

Surface Chemistry

SURFACE CHEMISTRY

- C1 Colloids :** A colloid is a heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance called dispersion medium. In a colloid, the dispersed phase may consist of particles of a single macromolecule (such as protein or synthetic polymer) or an aggregate of many atoms, ions or molecules. Colloidal particles are larger than simple molecules but small enough to remain suspended.

Difference between a solution and colloid is one of particle size.

True Solution :

1. Homogeneous mixture are transparent
2. In true solution, the particles are ions or small molecules and they are invisible under all circumstances
3. Particle size is of the order i.e. $1\text{ }\mu\text{m}$ or $10\text{ }\text{\AA}$ or $< 10^3\text{ pm}$ or $< \mu\text{mm}$
4. True solution passes easily through filter paper as well as animal membrane or parchment membrane
5. Does not scatter light
6. Particle do not settle on ultracentrifugation

Colloid :

- Heterogeneous mixture are translucent
- Particles are visible under powerful microscope but scattering effect by the particles can be observed under ultra microscope
- Size of particle range of diameter between 1 and 1000 nm.
- Colloidal particles passes easily through filter paper but slowly through parchment membrane
- Particle scatter light i.e. Tyndall effect
- Particle settle on ultracentrifugation

Practice Problems :

1. **Comment on the statement that “colloid is not a substance but a state of substance”.**

[Answers : (1) This is because the same substance may exist as a colloid under certain conditions and as a crystalloid under certain other conditions. For example, NaCl in water behaves as a crystalloid while in benzene, it behaves as a colloid. Similarly, dilute soap solution behaves like a crystalloid while concentrated solution behaves as a colloid. It is the size of the particles which decides whether it is a colloid or a crystalloid]

C2 Classification of colloids

Colloids are classified on the basis of the following criteria :

- (a) Physical state of dispersed phase and dispersion medium
- (b) Nature of interaction between dispersed phase and dispersion medium
- (c) Type of particles of the dispersed phase

(a) Classification based on physical state of dispersed phase and dispersion medium

Eight types of colloidal system are possible :

	(solute) Dispersed Phase	(solvent) Dispersed Medium	Type of colloid	Examples
1.	Solid	Solid	Solid Sol	Coloured glasses, Gemstone, Some alloys, minerals, rock salts.
2.	Solid	Liquid	Sol	Paints, cell fluids, starch or protein in water, glue, gold sol, Indian ink, muddy water, milk of magnesia, white of an egg
3.	Solid	Gas	Solid Aerosol	Smoke, dust, storm, fumes

4.	Liquid	Solid	Gel (solid emulsion)	Cheese, butter, jellies, boot polish, curd, $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$.
5.	Liquid	Liquid	Emulsion	Milk, hair cream, emulsified oils, cod liver oil, medicines.
6.	Liquid	Gas	Liquid Aerosol	Fog, mist, cloud, insecticide spray.
7.	Gas	Solid	Solid Foam	Styrene foam, rubber, occluded gases, pumice stone, bread
8.	Gas	Liquid	Foam or froth	Whipped cream, soap, lather, lemonade froth, beer, shaving cream, beaten egg

If dispersion medium is water, the solution is called aquasol or hydrosol and if the dispersion medium is alcohol, it is called alcosol and so on.

- (b) **Classification based on nature of interaction between dispersed phase and dispersion medium. They are :**

Lyophilic Colloidal Solution

1. Solvent attracting (If water is the dispersion medium term used in hydrophilic)
2. The word lyophilic means liquid loving
3. Colloidal sols directly formed by substances like gum, gelatine, starch, rubber etc. on mixing or warming with suitable liquid (dispersion medium).
4. If dispersion medium is separated from dispersed phase by evaporation, the sol can be reconstituted by simply remixing with the dispersion medium
5. Thus these sols are reversible sols

Lyophobic Colloidal Solution

- Solvent repelling (same here) i.e. if water is the dispersion medium the term used is hydrophobic
- The word lyophobic means liquid hating
- Substances like metals, their sulphides etc. when mixed simply with dispersion medium do not form colloidal sol. They can be prepared by special method.
- These sols are readily precipitated or coagulated on the addition of small amount of electrolytes by heating or by shaking and hence are not stable
- Once they precipitate they do not give back the colloidal sol by simple addition of the dispersion medium. These sols are Irreversible.

- (c) **Classification based on type of particles of the Dispersed Phase : They are**

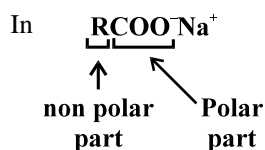
1. Multimolecular colloid
2. Macromolecular colloid
3. Associated colloid

1. **Multimolecular Colloid** : When on dissolution, a large number of atoms or smaller molecules of a substance aggregate together to form species having size (with diameter less than 1 nm) e.g. Gold sol may contain particles of various sizes having many atoms. Sulphur sol consists of particles containing a thousand or more of S_8 sulphur molecules.
2. **Macromolecular Colloid** : Macro molecules have large molecular masses. These on dissolution in a suitable solvent form a solution in which the size of the macromolecules may be in the colloidal range. Such systems are called macro-molecular colloid. These colloids are quite stable and resemble true solution in many respect. e.g. naturally occurring macromolecules are starch, cellulose, proteins, and enzymes. Examples of man-made macromolecules are polythene, nylon, polystyrene, synthetic rubber etc.

