Surface Chemistry

Surface chemistry is that branch of chemistry, which deals with the study of the phenomenon occurring at the surface or interface i.e. at the boundary separating two bulk phases.

Adsorption:- Surface of the solid is in state of unsaturation due to presence of residual forces acting along the surface of solid thus have tendency to attract the molecule of gas or solute from solution with which such surface come in contact. “The phenomenon of higher concentration of any molecular species on the solid surface than present in the bulk is known as adsorption”.

The solid that takes up the gas molecule is known as adsorbent (Ex. Such as Pt, Ni, Pd, colloids, silica gel etc.) and the gas molecule that bare held to the surface of the solid are known as adsorbate. Example- various gases such as He, Ne, O₂, N₂, NH₃ etc and substances in solution NaCl, KCl etc.

Adsorption in Action

i. When a gas like O₂, H₂, CO, Cl₂, NH₃ or SO₃ is taken in a closed vessel containing powdered charcoal, it is observed that the pressure of the gas in the enclosed vessel decreases. The gases molecules concentrate at the surface of the charcoal, i.e., gases are adsorbed at the surface.

ii. In a solution of an organic dye, say methylene blue, when animal charcoal is added and the solution is well shaken, it is observed that the filtrate turns colourless. The molecules of the dye, thus, accumulate on the surface of charcoal, i.e., are adsorbed.

iii. Aqueous solution of raw sugar, when passed over beds of animal charcoal, becomes colourless as the colouring substances are adsorbed by the charcoal.

iv. During adsorption, as the molecule of gas are held by adsorbent, entropy of gas decrease i.e., ΔS is negative. Adsorption is thus accompanied by decrease in enthalpy as well as decrease in entropy of the system. For a process to be spontaneous, at constant temperature and pressure, ΔG must be negative, i.e., there is a decrease in Gibbs energy. On the basis of equation, ΔG = ΔH – TΔS, ΔG can be negative if ΔH has sufficiently high negative value as – TΔS is positive. Thus, in an adsorption process, which is spontaneous, a combination of these two factors makes ΔG negative. As the adsorption proceeds, ΔH becomes less and less negative ultimately ΔH becomes equal to TΔS and ΔG becomes zero. At this state equilibrium is attained.

Types of adsorption:- Adsorptions are two types

i. Physical Adsorption or Physisorption: - When a gas is held on the surface of solid by weak van der waal’s forces without resulting in the formation of any chemical bond between the adsorbate and the adsorbent, is termed as physical adsorption or physisorption.

ii. Chemical Adsorption or Chemisorption: - When a gas molecule or atoms are held to the solid surface (adsorbent) by chemical bond (which may be covalent or ionic in nature) is termed as Chemical adsorption or chemisorptions.

Characteristics of physisorption:-

i. Lack of specificity: - Adsorbent do not show any preference for a particular gas as the van der waal’s forces are universal.

ii. Nature of adsorbate: - Easily liquefiable gases i.e. having high critical temperature are adsorbed more strongly because they have stronger van der Waal’s forces of attraction. Ex. SO₂ adsorbed more amounts in same time than CH₄.

iii. Reversible Nature: - Physical adsorption of a gas by a solid is generally reversible. Thus, Solid + Gas ↔ Gas/Solid + Heat

iv. Low Enthalpy of adsorption: - Enthalpy of physical adsorption is very low (20-40 kJ mol⁻¹). This is due to weak van der waal’s forces of attraction between gas and solid.

v. Surface area of adsorbent: - The adsorption increases with increases in surface area of adsorbent. Thus finely divided metal has large surface area are good adsorbent.

vi. No any appreciable amounts of activation energy involve.

vii. Equilibrium readily attained.

Characteristics of chemisorptions:-

i. Chemical Change: - It involve the formation of chemical bond between the adsorbate and the adsorbent.
ii. **High specificity**: Chemosorption is highly specific because it occurs only if there is a chance of chemical bond formation between the adsorbate and adsorbent. For example, oxygen is adsorbed on metals by virtue of oxide formation and hydrogen is adsorbed by transition metals due to hydride formation.

iii. **Irreversible in nature**: As chemisorption involves compound formation, it is usually irreversible in nature. Chemisorption is also an exothermic process but the process is very slow at low temperatures on account of high energy of activation. Like most chemical changes, adsorption often increases with rise of temperature. Physisorption of a gas adsorbed at low temperature may change into chemisorption at a high temperature. Usually high pressure is also favourable for chemisorptions.

iv. **Enthalpy of adsorption**: Enthalpy of chemisorptions is very high (80-240 kJ mol⁻¹) as it involves strong force of attraction heat evolved is much higher.

v. **Surface area**: Chemosorption also increases with increase of surface area of the adsorbent.

vi. Appreciable amount of activation energy is involved.

vii. Equilibrium attained very slowly.

