21. SURFACE CHEMISTRY

THE COLLOIDAL STATE

1. INTRODUCTION

The foundation of Colloidal Chemistry was laid down by an English Scientist, Thomas Graham, in 1861. He classified the soluble substances into categories depending on their rates of diffusion through animal and vegetable membranes or parchment paper. He observed that certain substances diffuse freely through the membrane whereas others do not diffuse. The former types of substances are crystalline in nature like sugar, common salt etc while the latter were termed as colloids. Thus,

Crystalloids: The ones having higher rates of diffusion.

Colloids: The one having slower rate of diffusion.

However, this classification has now been rejected because some substances, like NaCl, diffuse fast in water but slow in alcohol whereas, some other substances like RCOONa diffuse slowly in water and rapidly in alcohol. Therefore, a new term **colloidal state** was preferred.

Characteristics of Colloidal State

It is a particular state and not a class of compounds.

It is heterogeneous state, i.e., number of phases >= 2

It must have 2 phases: DISPERSED PHASE & DISPERSION MEDIUM

The one phase dispersed in other is known as dispersed phase (or D.P.) or internal phase or discontinuous phase whereas, the other in which dispersions are made is known as dispersion medium (or D.M.) or external phase or continuous phase.

Sol Particles

It is an intermediate state between true solution state and suspension state, i.e., particle size of dispersed phase usually called sol particles lies between true solution state and suspension state.

True solution	Colloidal state	Suspension
Solute + Solvent	D.P. + D.M.	Precipitate + Medium
Size Solute 1mμ or 10 Å	D.P. – 1mμ to 200 mμ	Precipitate – 200 mμ onwards

Characteristics of Sol particles:

(a) They have enormous surface area/gram as a result of their small size which gives rise to certain special properties of colloidal state.

(b) They are not detectable even under microscope.

(c) They do not settle down even under the influence of gravity.

(d) They usually carry charge: positive/negative

Illustration 1: What are the physical states of dispersed phase and dispersion medium of froth? **(JEE MAIN)**

Sol: Froth is a Mass of small bubbles in liquid that is caused by agitation.

Dispersed phase : Gas

Dispersion medium : Liquid

Illustration 2: Why medicines are more effective in colloidal state? **(JEE ADVANCED)**

Sol: Sol particles of a colloidal state has larger surface area and thus, shows more effective adsorption. So if the medicine is in colloidal state it will get adsorbed more effectively and will give better results.

2. CLASSIFICATION OF COLLOIDAL DISPERSIONS

(a) Classification based on the nature of D.M.

(i) D.M. is water : Hydrosols

(ii) D.M. is alcohol : Alcohols

(iii) D.M. is benzene : Benzosols

(iv) D.M. is air : Aerosols

(b) Classification based on the nature of charge

If dispersed phase particles carry +ve charge, it is +ve charge; it is +ve Sol If dispersed phase particles carry –ve charge; it is –ve Sol

(c) Classification based on the physical state

Table 21.1: Classification based on the physical state of D.P. and D.M.

Internal phase or Dispersed phase	External phase or dispersion medium	Colloidal Name	Examples
S	S	Solid sols	Alloys, ruby glass, gems or precious stones, marbles, optical and vision glasses
	L	Sols	Muddy water, gold sol, sols of protein, starch, agar and gelatin in water
	G	Aerosols of solids	Smoke, storm
L	S	Gels	Cheese, jams, jellies, curd, plants, fruits, vegetables, cementation

Internal phase or Dispersed phase	**External phase or dispersion medium**	**Colloidal Name**	**Examples**
	L	Emulsions	Butter, milk, blood, cosmetic products, e.g., shampoo, creams, emulsified oils, polish and medicines.
	G	Aerosols of liquids	Fog, clouds, mist
G	S	Solid foams	Pumice stone, styrene foam, rubber foam, porous pot, rubber pillows and mattresses
	L	Foam or froths	Froths, soap suds, air bubble
	G	Homogeneous system	Thus, not colloids

(d) Classification based upon interaction forces between the dispersed phase and dispersion medium:

(i) If strong interactive force exist between the dispersed phase and dispersion medium then such colloids are called Lyophilic colloids.

(ii) If no interactive forces exist between the dispersed phase and dispersion medium. Such colloids are called lyophobic colloids.

