

Surface chemistry

Surface of a solid has the tendency to attract and retain the molecules of the phase with which it comes into contact .

- **ADSORPTION** :The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed adsorption .
- **Adsorbate**: substance that concentrate on the surface.
- **Adsorbent**: surface on which adsorption occurs.
- Air becomes dry in the presence of silica gel because the water molecules get adsorbed to the surface of the gel.
- **DESORPTION**: The process of removing an adsorbed substance from a surface on which it is adsorbed.
- **ABSORPTION**: Substance is uniformly distributed in the bulk of the solid.
- Both adsorption and absorption can take place simultaneously.
- Sorption : BOTH PROCESSES
- Arises due to the fact that the surface particles of the adsorbent are not in the same environment as the particles inside the bulk.

- Surface possess unbalanced / residual attractive forces
- Attract the adsorbate particles on the surface.
- Adsorption increases with the increase in surface area / unit mass of the adsorbent at a given temperature and pressure .
- Decrease in residual forces = decrease in surface energy .
- Exothermic reaction $\Delta H < 0$.
- Entropy decreases $\Delta S < 0$
- $\Delta G < 0$: for spontaneous = $\Delta H - T \Delta S$
- Equilibrium when $\Delta H = - T \Delta S$ ie. $\Delta G = 0$
- Gas adsorption : vanderwaal forces : Physical adsorption

: chemical bonds : chemisorptions

Chemical bonds are of two types: covalent and ionic

- **Physical adsorption at low temperature can get converted into chemical adsorption when temperature increases.**
- **ADSORPTION ISOTHERM:** variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve.

- 1) Freundlich adsorption isotherm :

Quantity of gas adsorbed by unit mass of solid adsorbent and pressure at particular temperature .

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

Where $n > 1$

x = mass of the gas adsorbed on mass m of adsorbent and pressure P , k and n are constants which depend on the nature of adsorbent of the gas at particular temperature .

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

Adsorption from solution phase

charcoal

Acetic acid + water \longrightarrow a part of acid is adsorbed by charcoal

1. The extent of adsorption decreases with increase in temperature.
2. Adsorption increases with increase in surface area of the adsorbent .
3. Adsorption depends on the concentration of the solute in the solution
4. Depends on the nature of the adsorbent and the adsorbate

Freundlich equation:

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

c= equilibrium concentration = when adsorption is complete

APPLICATION:

1. Production of high vacuum :air with charcoal
2. Gas masks : coal mines to adsorb poisonous gases
3. Control humidity
4. Removal of colouring matter from solution
5. Heterogeneous catalysis
6. Separation of inert gases
7. Curing diseases
8. Froth floatation process

9. Adsorption indicators

10. Chromatographic analysis

Catalyst : homogenous catalysis: reactants and catalyst in the same phase.

: Heterogenous catalysis: different phases

MECHANISM OF HETEROGENOUS CATALYST

1. Diffusion of reactants to the surface of the catalyst .

2. Adsorption of reactants molecules on the surface of the catalyst

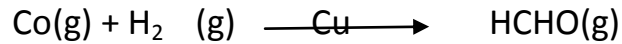
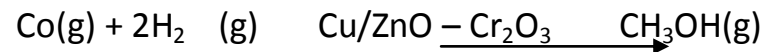
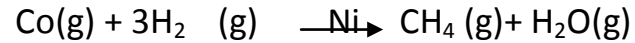
3. Occurrence of chemical reaction on the catalysts surface through formation of an intermediate .

4. Diffusion of reaction products away from the catalyst's surface .

FEATURES OF A CATALYST :

1. Acidity : Depends on the strength of chemisorptions

2. Selectivity: The ability to direct reaction to yield a particular product



SHAPE SELECTIVE CATALYSTS :

Depends on the pore structure of the catalyst and size of the reactant and product molecules.

Zeolites are good shape selective catalysts. Honey comb like structure .

Microporous aluminosilicates with 3D.

of silicates in which some Si atoms are replaced by Al atoms - Al -O -Si

In petrochemical industries :

Cracking of hydrocarbons and isomerization.

ZSM- 5 converts alcohols directly to gasoline.

COLLOIDS : Heterogenous system in which one substance is dispersed as very fine particles in another substance called dispersion medium .

- 1- 1000 nm
- Have very high surface area / unit mass as a result of their small size.

Colloids:

1. Physical state of dispersed phase and dispersion .
2. Nature of interaction between dispersed medium and dispersion medium.
3. Types of particulars of the dispersed phase .

LYOPHILIC COLLOIDS: If dispersed medium is separated from the dispersed phase the solution can be reconstructed by simply remixing.

- Reversible sols
- Stable and can't be easily coagulated

LYOPHOBIC COLLOIDS : readily coagulated on addition of electrolytes .

