SURFACE CHEMISTRY

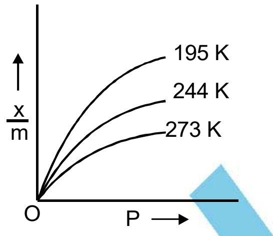
Adsorption: The existence of a substance at a surface in different concentration than in the adjoining bulk is called adsorption, The substance so Adsorbed is called Adsorbate and the substance upon which adsorption takes place is called adsorbent

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

Sorption: When adsorption and absorption take place simultaneously

	Physiosorption	Chemisorption
1.	Non specific	Specific
2.	Reversible	Irreversible
3.	Increases with increase in surface area	In creases with increase in surface area
4.	Weak vander waals forces between absorbate and adsorbent.	Chemical bond formation
5.	Low heat of adsorption (20 - 40 KJ mol^{-1})	High
6.	Occurs at low temperature	At moderate temperature
7.	Decreases with increase of T	It first increases, then decreases with T
8.	Increases with increase of P	It increases with increase in P at low P but is independent of P at high pressure
9.	Forms multimolecular layer	Forms unimolecular layer.

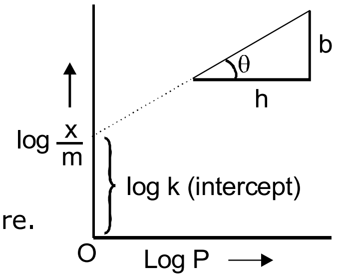
Adsorption isotherm: The graph plotted between x/m and p at constant T.



Frendulich adsorption isotherm

$$\boxed{\frac{x}{m} = kp^{1/n} \qquad n > 1 \\ \log\frac{x}{m} = \log k + \frac{1}{n}\log p}$$

Adsorption isotherm



When $\frac{1}{n} = 0$, $\frac{x}{m}$ = Constant, the adsorption is independent of pressure.

When $\frac{1}{n} = 1$, $\frac{x}{m}$ = kp, i.e., $\frac{x}{m} \propto$ p, the adsorption varies directly with pressure.

Adsorption from solution phase

When litmus solution is shaken with charcoal becomes colorless.

$\left(\frac{x}{m}\right)$ Extent of adsorption $\propto \frac{1}{T} \propto$ S.A. $\propto$ [Solute] and also on nature of adsorbate and adsorbent

$$\boxed{\frac{x}{m} = KC^{1/n}} \quad \Rightarrow \quad \log\frac{x}{m} = \log K + \frac{1}{n}\log C$$

Applications of adsorption

1. To create vacuum.
2. Gas masks to adsorb poisonous gases
3. Controlling humidity (Silica and Al gels)
4. Removing colouring matter from solutions.
5. Heterogeneous catalysis (eg. Fe catalyst to make NH_3)
6. Seperation of inert gases.
7. Drugs used to kill germs by getting adsorbed on it
8. Froth floatation process.
9. Adsorption indicators eg. Ag halides adsorbs eosin and fluorosin and give characteristic colour at end point.
10. Chromatographic analysis.

Catalysis : The process in which catalyst is used to increase the rate of reaction.

$$2KClO_3 \xrightarrow[473-633\,K]{MnO_2} 2KCl + 3O_2$$

*****Promoters** are substances that inhance the activity of a catalyst while **poisons** decrease the activity of a catalyst.

$$N_{2(g)} + 3H_{2(g)} \xrightarrow[Mo(s)]{Fe(s)} 2NH_{3(g)}$$

Homogenous catalysis : When the reactant and the catalyst are in the same phase.

