\right)^{11/9}$$

where γ_0 is an empirical parameter characteristic of the liquid. Since 11/9 is nearly 1, we have $\gamma = \gamma_0 - \gamma_0\,T/T_c$, and γ decreases almost linearly as T increases.

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When two phases α and β are in contact with each other assuming that the system has several components J, each one present in an overall amount n_J. If the components were in uniform distribution throughout the two phases upto the interface, assuming it to be a plane of surface area σ, the total Gibbs energy, G, would be the sum of the Gibbs energies of both phases,

G = G(α) + G(β). But, the components are not uniformly distributed and due to the nature of the interface, one may accumulate at the interface. Thus, the difference between the total Gibbs energy, G and sum of the two Gibbs is called the surface Gibbs energy, G(σ), given by

G(σ) = G – {G(α) + G(β)}

If the concentration of a species J is uniform throughout, then it contains an amount $n_J(α)$ of J in phase α and an amount $n_J(β)$ in phase β. However, due to accumulation at the interface, the total amount of J differs from the sum of the two amounts as $n_J(σ) = n_J – \{n_J(α) + n_J(β)\}$.

This difference is expressed as surface excess, Γ_J:

$$\Gamma_J = \frac{n_J(\sigma)}{\sigma}$$

Gibbs derived the relation between the change in surface tension and the surface composition (surface excess) and formulated the Gibbs isotherm, between the changes in the chemical potentials of the substances present in the interface and the change in surface tension:

$$d\gamma = -\sum_J \Gamma_J d\mu_J$$

The Gibbs Isotherm

dG is dependent upon changes in T, P, and the n_J. Thus, $dG = -SdT + VdP + \gamma d\sigma + \sum_J \mu_J dn_J$

When applied to G, G(α), and G(β) it becomes $dG(\sigma) = -S(\sigma)dT + \gamma d\sigma + \sum_J \mu_J dn_J(\sigma)$ ….eqn. (1)

Since at equilibrium the chemical potential of each component is the same in all phases,

$\mu_J(\alpha) = \mu_J(\beta) = \mu_J(\sigma)$. Integrating this equation (1) at constant temperature,

$G(\sigma) = \gamma\sigma + \sum_J \mu_J n_J(\sigma)$ *….eqn. (2)*

The change of surface tension $d\gamma$ and the change of composition at the interface are related. Therefore, we use the the Gibbs–Duhem equation , $\boxed{\sum_j N_j d\mu_j = -S\,dT + V\,dp}$ *[relationship between changes in chemical potential for components in a thermodynamical system], but on comparison with the expression $dG(\sigma) = \gamma\,d\sigma + \sum_J \mu_J dn_J(\sigma)$ (at constant temperature) with the expression for the same quantity but derived from eqn. (2):*

$dG(\sigma) = \gamma d\sigma + \sigma d\gamma + \sum_J \mu_J dn_J(\sigma) + \sum_J n_J(\sigma)d\mu_J$ *….eqn. (3)*

Comparing eqns. (2) & (3), it follows that at constant temperature, $\sigma d\gamma + \sum_J n_J(\sigma)d\mu_J = 0$

Dividing thro.'out by σ, we get $\boxed{d\gamma = -\sum_j \Gamma_j d\mu_j}$

Processes at Solid Surfaces

Processes at solid surfaces govern reactions from catalysis to corrosion. Adsorption is the attachment of particles to a solid surface. The substance that adsorbs is the adsorbate and the substance on which it is adsorbed is the adsorbent or substrate.

Desorption is the detachment of particles from a solid surface.

A solid–gas adsorption study requires an initially clean solid surface. To produce a clean surface, one may heat the solid strongly in high vacuum, a procedure called outgassing. In 1918 Langmuir used a simple model of the solid surface to derive an equation for an isotherm. He assumed that the solid has a uniform surface, that adsorbed molecules don't interact with one another, that the adsorbed molecules are localized at specific sites, and that only a monolayer can be adsorbed.

Growth and Structure of Solid Surfaces

In order to understand the catalytic role of a solid surface in heterogeneous catalysis, especially in gas-solid systems, the growth and structure of solid systems plays an important role.