### Comparison of Physisorption and Chemisorption

<table>
<thead>
<tr>
<th>Physical Adsorption</th>
<th>Chemical Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. It arises because of van der Waals’ forces.</td>
<td>1. It is caused by chemical bond formation.</td>
</tr>
<tr>
<td>2. It is not specific in nature.</td>
<td>2. It is highly specific in nature.</td>
</tr>
<tr>
<td>3. It is reversible in nature.</td>
<td>3. It is irreversible.</td>
</tr>
<tr>
<td>4. It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.</td>
<td>4. It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorption.</td>
</tr>
<tr>
<td>5. Enthalpy of adsorption is low (20-40 kJ mol⁻¹) in this case.</td>
<td>5. Enthalpy of adsorption is high (80-240 kJ mol⁻¹) in this case.</td>
</tr>
<tr>
<td>6. It forms multimolecular layer.</td>
<td>6. It forms unimolecular layer.</td>
</tr>
<tr>
<td>7. No appreciable activation energy is needed.</td>
<td>7. High activation energy is sometimes needed.</td>
</tr>
</tbody>
</table>

### Desorption

The process which involves removal of gaseous molecule from the surface of solid is known as desorption.

### Adsorption Isotherm

The variation in the amount of gas adsorbed by adsorbent with pressure at constant temperature can be expressed by means of curve as adsorption isotherm.

**Freundlich adsorption isotherm**

In 1909 Freundlich proposed an empirical relationship between quantity of gas adsorbed by unit mass of solid adsorbent and pressure at particular temperature. The relationship can be expressed by the following equation.

\[ \frac{x}{m} = k P^{1/n} \quad (n \neq 1) \]

Where \( x \) is the mass of adsorbate, \( m \) is the mass of adsorbent, \( P \) is the pressure, \( k \) and \( n \) are constants which depend on the nature of adsorbent and adsorbate at particular temperature.

A curve of \( x/m \) is plotted against \( P \). These curve indicate at a fixed pressure, there is decrease in physical adsorption with increase in temperature. These curves always seem to approach saturation at high pressure.

To test the validity of Freundlich adsorption isotherm, taking logarithms of both sides. We get

\[ \log \frac{x}{m} = \log k + \frac{1}{n} \log P \]

\( \log x/m \) is plotted against \( \log P \). If a straight line is obtained, the freundlich isotherm is valid otherwise not. The slope of the line gives the value of \( 1/n \) and the intercept on the y-axis gives the value of \( \log k \).

When \( \frac{1}{n} = 0 \), \( \frac{x}{m} = k \), the adsorption is independent of pressure.

When \( \frac{1}{n} = 1 \), \( \frac{x}{m} = k P \), i.e. \( \frac{x}{m} \propto P \)

Both the condition are supported by experimental results. The experiments isotherms always seems to be approach saturation at high pressure. This cannot be explained by Freundlich isotherm. Thus Freundlich’s equation has a limitation, that it is valid over a certain range of pressure only.

**Limitation of Freundlich adsorption isotherms**:

i. It is valid over a certain range of pressure only.

ii. The constant \( k \) and \( n \) vary with temperature.

iii. Freundlich adsorption equation is purely empirical formula without theoretical foundation.

### Adsorption From solution phase
Solid surface can also adsorb solute from solution. When a solution of acetic acid in water is shaken with charcoal, some amount of acetic acid from the solution is adsorbed on the charcoal and hence the concentration of acid in the solution decreases. Similarly, when litmus solution shaken with charcoal it becomes colourless because the colouring agent of the litmus is adsorbed by charcoal.

**Factor affecting adsorption from solution:-**

**Applications of Adsorption:-**
The phenomenon of adsorption finds a number of applications.

Important ones are listed here:

(i) **Production of high vacuum:** The remaining traces of air can be adsorbed by charcoal from a vessel evacuated by a vacuum pump to give a very high vacuum.

(ii) **Gas masks:** Gas mask (a device which consists of activated charcoal or mixture of adsorbents) is usually used for breathing in coal mines to adsorb poisonous gases.

(iii) **Control of humidity:** Silica and aluminium gels are used as adsorbents for removing moisture and controlling humidity.

(iv) **Removal of colouring matter from solutions:** Animal charcoal removes colours of solutions by adsorbing coloured impurities.

(v) **Heterogeneous catalysis:** Adsorption of reactants on the solid surface of the catalysts increases the rate of reaction. There are many gaseous reactions of industrial importance involving solid catalysts. Manufacture of ammonia using iron as a catalyst, manufacture of H2SO4 by contact process and use of finely divided nickel in the hydrogenation of oils are excellent examples of heterogeneous catalysis.

(vi) **Separation of inert gases:** Due to the difference in degree of adsorption of gases by charcoal, a mixture of noble gases can be separated by adsorption on coconut charcoal at different temperatures.

(vii) **In curing diseases:** A number of drugs are used to kill germs by getting adsorbed on them.

(viii) **Froth flotation process:** A low grade sulphide ore is concentrated by separating it from silica and other earthy matter by this method using pine oil and frothing agent.

(ix) **Adsorption indicators:** Surfaces of certain precipitates such as silver halides have the property of adsorbing some dyes like eosin, fluorescein, etc. and thereby producing a characteristic colour at the end point.

(x) **Chromatographic analysis:** Chromatographic analysis based on the phenomenon of adsorption finds a number of applications in analytical and industrial fields.