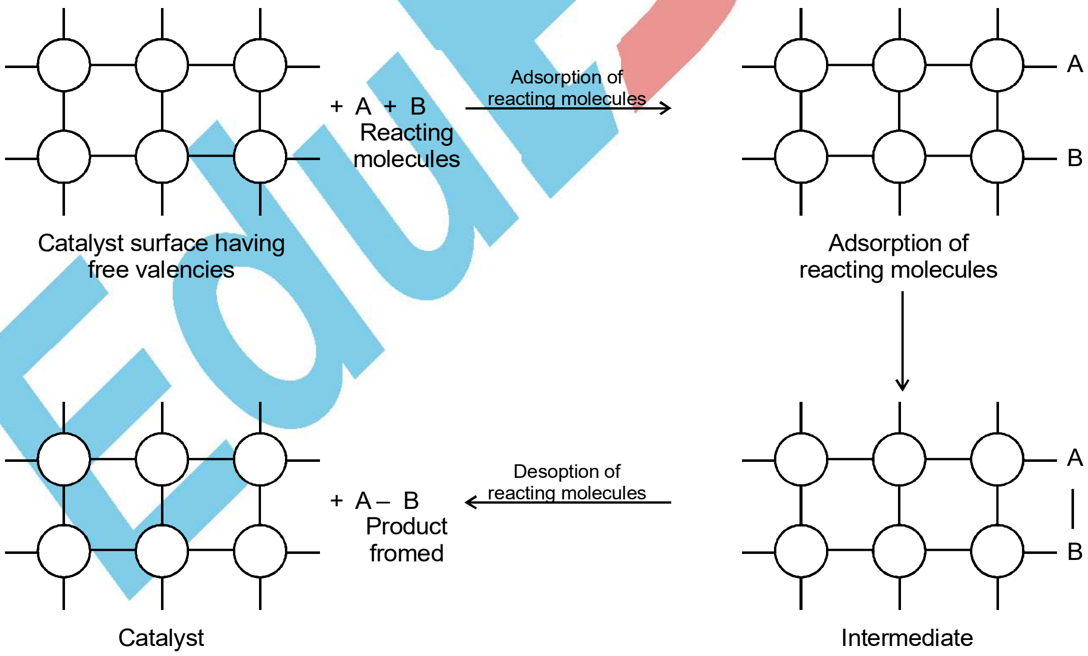
$$2SO_{2(g)} + O_{2(g)} \xrightarrow{NO(g)} 2SO_{3(g)}$$

$$C_{12}H_{22}O_{11}(aq) + H_2O_{(l)} \xrightarrow{H_2SO_4(l)} C_6H_{12}O_6(g) + C_6H_{12}O_6$$

Heterogeneous catalysis : The catalytic process in which the reactants and the catalyst are in different phases.

$$O_2 + 2SO_2(g) \xrightarrow{Pt(s)} 2SO_{3(g)}$$

$$4NH_3(g) + 5O_2(g) \xrightarrow{Pt(s)} 4NO(g) + 6H_2O(g)$$



Adsorption of reacting molecules, formation of intermediate and desorption of products

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 catalysis.

Zeolites are good shape–selective catalysts because of their honey comb structure . They are microporous. Aluminosilicates. A zeolite catalyst ZSM – 5 converts alcohol to gasolene.

Enzymes (biocatalysts):

Nitrogenous organic compounds produced by living cells that catalyse biochemical reactions in living organisms.

Examples of enzyme catalysed reactions.

1. Inversion of cane sugar.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{Fructose}}{C_6H_{12}O_6(aq)}$$

2. $$\underset{\text{Glucose}}{C_6H_{12}O_6(aq)} \xrightarrow{\text{Zymase}} 2\,C_2H_5OH(aq) + 2CO_2(g)$$

3. $$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}(aq)}$$

4. $$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6(aq)}$$

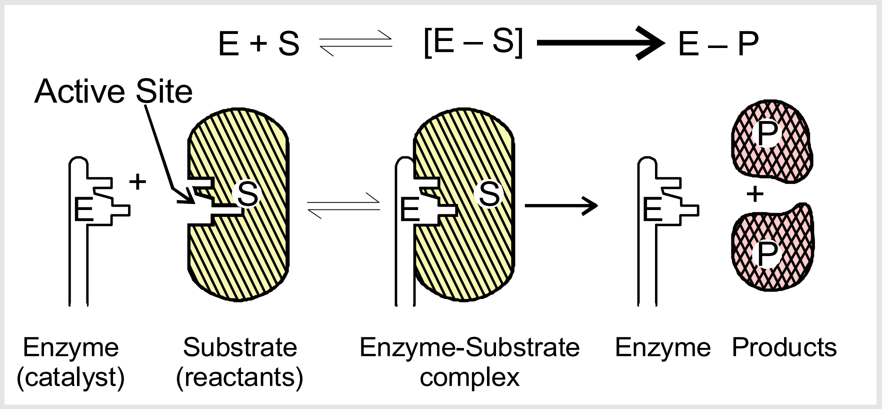
5. $$\underset{\text{Urea}}{NH_2CONH_2} + H_2O \xrightarrow{\text{Urease}} 2NH_3 + CO_2$$