Table 21.2: Essential Differences between Lyophobic and Lyophilic Sols

Property	**Lyophobic Sols**	**Lyophilic Sols**
1. Surface Tension	Surface tension is usually the same as that of the medium (i.e. the liquid in which the particles are dispersed)	Surface tension is generally lower than that of the medium (i.e. the liquid in which the particles are dispersed)
2. Viscosity	Viscosity is about the same as that of the medium	Viscosity is much higher than that of the medium
3. Visibility	The particles, though invisible, can be readily detected under an ultra-microscope.	The particles cannot be readily detected even under an ultra-microscope.
4. Migration in an electric field	The particles migrate either towards anode or towards cathode in an electric field.	The particles migrate in either direction or not at all in an electric field.
5. Action of electrolytes	The addition of small quantities of electrolytes can cause precipitation (coagulation).	The addition of small quantities of electrolytes has little effect. Much larger quantities are needed to cause precipitation.
6. Reversibility	These are irreversible	These are reversible.
7. Hydration	The particles are not hydrated to a large extent	The particles are extensively hydrated. This is due to the presence of a number of polar groups in the molecules of lyophilic colloids as, for example, in polysaccharides, proteins, etc.

PLANCESS CONCEPTS

- Stability of lyophilic sols (reversible) is due to a thin layer of dispersion medium round dispersed phase particles whereas, the stability of lyophobic sols (irreversible) is due to the presence of charge on dispersed phase particles.
- If water is used as dispersion medium, lyophilic sols are called hydrophilic and lyophobic sols as hydrophobic sols.
- Inorganic sols, e.g. AgI, SnO_2, $Fe(OH)_3$, As_2S_3, CdS, S, in water etc are usually hydrophobic whereas organic sols, e.g. protein, gelatin, agar-agar, polymers, etc. in water are hydrophilic.

Vaibhav Krishnan (JEE 2009, AIR 22)

Illustration 3: Lyophilic sols are more stable than lyophobic colloids. Why? **(JEE MAIN)**

Sol: The lyophilic system contains highly solvated colloidal entities.

3. PREPARATION OF COLLODIAL SOLUTIONS

The primary consideration in the preparation of colloidal solution is that the dispersed particles should be within the size range of 1nm-100 nm. The lyophilic sols can be readily prepared since colloidal materials such as starch, gelatin, acacia, etc, when added to water swell up and spontaneously break into particles of matter of colloidal range. The lyophobic sols, however, require special techniques for their preparation. The methods consist either in

1. Breaking down the coarser aggregates into particles of colloidal size
2. Grouping molecules into larger aggregates of colloidal size. The methods belonging to these two categories are known as dispersion and condensation methods, respectively.

(a) Mechanical Dispersion: By breaking up suspension particles into colloidal size. The goal is achieved by:

(i) Grinding: Freshly precipitated mass + medium $\xrightarrow[\text{in grinder}]{\text{Grind}}$ sols

(ii) Peptization: Certain freshly precipitates, such as silver chloride, ferric hydroxide, aluminum hydroxide, can be converted into colloidal solutions by the addition of a small amount of a suitable electrolyte. An electrolyte having an ion in common with the material to be dispersed is required for sol formation. The peptization action is due to the preferential adsorption of one of the ions of the electrolyte by the particles of the material. As would be illustrated a little later in this chapter, as a result of the preferential adsorption of the ion which is more closely related chemically to the precipitate, the particles acquire a positive or a negative charge depending upon the charge on the ion adsorbed. Because of the presence of the same type of charge, the particles of the precipitate are pushed apart. The precipitate thus gets dispersed resulting in the formation of a stable sol.

(iii) Bredig arc method: Two metal electrodes are immersed in a liquid medium. Both of them are connected to a high tension battery by which an electric arc is produced between the electrodes. High temperature of the arc vaporizes some of the metal, which condenses on cooling to form sols. The heat generated during process is removed by putting system under ice cold water. The method is generally used for preparation of metal sols in water. A little amount of KOH in water prevents growth of sol particles and stabilizes the dispersion. Au sol in water, i.e., Purple of Cassius is obtained by this method.

(iv) Condensation Methods: Colloidal stems can be obtained by various chemical reactions such as double decomposition, oxidation, reduction, hydrolysis etc.