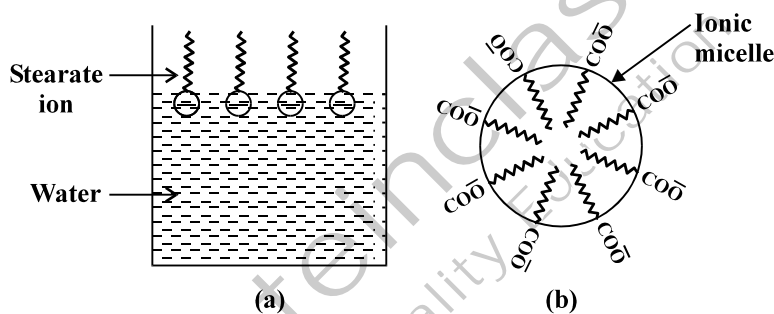
3. **Associated Colloids (Micelles) :** These are some substance which at low concentrations behave as normal, strong electrolytes but at higher concentrations exhibit colloidal behaviour due to formation of aggregated particles. The aggregated particles thus formed are called micelles. These are known as associated colloid. The formation of micelles takes place only above a particular temperature called “Kraft Temperature” (T_k) and above particular concentration called “Critical Micelle concentration (CMC)”. On dilution, these colloids revert back to individual ions. e.g. surface active agents soaps, detergents belong to this class. For soaps CMC is $\sim 10^{-4}$ to 10^{-3} mol L^{-1} . These colloid have both lyophilic and lyophobic part. Micelles may contain as many as 100 molecules or more

Mechanism of Formation of Micelle

e.g. let us take example of soap solution i.e. $RCOO^-Na^+$ (soap is sodium salt of high fatty acids e.g. sodium stearate) i.e. $CH_3(CH_2)_{16}COO^-Na^+$ or sodium Lauryl Sulphate $CH_3(CH_2)_{11}SO_4^-Na^+$



The $RCOO^-$ ions are, therefore, present on the surface with their COO^- groups in water and the hydrocarbon chains R staying away from it and remain at the surface. But at critical micelle concentration, the anions are pulled into the bulk of the solution and aggregate to form a spherical shape with their hydrocarbon chains pointing towards the centre of the sphere with COO^- part remaining outward on the surface of the sphere. An aggregate thus formed is known as ‘ionic micelle’. These micelles may contain as many as 100 such ions.



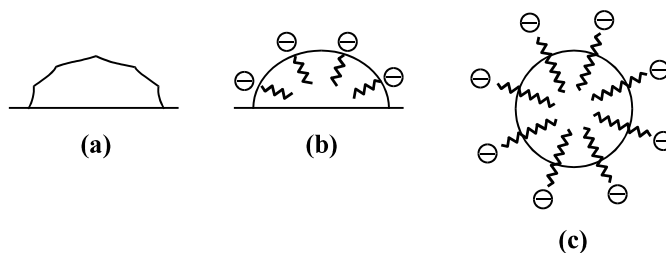
(a) Arrangement of stearate ions on the surface of water at low concentration of soaps

(b) Arrangement of stearate ions inside the bulk of water (ionic micelle) at critical micelle concentration of soap

Similarly, in case of detergents, e.g., sodium laurylsulphate, $CH_3(CH_2)_{11}SO_4^-Na^+$, the polar group is SO_4^- along with the long hydrocarbon chain. Hence, the mechanisms of micelle formation here also is same as that of soaps.

Cleaving action of soaps

It has been mentioned earlier that a micelle consists of a hydrophobic hydrocarbon – like central core. The cleansing action of soap is due to the fact that soap molecules form micelle around the oil droplet in such a way that hydrophobic part of the stearate ions is in the oil droplet and hydrophilic part projects out of the grease droplet like the bristles. Since the polar groups can interact with water, the oil droplet surrounded by stearate ions is now pulled in water and removed from the dirty surface. Thus soap helps in emulsification and washing away of oils and fats. The negatively charged sheath around the globules prevents them from coming together and forming aggregates.



(a) Grease on cloth (b) Stearate ions arranging around the grease droplet and (c) Grease droplet surrounded by stearate ions (micelle formed)

Practice Problems :

- How are colloidal solutions classified, on the basis of physical states of the dispersed phase and dispersion medium ?
- What are lyophilic and lyophobic sols ? Give one example of each type. Why are hydrophobic sols easily coagulated ?
- What is the difference between multimolecular and macromolecular colloids ? Give one example of each. How are associated colloids different from these two types of colloids ?
- How are colloids classified on the basis of
 - physical states of components
 - nature of dispersion medium and
 - interaction between dispersed phase and dispersion medium ?
- Explain the terms with suitable examples : (i) Alcosol (ii) Aerosol and (iii) Hydrosol.
- In what way is a sol different from a gel ?

[Answers : (5) Alcosol : It is a colloidal sol of cellulose nitrate in ethyl alcohol. Aerosol : It is a colloidal dispersion of a liquid in a gas. For example, fog. Hydrosol : It is a colloidal sol of a solid in water as the dispersion medium. For example, starch sol. (6) Sols are colloidal solutions of solid dispersed in liquid while gels are colloidal solutions of liquid dispersed in solid]

C3 Preparation of colloidal solution :

1. Preparation of Lyophobic solutions :

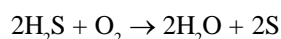
(a) Condensation method (b) Dispersion method

(a) Condensation Method :

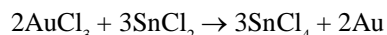
- Chemical Method
- Physical Method
 - Exchange of solvent
 - Excessive cooling

1. **Chemical Method :** Colloidal solutions can be prepared by chemical reactions leading to formation of molecules by double decomposition, oxidation, reduction and hydrolysis. These molecules then aggregate leading to formation of sols, provided a suitable stabiliser is present.