**Catalysis:-**

In 1835 Berzelius was first observed that rate of chemical reaction altered (changed or influenced) due to presence of certain foreign substance. He suggested the term catalyst for such substances and the process is termed as catalysis.

“Such substances which alter the rate of reaction without itself undergoing any change in mass and chemical composition at the end of the reaction, known as catalyst and the phenomenon is known as catalysis.”

**Types of catalysis:** Catalysis can be broadly divided in two types-

(i) Homogeneous catalysis (ii) Heterogeneous catalysis

(i) **Homogeneous catalysis:** When the reactant and catalyst are in same phase (i.e. liquid or gas) the process is said to be homogeneous catalysis

**E.g. i.** In manufacture of sulphuric acid by lead chamber process SO2 is oxidize into SO3 by air in presence of catalyst NO(g), in which reactant and catalyst are in the same phase

\[
2\text{SO}_2 (g) + \text{O}_2 (g) \overset{\text{NO(g)}}{\rightarrow} 2\text{SO}_3 (g)
\]

**ii.** Hydrolysis of methylacetate is catalysed by HCl

\[
\text{CH}_3\text{COOCH}_3 (l) + \text{H}_2\text{O(l)} \overset{\text{HCl(l)}}{\rightarrow} \text{CH}_3\text{COOH(aq)} + \text{CH}_3\text{OH (aq)}
\]

**iii.** Hydrolysis of sugar catalysed by sulphuric acid

\[
\text{C}_{12}\text{H}_{22}\text{O}_{11}(l) + \text{H}_2\text{O}(l) \overset{\text{H}_2\text{SO}_4(l)}{\rightarrow} \text{C}_6\text{H}_{12}\text{O}_6 (aq) + \text{C}_6\text{H}_{12}\text{O}_6 (aq)
\]

(ii) **Heterogeneous catalysis:** When the reactant and the catalyst are in different phases is known as heterogeneous catalysis.

**E.g. i.** In manufacture of H2SO4 by contact process, oxidation of SO2 into SO3 by air in presence of catalyst Pt.

\[
2\text{SO}_2 (g) + \text{O}_2 (g) \overset{\text{Pt(s)}}{\rightarrow} 2\text{SO}_3 (g)
\]

The reactant is in gaseous state while the catalyst is in solid state.

**ii.** N2(g) + 3H2(g) \overset{\text{Fe(s)}}{\rightarrow} 2NH3 (g) (Haber’s process)

**iii.** 4NH3(g) + 5O2(g) \overset{\text{Pt(s)}}{\rightarrow} 4NO(g) + 6 H2O(g) (Ostwald’s process)

**iv.** Hydrogenation of vegetable oils

\[
\text{Vegetable oil} (l) + \text{H}_2(g) \overset{\text{Ni(s)}}{\rightarrow} \text{Vegetable ghee} (S)
\]

One of the reactant is in liquid state and the other in gaseous state while the catalyst is in solid state.

**v.** In friedel craft reaction - \[
\text{C}_6\text{H}_5 \text{(l)} + \text{CH}_3\text{COCl} (l) \overset{\text{AlCl}_3(s)}{\rightarrow} \text{C}_6\text{H}_5\text{COCH}_3
\]

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Promoter and Poisons-
A substance which enhances the activity of a catalyst is known as catalytic promoter.
Eg. Molybdenum acts as a promoter for iron catalyst in manufacture of ammonia by Haber’s process

\[ \text{N}_2(g) + 3\text{H}_2(g) \xrightarrow{\text{Fe (Mo)}} 2\text{NH}_3(g) \]

ii. Synthesis of methanol by water gas in presence of ZnO and CuO mixture act as a catalyst, but the catalytic activity of this mixture increases in presence of Cr_2O_3 act as promoter.

\[ \text{CO} + \text{H}_2 + \text{H}_2 \xrightarrow{\text{ZnO+CuO} (\text{Cr}_2\text{O}_3)} \text{CH}_3\text{OH} \]

Those substances, which decrease the activity of catalyst (or destroy the activity of catalyst) known as catalytic poisons. Ex. In Rosenmund reduction reaction, BaSO_4 act as catalytic poison for the Pd catalyst.

\[ \text{CH}_3\text{COCl} + \text{H}_2 \xrightarrow{\text{Pd (Catalyst)}} \text{BaSO}_4 (\text{poison}) \rightarrow \text{CH}_3\text{CHO} + \text{HCl} \]

Absorption Theory of Heterogeneous catalysis-
Catalysis is explained by many theories but some important is given below-

1. Intermediate compound formation theory- According to this theory, a catalyst participating in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex which decompose to yield products and regenerate the catalysts. Suppose AB and C is reactant and X is a catalyst, therefore according to this theory-

   \[ \text{AB} + X \rightarrow \text{AX} + B \]

   \[ \text{AX} + C \rightarrow \text{AC} + X \]

Example- Friedel Craft reaction-

[Diagram of Friedel Craft reaction]

Mechanism-

\[ \text{CH}_3\text{Cl} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{Cl} \text{---AlCl}_3 \rightarrow \text{CH}_3^+ + \text{AlCl}_4^- \]

Adsorption Theory- According to old adsorption theory of heterogeneous catalysis, the reactants in gaseous state or in solution are adsorbed on the surface of the solid catalyst. As a result the concentration of reactant increases on the surface hence increase the rate of reaction. Adsorption is always an exothermic process, the heat of adsorption is utilized in enhancing the rate of reaction.