6. $$\text{Milk} \xrightarrow[\text{enzyme}]{\text{Lacto bacilli}} \text{curd}$$

7. $$\text{Protein} \xrightarrow{\text{Pepsin}} \text{Amino acid.}$$

Characteristics of enzyme-catalysis

1. Highly efficient -1 molecule of enzyme may transform one million molecules of reactant per minute.
2. Specific for given reaction.
3. Highly active under optimum temperature (298 -310K) and optimum pH (b/w 5–7)
4. Increasing activity in presence of activators and co-enzymes (non protein part) eg. Amylase in presence of NaCl i.e., Na^+ are catalytically very active.
5. Influence of inhibitors and poisoned.



Mechanism of enzyme catalysed reaction

Step I $E + S \rightarrow ES^+$

Step II $ES^+ \rightarrow E + P$

Industrial catalytic processes

Habers process $N_2 + 3H_2 \rightarrow 2NH_3$	**Catalyst** Fe, Mo as promoters
Ostwald's process $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$ $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $4NO_2(g) + 2H_2O(l) + O_2(g) \rightarrow 4HNO_2(g)$	Platinsed asbestos
Contact process $2SO_2(g) + O_2(g) \rightarrow 2SO_3$ $SO_3(g) + H_2SO_4 \rightarrow H_2S_2O_7(l)$ Oleum $H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(aq)$	Platinsed Asbestos or V_2O_5

Colloids : colloidal solutions are intermediate between true solution and suspension

* Heterogenous mixture

* Size of colloidal particles varies from 1 nm to 1000 nm

Dispersed phase (DP) : The component present in a small proportion (like solute in solution)

Dispersion medium (DM): The component present in large proportion.

Types of colloids	DP $\longrightarrow$ DM	example
Foam	$G \xrightarrow{in} L$	Soap lather
Solid sol	G or $S \xrightarrow{in} S$	Pumice stone, Gems
Aerosol	S or $L \xrightarrow{in} G$	fog, cloud, Smoke
Emulsion	$L \xrightarrow{in} L$	milk
Gel	$L \xrightarrow{in} S$	Cheese
Sol	$S \xrightarrow{in} L$	Paints

Lyophilic Colloids : The colloidal solution in which the particles of the dispersed phase have great affinity for the dispersion medium

* Liquid loving in nature.

* Reversible sols. (reconstituted by remixing)

* Cannot be easily coagulated.

Lyophobic colloids :

The colloidal solutions in which the particles of the dispersed phase have no affinity for the dispersion medium are called lyophobic colloids.

* liquid hating in nature

* Irreversible sols

* Need stabilising agent for their preservation

* prepared by special methods.

Multimolecular colloids :

On dissolution , a large number of atoms or smaller molecules aggregate together to form species having size in the colloidal range. The colloid so formed is called multimolecular colloid eg gold, sulphur sol.

Macromolecular colloids :

If the size of particles of substance (dispersed phase) is in colloidal range. eg starch cellulose, protein, enzymes, polythene, nylon, rubber.