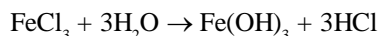
(i) **Oxidation :** A colloidal solution of sulphur can be obtained by bubbling oxygen or any other oxidising agent like HNO_3 , Br_2 etc. through a solution of hydrogen sulphide in water



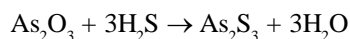
- (ii) **By reduction :** A number of metals, such as silver, gold and platinum have been obtained in colloidal state by treating the aqueous solution of their salts with a suitable reducing agent, such as formaldehyde, hydrazine, H_2O_2 , SnCl_2 etc.



- (iii) **By hydrolysis :** Many salt solutions are easily hydrolysed by boiling dilute solutions of their salts. e.g. $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ sol are obtained by boiling solutions of corresponding chlorides.



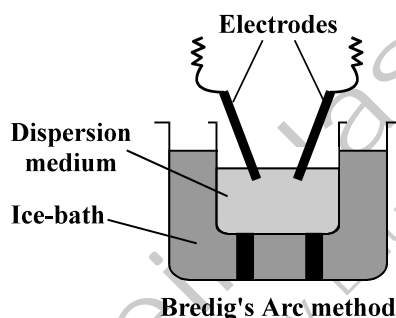
- (iv) **By double decomposition :** A solution of arsenic sulphide is obtained by passing H_2S through a cold solution of arsenious oxide in water.



- (b) **Dispersion Method :** In these methods the coarser particles are broken to smaller particles of colloidal size in the presence of dispersion medium. These are stabilized by adding suitable stabilizer.

- (i) **Mechanical Dispersion :** In this method, the coarse suspension of the substance is brought into colloidal state in the dispersion medium by grinding in a colloid mill.

- (ii) **Electrical dispersion or Bredig's Arc method :** This process involve dispersion as well as condensation. Colloidal sols of metals such as gold, silver, platinum, etc., can be prepare 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.



- (iii) **Peptization :** The process of converting precipitate into colloidal solution by shaking it with dispersion medium in the presence of (small amount of) electrolyte. The electrolyte used for this purpose is called peptizing agent or stabilizing agent. During peptization, the precipitate absorbs one of the ions of the electrolyte on its surface. The ion adsorbed on the surface is common either with the anion or cation of the electrolyte. This causes the development of positive or negative charge on precipitates which ultimately break-up into small particles having the dimensions of colloids. e.g. Freshly prepared $\text{Fe}(\text{OH})_3$ can be converted into colloidal state by shaking it with H_2O containing FeCl_3 or NH_4OH



Stable solution of stannic oxide colloidal is obtained by adding small amount of dilute HCl to stannic oxide precipitate. Similarly colloidal solution $\text{Al}(\text{OH})_3$ and AgCl are obtained by treating corresponding ppt. with dilute HCl and AgNO_3 or KCl respectively. Gelatin stabilised colloidal state of ice-cream. Lamp black is peptised by gums to form indian ink.

Practice Problems :

1. Why is it essential to wash the precipitate with water before estimating it quantitatively ?
2. On passing H_2S through dilute HNO_3 , the colourless solution becomes turbid. Why ?
3. What is collodion ?

[Answers : (1) Some amount of the electrolytes added to form the precipitate remains adsorbed on the surface of the particles of the precipitate. Hence, it is essential to wash the precipitate with water to remove the sticking electrolytes, otherwise peptisation (conversion of ppt. into colloidal solution) might take place

(2) $\text{H}_2\text{S} + \text{O} \longrightarrow \text{H}_2\text{O} + \underset{\text{Colloidal}}{\text{S}}$. Colloidal solution of sulphur is obtained which is turbid (3) Collodion is cellulose nitrate peptised by ethanol]

C4A Purification of Colloidal Solution :

1. **Dialysis :** Dialysis may be defined as the process of separating a crystalloid from a colloid by diffusion or filtration through a fine membrane, the membrane (or apparatus) used for this purpose is called Dialyser. The process of dialysis can be quickened by using hot water or by applying electric field (electrodialysis).
2. **Ultra filtration :** Solution particles pass directly through the ordinary filter paper because their pores are larger (more than $1\ \mu$ or $1000\ \text{m}\mu$) than the size of solution particles (less than $200\ \text{m}\mu$). But if the pores of ordinary filter paper made smaller by soaking the filter paper in a solution of gelatin and subsequently hardened by soaking in formaldehyde, the filter paper may retain colloidal particles and allow true solution particle to escape. Such filter is known as ultrafilter paper.
3. **Ultra-Centrifugation :** In this method, the colloidal solution is taken in a tube which is placed in a ultra-centrifuge on rotation the colloid particle settle down at the bottom of the tube.