The modern adsorption theory is the combination of intermediate compound formation theory and old adsorption theory.

The mechanism of catalysis involves the following five steps-

i. Diffusion of reactant on the surface of catalyst.
ii. Adsorption of reactants on the solid surface of the catalyst.
iii. Occurrence of chemical reaction and the catalyst surface.
iv. Desorption of the product and the catalyst surface available again for more reaction to occur.
v. Diffusion of products away from catalyst surface.
The surface of the catalyst unlike the inner parts of the bulk has free valencies which provide the seat for chemical force of attraction. When a gas comes in contact of such a surface, its molecule are held up there due to loose chemical combination. If different molecules are adsorbed side by side they may reacts with other resulting in the formation of new molecules. Thus formed molecule may evaporate

**Important feature of solid catalyst:-**

**i. Activity:-** Activity of catalyst means its capacity to increase the speed of chemical reaction. The activity depends upon the extent of chemisorptions. The adsorption should be reasonably strong but not so strong that the adsorbed molecules become immobile and no space is available for other reactant to get adsorbed.

**ii. Selectivity:-** The selectivity of the catalyst is its ability to direct a reaction to yield a particular products in presence of different catalysts as follows.

\[
\begin{align*}
(i) & \quad CO + 3H_2(g) \xrightarrow{Ni} CH_3(g) + H_2O(g) \\
(ii) & \quad CO + 2H_2(g) \xrightarrow{Cu/ZnO-Cr2O3} CH_3OH(g) \\
(iii) & \quad CO + H_2(g) \xrightarrow{Cu} HCHO(g)
\end{align*}
\]

Catalyst is highly selective in nature i.e. a given substance can act as a catalyst in a particular reaction and not for all reactants. It means that a substance which acts a catalyst in one reaction may fail to catalyses another reaction.

**Shape-selective catalysis by Zeolites:-** The catalytic reaction that depends upon pore structure of the catalyst and the size of the reactant and product molecules is called shape selective catalysis. Zeolites are good shape selective catalyst, because of honey-comb like structure. They are micro porous aluminosilicates with three dimensional network of silicates in which some silicon atom are replaced by aluminium atom giving Al–O–Al framework. Zeolites are being very widely used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerisation. An important zeolite catalyst used in the petroleum industry is ZSM-5.

**Enzyme catalysis:-** Enzymes are complex nitrogenous organic compound (protein molecule) with higher molecular mass form colloidal solution water. Numerous reactions that occur in the bodies of animals and plants to maintain the life process are catalysed by enzymes. Thus enzymes are termed as biocatalyst or biochemical catalyst and the phenomenon is known as biocatalysis or biochemical catalysis.

Many enzymes have been obtained in pure crystalline state from living cells. However the first enzyme was synthesized in laboratory in 1969.

Some enzyme catalyse reaction are:

1. Inversion of cane sugar - C_{12}H_{22}O_{11} (aq) + H_2O(l) \xrightarrow{Invertase} C_6H_{12}O_6 + C_6H_{12}O_6
2. Conversion of glucose into ethyl alcohol - C_6H_{12}O_6 (aq) \xrightarrow{Zymase} 2C_2H_5OH + CO_2
3. Conversion of starch into maltose: 2(C_6H_{10}O_5)n (aq) nH_2O(l) \xrightarrow{Diastase} n C_6H_{12}O_11 (aq)
4. Conversion of maltose into glucose: C_6H_{12}O_{11} (aq) + H_2O(l) \xrightarrow{Maltase} 2C_6H_2O_6(aq)
5. Decomposition of urea into NH_3 and CO_2 - NH_2CONH_2 (aq) + H_2O (l) \xrightarrow{Urease} 2NH_3 + CO_2
6. Fat \xrightarrow{Amylase} Fatty acid + Glycerol
7. Starch \xrightarrow{Amylase} Glucose

**Characteristics of enzyme catalysis**

Enzyme catalysis is unique in its efficiency and high degree of specificity. The following characteristics are exhibited by enzyme catalysts:

(i) **Most highly efficient:** One molecule of an enzyme may transform one million molecules of the reactant per minute.

(ii) **Highly specific nature:** Each enzyme is specific for a given reaction. For example, the enzyme urease catalyses the hydrolysis of urea only. It does not catalyse hydrolysis of any other amide.

(iii) **Highly active under optimum temperature:** The rate of an enzyme reaction becomes maximum at a definite temperature, called the optimum temperature. On either side of the optimum temperature, the enzyme activity decreases. The optimum temperature range for enzymatic activity is 298-310K. Human body temperature being 310 K is suited for enzyme-catalysed reactions.

(iv) **Highly active under optimum pH:** The rate of an enzyme-catalysed reaction is maximum at a particular pH called optimum pH, which is between pH values 5-7.