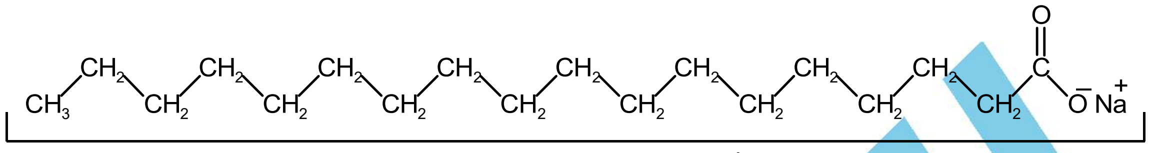
Associated colloids :

Some substances (D.P) at low concentration behave as electrolytes, but at higher concentration behave as colloids. (Due to formation of aggregates – micelles)

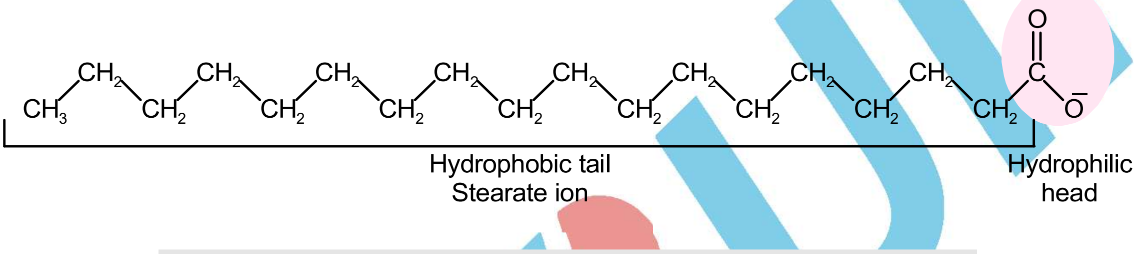
CMC -(Critical micelleconcentration)

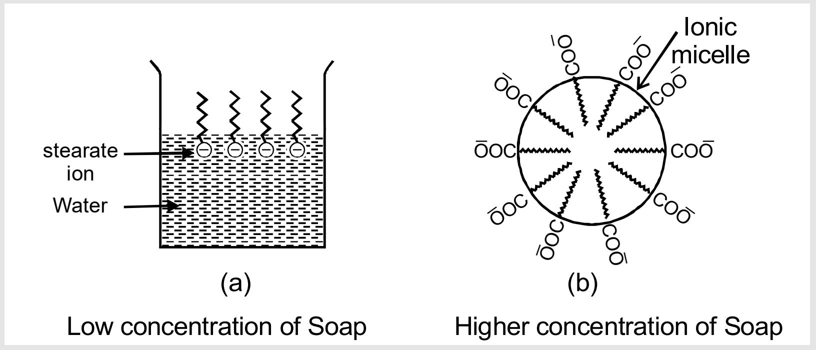
(T_k) Kraft temperature – micelle formation above particular temperature.

Soap – Na or K salt of higher fatty acids eg sodium stearate $C_{17}H_{35}COO^-Na^+$



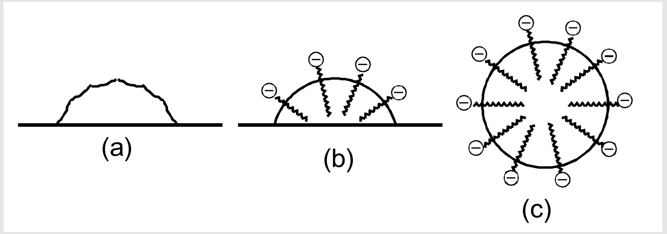
Sodium stearate ($C_{17}H_{35}\overset{-}{COO}\ \overset{+}{Na}$)





(a) Low concentration of Soap

(b) Higher concentration of Soap



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

Methods of preparation of colloids :

(1) Chemical methods

$2H_2S + SO_2 \xrightarrow{\text{Oxidation}} 3S(sol) + 2H_2O$

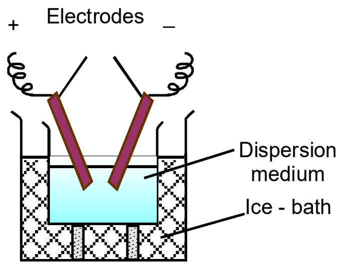
$As_2O_3 + 3H_2S \xrightarrow[\text{decomposition}]{\text{double}} As_2S_3(sol) + 3H_2O$

$2AuCl_3 + 3HCHO + 3H_2O \xrightarrow{\text{reduction}} 2Au(Sol) + 3HCOOH + 6HCl$

$FeCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} Fe(OH)_3(Sol) + 3HCl$

2. **Bredig's Arc method (Electrical disintegration):**

Electric spark 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.