Factors affecting adsorption of gases on solids

1. Nature of adsorbate
2. Nature of adsorbent
3. Surface area of adsorbent
4. Pressure
5. Temperature
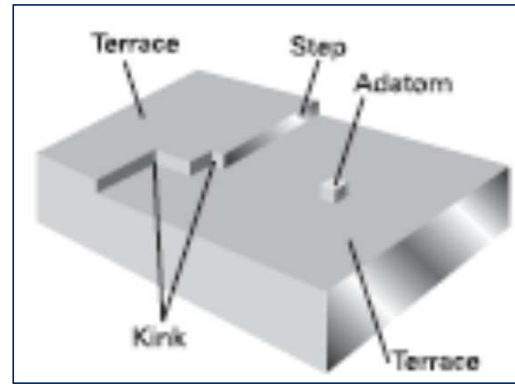6. Activation of solid adsorbent

Surface Growth

A common type of surface defect is a step between two otherwise flat layers of atoms called terraces. A step defect may have sub-defects like corners or kinks.

A special kind of dislocation is the screw dislocation. wherein a cut in the crystal, with the atoms to the left of the cut are pushed up through a distance of one unit cell. The unit cells now form a continuous spiral around the end of the cut, which is called the screw axis. A path encircling the screw axis spirals up to the top of the crystal, and where the dislocation breaks through to the surface it takes the form of a spiral ramp. The surface defect formed by a screw dislocation is a step, possibly with kinks, where growth can occur. When growth occurs simultaneously at neighbouring left- and right-handed screw dislocations, terraces are formed.

Growth and Structure of Solid Surfaces

In order to understand the catalytic role of a solid surface in hetero

Processes at Solid Surfaces

*Processes at solid surfaces govern reactions from catalysis to corrosion. **Adsorption is** the attachment of particles to a solid surface. The substance that adsorbs is the **adsorbate** and the substance on which it is adsorbed is the **adsorbent** or **substrate**. The reverse of adsorption is **desorption**.*

A solid–gas adsorption study requires an initially clean solid surface. To produce a clean surface, one may heat the solid strongly in high vacuum, a procedure called <u>outgassing</u>. In 1918 Langmuir used a simple model of the solid surface to derive an equation for an isotherm. He assumed that the solid has a uniform surface, that adsorbed molecules don't interact with one another, that the adsorbed molecules are localized at specific sites, and that only a monolayer can be adsorbed.

Surface Growth

*A common type of surface defect is a **step** between two otherwise flat layers of atoms called **terraces.***

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The extent of adsorption

The extent of surface coverage is expressed as the fractional coverage, θ : ratio of number of adsorption sites occupied to the number of adsorption sites available.

$$\theta = \frac{\text{number of adsorption sites occupied}}{\text{number of adsorption sites available}}$$

θ may also be expressed in terms of the volume of adsorbate adsorbed as $\theta = V/V_\infty$, where V_∞ is the volume of adsorbate corresponding to complete monolayer coverage.

The rate of adsorption, $d\theta/dt$, is the rate of change of surface coverage, and can be determined by observing the change of fractional coverage with time. Methods for measuring $d\theta/dt$ are gravimetry on a quartz crystal microbalance (QCM), flash desorption, and other flow methods.

Adsorption isotherms

The free gas and the adsorbed gas are in dynamic equilibrium, and the fractional coverage of the surface depends on the pressure of the overlying gas. The variation of θ with pressure at a chosen temperature is called the adsorption isotherm.

(a) The Langmuir isotherm

The simplest physically plausible isotherm is based on three assumptions:

1. Adsorption cannot proceed beyond monolayer coverage.

2. All sites are equivalent and the surface is uniform (that is, the surface is perfectly flat on a microscopic scale).

3. The ability of a molecule to adsorb at a given site is independent of the occupation of neighbouring sites (that is, there are no interactions between adsorbed molecules).

(b) The BET isotherm

The isotherm proposed for multilayer adsorption was derived by Brunauer, Emmett, and Teller, and is called the BET isotherm:

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$$\frac{V}{V_{mon}} = \frac{cz}{(1-z)\{1-(1-c)z\}} \quad \text{with} \quad z = \frac{p}{p^*}$$ *where p* is the vapour pressure above a layer of adsorbate, more than one molecule thick and resembling a pure bulk liquid, V_{mon} is the volume corresponding to monolayer coverage, and c is a constant which is large when the enthalpy of desorption from a monolayer is large compared with the enthalpy of vaporization of the liquid adsorbate* $$c = e^{(\Delta_{des}H^{\oplus} - \Delta_{vap}H^{\oplus})/RT}$$

When c>>1, the BET isotherm becomes $$\frac{V}{V_{mon}} = \frac{1}{1-z}$$

(c) Other isotherms such as the Temkin isotherm $$\theta = c_1 \ln(c_2 p)$$ *supposes that the adsorption enthalpy changes linearly with pressure, where c_1 and c_2 are constants.*