C4B Properties of Colloidal System :

- (i) **Heterogeneous character :** As it contain two phases i.e. dispersed phase and dispersion medium.
- (ii) **Non-Settling :** Colloidal solutions are stable systems.
- (iii) **Filterability :** Colloidal particles readily pass through ordinary filter paper. However they can be retained by special filters known as ultrafilters.
- (iv) **Visibility :** Visible under most powerful microscope.
- (v) **Colour :** Colour of a colloidal solution depends on the size and shape of particle.
- (vi) **Colligative Properties :** Colloidal solutions shows colligative properties i.e. relative lowering in V.P., osmotic property, elevation in boiling point. Depression in freezing point. However due to high molecular masses of colloidal particles, mole fraction of the dispersed phase is very low. Thus value of colligative properties determined experimentally is very low. Only osmotic pressure measurement is used to determine the molecular mass of polymer.
- (vii) **Tyndall Effect (optical property) :** Tyndall in 1869, observed that when a beam of light is passed through a true solution it can not be seen. When a same light is passed through a colloidal solution it become visible as a bright streak. This phenomenon is called Tyndall effect and illuminated path (streak of light) is known as Tyndall cone. The appearance of dust particles in a semidarkened room when a sun beam enters or when a light is thrown from a projector in cinema hall are well known example of Tyndall effect. The dust particles are large enough to scatter light which renders the path of light visible.
- (viii) **Brownian Movement :** Robert Brown, observed that pollen grain in aqueous suspension were in constant motion. When colloidal solutions are observed in ultramicroscope, the particles are in constant, random or zig-zag motion, not following the definite path called as Brownian motion. Brownian movement is due to collision of colloidal particles with dispersion medium which are in constant motion. Since colloidal particles are heavier than dispersion medium molecules their movement is considerably slower than that of medium molecules. The mass of particle of ordinary suspension is so large that the bombardment of molecules of the dispersion medium produces little effect and thus ordinary suspension do not exhibit brownian movement.
- (ix) **Electrical Property :** Colloidal particles are electrically charged. All the particles of a colloidal system carry the same charge while the dispersion medium has an equal but opposite charge with the result the system as a whole is electrically natural. Colloidal particles having similar charge, repel each other, and do not combine to form bigger particles and thus solution is stable and particles do not settle down. When an electric current is passed through a colloidal solution the solid particles and the liquid medium being

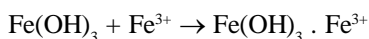
oppositely charged move in opposite direction. In case the experiment is so arranged that only the particles can move and no liquid medium, the phenomenon is known as **Cataphoresis or Electrophoresis**.

When only the medium is allowed to migrate and not the particles, then is known as **electrosmosis**.

Distance travelled by colloidal particles in one second under a potential gradient of 1 volt per cm is called electrophoretic mobility of colloidal particles.

(x) **Origin of the charge on colloidal particles :**

The origin of the charge on the sol particles in most cases is due to the preferential of either positive or negative ions on their surface. When two or more ions are present in the dispersion medium differential adsorption of common to the colloidal particle usually takes place. e.g. $\text{Fe}(\text{OH})_3$ sol prepared by the hydrolysis of ferric chloride has positive charge because of the preferential adsorption of ferric ions i.e. Fe^{3+} on the surface of the ferric hydroxide particles.



Some other positively charged colloidal sols are $\text{Al}(\text{OH})_3$, Hemoglobin, basic dyes etc. Similarly, the negative charge on the arsenic sulphide sol is found to be due to preferential adsorption of sulphide ions, produced by the ionization of H_2S . Other negatively charged sol are starch acidic dyes etc.

Practice Problems :

1. **Explain what is observed**

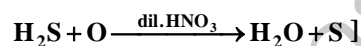
- (i) when a beam of light is passed through a colloidal sol.
- (ii) an electrolyte, NaCl is added to sol.
- (iii) electric current is passed through a colloidal sol ?

2. **What causes Brownian movement in colloidal solution ?**

3. **How is dialysis carried out ? Mention its one application.**

4. **How can colloidal solution of sulphur in water be prepared ?**

[Answers : (1) (i) Scattering of light by the colloidal particles takes place and the path of light becomes visible. This is known as Tyndall effect. (ii) The positively charged colloidal particles of $\text{Fe}(\text{OH})_3$ get coagulated by the oppositely charged Cl^- ions provided by NaCl. (iii) On passing an electric current, colloidal particles move towards the oppositely charged electrode where they lose their charge and get coagulated. This process is called electrophoresis (3) Dialysis is carried out by placing the bag contains impure colloidal solution in running distilled water. It is used for purification of impure colloidal solution (4) It is prepared by oxidation of H_2S by dil. HNO_3 .



C5 Co-agulation of colloidal solutions :

As stability of the colloidal state is due to existence of electrical charge on the particles. If charge is lowered to a certain critical value or neutralised, the particles approach close enough to coalesce to form bigger particles of the suspension range.

This phenomenon of change of colloidal state to suspension state is known as coagulation or flocculation of colloidal solution. It is generally brought about by following treatments :

- (i) **By the mutual action of sols (mutual precipitation) :** When the two oppositely charged sols e.g. As_2S_3 and $\text{Fe}(\text{OH})_3$ sols are mixed in approximately equal proportions, the charge of one sol is neutralised by the opposite charge on the other sol with the result the dispersed phase of both the sols are precipitated out.
- (ii) **By the addition of electrolytes :** Although traces of an electrolyte are essential for stabilising the sols, presence of large amounts causing their coagulation or flocculation.

As colloidal particles carry opposite charge ions, they take up oppositely charged ions from electrolytes with the result the charge on the sol particles is neutralised and thus these are precipitated. The ion carry opposite charge is called Flocculating ion. e.g. the amount of electrolyte required to coagulate a fixed

amount of a sol depends upon the valency of the flocculating ion. In general, greater the valency of the flocculating ion the higher is its power to cause precipitation. This is known as **Hardy - Schulze rule**.