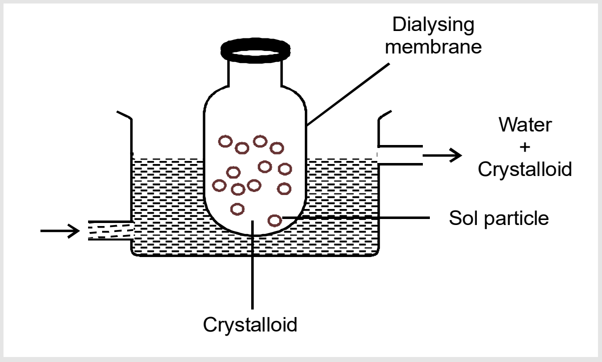
Bredig's Arc method

3. **Peptization:**

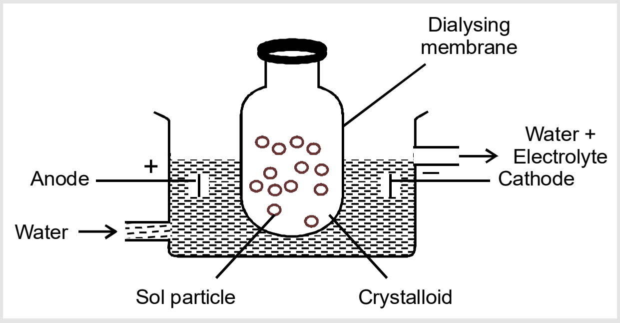
The process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte (peptizing agent)

Purification of colloidal solution

Dialysis: The process of removing a dissolved substance from a colloidal solution by means of diffusion. through a suitable membrane [animal membrane (bladder), parchment Paper or cellophane sheet.)



Dialysis



Electro-dialysis

Ultrafiltration :

Separating the colloidal particles by specially designed filters (prepared by soaking the filter paper in a collodion solution). To speed up the process pressure or suction is applied

Collodion - 4% solution of nitrocellulose in mixtures of alcohol and ether.

Properties of colloidal solution

1. **Colour -** depends on λ of light scattered eg (1) Mixture of milk and water appears blue when viewed by reflected light and red when viewed by transmitted light (2) Finest gold sol is red in colour: as the size increases, it appears purple, their blue and finallty golden.

2. Colloidal particles are always charged: either + or –)

	Positive charged sols	**Negative charged sols**
1	Hydrated metal oxides eg. $Al_2O_3.xH_2O$, $CrO_3.xH_2O$ $Fe_2O_3.xH_2O$ etc.	Metals eg Cu, Ag, Au Sols
2.	Basic dye stuffs eg. methylene blue Sol.	*Acid dye stuffs eg eosin,congo red Sols.
3.	Haemoglobin (blood)	Metallic sulphides eg As_2S_3,Sb_2S_3,CdS Sols
4.	Oxides eg. TiO_2 Sol.	*Sols of starch, gum, clay, Charcoal,

Helmholtz electrical double layer : When the colloidal particles acquire (–) or (+) charge by selective adsorption of one of the ions it attracts counter ions from the medium forming a second layer as shown below

AgI/ I^- K^+ AgI/Ag^+ I^-

The combination of these 2 layers of opposite charge around colloidal particles is called helm holtz electrical double layer

Electrokinetic potential (Zeta potential):

The potential difference between the fixed layer and the diffused layer of colloidal solution having opposite charges is called zeta potential.

3. **Colligative properties :** (RLVP, Osmotic pressure, depression in freezing pt, elevation in boiling point) are small or lower as compared to true solution
4. Heterogeneous, stable solution
5. **Show Tyndall effect :**
6. **Brownian movement**
7. **Electrophoresis :** The movement of colloidal particles under an applied electric field is called electrophoresis.
8. **Electro-osmosis :** The movement of molecules of dispersion medium in an electric field is called electroosmoses.
9. **Coagulation or Precipitation :** The process of settling of colloidal partcles. When an electrolyte is added to the solution, the colloidal particles take up the ions having opposite charge from the electrolyte and get neutralised and thus, coagulated.

