

# ST. LAWRENCE HIGH SCHOOL A JESUIT CHRISTIAN MINORITY INSTITUTION STUDY MATERIAL FOR CHEMISTRY (CLASS-12) TOPIC-SURFACE CHEMISTRY PREPARED BY: MR. ARNAB PAUL CHOWDHURY SET NUMBER-15 DATE: 18.01.2021



Surface chemistry is referred to as the study of the phenomenon occurring on the surfaces of substances. This is very applicable in industries and day to day lives. In other words, surface chemistry deals with all types of surface phenomenon.

# **Adsorption**

Due to unbalanced attraction forces, accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed as adsorption. The molecular species accumulates at the surface is termed as adsorbate and the material on the surface of which the adsorption takes place is called adsorbent, e.g.

(i) O<sub>2</sub>, H<sub>2</sub>, Cl<sub>2</sub> gases are adsorbed on the surface of charcoal.
(ii) Silica gels adsorb water molecules from air.
Charcoal, silica gel, metals such as Ni, Cu, Ag, Pt and colloids are some adsorbents.

# **Important Characteristics of Adsorption**

1. It is specific and selective in nature.

2. Adsorption is spontaneous process, therefore change in free energy ( $\Delta G$ )is negative.

 $\Delta G = \Delta H - T \Delta S$ ,

For the negative value of  $\Delta$ G, in a system, in which randomness decreases,  $\Delta$ H must be negative. Hence, adsorption is always exothermic.

Adsorption of hydrogen over Pt is called occlusion.

# **Desorption**

It is a process of removing an adsorbed substance from a surface on which it is adsorbed, is known as desorption.

# **Distinction between Adsorption and Absorption**

	Adsorption	Absorption
1.	It involves unequal distribution of the molecular species in bulk and at the surface.	It involves uniform distribution of the molecular species throughout the bulk.
2.	It is a surface phenomenon.	It occurs throughout the body of material.
3.	It is rapid in the beginning.	It occurs at a uniform rate.

# Sorption

It is a process in which both adsorption and absorption take place simultaneously, the term sorption is simply used.

# Positive and Negative Adsorption

When the concentration of the adsorbate is more on the surface of the adsorbent than in the bulk, it is called positive adsorption.

On the other hand, if the concentration of the adsorbate is less relative to its concentration in the bulk, it is called negative adsorption, e.g., when a dilute solution of KCl is shaken with blood charcoal, it shows negative adsorption.

# Distinction between Physisorption and Chemisorption

	Physisorption	Chemisorption		
1.	It arises when the adsorbate molecules accumulate on the surface of adsorbent on account of weak van der Waals' forces.	It arises when the adsorbate molecules accumulate on the surface of adsorbent on account of chemical bonds.		
2. It occurs at low temperature.		It occurs at high temperature.		
3.	Heat of adsorption is low and it is in the range of 20-40 kJ/mol.	Heat of adsorption is high and it is in the range of 80-240 kJ/mol.		
4.	It is reversible process.	It is an irreversible process.		
5. Multilayer adsorption and thus, adsorbed layer is several molecules thick.		Monolayer adsorption. Thus, adsorbed layer is only unimolecular in thickness.		

# Factors Affecting Adsorption

(a) **Nature of adsorbent**: Same gas may be adsorbed to different extents on different adsorbent.

(b) Surface area of the adsorbent: Greater the surface area, greater is the extent of adsorption.(c) Nature of the gas being adsorbed: Greater is the critical temperature of a gas, greater are

the van der Waals' forces of attraction and thus, greater is the adsorption.

Gas	Ha	$N_2$	CO	$CH_4$	CO2	HCI	NH <sub>3</sub>	SO2
Critical temp. (K)	33	126	134	190	304	324	406	430

(d) **Temperature** Adsorption is an exothermic process involving the equilibrium : Gas (adsorbate) + Solid (adsorbent) ⇔ Gas adsorbed on solid + Heat

Applying Le-Chatelier principle, increase of temperature decreases the adsorption and vice-versa.

(e) **Pressure** Adsorption increases with pressure at constant temperature. The effect is large if temperature is kept constant at low value.