(b) Double Decomposition: A sol of arsenious sulphide is prepared by passing H_2S gas through a dilute solution of arsenious oxide and removing the excess H_2S by boiling

(i) $NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$

(ii) $As_2O_3 + 3H_2S \longrightarrow As_2S_3 + As_2S_3 + 3H_2O$

(c) Oxidation: A colloidal sulphur sol is obtained by the oxidation of an aqueous solution of hydrogen sulphide with air or sulphur dioxide.

(i) $H_2S + 2HNO_3 \longrightarrow 2NO_2 + S + 2H_2O$

(ii) $2H_2S + O_2 \longrightarrow 2S + 2H2O$

(iii) $2H_2S + SO_2 \longrightarrow 3S + 2H_2O$

(d) Reduction: Sols of metals such as silver, copper, gold and platinum are obtained by reducing the aqueous solutions of their salts by non-electrolytes such as formaldehyde, tannin, phenyl hydrazine, carbon monoxide and phosphorus. Zsigmondy prepared the gold hydrosol by reducing potassium aurate with formaldehyde. In the reaction, chlorauric acid, $H[AuCl_4].4H_2O$ first formed, is made to react with potassium carbonate in an aqueous solution to yield potassium aurate:

(i) $2H[AuCl_4] + 5K_2CO_3 \longrightarrow 2KAuO_2 + 5CO_2 + 8KCl + H_2O$

The resulting solution is heated and a dilute solution of formaldehyde is added drop-wise when reduction occurs according to the reaction:

(ii) $2KAuO_2 + 2CH_2O + K_2CO_3 \xrightarrow{\Delta} 2Au\ (sol) + 3HCO_2K + KHCO_3 + H_2O$

(e) Hydrolysis: Colloidal sols of heavy metals are obtained by the hydrolysis of the solutions of their salts. Thus, when a small amount of ferric chloride is added to boiling water, a red-brown sol of ferric hydroxide is obtained:

(i) $FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 + 3HCl$

(ii) This is because $FeCl_3 \longrightarrow Fe^{3+} + 3Cl^-$

(iii) And $Fe^{3+} + H_2O^- \longrightarrow \underset{\text{Sol}}{Fe(OH)_3} + 3H^+$

Boiling promotes the reactions because HCl formed is removed with water vapors from the system. In this reaction, iron oxychloride, FeOCl, formed as a result of incomplete hydrolysis of $FeCl_3$, is believed to act as the stabilizer:

(i) $FeCl_3 + H_2O \longrightarrow FeOCl + 2HCl$

Thus, the structure of the $Fe(OH)_3$ sol can be expressed by any of the following formulas depending upon which substance acts as a stabilizer:

1. $(m\ [Fe(OH)_3]_n FeO^+.(n - x)^- Cl^-)^* Cl^-$

2. $(m\ [Fe(OH)_3]_n Fe^+.3(n - x)Cl^-)3^* Cl^-$

3. $(m\ [Fe(OH)_3]_n H^+.(n - x)Cl^-)^* Cl^-$

(f) Exchange of Solvents: Sols can also be obtained by exchange of solvents. For instance, when a concentrated solution of sulphur in alcohol is poured in a large amount of boiling water, the alcohol evaporates leaving behind sulphur particles which form nuclei that rapidly grow into a colloidal solution.

Illustration 4: On passing H_2S in cold, dilute solution during group II qualitative analysis of basic radicals sometimes yellow turbid solution is obtained instead of precipitate. Explain. **(JEE ADVANCED)**

Sol: It is because of the formation of sol of As_2S_3 or CdS.

$As_2O_3 + 3H_2S \longrightarrow \underset{\text{sol}}{As_2S_3} + 3H_2O$

Illustration 5: Describe a chemical method each for the preparation of sols of sulphur and platinum in water. **(JEE ADVANCED)**

Sol: By bubbling H_2S gas in cold solution of an oxidizing agent like HNO_3 SO_2 or Br_2

(a) $H_2S + 2HNO_3 \longrightarrow 2H_2O + 2NO_2 + \underset{sol}{S}$

(b) $H_2S + Br_2 \longrightarrow 2HBr + \underset{sol}{S}$

(c) $2H_2S + SO_2 \longrightarrow 2H_2O + \underset{sol}{3S}$

Platinum sol can be prepared by reducing its salt solution by using suitable reducing agent like formaldehyde, $SnCl_2$, hydrazine, carbon monoxide etc.