(v) **Increasing activity in presence of activators and co-enzymes:** The enzymatic activity is increased in the presence of certain substances, known as co-enzymes. It has been observed that when a small non-protein (vitamin) is present along with an enzyme, the catalytic activity is enhanced considerably. Activators are generally metal ions such as Na^+, Mn^{2+}, Co^{3+}, Cu^{2+}, etc. These metal ions, when weakly bonded to enzyme molecules, increase their catalytic activity. Amylase in presence of sodium chloride i.e., Na^+ ions are catalytically very active.

(vi) **Influence of inhibitors and poisons:** Like ordinary catalysts, enzymes are also inhibited or poisoned by the presence of certain substances. The inhibitors or poisons interact with the active functional groups on the enzyme surface and often

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reduce or completely destroy the catalytic activity of the enzymes. The use of many drugs is related to their action as enzyme inhibitors in the body.

**Mechanism of enzyme catalysis**

There are a number of cavities present on the surface of colloidal particles of enzymes. These cavities are of characteristic shape and possess active groups such as -NH₂, -COOH, -SH, -OH, etc. These are actually the active centres on the surface of enzyme particles. The molecules of the reactant (substrate), which have complementary shape, fit into these cavities just like a key fits into a lock. On account of the presence of active groups, an activated complex is formed which then decomposes to yield the products. Thus, the enzyme-catalysed reactions may be considered to proceed in two steps.

**Step 1:** Binding of enzyme to substrate to form an activated complex.

$$E + S \rightarrow ES≠$$

**Step 2:** Decomposition of the activated complex to form product.

$$ES≠ \rightarrow E + P$$

**Colloids** - A Colloid is a heterogenous system in which one substance is dispersed (dispersed phase) as fine particle (10⁻⁷ to 10⁻⁴ cm) in another substance called dispersion medium.

Colloidal system = disperse phase + dispersion medium

The essential difference between a true solution and suspension is that of particle size.

<table>
<thead>
<tr>
<th>True Solution</th>
<th>Colloidal solution</th>
<th>Suspension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less than 10⁻⁷ cm</td>
<td>Lies between 10⁻⁷ to 10⁻⁴ cm</td>
<td>More than 10⁻⁴ cm</td>
</tr>
</tbody>
</table>

Thus the size of colloidal particle is intermediate between the particle of true solution and suspension.

**Dispersed Phase and dispersion medium**

Like true solution, the term solute and solvent are replaced by the term dispersed phase and dispersion medium respectively in colloidal system. Thus dispersed phase means the substance distributed in the dispersion medium in the form of colloidal particles and the dispersion medium means the medium in which the substance is dispersed in the form of colloidal particle.

**Classification of colloids**

Classification based on the physical state of dispersed phase and dispersion medium-

Depending upon the physical state of dispersed phase and the dispersion medium eight type of colloidal system is possible. A gas mix with another gas forms a homogenous mixture and hence is not a colloidal system. Example-

<table>
<thead>
<tr>
<th>Dispersed phase</th>
<th>Dispersion Medium</th>
<th>Types of colloids</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Solid</td>
<td>Solid</td>
<td>Solid sol</td>
<td>Coloured glasses and gem stones</td>
</tr>
<tr>
<td>2. Solid</td>
<td>Liquid</td>
<td>Sol</td>
<td>Paints</td>
</tr>
<tr>
<td>3. Solid</td>
<td>Gas</td>
<td>Aerosol</td>
<td>Smoke, dust</td>
</tr>
<tr>
<td>4. Liquid</td>
<td>Solid</td>
<td>Gel</td>
<td>Cheese, butter, jellies</td>
</tr>
<tr>
<td>5. Liquid</td>
<td>Liquid</td>
<td>Emulsion</td>
<td>Milk</td>
</tr>
<tr>
<td>6. Liquid</td>
<td>Gas</td>
<td>Liquid Aerosol</td>
<td>Fog, mist, cloud</td>
</tr>
<tr>
<td>7. Gas</td>
<td>Solid</td>
<td>Solid sol</td>
<td>Pumice stone, Foam rubber</td>
</tr>
<tr>
<td>8. Gas</td>
<td>Liquid</td>
<td>Foam</td>
<td>Froath, Soap leather</td>
</tr>
</tbody>
</table>

The most common are **sols** (solids in liquids), **gels** (liquids in solids) and **emulsions** (liquids in liquids). However, in the present Unit, we shall take up discussion of the ‘sols’ and ‘emulsions’ only. Further, it may be mentioned that if the dispersion medium is water, the sol is called aquasol or hydrosol and if the dispersion medium is alcohol, it is called alcosol and so on.

**Classification Based on Nature of Interaction between Dispersed Phase and Dispersion Medium**

Depending upon the nature of interaction between the dispersed phase and the dispersion medium, colloidal sols are divided into two categories-

(i) **Lyophilic colloids**: The word ‘lyophilic’ means liquid-loving. Colloidal sols directly formed by mixing substances like gum, gelatine, starch, rubber, etc, with a suitable dispersion medium are called lyophilic sols. It is **reversible in nature**. These sols are quite stable and cannot be easily coagulated.

(ii) **Lyophobic colloids**: The word ‘lyophobic’ means liquid-hating. Substances like metals, their sulphides, etc., when simply mixed with the dispersion medium do not form the colloidal sol. Such sols are called lyophobic sols. These sols are readily precipitated (or coagulated) on the addition of small amounts of electrolytes, by heating or by shaking.