(f) **Activation of the solid adsorbent** Activation means increasing the adsorbing power of the solid adsorbent. This can be done by subdividing the solid adsorbent or by removing the gases already adsorbed by passing superheated steam.

# **Adsorption Isotherms**

It is the plot of the mass of gas adsorbed per gram of adsorbent (x / m) versus equilibrium pressure at constant temperature.

# Freundlich Adsorption Isotherm

It gave an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature. It can be expressed by the equation.

# $x / m = kp^{1/n} ...(i)$

Where, x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p, k and n are constants which depend on the nature of the adsorbent and the gas at a particular temperature.



At low pressure, n = 1, i.e., x / m = kp

At high pressure, n > 1, i.e., x / m = k (independent of p)

Taking logarithm of Eq. (i)

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$
Plot of log  $\frac{x}{m}$  vs log p is a straight line with  
slope  $\frac{1}{n}$  and intercept on y-axis = log k.  
The factor  $\frac{1}{n}$  can have values between 0 and 1.

# Freundlich Adsorption Equation for Solutions

 $x / m = kC^{1/n}$ where, C is the equilibrium concentration. On taking logarithm of the above equation, we have

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

#### Langmuir Adsorption Isotherm

According to Langmuir, the degree of adsorption is directly ProPOrtional to e, i.e., the fraction of surface area occupied.

 $x / m \alpha \theta = k\theta$ 

As, 
$$\theta = \frac{kp}{1+k_p}$$

...

 $\frac{x}{m} = \frac{k' p}{1 + k_p}$ 

If  $\frac{p}{x/m}$  is plotted against p, it will give a straight line



At very high pressure,  $1 + k_p = k_p$ 

$$\frac{x}{m} = \frac{k' p}{kp} = \text{constant}$$

At low pressure, 1 + kp = 1

$$\frac{x}{m} = k' p$$

At moderate p,

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

where, 
$$\frac{1}{n} = 0$$
 to 1.

# Adsorption Isobars

These are plots of x / m us temperature t at constant pressure. For physical and chemical adsorption, they are shown below.



#### Adsorption Isostere

These are the plot of temperature versus pressure for a given amount of adsorption



#### **Applications of Adsorption**

- 1. For production of high vacuum.
- 2. Gas masks containing activated charcoal is used for breathing in coalmines. They adsorb poisonous gases.
- 3. Silica and aluminium gels are used as adsorbents for controlling humidity.
- 4. Removal of colouring matter from solutions.
- 5. It is used in heterogeneous catalysis.
- 6. In separation of inert gas.
- 7. As adsorption indicators.
- 8. In chromatographic analysis.
- 9. Qualitative analysis, e.g., lake test for Al<sup>3</sup>+.

#### **Catalysis**

Catalyst is a chemical substance which can change the rate of reaction without being used up in that reaction and this process is known as catalysis

	Process	Catalyst
1.	Haber's process of NH <sub>3</sub>	finely divided Fe (Mo acts as promoter)
2.	Ostwald's process for manufacture of nitric acid	Platinised asbestos
3.	Contact process for H2SO4	Platinised asbestos or V205
4.	Lead chamber process for H <sub>2</sub> SO <sub>4</sub>	Nitric oxide
5.	Decon's process	CuCl <sub>2</sub>

A catalyst may be positive (i.e., increases rate of reaction) or negative (i.e., decreases rate of reaction).

# **Types of Catalysis**

(a) **Homogeneous catalysis** In this catalysis, and the catalyst reactants are in the same physical state [phase], e.g.,

$$2\operatorname{SO}_2(g) + \operatorname{O}_2(g) \xrightarrow{\operatorname{NO}(g)} 2\operatorname{SO}_3(g)$$

(b) **Heterogeneous catalysis** In heterogeneous catalysis, catalyst is present in a different phase than that of reactants, e.g.,

$$2\text{KClO}_3(s) \xrightarrow{\text{MnO}_2} 2\text{KCl}(s) + 3\text{O}_2(g)$$

(c) **Autocatalysis**: When one of the product of a reaction acts as catalyst, the process is called autocatalysis.