$PtCl_2 + 2SnCl_2 \longrightarrow \underset{sol}{Pt} + 2SnCl_4$

4. PURIFICATION OF SOLS

Sols so obtained are contaminated with two types of impurities and need purification:

(a) **Insoluble impurities:** These are removed by simple filtration of impure sols. Impurities are retained on filter paper and sols are filtered.

(b) **Soluble impurities:** Special methods are required to separate these impurities.

  (i) **Dialysis:** The separation of soluble impurities from sols on the basis of their different rates of diffusion through parchment membrane (known as dialyser) is known as dialysis. If impurities are of electrolytic nature electro dialysis is preferred. The ions of electrolyte move faster than sol particles towards opposite electrodes and thus removed from sol.

  (ii) **Ultra filtration:** Ultra filters used for separation of soluble impurities from sols are specially prepared filters of uniform pore sizes obtained by dipping filters in colloid ion solution (4% nitrocellulose in alcohol + ether)

  (iii) **Ultra centrifuge:** Based on sedimentation technique.

PLANCESS CONCEPTS

The process of dialysis finds applications in the purification of blood by artificial machine when kidney fails.

Nikhil Khandelwal (JEE 2009, AIR 94)

5. PROPERTIES OF COLLOIDAL SOLUTIONS

(a) **Physical properties**

  (i) **Heterogeneity:** Sols are heterogeneous in nature.

  (ii) **Diffusibility:** Sol particles have slow rate of diffusion through parchment membrane.

  (iii) **Filterability:** Sol particles are passed through ordinary filter papers.

  (iv) **Non-Settling nature:** Sol particles do not settle down due to gravity.

- **(v) Viscosity and surface tension:** Viscosity and surface tensions of sols are almost similar to those of pure solvent in case of lyophobic colloidal solutions, viscosity is higher than the solvent and surface tension being lesser than the solvent used as dispersed medium for sols.
- **(vi) Visibility and size of the particles:** It is not possible even by the help of a most powerful microscope to see colloidal particles because clear image formation of a particle smaller in size than the wavelength of light used is not possible. However, zones of scattered light can be seen by a microscope and sometimes with naked eyes also.
- **(vii) Surface area and adsorption:** The surface area of the particles in colloidal state is appreciably larger than compared with an equal mass of the matter in coarse grained size. It is due to the larger surface area, sol particles show high tendency for adsorption. The property has got application in medicinal chemistry, where drugs are sold in form of sols.
- **(viii) Shape of sol particles and color:** The sol particles possess different shapes and size. Due to their different size and shape, they acquire different colors, because the nature of light absorbed and transmitted out depends upon size and shape of particle. A larger particle will absorb larger wavelength and will transmit shorter ones. Therefore, as the size of particles increases, the color approaches to violet one. That is why red gold sol on slow coagulation shows a color change from red to blue. Also, red sol particles are spherical and blue sol particles are disc like in gold Sol

(b) Colligative Properties: Like true solutions, colloidal solutions also exhibit colligative properties such as osmotic pressure, elevation in b. pt., depression in freezing point, lowering in vapor pressure.

(c) Optical Properties vis-a-vis Tyndall effect

- **(i)** All colloidal solutions are capable of scattering of light or opalescence.
- **(ii)** A beam of converging rays on passing through a colloidal solution, scattering of light by sol particles in all the directions, gives rise to a bright glowing cone (fig.1) when looking at it sideways. This is known as Tyndall effect.

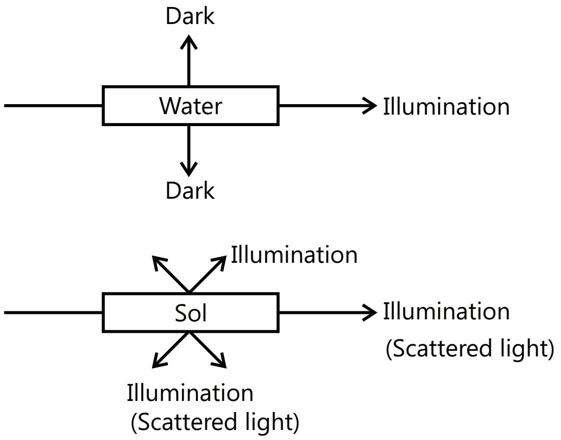


Figure 21.1: Scattering of light-Tyndall Effect

Some examples of Tyndall effects are:

- Blue color of sky and sea water.
- Visibility of tails of comets.
- Twinkling of stars.
- Visibility of sharp ray of sunlight entering through a slit in dark room.
- Visibility of projector path and circus light.