Flocculation power of the various ions follows the following order :

Cations : $\text{Al}^{3+} > \text{Mg}^{2+} > \text{Na}^+$

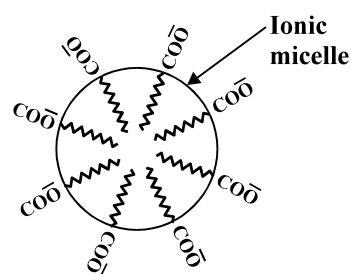
Anions : $[\text{Fe}(\text{CN})_6]^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$

Flocculating cations and anions cause coagulation (flocculation) of the negatively and positively charged colloids respectively. The minimum concentration required to cause flocculation is known as **Flocculation value**, which is generally expressed in milli mol per litre.

Practice Problems :

1. What modification can you suggest in the Hardy-Schulze law ?
2. Explain the following terms :
(i) Electrophoresis (ii) Coagulation (iii) Dialysis (iv) Tyndall effect.
3. Describe electrophoresis briefly.
4. How does soap help in washing clothes ?
5. Show with the help of a diagram arrangement of stearate ions inside the bulk of water (ionic micelle) at critical micelle concentration of soap.
6. Explain the following observations :
(a) Lyophilic colloid is more stable than lyophobic colloid.
(b) Coagulation takes place when sodium chloride solution is added to a colloidal solution of ferric hydroxide.
(c) Sky appears blue in colour.
7. Why is water alone not very effective for removing dirt from clothes ?

[Answers : (1) The coagulating ion has charge opposite to that on the colloidal particles. Hence, the charge on colloidal particles is neutralised and coagulation occurs. The law can be modified as : When oppositely charged sols are mixed in proper proportions to neutralise the charges of each other, coagulation of both the sols occurs (3) Movement of colloidal particles towards oppositely charged electrodes on passing electricity is called electrophoresis (4) Soap forms micelles around grease and dust particles. The lyophobic hydrocarbon parts of the $\text{R} - \text{COO}^-$ (of soap) are oriented towards grease droplets while the lyophilic COO^- parts of RCOO^- are oriented towards water.



Water washes away the micelles along with grease and dirt (5)

(6) (a) The stability of the lyophobic colloid is only on account of charge while the stability of lyophilic colloid is on account of charge as well as solvation of colloidal particles. (b) $\text{Fe}(\text{OH})_3$ sol is positively charged which is coagulated by negatively charged Cl^- present in sodium chloride solution. (c) Sky appears blue in colour due to scattering of light by colloidal particles like dust, mist etc. (7) Water does not dissolve dirt, grease etc., therefore, alone it cannot be used for removing dirt from clothes. It cannot form an emulsion with dirt, grease etc., because water cannot form micelle with grease particles. Soap is needed to form micelle which surround dirt and grease, and are finally washed away by water]

- C6** **Protective colloids** : Lyophilic sol added to a lyophobic colloid prevent from precipitation by electrolyte, the lyophilic sol added to a lyophobic sol, provide envelop to the particles of lyophobic sol, and thus protect is from the action of electrolytes. This lyophilic colloids used for such purposes are known as protective colloids. e.g. addition of gelatin (lyophilic colloid) to a gold sol (lyophobic sol) protects the latter by the action of limited amount of NaCl. The lyophilic colloids differ in their protective powers.

Gold Number : is used to measure the protective power of different colloids. It is defined as weight in milligrams of a protective colloid which checks the co-agulation of 10mL of a given gold solution by adding 1 mL of a 10% solution of sodium chloride. Thus smaller the gold no. of a lyophilic colloid greater is the protective power.

- Q.** **0.025 g of starch sol. is required to prevent coagulation of 10mL gol sol when 1 ml of 10% NaCl solution is present. What is the gold number.**

Solution :

By def. amount of protective sol. in mg is required to prevent the coagulation of 10 mL gold sol when 10% NaCl solution is added. Thus amount of starch required is 0.025 g i.e. 25 mg thus gold number is 25.

There is another term called “Rubin number” which is defined as the amount of protective colloid in milligrams which prevents the colour change in 100 mL of 0.01% congo rubic dye to which 0.16 gm equivalent of KCl is added.

Practice Problems :

- 1.** **How does the addition of alum purify water ?**

[Answers : (1) Alum is an electrolyte. It coagulates colloidal muddy particles and helps in purification of water]

- C7** **Emulsions** : Emulsions are those colloidal systems in which the dispersed phase is liquid normally.

The two common examples are :

Milk : Which consists of particles of liquid fat dispersed in water.

Cod Liver Oil : in which particles of water are dispersed in oil.

Particles of dispersed phase are generally bigger than those in sols and are sometime visible in microscope. Emulsions, particles carry a negative charge and are sensitive to addition of electrolytes. They show Tyndall effect and Brownian movement. In most of emulsions the two liquid phases are oil and water and thus emulsions may be of following two types.

- 1.** **Oil in water emulsion** : In these emulsions, oil is the dispersed phase and water is dispersion medium milk and vanishing cream are two important examples.
- 2.** **Water in oil emulsion** : Water is dispersed phase and oil is dispersion medium e.g. Butter and Cold Cream.

FOAM : are colloidal dispersions of gas in liquid, which is stabilized by soap or other surface active agents. Industrial application of foam : (i) in ore floatation (ii) in detergency (iii) in fire fighting etc.