(d) Freundlich isotherm $$\theta = c_1 p^{1/c_2}$$ *corresponds to a logarithmic change, incorporating the role of substrate–substrate interactions on the surface.*

The relationship between x/m and pressure of the gas at constant temperature is called adsorption isotherm and is given by

$$\frac{x}{m} = kP^{1/n} \quad (n > 1)$$
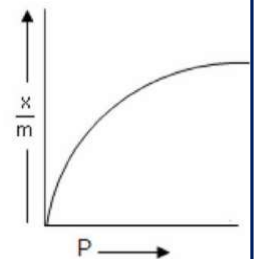
Physisorption

In physical adsorption, the gas molecules are held to the solid's surface by relatively weak intermolecular van der Waals forces. Physical adsorption is nonspecific. For example, N_2 will be physically adsorbed on any solid provided the temperature is low enough. For physical adsorption, once a monolayer has formed, intermolecular interactions between adsorbed B molecules in the monolayer and gas-phase B molecules can lead to formation of a second layer of adsorbed gas.
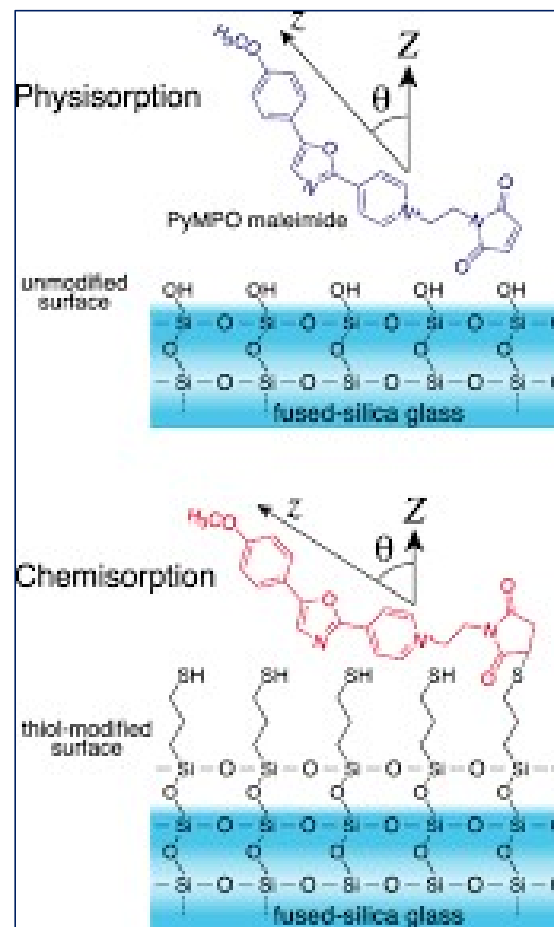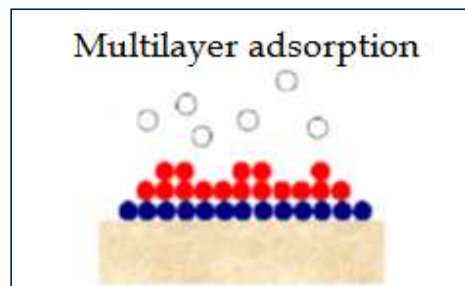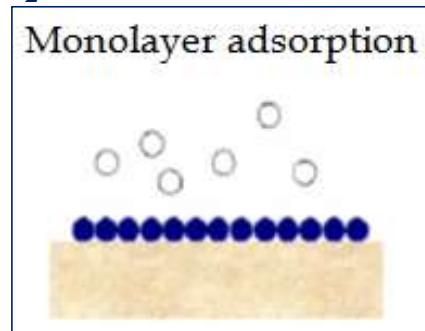
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Chemisorption

In chemisorption, a chemical reaction occurs at the solid's surface, and the gas is held to the surface by relatively strong chemical bonds. Chemisorption is similar to ordinary chemical reactions in that it is highly specific. Solid Au chemisorbs O_2, C_2H_2, and CO but not H_2, CO_2, or N_2. For chemisorption, once a monolayer of adsorbed gas covers the solid's surface, no further chemical reaction between the gas (species B) and the solid (species A) can occur. The enthalpy changes for chemisorption are usually substantially greater in magnitude than those for physical adsorption. Typically H_m for chemisorption lies in the range 40 to 800 kJ/mol (10 to 200 kcal/mol), whereas H_m for physical adsorption is usually from 4 to 40 kJ/mol (1 to 10 kcal/mol), similar to enthalpies of gas condensation. Chemical bonds may be broken as well as formed in chemisorption (for example, H_2 is chemisorbed on metals as H atoms).