*** Hardy-Schulze rule :** It states that the coagulating power of an electrolyte is directly proportional to the fourth power of the valency of the oppositively charged ion of the electrolyte.

$$\text{Coagulating power} \propto (\text{ valency })4$$

For example : Negative solution As_2S_3 is coagulated faster by $AlCl_3$ than $MgCl_2$

In coagulation of negative sol, the flocculating power is in the order: $Al^{3+} > Ba^{+2} > Na^+$

Similarly, in the coagulation of a positive sol, the flocculating power is in the order

$[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{3-} > Cl^-$

Coagulating value : Min conc of an electrolyte in millimoles per litre required to cause precipitation of a sol in 2 hours.

*The smaller the quantity needed, the higher will be the Coagulating power of the ion.

Coagulation of lyophilic sols:

By adding (i) electrolyte or (ii) suitable solvent.

Protection of colloids:

When lyophilic colloid is added to 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.

*Protective power of different colloids is expressed in gold number.

$$\text{Protecting Power} \propto \frac{1}{\text{Gold number}}$$

Emulsions :

The colloidal system in which both the dispersed phase and dispersion medium are in liquid state is called emulsion. eg. Milk, cod liver oil.

Emulsification: The process of making emulsion

Emulsions are of 2 types

1. (O/W) Oil - in - Water : Emulsion in which, oil acts as the dispersed phase and water act as dispersion medium eg. Vanishing cream.

eq. Milk
Fat or oil (D.P)
Water (D.M)

2. (W/O) Water - in - Oil: Emulsion in which water acts as the dispersed phase and oil act as dispersion medium

eg. Butter, Cream cod liver oil

Water (D.P) Oil (D.M)

Emulsifying agent : The emulsions are stabilized by adding a stabilizing substance called emulsifying agent eg soaps, detergents etc.

*Emulsifying agent for O/W emulsion are proteins gums, soaps etc.

*Emulsifying agent for W/O emulsion are lamp black heavy metal salts of fatty acids, long chain alcohols, etc.

Demulsification : The separation of an emulsion into it components

* It is done by centrifugation, heating, freezing etc.

*Soil is a colloid in which humus act as protective colloids

***Delta :** when river water meets sea water the electrolytes present in sea water coagulate the colloidal solution of clay resulting in its deposition.

Applications of colloids

1. Precipitation of smoke - By contrell precipitator.
2. Purification of drinking water - by Alum.
3. Medicines -eg(1) colloidal antimony is used in kalaazar (ii) argyrol is silver sol. used as eye lotion (iii) Milk of magnesia for acidity in stomach
4. Tanning -The process of hardening leather.
5. Cleansing action of soap.
6. Photo graplic films are coated with emulsions of light sensitive silver bromide in gelatin over cellulold film.
7. Rubber is obtained by coagulation of latex.
8. Paint, ink, synthetic plastic, cement etc are colloidal solutions.

SOLVED PROBLEMS

Q.1 Give the sign of ΔH and ΔS for adsorption process.

Or

What is the sign of ΔH and ΔS when bromine gas gets adsorbed on charcoal?

Ans. ΔH is –ve (enthalpy decreases) and ΔS = – ve (entropy decreases).

Q.2 How can we make dialysis fast ?

Ans. By applying electric field.

Q.3 Write down the heterogeneous catalyst involved in the polymerisation of ethylene.

Ans. $((C_2H_5)_3Al + TiCl_4)$ Zeigler – Natta catalyst.

Q.4 Artificial rain can be caused by spraying common salt on the clouds. How ?

Ans. Clouds are colloidal dispersion of water particles in air. These colloidal water particles cause some change on applying salt in the cloud, coagulation of water particles takes place.

Q.5 What do you understand by activation of adsorbent? How is the achieved ?