PLANCESS CONCEPTS

The scattering of light depends upon wavelength of light used: Scattering $\alpha(1/\lambda^4)$: that is why scattering of blue-violet light is maximum.

Saurabh Gupta (JEE 2010, AIR 443)

(d) **The Brownian movement:** Robert Brown noticed the irregular or chaotic motion of (pollen grains) particles suspended in water. This was later on named as Brownian motion. Later on Zsigmondy after the discovery of ultramicroscope (based on Tyndall effect) noticed the similar irregular motion of the images of sol particles (figure) and concluded that colloidal particles move much more vigorously than small particles.

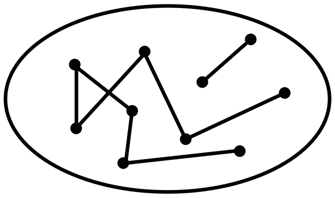


Figure 21.2: Brownian movement - zig-zag motion of a colloidal particle.

Applications of Brownian motion are

- **(i)** For an explanation for the stability of colloidal solutions.
- **(ii)** For an experimental set up to determine Avogadro's number
- **(iii)** For an explanation of kinetic theory of matter.

PLANCESS CONCEPTS

Brownian motion is not observed in suspension, however spontaneous movement of solute particles in solvent (i.e., true solution) also show Brownian motion.

Neeraj Toshniwal (JEE 2009, AIR 21)

6. ELECTRICAL PROPERTIES

The charge:

(a) Charge on sol particles is a fundamental factor for their existence, i.e., no charge on dispersed phase particles, no stability to colloidal solutions.

(b) It is the charge on sol particles, which keeps them apart and prevents them from coming closer to each other to coagulate.

(c) Sol particles either carry +ve or –ve charge.

(d) Metal sols are –ve; blood is –ve, smoke is –vely charged.

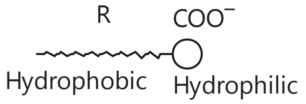
6.1 Origin of Charge

(a) Frictional electricity; Due to friction between D.P. and D.M.

(b) Due to electron capture by sol particles.

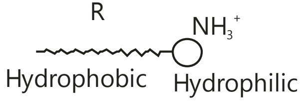
(c) Nature of dispersed phase: The nature of dispersed phase also contributes for the charge on sol particles.

(a) $RCOONa \rightarrow RCOO^- + Na^+$



$RCOO^-$ ions undergo aggregation to from sol particles and thus, they carry -ve charge.

(b) $RNH_3Cl \rightarrow RNH_3^+ + Cl^-$



RNH_3^+ ions undergo aggregation to form sol particles and thus, they carry +ve charge.

(d) **Preferential ion adsorption theory:** According to this theory sol particles possesses the tendency for adsorption of common ion present in solution and thereby, acquiring their charge, e.g.

Addition of KI drop by drop to dilute, cold solution of $AgNO_3$ gives rise to +ve sol of AgI, since, AgI particles adsorb Ag^+ ions present in excess in solution.