Monolayer adsorption

Differences

	Physisorption	Chemisorption
1	Occurs due to van der Waals' force	Chemical Bond
2	Reversible	Irreversible
3	Not specific	Specific
4	Enthalpy of adsorption is low	Enthalpy of adsorption is high
5	More liquefiable gases are adsorbed readily	Gases which form compounds with adsorbent alone undergo chemisorption
6	Decreases with increase of temperature	Increases with increase of temperature
7	Low temperature is favorable.	High temperature is favorable
8	High pressure favors physisorption and decrease of pressure causes desorption	High pressure is favorable but decreases of pressure does not cause desorption
9	Results in multimolecular layers	Only unimolecular layer are formed
10	No activation energy is needed	High activation energy is needed
11	It is instantaneous	It is a slow process

Surfactants

Surfactants: are compounds that lower the surface tension (or interfacial tension) between two liquids or between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants.

Classification of surfactants:

1. Anionic: (1) Sulfate, sulfonate, and phosphate esters (2) carboxylates

2. Cationic head groups

3. Zwitterionic surfactants

4. Nonionic surfactant

5. According to composition

of their counter-ion

6. Biosurfactants
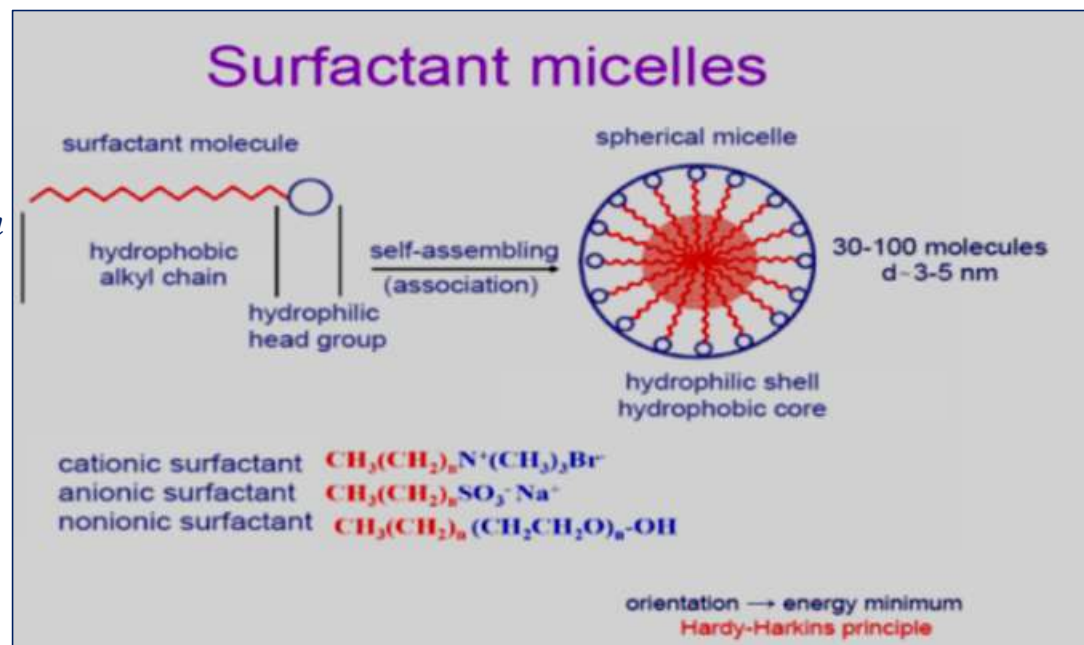
Surfactant micelles

surfactant molecule

spherical micelle

self-assembling (association)

hydrophobic alkyl chain

hydrophilic head group

30-100 molecules
d~3-5 nm

hydrophilic shell
hydrophobic core

cationic surfactant $CH_3(CH_2)_nN^+(CH_3)_3Br^-$
anionic surfactant $CH_3(CH_2)_nSO_3^-Na^+$
nonionic surfactant $CH_3(CH_2)_n(CH_2CH_2O)_n\text{-}OH$

orientation → energy minimum
Hardy-Harkins principle

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Colloidal systems

A **colloidal system** consists of particles that have in at least one direction a dimension lying in the approximate range *1 to 1000 nm* and a medium in which the particles are dispersed. E.g. Polymer solutions.