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Further, once precipitated, they do not give back the colloidal sol by simple addition of the dispersion medium. Hence, lyophobic sols are irreversible in nature. Lyophobic sols need stabilizing agents for their preservation.

Classification Based on Type of Particles of the Dispersed Phase, Multimolecular, Macromolecular and Associated Colloids

(i) Multimolecular colloids: On dissolution, a large number of atoms or smaller molecules of a substance aggregate together to form species having size in the colloidal range (diameter < 1nm). The species thus formed are called multimolecular colloids. For example, a gold sol may contain particles of various sizes having many atoms. Sulphur sol consists of particles containing a thousand or more of S₈ sulphur molecules.

(ii) Macromolecular colloids: Macromolecules in suitable solvents form solutions in which the size of the macromolecules may be in the colloidal range. Such systems are called macromolecular colloids. Examples of naturally occurring macromolecules are starch, cellulose, proteins and enzymes; and those of man-made macromolecules are polythene, nylon, polystyrene, synthetic rubber, etc.

(iii) Associated colloids (Micelles): There are some substances which at low concentrations behave as normal strong electrolytes, but at higher concentrations exhibit colloidal behaviour due to the formation of aggregates. The aggregated particles thus formed are called micelles. These are also known as associated colloids. The formation of micelles takes place only above a particular temperature called Kraft temperature (Tk) and above a particular concentration called critical micelle concentration (CMC). On dilution, these colloids revert back to individual ions.

Preparation of Colloids

A few important methods for the preparation of colloids are as follows:

(a) Chemical methods

Colloidal solutions can be prepared by chemical reactions leading to formation of sols.

By double decomposition As₂O₃ + 3H₂S → As₂S₃(sol) + 3H₂O

By oxidation: SO₂ + 2H₂ → 3S(sol) + 2H₂O

By reduction: 4AuCl₃ + 3 NH₃ → 4Au(sol) + 12HCl + 3N₂

By hydrolysis: FeCl₃ + 3H₂O → Fe(OH)₃(sol) + 3HCl

(b) Electrical disintegration or Bredig’s Arc method: This process involves dispersion as well as condensation. Colloidal sols of metals such as gold, silver, platinum, etc., can be prepared by this method. In this method, electric arc is struck between electrodes of the metal immersed in the dispersion medium. The intense heat produced vapourises the metal, which then condenses to form particles of colloidal size.

(c) Peptization: The process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte is known as peptization. The electrolyte used for this purpose is called peptizing agent.

Purification of Colloidal Solutions

The process used for reducing the amount of impurities to a requisite minimum is known as purification of colloidal solution. The purification of colloidal solution is carried out by the following methods:

(i) Dialysis: It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane. The apparatus used for this purpose is called dialyser.

(ii) Electro-dialysis: The process of dialysis is quite slow. It can be made faster by applying an electric field if the dissolved substance in the impure colloidal solution is only an electrolyte. The process is then named electrodialysis. The ions present in the colloidal solution migrate out to the oppositely charged electrodes.

(iii) 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. Colloidal particles can pass through ordinary filter paper because the pores are too large. However, the pores of filter paper can be reduced in size by impregnating with colloidion solution to stop the flow of colloidal particles. Ultrafiltration is a slow process. To speed up the process, pressure or suction is applied. The colloidal particles left on the ultra-filter paper are then stirred with fresh dispersion medium (solvent) to get a pure colloidal solution.

Properties of Colloidal Solutions

(i) Colligative properties: Colloidal particles being bigger aggregates, the number of particles in a colloidal solution is comparatively small as compared to a true solution. Hence, the values of colligative properties (osmotic pressure, lowering in vapour pressure, depression in freezing point and elevation in boiling point) are lower as compared to values shown by true solutions at same concentrations.

(ii) Tyndall effect: The scattering of light by colloidal particle in colloidal solution is known as tyndall effect. Tyndall effect can be observed during the projection of picture in the cinema hall due to scattering of light by dust and smoke particles present there. Tyndall effect is observed only when the following two conditions are satisfied.

(i) The diameter of the dispersed particles is not much smaller than the wavelength of the light used; and

(ii) The refractive indices of the dispersed phase and the dispersion medium differ greatly in magnitude.

Tyndall effect is used to distinguish between a colloidal and true solution.

(iii) Brownian movement: The continuous zig-zag motion of colloidal particle is known as Brownian movement.
The Brownian movement is due to the unbalanced bombardment of the particles by the molecules of the dispersion medium. The Brownian movement has a stirring effect which does not permit the particles to settle and thus, is responsible for the stability of sols.