# **Characteristics of Catalysts**

1 The catalyst remains unchanged in mass and chemical composition.

2. In case of reversible reactions, the catalyst does not influence the composition of reaction mixture at equilibrium. It only helps to attain the equilibrium quickly.

# **Promoters and Poisons**

Promoters are chemical substances that enhance the activity of a catalyst while poisons decreases the activity of a catalyst

# Adsorption Theory of Heterogeneous Catalysis

The mechanism involves five steps:

- (i) Diffusion of reactants to the surface of the catalyst
- (ii) Adsorption of reactant molecules on the surface of the catalyst.
- (ill) Occurrence of chemical reaction on the catalyst's surface through formation of an

intermediate.

(iv) Desorption of reaction products from t he catalyst surface.

(v) Diffusion of reaction products away from the catalyst's surface



#### **Important Features of Solid Catalysts**

(i) **Activity** The activity of a catalyst depends upon the strength of chemisorption to a large extent. The adsorption should be reasonably strong but not so strong that they become immobile and no space is available for other reactants to get adsorbed.

(ii) **Selectivity** The selectivity of a catalyst is its ability to direct a reaction to yield a particular product, e.g., starting with Hz and CO using different catalysts, we get different products.

$$\begin{array}{ccc} \mathrm{CO}(g) + 3\mathrm{H}_{2}(g) & \xrightarrow{\mathrm{Ni}} & \mathrm{CH}_{4}(g) + \mathrm{H}_{2}\mathrm{O}(g) \\ \\ \mathrm{CO}(g) + 2\mathrm{H}_{2}(g) & \xrightarrow{\mathrm{Cu}, \ \mathrm{ZnO} \cdot \mathrm{Cr}_{2}\mathrm{O}_{3}} & \mathrm{CH}_{3}\mathrm{OH}(l) \\ \\ \mathrm{CO}(g) + \mathrm{H}_{2}(g) & \xrightarrow{\mathrm{Cu}} & \mathrm{HCHO}(g) \end{array}$$

**Shape–selective catalysis** The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules is called shape-selective 8atalysis. Cracking Isomerization of hydrocarbons in the presence of zeolites is an example of shape-selective catalysis.

An important zeolite catalyst used in the petroleum industry is ZSM-S.It converts alcohols directly into gasoline.

# Enzyme Catalysis:

Enzymes are complex nitrogenous organic compounds which are Produced by living plants and animals. They are actually protein molecules of high molecular mass and form colloidal solutions in water.

They are also known as biochemical catalysis.





Some examples of enzyme catalysed reactions are:

(i) 
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} C_6H_{12}O_6 + C_6H_{12}O_6$$
  
sucrose  
(ii)  $C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$   
(iii)  $n(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{Diastase}} nC_{12}H_{22}O_{11} \xrightarrow{\text{Maltose}} \text{Glucose}$   
(iv)  $NH_2CONH_2 + H_2O \xrightarrow{\text{Urease}} 2NH_3 + CO_2$ 

(Source of invertase, zymase and maltose is yeast and that of diastase is malt. Soybean is the source of urease.)

(v) In stomach, the pepsin enzyme converts proteins into peptides while in intestine, the pancreatic trypsin converts proteins into amino acids by hydrolysis.

(vi) Lactobacilli is used to convert milk into curd.

#### **Characteristics of Enzyme Catalysis:**

- **High efficiency** One molecule of an enzyme may transform one million molecule of reactant per minute.
- **Highly specific nature** Each enzyme catalyst cannot catalyse more than one reaction.
- **Optimum temperature** Enzyme catalyst gives higher yield at optimum temperature i.e., at 298-310 K. Human body temperature, i.e., at being 310 K is suited for enzyme catalysed reactions.
- **Optimum pH** The rate of an enzyme catalysed reaction is maximum at optimum pH range 5 to 7.
- Activators Activators like ions such as Na<sup>+</sup>, Ca<sup>2+</sup>, Mn<sup>2+</sup> help in the activation of enzymes which cannot act on their own strength.
- **Co-enzyme** Co-enzymes are the substance having nature similar to the enzyme and their presence increases the enzyme activity. Mostly vitamins act as co-enzymes.
- Effect of Inhibitors Inhibitors slow down the rate of an enzymatic reaction. The use of many drugs is based on enzyme inhibition action of those drugs in the body.