The particles are called **colloidal particles** or the dispersed phase. The colloidal particles may be in the solid, liquid, or gaseous state, or they may be individual molecules. The medium is called the **dispersion medium** or the continuous phase. The dispersion medium may be solid, liquid, or gas.

The term **colloid** can mean either colloidal system of particles plus dispersion medium or just colloidal particles.

A **sol** is a colloidal system whose dispersion medium is a gas or liquid.

- When the dispersion medium is a gas, the sol is called an **aerosol**. E.g. Fog: aerosol with liquid particles, Smoke: aerosol with liquid/solid particles. The earth's atmosphere contains an aerosol of aqueous H_2SO_4 and $(NH_4)_2SO_4$ droplets resulting from the burning of sulfur-containing fuels and volcanic eruptions. This sulfate aerosol produces acid rain and reflects some of the incident sunlight, thereby cooling the earth.

- A sol that consists of solid particles suspended in a liquid is a **colloidal suspension.** E.g. aq. AgCl system.
  A sol that consists of a liquid dispersed in a liquid is an **emulsion.**
  A sol that consists of gas bubbles are dispersed in a liquid or solid is a **foam.** E.g. pumice stone.

True solution	Colloids	Suspension
It is homogeneous	It appears to be homogeneous but is actually heterogeneous	It is heterogeneous
The diameter of the particles is less than 1 nm	The diameter of the particles is 1 nm to 1000 nm	The diameter of the particles are larger that 1000 nm
It passes through filter paper	It passes through ordinary filter paper but not through ultra-filters	It does not pass through filter paper
Its particles cannot be seen under a microscope	Its particles can be seen by a powerful microscope due to scattering of light	Its particles can be seen even with naked eye

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Colloidal systems can be classified based on type of particles in dispersed phase: into those in which dispersed particles are single molecules (monomolecular particles) & those in which particles are aggregates of many molecules (polymolecular particles).

Colloidal systems can also be classified based on the nature of interaction, into:

Lyophilic Colloids: *thermodynamically more stable than the two-phase system of dispersion medium and bulk colloid material. E.g. protein in water. These are due to micelles (aggregates of lyophilic colloidal systems due to spontaneous association of molecules)*

Lyophobic Colloids: *thermodynamically unstable w.r.t. separation into two unmixed bulk phases. - aq. AgCl system.*

Emulsions are classified as

A colloidal dispersion of one liquid in another immiscible liquid is known as an emulsion, e.g. milk, Na-soaps, vanishing cream, etc.

- *Oil-in-water (O/W) : water is the continuous phase and the oil is present as tiny droplets, e.g. milk or*

- *Water-in-oil (W/O) : the oil (organic liquid immiscible with water) is the continuous phase, e.g. margarine*

•Emulsions are lyophobic colloids. They are stabilized by the presence of an emulsifying agent, (amphipathic species that forms a surface film at the interface)

*A **gel** is a semirigid colloidal system of at least two components in which both components extend continuously throughout the system. E.g. cooled aq. solution of the protein gelatin.*

*If the liquid phase of a gel is removed by heating and pressurizing the gel above the critical temperature and pressure of the liquid, one obtains an **aerogel**. E.g. silica aerogel.*

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S.N.	Property	True solution	Colloidal	Suspension
1	Particle size	>1nm	1 nm to 1000 nm	<1000 nm
2	Filtration	Not possible	Possible only by ultrafiltration	Possible by ordinary filtration
3	Settling of particles	Do not settle	Settle only on centrifugation	Settle under gravity
4	Appearance	Transparent	May or may not transparent	Opaque
5	Tyndall Effect	Does not show	shows	Shows
6	Diffusion of particles	Diffuse rapidly	Diffuse slowly	Do not diffuse
7	Brownian Motion	May or may not show	shows	May show
8	Nature	Homogeneous	Heterogeneous	Heterogeneous

Types of colloids

Colloids are usually classified according to:
The original states of their constituent parts

Dispersed phase	Dispersion medium	Type of colloid	Example
Solid	Solid	Solid sol	Some coloured glasses, and gem stones
Solid	Liquid	Sol	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, cloud, insecticide sprays
Gas	Solid	Solid sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream, soap-lather

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Cleaning Action of Soap

Soap contains a non polar carbon end that dissolves in non polar fats and oils, and a polar end that dissolves in water.