(v) 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 preferential adsorption of ions from solution and/or due to formulation of electrical double layer. The sol particles acquire positive or negative charge by preferential adsorption of +ve or −ve ions. When two or more ions are present in the dispersion medium, preferential adsorption of the ion common to the colloidal particle usually takes place. This can be explained by taking the following examples:
(a) When silver nitrate solution is added to potassium iodide solution, the precipitated silver iodide adsorbs iodide ions from the dispersion medium and negatively charged colloidal solution results. However, when KI solution is added to AgNO₃ solution, positively charged sol results due to adsorption of Ag⁺ ions from dispersion medium.

\[
\text{AgI/I}^-
\quad \text{AgI/Ag}^+
\]

Negatively charged
Positively charged

Having acquired a positive or a negative charge by selective adsorption on the surface of a colloidal particle as stated above, this layer attracts counter ions from the medium forming a second layer, as shown below.

\[
\text{AgI/I}^-\ K^+
\quad \text{AgI/Ag}^+\ I^-
\]

The combination of the two layers of opposite charges around the colloidal particle is called Helmholtz electrical double layer. The first layer of ions is firmly held and is termed fixed layer while the second layer is mobile which is termed diffused layer. This potential difference between the fixed layer and the diffused layer of opposite charges is called the electrokinetic potential or zeta potential. The presence of equal and similar charges on colloidal particles is largely responsible in providing stability to the colloidal solution.

(vi) Electrophoresis: The movement of colloidal particles under an applied electric potential towards opposite charged electrode is called electrophoresis.

(vii) Coagulation or precipitation: The process of settling of colloidal particles is called coagulation or precipitation of the sol.

The coagulation of the lyophobic sols can be carried out in the following ways:
(i) By electrophoresis: The colloidal particles move towards oppositely charged electrodes, get discharged and precipitated.
(ii) By mixing two oppositely charged sols: Oppositely charged sols when mixed in almost equal proportions, neutralise their charges and get partially or completely precipitated.
(iii) By boiling: When a sol is boiled, the adsorbed layer is disturbed due to increased collisions with the molecules of dispersion medium. This reduces the charge on the particles and ultimately lead to settling down in the form of a precipitate.
(iv) By persistent dialysis: On prolonged dialysis, traces of the electrolyte present in the sol are removed almost completely and the colloids become unstable and ultimately coagulate.
(v) By addition of electrolytes: When excess of an electrolyte is added, the colloidal particles are precipitated. The reason is that colloids interact with ions carrying charge opposite to that present on themselves. This causes neutralisation leading to their coagulation.

The ion responsible for neutralisation of charge on the particles is called the coagulating ion. A negative ion causes the precipitation of positively charged sol and vice versa. It has been observed that, generally, the greater the valence of the opposite charged ion added, the greater is its power to cause precipitation. This is known as Hardy-Schulze rule.

For negative sol- \( \text{Al}^{3+} > \text{Ba}^{2+} > \text{Na}^+ \)

For positive sol- \( \text{Fe(CN)}_6^{3+} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^- \)

The minimum concentration of an electrolyte in millimoles per litre required to cause precipitation of a sol in two shours is called coagulating value. The smaller the quantity needed, the higher will be the coagulating power of an ion.

Coagulation of lyophilic sols
There are two factors which are responsible for the stability of lyophilic sols. These factors are the charge and solvation of the colloidal particles. When these two factors are removed, a lyophilic sol can be coagulated. This is done (i) by adding an electrolyte and (ii) by adding a suitable solvent. When solvents such as alcohol and acetone are added to hydrophilic sols, the dehydration of dispersed phase occurs. Under this condition, a small quantity of electrolyte can bring about coagulation.

Protection of colloids
Lyophilic sols are more stable than lyophobic sols. This is due to the fact that lyophilic colloidal particles are covered by a sheath of the liquid in which they are dispersed. When a lyophobic 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
A colloidal system in which both the dispersed phase and dispersion medium are liquids 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)- In such emulsions, oil is the dispersed phase and water is dispersion medium, Examples- milk and vanishing cream.
(ii) Water dispersed in oil (W/O type). In such emulsions, water is the dispersed phase and oil is dispersion medium, Examples- butter, cod liver oil 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.

They also show Brownian movement and Tyndall effect.

The process of decomposing an emulsions into its constituent liquids is called demulsification. It can carried out by heating, freezing, centrifuging, etc.

**Colloids Around Us**

Following are the interesting and noteworthy examples of colloids:

(i) **Blue colour of the sky:** Dust particles along with water suspended in air scatter blue light which reaches our eyes and the sky looks blue to us.

(ii) **Fog, mist and rain:** When a large mass of air containing dust particles, is cooled below its dewpoint, the moisture from the air condenses on the surfaces of these particles forming fine droplets. These droplets being colloidal in nature continue to float in air in the form of mist or fog. Clouds are aerosols having small droplets of water suspended in air. On account of condensation in the upper atmosphere, the colloidal droplets of water grow bigger and bigger in size, till they come down in the form of rain. Sometimes, the rainfall occurs when two oppositely charged clouds meet. It is possible to cause artificial rain by throwing electrified sand or spraying a sol carrying charge opposite to the one on clouds from an aeroplane.

(iii) **Food articles:** Milk, butter, halwa, ice creams, fruit juices, etc., are all colloids in one form or the other.

(iv) **Blood:** It is a colloidal solution of an albuminoid substance. The styptic action of alum and ferric chloride solution is due to coagulation of blood forming a clot which stops further bleeding.

(v) **Soils:** Fertile soils are colloidal in nature in which humus acts as a protective colloid. On account of colloidal nature, soils adsorb moisture and nourishing materials.