Ans. **Activation of adsorbent :** The phenomenon which involves the increasing of the adsorbing power of an adsorbent by suitable means is known as activation of adsorbent. Activation of adsorbent refers to its clean surface and fine particle size. Cleaning can be done by ultra high vacuum while large surface area can be achieved by grinding.

Q.6 What role does adsorption play in heterogeneous catalysis?

Ans. Heterogeneous catalysis generally proceeds through the adsorption of reactants on the surface of catalyst. In such type of catalysis generally adsorbent is solid while the reactants are gaseous. The reactions occur at the surface of the catalyst where the gaseous molecules get adsorbed either by physical adsorption or by chemical adsorption.

Q.7 Why is adsorption always exothermic?

Ans. When a gas is adsorbed on the surface of solid its entropy decreases, it means Δs is –(ve). Now, $\Delta G = \Delta H - T\Delta S$ and for the process to be spontaneous, free energy change (ΔG),must be negative. If ΔH has sufficient high –(ve) value as $T\Delta S$ is positive. Thus, in an adsorption process, which is spontaneous, a combination of these two factors makes ΔG negative. As the adsorption proceeds, ΔH become less and less negative ultimately ΔH becomes equal to $T\Delta S$ and ΔG become zero at equilibrium state.

Q.8 Action of soap is due to emulsification and micelle formation. Comment.

Ans. Soap molecules adsorb on to the dirty (oily) surface and try to emulsify it. Soap micelles do solubilize the insoluble dirt as greasy material.

Q.9 What do you mean by activity and selectivity of catalysts?

Ans. **Activity :** Activity of a catalyst refers to the chemisorption of reactants reasonable strongly. It has ability to increase chemical reaction. For example : Transition metals show catalytic activity. (Maximum activity group 7-9 metals).

Selectivity : Selectivity of a catalysts is its ability to speed up a reaction to yield a particular product. For example: $CO + H_2$ combine to form CH_4 when Ni is the catalyst and methanal when Cr_2O_3 is catalyst.

$CO + 3H_2 \xrightarrow{Pt} CH_4 + H_2O$ Methane

$CO + 2H_2 \xrightarrow{Cu/ZnO\text{-}Cr_2O_3} CH_3OH$ Methyl alcohol

$CO + H_2 \xrightarrow{Cu} HCHO$ Formaldehyde

Q.10 Explain the term with suitable examples :

(i) Alcosol (ii) Aerosol (iii) Hydrosol.

Ans. **(i) Alcosol :** Alcosols are those sols in which the dispersion medium is alcohol.

For example : Collodion (a colloidal solution of cellulose nitrate in ethyl alcohol).

(ii) Aerosol : Aerosol are those sols in which the dispersion medium is air.

For example : Smoke, dust.

(iii) Hydrosol : Hydrosol are those sols in which the dispersion medium is water.

For example : Starch solution, gold solution.

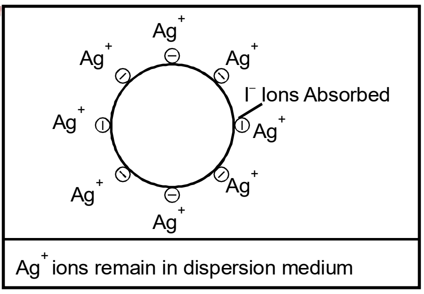
Q.11 Comment on the statement that "colloid is not a substance but a state of substance."

Ans. Colloidal solution is made up of dispersed phase and dispersion medium. The size of the particles of dispersed phase varies between 1 nm to 1000 nm in colloidal solution. On the basis of size of particles, we can distinguish between colloidal solution and true solution. For example : NaCl in water forms true solution but in benzene forms colloidal solution. A soap forms true solution in alcohol but colloidal solution in water.

Q.12 Discuss the origin of charge on colloidal particles.

Or

How does the theory of selective adsorption, explain the origin of charge on colloidal particles.