Practice Problems :

- 1.** **What are emulsions ? What are their different types ? Give one example of each type.**
- 2.** **What is demulsification ? Name two demulsifiers.**
- 3.** **Action of soap is due to emulsification and micelle formation. Comment.**
- 4.** **Give four uses of emulsions.**
- 5.** **What are micelles ? Give an example of micellers system.**
- 6.** **Explain the following term giving a suitable example : Emulsification.**

[Answers : (2) The process of separation of the constituent liquids of an emulsion is called demulsification. Demulsification can be done by centrifuging, boiling or freezing (3) Soap stabilises the emulsion between grease and water by forming micelles around the grease (and dirt) (4) (i) Cleansing action of soaps and detergents (ii) Medicines are effective because of emulsions (iii) Emulsions of AgBr is coated on the surface of photographic film (iv) Paints are emulsions]

C8A ADSORPTION

Adsorption is defined as phenomenon of attracting & retaining the molecules on the surface of a liquid or a solid resulting into a higher concentration of the molecules on the surface is called adsorption.

Process of removal of adsorbed particle called as desorption. The substance which is adsorbed on surface is called adsorbate. The substance on which adsorption takes place is adsorbent e.g. charcoal, silica gel, alumina gel, clay etc. are very good adsorbent

Absorption : The molecule of substance are uniformly distributed throughout the body of a solid or a liquid. In certain cases both absorption & adsorption takes place simultaneously called as sorption.

Adsorption is of two types :

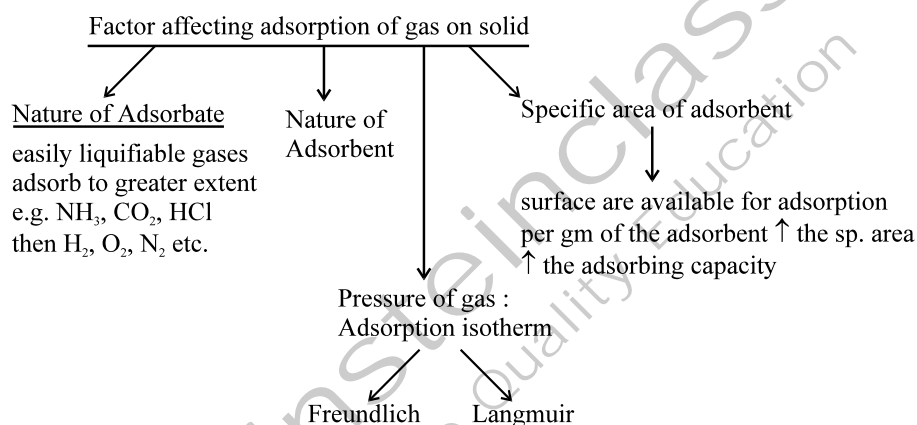
Physisorption

ΔH adsorption is low ≈ 20 kJ/mol
Molecule of adsorbate & adsorbent are held by weak vander wall forces
Take place at low temperature & decreases with $\uparrow T$
Not very specific
Multimolecular layer formed

Chemisorption

ΔH adsorption is high ~ 200 kJ/mol
Held by chemical bonds
Take place at high temperature
Very specific
Usually monomolecular layer is formed.

C8B



1. Freundlich Adsorption Isotherm (at temp. T)

$x \rightarrow$ Amount of Adsorbate

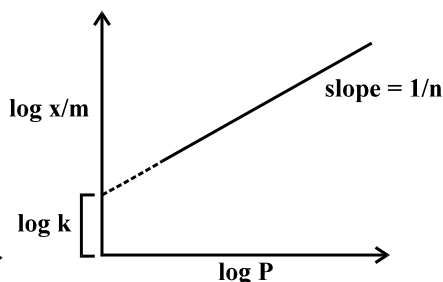
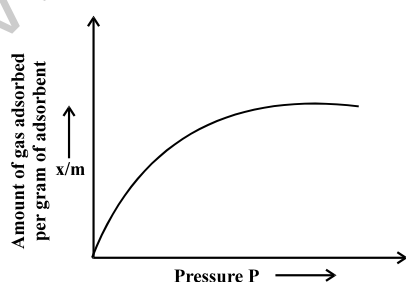
$m \rightarrow$ Amount of Adsorbant

$kP^{1/n}$, $n > 1$, $P \rightarrow$ Pressure of gas adsorbed

k , n are parameter depend on nature of gas and solid.

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

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



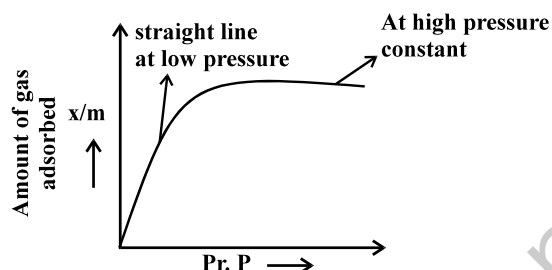
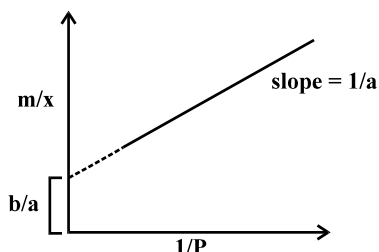
value of k & n can be find out.