#### True solution:

- (i) It is homogeneous.
- (ii) The diameter of the particles is less than 1 nm.
- (iii) It passes through filter paper.
- (iv) Its particles cannot be seen under a microscope.

Name	Dispersed phase	Dispersed medium	Examples
Solid sol	solid	Solid	Coloured gem stones
Sol	Solid	Liquid	Paints
Aerosol	Solid	Gas	Smoke, dust
Gel	Liquid	Solid	Cheese, jellies
Emulsion	Liquid	Liquid	Hair cream, milk
Aerosol	Liquid	Gas	Mist, fog, cloud

Solid sol	Gas	Solid	Foam rubber, pumice stone
Foam	Gas	Liquid	Whipped cream

Colloids:

(i) It appears to be homogeneous but is actually heterogeneous.

- (ii) The diameter of the particles is 1 nm to 1000 nm.
- (iii) It passes through ordinary filter paper but not through ultra-filters.
- (iv) Its particles can be seen by a powerful microscope due to scattering of light.

# Suspension:

- (i) It is heterogeneous.
- (ii) The diameter of the particles are larger than 1000 nm.
- (iii) It does not pass through filter paper.
- (iv) Its particles can be seen even with naked eye.

Classification of colloids on the basis of the physical state of dispersed phase and dispersion medium:

Classification of colloids on the basis of nature of interaction between dispersed phase and dispersion medium, the colloids are classified into two types namely,

# A) **Dispersed phase**: It is the substance which is dispersed as very fine particles.

# B) **Dispersion medium**: It is the substance present in larger quantity.

- 1. Lyophobic sols
- 2. Lyophilic sols

# Lyophobic sols:

(i) These colloids are liquid hating.

(ii) In these colloids the particles of dispersed phase have no affinity for the dispersion medium.

- (iii) They are not stable.
- (iv) They can be prepared by mixing substances directly.
- (v) They need stabilizing agents for their preservation.
- (vi) They are irreversible sols.

# Lyophilic sols:

(i) These colloids are liquid loving.

(ii) In these colloids, the particles of dispersed phase have great affinity for the dispersion medium.

(iii) They are stable.

(iv) They cannot be prepared by mixing substances directly. They are prepared only by special methods.

(v) They do not need stabilizing agents for their preservation.

(vi) They are reversible sols.

# Classification of colloids on the basis of types of particles of the dispersed phase:

There are three types of colloids based on the type of dispersed phase, namely,

- 1. Multimolecular colloids: The colloids in which the colloidal particles consist of aggregates of atoms or small molecules. The diameter of the colloidal particle formed is less than 1 nm.
- 2. Macromolecular colloids: These are the colloids in which the dispersed particles are themselves large molecules (usually polymers). Since these molecules have dimensions comparable to those of colloids particles, their dispersions are called macromolecular colloids, e.g., proteins, starch and cellulose form macromolecular colloids.
- 3. Associated colloids (Micelles): Those colloids which behave as normal, strong electrolytes at low concentrations, but show colloidal properties at higherconcentrations due to the formation of aggregated particles of colloidal dimensions. Such substances are also referred to as associated colloids.
- Kraft Temperature (Tk):Micelles are formed only above a certain temperature called Kraft temperature.
- Critical Micelle Concentration (CMC): Micelles are formed only above a particular concentration called critical micelle concentration.
- Soaps: These are are sodium or potassium salts of higher fatty acids e.g., sodium stearate CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>COO-Na<sup>+</sup>

# Methods of preparation of colloids:

- 1. Chemical methods: Colloids can be prepared by chemical reactions leading to the formation of molecules. These molecules aggregate leading to formation of sols.
- 2. Electrical disintegration or Bredig's Arc method: In this method, electric arc is struck between electrodes of the metal immersed in the dispersion medium. The intense heat produced vaporizes the metal which then condenses to form particles of colloidal size.
- 3. Peptization: It is the process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte. The electrolyte used for this purpose is called peptizing agent.

# Purification of colloids:

1. <u>Dialysis:</u> It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane.