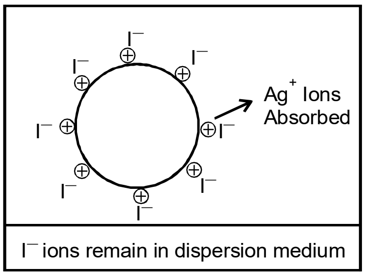


Ag⁺ ions remain in dispersion medium

Ans. **Due to selective adsorption of ions:** These particles constituting the dispersed phase adsorb those ions preferentially which are common with their own lattice ions. For example, if silver nitrate solution is added to an aqueous solution of potassium iodide, the silver iodide will adsorb the I^- (Common ions) from the dispersion medium to form a negatively charged sol.

$$AgNO_3 + KI \rightarrow AgI$$

$$AgNO_3 + \underset{\text{Dispersion medium}}{I^-} \rightarrow \underset{\text{Negative sol.}}{AgI/I^-}$$



I⁻ ions remain in dispersion medium

However, if silver iodide is formed by adding potassium iodide to silver nitrate solution, the sol is positively charged due to the adsorption of Ag^+ ions (Common ions) present in the dispersion medium.

$$KI + AgNO_3 \rightarrow AgI$$

$$AgI + \underset{\text{Dispersion medium}}{Ag^+} \rightarrow \underset{\text{Positive sol.}}{AgI / Ag^+}$$

EXERCISE – I UNSOLVED PROBLEMS

Q.1 Illustrate with examples :

(i) Lyophillic and lyophobic solutions,

(ii) Multimolecular and macromolecular colloids.

(iii) Homogeneous and heterogeneous catalysis.

Q.2 What are the two classes of emulsions ? Give one example of each class. State one activity to test the type of an emulsion.

Q.3 How do size of particles of adsorbent, pressure of gas and prevailing temperature influence the extent of adsorption of a gas on a solid?

Q.4 Explain the following observation:

(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.

Q.5 What is meant by adsorption isotherm ?

What is the effect of pressure on physical adsorption?

Explain freundlich adsorption isotherm

Q.6 (a) What are micelles ? How do they differ from ordinary colloidal particles ? Give two example of micelles forming substances.

(b) State Hardy-Schulze rule.

Q.7 Define adsorption. Write any two features which distinguish physisorption from chemisorption.

Q.8 Explain the following terms with a suitable example in each case:

(i) Shape - selective catalysis (ii) Dialysis

(iii) Emulsification (iv) Tyndall effect

EXERCISE – II BOARD PROBLEMS

Q.1 What causes Brownian movement of a colloidal solution?

Q.2 Which has a higher enthalpy of absorption physisorption or chemisorption?

Q.3 Describe electrophoresis briefly.

Q.4 Why does physisorption decrease with the increase of temperature

Q.5 In chemisorption why x/m initially increases and then decreases with rise in temperature?

Q.6 Distinguish between homogeneous and heterogeneous catalysis. What role does adsorption play in heterogeneous catalysis?

Q.7 Distinguish between micelles and colloidal particles. Give one example of each.

Q.8 What is the 'coagulation process?

Q.9 What happens in the following activities and why?

(i) An electrolyte is added to a hydrated ferric oxide sol in water.

(ii) A beam of light is passed through a colloidal solution.

(iii) An electric current is passed through a colloidal solution.

Q.10 Describe the following:

(i) Tyndall effect (ii) Shape-selective catalysis

Q.11 What is meant by coagulation of a colloidal solution? Name any method by which coagulation of lyopholic sols can be carried out.

Q.12 Define the following

(i) Peptization (ii) reversible sols

Q.13 Classify colloids where the dispersion medium is water. State their characteristics and write an example of each of these classes.

Q.14 Explain what is observed when

(i) an electric current is passed through a sol (ii) a beam of light is passed through a sol.

(iii) an electrolyte (say NaCl) is added to freeic hydroxide sol.

Q.15 Define 'peptization'.

Q.16 Write three distinct features of chemisorptions which are not found in physisorptions.

Q.17 What is meant by coagulation of a colloidal solution ? Name any method by which coagulation of lyophobic sols can be carried out.

Q.18 What is especially observed when a beam of light is passed through a colloidal solution ?

Q.19 Define the following terms with an example in each case :
(i) Macromolecular sol (ii) Peptization (iii) Emulsion