2. **Langmuir Adsorption Isotherm** : Applicable to chemisorption $\frac{x}{m} = \frac{ap}{1 + bp}$

a, b → Langmuir Parameter

By reversing equation :

$$\frac{m}{x} = \frac{1 + bp}{aP} = \frac{b}{a} + \frac{1}{a} \cdot \frac{1}{P}$$



a, b can be calculated

$$\frac{x}{m} = \frac{ap}{1 + bp}$$

At. low pressure $bp \ll 1$, thus $\frac{x}{m} = aP$

At high pressure $bp \gg 1$, thus $\frac{x}{m} = \frac{aP}{bP} = \frac{a}{b}$ (constant)

Effect of Temperature : (Adsorption isobar) Adsorption is temperature dependent. Mostly adsorption is exothermic thus it decreases with ↑ temperature, $\Delta G = \text{negative}$ $\Delta G = \Delta H - T\Delta S$

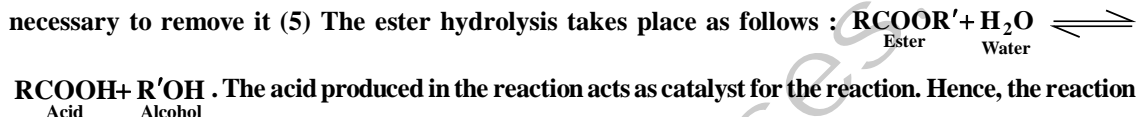
Practic Problems :

- Why are substances like platinum and palladium often used for carrying out electrolysis of aqueous solution ?
- Why does physisorption decrease with the increase of temperature ?
- Why are powdered substances more effective adsorbent than their crystalline forms ?
- Why is it necessary to remove CO when ammonia is obtained by Haber's process ?
- Why is the ester hydrolysis slow in the beginning and becomes faster after sometime ?
- What is the role of desorption in the process of catalysis ?
- Distinguish between the meaning of the terms adsorption and absorption. Give one example of each.
- What is the difference between physisorption and chemisorption ?
- Give reason why a finely divided substance is more effective as an adsorbent.
- What are the factors, which influence the adsorption of a gas on a solid ?
- What is an adsorption isotherm ? Describe Freundlich adsorption isotherm.
- What do you understand by activation of adsorbent ? How is it achieved ?
- What role does adsorption play in heterogeneous catalysis ?
- Why is adsorption always exothermic ?
- Discuss the effect of pressure and temperature on the adsorption of gases on solids.
- What are enzymes ? Write in brief the mechanism of enzyme catalysis.
- Give four examples of heterogeneous catalysis.
- What do you mean by activity and selectivity of catalyst ?
- Describe some features of catalysis by zeolites.
- What is shape selective catalysis ?
- Of physisorption and chemisorption, which type of adsorption has a higher enthalpy of adsorption ?
- Of NH_3 and N_2 , which gas will be adsorbed more readily on the surface of charcoal and why ?
- What is meant by specific surface area of a solid ?
- What are zeolites ? Describe some of their features.
- Explain Freundlich adsorption isotherm.
- What do you mean by adsorption isobar ?
- Draw a plot of variation in quantity of gas adsorbed $\left(\frac{x}{m}\right)$ with the pressure of the gas. Also plot the graph

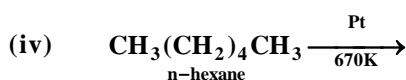
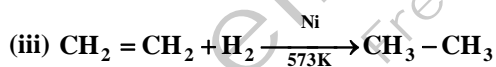
between $\log \frac{x}{m}$ vs $\log P$ at constant temperature. What is slope of this line ?

28. (a) In which of the following does adsorption take place and why ?
 (i) Silica gel placed in the atmosphere saturated with water.
 (ii) Anhydrous CaCl_2 placed in the atmosphere saturated with water.
 (b) How does BF_3 act as a catalyst in industrial process ?
 (c) Give an example of shape-selective catalysis.
29. Explain with the help of diagram :
 (i) Adsorption of reacting molecules on the surface of catalyst.
 (ii) Formation of intermediate.
 (iii) Desorption of products.
30. Draw a labelled diagram to represent mechanism of enzyme catalysed reaction.

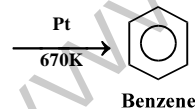
[Answers : (1) Platinum and palladium are inert materials for electrodes. They are not attacked by the ions of the electrolyte or the products of electrolysis. Hence, they are used as electrodes for carrying out the electrolysis (2) Physisorption is an exothermic process i.e., heat is produced in the process. According to Le-Chatelier's principle, if we increase the temperature, equilibrium will shift in the backward direction. i.e., gas is released from the adsorbed surface (3) Powdered substances have greater surface area as compared to their crystalline forms for the same mass. Greater the surface area, greater is the adsorption (4) CO acts as a poison for the catalyst in the manufacture of ammonia by Haber's process. Hence, it is necessary to remove it (5) The ester hydrolysis takes place as follows :



The acid produced in the reaction acts as catalyst for the reaction. Hence, the reaction becomes faster after sometime. This phenomenon is known as autocatalysis (6) Desorption makes the surface of the solid catalyst free for fresh adsorption of the reactants on the surface. It is necessary for the continuation of the process (12) Activating an adsorbent means increasing its adsorption capacity. This can be achieved by evacuating it under vacuum of the order of 10^{-8} to 10^{-9} Pascal (13) In heterogeneous catalysis, the reactant molecules are adsorbed on the surface of the solid catalyst by physical adsorption or chemisorption. As a result, concentration of the reactant molecules on the surface increases and hence the rate of reaction increases. The product molecules have no affinity for the solid catalyst and are desorbed making the surface free for fresh adsorption (14) When a gas is adsorbed on the surface of a solid, its entropy decreases, i.e., ΔS is -ve. Now, $\Delta G = \Delta H - T\Delta S$ is +ve, therefore, ΔG can be -ve only if ΔH is -ve. Hence, adsorption is always exothermic (15) With the increase of pressure, adsorption increases. With the increase of temperature adsorption decreases (16) Mechanism of enzyme catalysis : Step 1 : Binding of enzymes to substrate to form an activated complex $\text{E} + \text{S} \rightarrow \text{ES}^*$. Step 2 : Decomposition of the activated complex to form products. $\text{ES}^* \rightarrow \text{E} + \text{P}$ (E = Enzyme, S = Substrate, ES^* = Activated complex, P = Product