- 2. <u>Electro dialysis</u>. 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.
- 3. <u>Ultrafiltration</u>: It 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.
- 4. <u>Ultracentrifugation</u>: In this process, the colloidal solution is taken in a tube which is placed in ultracentrifuge. On rotating the tube at very high speed, the colloidal particles settle down at the bottom of the tube and the impurities remain in solution. The settled particles are mixed with dispersion medium to regenerate the sol.

**Properties of colloids**: Positively charged colloidal particles:

(i) These include hydrated metallic oxides such as  $Fe_2O_3$ .  $H_2O$ ,  $Cr_2O_3$ .  $H_2O$ ,

 $AI_2O_3$ .  $H_2O$ 

(ii) Basic dye stuff like malachite green, methylene blue sols.

(iii) Example – Haemoglobin (blood).Negatively charged colloidal particles:(i) Metallic sulphides like As<sub>2</sub>S<sub>3</sub>, Sb<sub>2</sub>S<sub>3</sub> sols.

(ii) Acid dye stuff like eosin, methyl orange, Congo red sols.

(iii) Examples – Starch sol, gum, gelatin, clay, charcoal, egg albumin, etc.

- 1. <u>Colour:</u> The colour of colloidal solution depends upon the wavelength of light scattered by the colloidal particles which in turn depends upon the nature and size of particles. The colour also depends upon the manner in which light is received by the observer.
- <u>Brownian movement</u>: Colloidal particles move in zig zag path. This type of motion is due to colliding molecules of dispersion medium constantly with colloidal particles.
- 3. <u>Colligative properties</u>: The values of colligative properties (osmotic pressure, lowering in vapour pressure, depression in freezing point and elevation in boiling point) are of small order as compared to values shown by true solutions at the same concentrations.
- 4. <u>Tyndall effect</u>: The scattering of a beam of light by colloidal particles is called Tyndall effect. The bright cone of light is called the Tyndall cone.
- 5. <u>Charge on colloidal particles</u>: 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.
- 6. <u>Helmholtz electrical double layer</u>: When the colloidal particles acquire negative or positive charge by selective adsorption of one of the ions, it attracts counter ions from the medium forming a second layer. The combination of these two layers of opposite charges around colloidal particles is called Helmholtz electrical double layer.

- 7. Electrokinetic potential or zeta potential: The potential difference between the fixed layer and the diffused layer of opposite charges is called electrokinetic potential or zeta potential.
- 8. Electrophoresis: The movement of colloidal particles under an applied electric potential is called electrophoresis.
- 9. Coagulation or precipitation: The process of settling of colloidal particles as precipitate is called coagulation.

#### Hardy – Schulze rules:

i) Oppositely charged ions are effective for coagulation.

ii) The coagulating power of electrolyte increases with increase in charge on the ions used for coagulation. Examples  $- Al^{3+} > Ba^{2+} > Na^+$  for negatively charged colloids. Fe  $(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$  for positively charged colloids.

# Types of emulsions:

- 1. Water dispersed in oil: When water is the dispersed phase and oil is the dispersion medium. E.g. butter
- 2. Oil dispersed in water: When oil is the dispersed phase and water is the dispersion medium. E.g. milk
- Emulsification: It is the process of stabilizing an emulsion by means of an emulsifier.
- Emulsifying agent or emulsifier: These are the substances which are added to stabilize the emulsions. Examples soaps, gum
- Demulsification: It is the process of breaking an emulsion into its constituent liquidsby freezing, boiling, centrifugation or some chemical methods.

The colloidal solutions in which both dispersed phase and dispersion medium are liquids are called as <u>Emulsions</u>.

**Example:** Paints, dyes, milk, vanishing cream. On the basis of dispersion medium emulsions in surface chemistry are classified into two types:

# Oil in Water Emulsions

In this, the oil or fat droplets are dispersed in water. Example: Milk.

# Water in Oil Emulsions

In this, the water droplets are dispersed in oil. Example: Vanishing cream.

Emulsions are unstable, to increase the stability another substance called as emulsifiers are added. **Example:** Milk contains natural emulsion casein.

# **Applications of Emulsions**

- These are used in syrups
- Paints
- Toothpaste
- Digestion of fats
- Pigment and dye

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