(vi) **Formation of delta:** River water is a colloidal solution of clay. Sea water contains a number of electrolytes. When river water meets the sea water, the electrolytes present in sea water coagulate the colloidal solution of clay resulting in its deposition with the formation of delta.

**Applications of colloids**

Colloids are widely used in the industry. Following are some examples:

(i) **Electrical precipitation of smoke:** Smoke is a colloidal solution of solid particles such as carbon, arsenic compounds, dust, etc., in air. The smoke, before it comes out from the chimney, is led through a chamber containing plates having a charge opposite to that carried by smoke particles. The particles on coming in contact with these plates lose their charge and get precipitated. The particles thus settle down on the floor of the chamber. The precipitator is called Cottrell precipitator.

(ii) **Purification of drinking water:** The water obtained from natural sources often contains suspended impurities. Alum is added to such water to coagulate the suspended impurities and make water fit for drinking purposes.

(iii) **Medicines:** Most of the medicines are colloidal in nature. For example, argyrol is a silver sol used as an eye lotion. Colloidal antimony is used in curing kalaazar. Colloidal gold and calcium are used for intramuscular injection. Milk of magnesia, an emulsion, is used for stomach disorders. Colloidal medicines are more effective because they have large surface area and are therefore easily assimilated (digested).

(iv) **Tanning:** Animal hides are colloidal in nature. When a hide, which has positively charged particles, is soaked in tannin, which contains negatively charged colloidal particles, mutual coagulation takes place. This results in the hardening of leather. This process is termed as tanning. Chromium salts are also used in place of tannin.

(v) **Cleansing action of soaps and detergents:**

(vi) **Photographic plates and films:** Photographic plates or films are prepared by coating an emulsion of the light sensitive silver bromide in gelatin over glass plates or celluloid films.

(vii) **Rubber industry:** Latex is a colloidal solution of rubber particles which are negatively charged. Rubber is obtained by coagulation of latex.

(viii) **Industrial products:** Paints, inks, synthetic plastics, rubber, graphite lubricants, cement, etc., are all colloidal solution.

**Exercise**

1. Why the ester hydrolysis is slow in the beginning and becomes faster after sometime?
2. What is the role of desorption in process of catalysis?
3. Why does physisorption decrease with the increase of temperature?
4. What is shape selective catalysis?

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5. Why are powdered substances more effective adsorbents than their crystalline forms?

6. Why does a gas mixed with another gas not form a colloidal system?

7. Why adsorbate particles are attracted and retained on the surface of adsorbent?

8. Explain the terms sorption and desorption.

9. “Chemisorption is highly specific.” Illustrate with an example.

10. “Adsorbents in finely divided form are more effective.” Why?

11. Name two compounds used as adsorbent for controlling humidity.

12. ‘Generally high temperature is favourable for chemisorption.’ Why?

13. Name the catalyst used in the following process:
   (a) Haber process for the manufacture of NH3 gas.
   (b) Ostwald process for the manufacture of nitric acid.

14. Explain the relationship given by Freundlich in Freundlich adsorption isotherm.

2-Marks-

1. What is the difference between physisorption and chemisorption?

2. Explain the effect of temperature on the extent of physical and chemical adsorption.

3. Define the term peptization and also mention its cause.

4. Arrange the gases CO, N2, and CH4 in increasing order of adsorption on the surface of charcoal in a closed vessel. Give reasons also.

5. What happens:
   (a) When animal charcoal is added to a solution of methylene blue dye.
   (b) When aqueous solution of raw sugar is passed over beds of animal charcoal.

6. Mention two examples of emulsifying agents for o/w emulsions and w/o emulsions.

7. Suggest a mechanism of enzyme catalysed reaction along with the diagram.

8. What are the conditions for the occurrence of (a) Electrophoresis and (b) Electroosmosis.

9. A small amount of silica gel and a small amount of anhydrous calcium chloride are placed separately in two beakers containing water vapour. Name of phenomenon that takes place in both the beakers.

   [Hint: Silica gel – Adsorption, Anhydrous CaCl2 – Absorption, as it forms CaCl2. 2H2O]

10. State “Hardy Schulze Rule” with one example.

11. What is an emulsifying agent? What role does it play in forming an emulsion?

12. Define the terms:
   (a) Helmholtz electrical double layer.
   (b) Zeta potential.

13. Explain the mechanism of heterogeneous catalysis.

14. Explain the following terms-
   (i) Electrophoresis
   (ii) Tyndall effect

3-Marks-

1. What are emulsions? What are their different types? Give example of each type.

2. What are lyophilic and lyophobic sols? Give one example of each type. Why hydrophobic sols are easily coagulated?

3. Explain what is observed
   (i) When a beam of light is passed through a colloidal sol.
   (ii) An electrolyte, NaCl is added to hydrated ferric oxide sol.
   (iii) Electric current is passed through a colloidal sol?

4. Explain the following terms-
   (i) Peptization
   (ii) Brownian movement
   (iii) Coagulation

5. Explain the following terms giving a suitable example for each:
   (i) Aerosol
   (ii) Micelle
   (iii) Adsorption