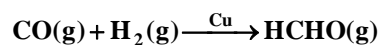
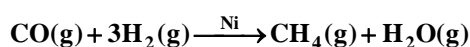


Cyclohexane



Benzene

(18) Activity : Ability of a catalyst to accelerate chemical reactions is known as its activity. For example, Pt catalyses the combination of H_2 and O_2 to form water. It has been found that for hydrogenation reactions, the catalytic activity increases from Group 5 to Group 11 metals with maximum activity being shown by group 7-9 elements of the periodic table. Selectivity : The ability of a catalyst to direct a reaction to yield a particular product is called its selectivity. Combination of CO and H_2 yields different products with different catalysts as given:

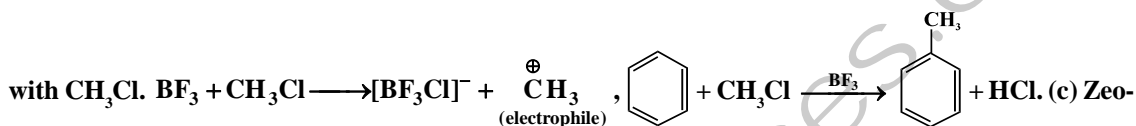


$\text{CO}(\text{g}) + \text{H}_2(\text{g}) \xrightarrow{\text{Cu/ZnO-Cr}_2\text{O}_3} \text{CH}_3\text{OH}(\text{g})$ (19) (i) Zeolites are hydrated aluminosilicates which have a three-dimensional network structure containing water molecules in their pores. (ii) On heating, water of

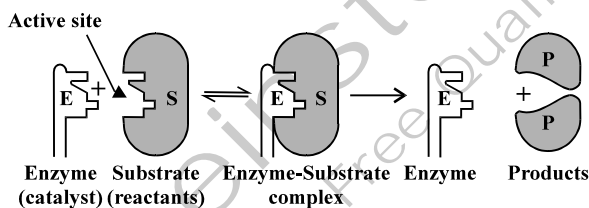
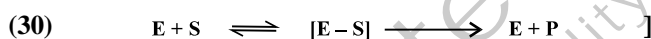
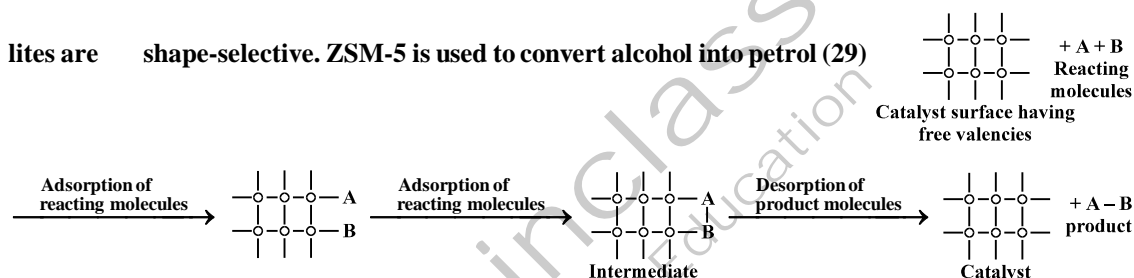
hydration present in the pores is lost and the pores become vacant to carry out catalysis. (iii) The size of the pores varies from 260 to 740 pm. Thus, only those molecules can be absorbed in these pores and catalysed whose size fits these pores. Hence, they act as molecular sieves or shape selective catalysts. An important catalyst used in petroleum industry is ZSM-5 (Zeolite sieve of molecular poririty-5). It converts alcohols

into petrol by dehydrating them to form a mixture of hydrocarbons. Alcohols $\xrightarrow[\text{Dehydration}]{\text{ZSM-5}}$ Hydrocar-

bons (20) Catalysis by zeolites is called shape selective catalysis. It depends upon the pore structure of the catalyst. Specific reactions take place keeping in view the molecular sizes of reactants and products and pore sizes of the zeolite catalyst (21) Chemisorption has higher enthalpy of adsorption on account of formation of chemical bond (22) NH_3 is adsorbed more readily as it is more easily liquefiable compared to N_2 . Moreover, NH_3 molecule has greater molecular size (23) Area available for adsorption per gram of the adsorbent is called specific surface area (24) Zeolites are aluminosilicates, i.e., three dimensional network silicates in which some silicon atoms are replaced by aluminium atoms. They are found in nature as well as synthesised for catalytic selectivity. They have honeycomb like structure. Features of Zeolites : (i) Zeolites have high porosity due to presence of cavities of molecular dimensions. (ii) Elements such as Ba, Mg, B, Ga and P can take place of Si and Al in the zeolite framework. (iii) New class of highly siliceous zeolites has catalytic properties. (iv) They are shape-selective catalyst (28) (a) (i) In silica gel, adsorption takes place. Silica gel can adsorb water molecules on its surface. (ii) It is adsorption that takes place with anhydrous CaCl_2 . (b) It is because it is electron deficient. For example, it produces electrophile on reaction



lites are shape-selective. ZSM-5 is used to convert alcohol into petrol (29)



Mechanism of enzyme catalysed reaction