- They are not reversible .
- Need stabilizing agents for preservation

3. Multimolecular colloids

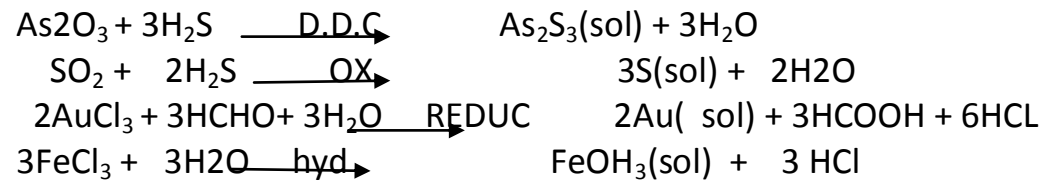
Macromolecular colloids

Associated colloids

PREPARATION OF COLLOIDS

(a) CHEMICALLY :double decomposition , oxidation , reduction or
Hydrolysis.

Eqns:



b) Electrical disintegration / Bredig's arc method :

involves dispersion as well as condensation.

sols of metals such as gold , silver etc.

c)Peptization : Process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte .

PURIFICATION:

1. DIALYSIS : remove dissolved substance from a colloidal solution by means of diffusion through a suitable membrane .
2. ELECTRO-DIALYSIS : dialysis can be made faster by applying an electric field if the dissolved substance in colloid is only an electrolyte ,
3. ULTRAFILTRATION:Ultrafiltration is the process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution by specially prepared filters, which are permeable to all substances except the colloidal particles.By using ultra-filter paper, the colloidal particles are separated from rest of the materials. Ultrafiltration is a slow process. To speed up the process, pressure or suction is applied.

Properties exhibited by the colloidal solutions

Tyndall effect: The Tyndall effect is the scattering of light as a light beam passes through a colloid. The individual suspension particles scatter and reflect light, making the beam visible. The amount of scattering depends on the frequency of the light and density of the particles.

Conditions for Tyndall effect:

- The diameter of the dispersed particles is not much smaller than the wavelength of the light used.
- The refractive indices of the dispersed phase and the dispersion medium differ greatly in magnitude.

Brownian movement:

When colloidal solutions are viewed under a powerful ultra microscope, the colloidal particles appear to be in a state of continuous zigzag motion all over the field of view. This motion was first observed by the British botanist, Robert Brown, and is known as Brownian movement.

This motion is independent of the nature of the colloid but depends on the size of the particles and viscosity of the solution. Smaller the size and lesser the viscosity, faster is the motion. The Brownian movement has been explained to be due to the unbalanced bombardment of the particles by the molecules of the dispersion medium.

Charge on colloidal particles:

Colloidal particles always carry an electric charge. The nature of this charge is the same on all the particles in a given colloidal solution and may be either positive or negative.

The charge on the sol particles is due to one or more reasons, viz., due to electron capture by sol particles during electro dispersion of metals, due to preferential adsorption of ions from solution and/or due to formulation of electrical double layer.

Coagulation or precipitation:

The stability of the lyophobic sols is due to the presence of charge on colloidal particles. If, somehow, the charge is removed, the particles will come nearer to each other to form aggregates (or coagulate) and settle down under the force of gravity.

The process of settling of colloidal particles is called coagulation or precipitation of the sol.

It can be achieved by electrophoresis, mixing two oppositely charged sols, boiling, persistent dialysis and addition of electrolytes.

It has been observed that, generally, the greater the valence of the flocculating ion added, the greater is its power to cause precipitation. This is known as **Hardy-Schulze rule**. In the coagulation of a negative sol, the flocculating power is in the order: $\text{Al}^{3+} > \text{Ba}^{2+} > \text{Na}^+$. Similarly, in the coagulation of a positive sol, the flocculating power is in the order: $[\text{Fe}(\text{CN})_6]^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$

Protection of colloids

Lyophilic sols are more stable than lyophobic sols. This is due to the fact that lyophilic colloids are extensively solvated, i.e., colloidal particles are covered by a sheath of the liquid in which they are dispersed. Lyophilic colloids have a unique property of protecting lyophobic colloids. When a lyophilic sol is added to the lyophobic sol, the lyophilic particles form a layer around lyophobic particles and thus protect the latter from electrolytes. Lyophilic colloids used for this purpose are called protective colloids.

Emulsions

These are liquid-liquid colloidal systems, i.e., the dispersion of finely divided droplets in another liquid. If a mixture of two immiscible or partially miscible liquids is shaken, a coarse dispersion of one liquid in the other is obtained which is called emulsion. Generally, one of the two liquids is water. There are two types of emulsions.

- (i) Oil dispersed in water (O/W type) and
- (ii) Water dispersed in oil (W/O type).

In the first system, water acts as dispersion medium. Examples of this type of emulsion are milk and vanishing cream. In milk, liquid fat is dispersed in water. In the second system, oil acts as dispersion medium. Common examples of this type are butter and cream.

Emulsions of oil in water are unstable and sometimes they separate into two layers on standing. For stabilisation of an emulsion, a third component called emulsifying agent is usually added. The emulsifying agent forms an interfacial film between suspended particles and the medium. The principal emulsifying agents for O/W emulsions are proteins, gums, natural and synthetic soaps, etc., and for W/O, heavy metal salts of fatty acids, long chain alcohols, lampblack, etc.