$$KI + \underset{\text{Excess}}{AgNO_3} \longrightarrow AgI + KNO_3$$

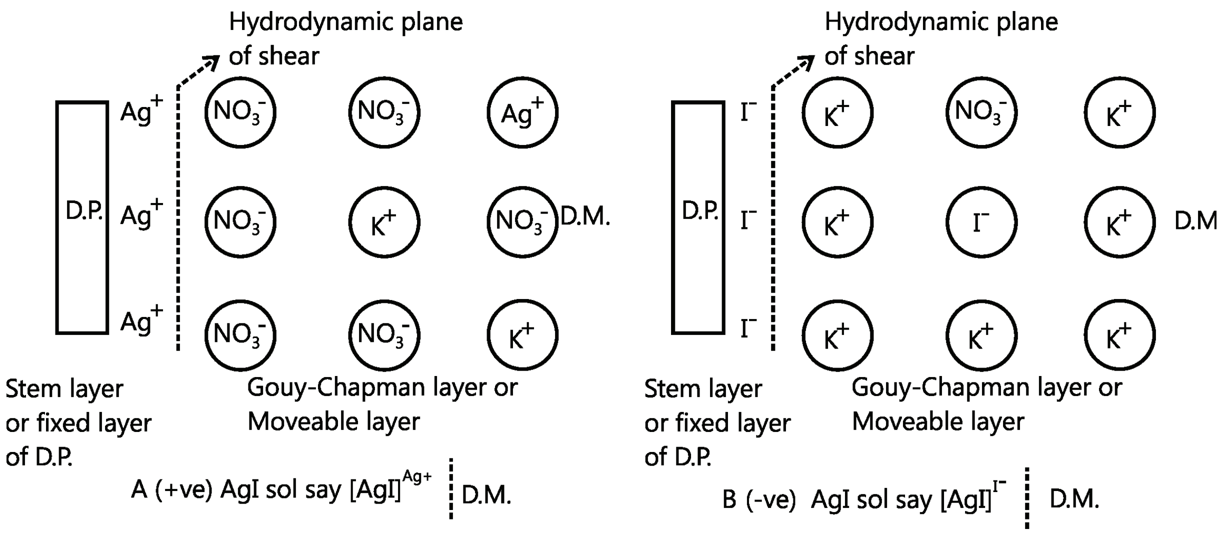
$$[AgI]^{Ag^+} \ \vdots \ Ag^+, NO_3^-, K^+$$

Similarly, addition of $AgNO_3$, drop by drop to dilute, cold solution of KI gives rise to –ve sol of AgI, since, AgI particles adsorb I^- ions present in excess in solution.

$$AgNO_3 + \underset{\text{Excess}}{KI} \longrightarrow AgI + KNO_3$$

$$\left[AgI\right] \vdots I^-, NO_3^-, K^+$$

6.2 Distribution of Charge



A (+ve) AgI sol say $[AgI]^{Ag^+} \vdots$ D.M.

B (-ve) AgI sol say $[AgI]^{I^-} \vdots$ D.M.

Figure 21.3: Distribution of charge

(a) Helmholtz gave electrical double layer concept for distribution of charge on sol particles.

(b) One layer is made up of dispersed phase carrying either +ve or –ve charge adhered on it. This is fixed layer.

(c) Other layer is made up of dispersion medium carrying +ve as well as –ve charges distributed in it. This is movable layer.

(d) Two layers are separated by an imaginary plane known as hydrodynamic plane of shear.

(e) The net charge on fixed layer is just equal and opposite to that on movable layer.

(f) The potential difference set-up across the surface of separation of two oppositely charged layers just in contact with each other is known as electro kinetic potential or zeta potential.

7. SOME OTHER IMPORTANT PHENOMENA

7.1 Cataphoresis or Electrophoresis

(a) Reuss observed the migration of colloidal particles under the influence of electrical field and the phenomenon was named as cataphoresis or electrophoresis.

(b) Sol particles carry charge and thus, move towards opposite electrodes.

(c) The migration velocity of sol particles is almost equal to the velocity of ions and is of the order of 10–5 cm sec–1 under a potential gradient of 1 volt cm–1.

(d) The phenomenon has found applications in:

  (i) Determining nature of charge on sol particles.

  (ii) Determining electrokinetic potential.

  (iii) Coagulation

7.2 Electro-Osmosis

The movement of the dispersion medium under the influence of electrical field when the dispersed phase particles are prevented from moving is known as electro-osmosis.

7.3 Coagulation or Flocculation

When an electrolyte is added to colloidal solution, the particles of the solution take up oppositively charged ions and thus, get neutralized. The neutral particles then comes closer and get accumulated to form bigger particles which settle down. Hence coagulations is defined as a process which involves precipitation of a colloidal solution by addition of excess of electrolyte.

Coagulation Value

Coagulation value is the minimum amount of electrolyte required to coagulate a definite amount of sol.