Dust and soap molecules form micelles that dissolve in water and are washed away.

Soap forms a precipitate with ions in hard water (Ca^{2+}, Mg^{2+}, Fe^{3+})

Nonpolar   Polar

Soap molecule ~~~~ $C \overset{O}{\underset{O^-}{\lessgtr}}$ Na^+

Fatty acid chain

H_2O

Hydrophilic — Oil and grease

Hydrophobic

At low concentrations, behave as normal, strong electrolytes

At higher concentrations exhibit colloidal state properties due to the formation of aggregated particles (micelles)

The formation of micelles takes place only above a particular temperature called Kraft temperature (T_k) and above a particular micelle concentration called Critical Micelle Concentration
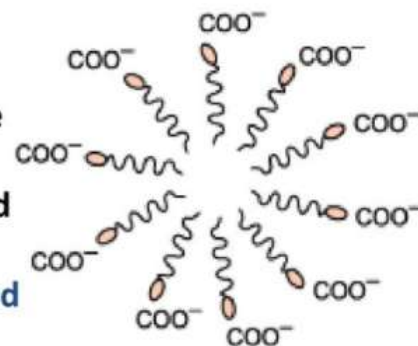
COO⁻ (multiple, in radial arrangement)

Properties of Colloidal Systems

Optical Properties of Colloids
- ✓ The Faraday-Tyndall Effect
- ✓ Light Scattering

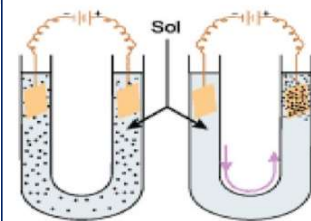## Kinetic Properties of Colloids
- ✓ Brownian Motion
- ✓ Diffusion
- ✓ Osmotic pressure
- ✓ Sedimentation
- ✓ Viscosity

Electrical Properties of Colloids
- ✓ Electric double layer
- ✓ Nernst and Zeta potential

When a strong beam of light is passed through a colloidal sol, a visible cone, resulting from the scattering of light by the colloidal particles, is formed. This is the Faraday-Tyndall

This property depends on the Faraday-Tyndall effect

It is used for determining the molecular weight of colloids.

It can also be used to obtain information on the shape and size of these particles.

Scattering can be described in terms of **turbidity** (τ).

Electrophoresis

Movement of colloidal particles under influence of electric field

Sol

Optical properties: Tyndall effect
When a beam of light falls at right angles to the line of view through a solution, the solution appears to be luminescent and due to scattering of light the path becomes visible.

Source of light — True solution — Sol — Screen
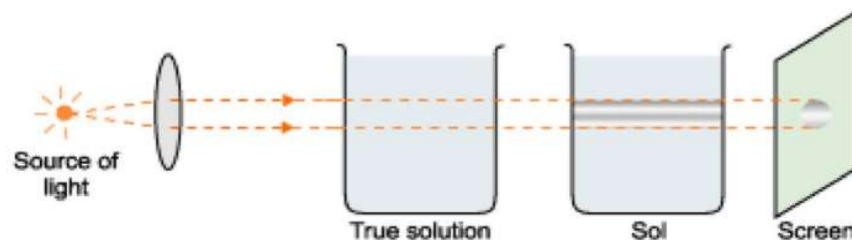
Electro-osmosis: molecules of dispersion medium are allowed to move under influence of electric field

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Coagulation or flocculation: Process which involves coming together of colloidal particles so as to change into large sized particles which ultimately settle as a precipitate or float on surface. It is generally brought about by addition of electrolytes.

Hardy Shulze law : Coagulating power of an electrolyte increases rapidly with the increase in the valency of cation or anion.

For negatively charged sol, the coagulating power of electrolytes are

$AlCl_3 > BaCl_2 > NaCl$ or $Al^{3+} > Ba^{2+} > Na^+$

For positively charged, then the coagulating power of electrolytes follow the following order:

$PO_4^{3-} > SO_4^{2-} > Cl^-$

The minimum amount of an electrolyte that must be added to one litre of a colloidal solution so as to bring about complete coagulation or flocculation is called coagulation or flocculation value. Smaller is the flocculation value of an electrolyte, greater is the coagulating or precipitating power

Applications of colloids

1. Rubber plating
2. Sewage disposal
3. Smoke screen
4. Purification of water
5. Cleaning action of soap
6. In medicine
7. Formation of delta
8. Photography
9. Artificial rain