E.g. For +ve sol -ve ion of electrolyte is effective ion:

Coagulation value: $KNO_3 > K_2SO_4 > K_3PO_4 > K_4Fe(CN)_6$

Coagulation power: $NO_3^- < SO_4^{2-} < PO_4^{3-} < Fe(CN)_6^{4-}$

For –ve sol +ve ion of electrolyte is effective ion:

Coagulation value: $KNO_3 > Ba(NO_3)_2 > Al(NO_3)_3 > Th(NO_3)_4$

Coagulation power: $K^+ < Ba^{2+} < Al^{3+} < Th^{4+}$

Illustration 6: A negatively charged yellow sol of As_2S_3 on mixing with a +vely charged $Fe(OH)_3$ red sol in equivalent amount give rise to colorless solution. Why? **(JEE MAIN)**

Sol: This is because the charges on sol particles neutralize to cause mutual coagulation and thus dispersed particles of As_2S_3 and $Fe(OH)_3$ are settled down leaving water, which is colorless.

7.4 Lyotropic Series

Hofmeister studied the efficacy of various ions on coagulation of lyophobic sols and the results obtained were known as Lyotropic series of Hofmeister series

For –ve sol: $Mg^{2+} > Ca^{2+} > Ba^{2+} > Na^{+} > K^{+}$

For +ve sol: $SO_4^{2-} > Cl^{-} > NO_3^{-} > ClO_3^{-} > I^{-}$

7.5 Isoelectric Point

Addition of electrolyte to sol particles, neutralizes their charge and thus, electrokinetic potential approaches to zero. At this point sol particles do not carry charge and are either coagulated or just to coagulate; however, they become inert towards cataphoresis. This condition is known as isoelectric point, at which the colloidal particles do not carry charge and possess minimum stability.

7.6 Protective Action of Lyophobic Colloids and Gold Number

We know that lyophobic sols (like metal sols) are unstable and are easily coagulated by addition of electrolytes. However, it is observed that if a lyophilic colloid is added to lyophobic one, the latter is not coagulated easily by the addition of electrolytes. The process is called protection and the lyophilic sols used for protection are known as protective colloids. The protective action is generally so strong that the resulting sol is reversible i.e. it can be evaporated to dryness and then peptized simply by shaking with water to get the Sol Protargol and Argyrol used as eye drops are protected forms of colloidal silver.

Zsigmondy introduced the term gold number to measure the protective powers of different colloids. Gold number is number of milligrams of dry colloids which when added to 10 mL of a standard red gold sol (0.0055% AU) will just prevent its coagulation (indicated by change of color from red to blue) on addition of 1 mL of 10% sodium chloride solution rapidly to it. Smaller the value of the gold number of a protective colloid, the greater is its protective action.

Illustration 7: What is electrostatic precipitation of carbon? **(JEE ADVANCED)**

Sol: The method is used to control air and soil pollution. The apparatus is known as Cottrell's precipitator. Smoke formed in industries contains carbon particles which are negatively charged. Before it comes out from the chimney, it is passed through a chamber containing plates at high tension, i.e., high electrode potential. The carbon particle gets attracted towards anode and loses their charge at anode and get precipitated.

Illustration 8: Gold number for different lyophilic (A, B, C, D) are in the order A > B > C > D. Which one is more powerful protective colloid and why? **(JEE MAIN)**

Sol: Smaller the value of the gold number of a protective colloid, the greater is its protective action.

Thus D is most powerful protective colloid.

Illustration 9: The coagulation of 100 mL of colloidal solution of gold is completely prevented by 25g of starch to it before adding 10 mL of 10% NaCl solution. Find out the gold no. of starch. **(JEE ADVANCED**)

Sol: The values given cannot be altered as this is experimental fact. Thus, such type of calculations should not be made. In order to find out gold no. we have to use 10 mL gold solution of given sample and must observe the coagulation by adding 1 mL of 10% NaCl taking different amount of protective colloid each time.

8. EMULSIONS

(a) A dispersion of liquid droplets in another liquid, the two liquids should be immiscible.

(b) Emulsions are of two types; normally one of the two constituents of emulsions is water.

  (i) Water in oil or w/o: D.P. is water; D.M. is oil, e.g., butter, cream

  (ii) Oil in water or o/w/: D.P. is oil; D.M. is water, e.g., milk.

(c) The interconversion of phases in emulsion is known as phase inversion, e.g. creaming of milk (milk: fat in water, cream: water in fat.)

Emulsifying agents: Emulsions, like other colloidal systems are unstable and are stabilized by the addition of a third component known as emulsifying agent or emulgents or emulsifiers. In the absence of an emulsifying agent the dispersed droplets coalesce together and the two liquids are separated into separate layers.

Commonly used emulsifiers are surfactants, polymers and metal oxides and hydroxides in finely divided states.

9. GELS

Liquid dispersions in solid are known as gels, e.g. curd, cheese, etc. Liquid rich systems are known as jellies. Gels too are unstable and stabilized by gelling agent, e.g. gelatin.

Some remarkable properties of gels are:

(a) **Syneresis or weeping of gels:** Spontaneous outcome of internal liquid without disturbing gel structure.

(b) **Imbibition or swelling:** Gels on keeping in contact with their dispersed phase takes in considerable amount of it and swells up.

(c) **Thixotropy or melting by touch:** Outcome of internal liquid on applying shear to gels and thus, gel structure is also disturbed.

(d) **Periodic precipitation:** Precipitation reactions, if carried out in gel medium, layers or rings of precipitates are formed at definite intervals in order of geometrical progression.

10. ASSOCIATED COLLOIDS

10.1 Micelles

The substances which at low concentration in a medium behave as normal strong electrolytes but at higher concentration exhibit colloidal properties due to the formation of aggregated particles are called associated colloids. The aggregated particles thus formed are called micelles.

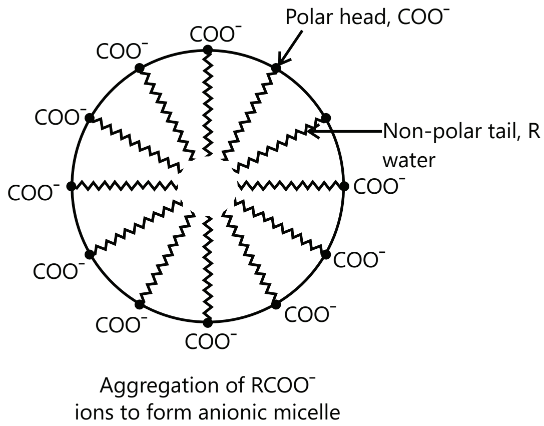


Figure 21.4: Micelle Formation

Their formation takes place above a particular temperature called Kraft temperature (T_K) and above a particular concentration called **Critical Micelle concentration** (CMC). The minimum concentration of surfactant at which micelle formation starts is Critical Micelle Concentration (CMC).

PLANCESS CONCEPTS

Lesser is CMC of surfactant, more is its surface activity and detergency.

The micellisation nature depends upon the hydrophilic lipophilic balance (HLB) in a surfactant molecule. More is the hydrophobic character in hydrocarbon tail lesser is the CMC of surfactant molecule in aqueous solution, i.e., CMC of $CH_3(CH_2)_{n_1}SO_4Na$ is lower than CMC of $CH_3(CH_2)_{n_2}SO_4Na$ when $n_1 > n_2$ in aqueous solution.

In other words longer is hydrocarbon chain lesser is its CMC. The surfactant molecules with linear hydrophobic chain possess the lower CMC than the corresponding surfactant molecules with branched chain in aqueous solution.

Aman Gour (JEE 2012, AIR 230)

Multimolecular Colloids: A multimolecular colloid consists of aggregated atoms or molecules as colloidal particles of diameter less than 1 nm, e.g. gold, sulphur Sol

Macromolecular Colloids: In a macromolecular colloids, the dispersed phase particles are themselves macromolecules (polymers), e.g., protein Sol

PLANCESS CONCEPTS

- Macromolecular colloids partly dissolves to form homogeneous solution and partly in colloidal nature (heterogeneous).
- Macromolecular colloids possess higher viscous nature due to high degree of solution.
- Macromolecular colloidal solution show larger deviations from ideal nature because of larger size and shape.

Nitin Chandrol (JEE 2012, AIR 134)

Illustration 10: What is the difference between multimolecular and macromolecular colloids? Give one example of each. How are association colloids different from these two types of colloids? **(JEE MAIN)**

Sol:

Multimolecular Colloids	Macromolecular colloids
Multimolecular colloids are dispersed particles made of aggregates of many molecules.	Macromolecular colloids are molecularly dissolved solutions of a polymer (due to large size of polymer molecular, it takes colloidal state)
These are lyophobic colloids.	They are lyophilic colloids.
E.g. As_2S_3 Sol	E.g. Starch solution

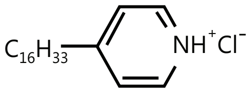
Association colloids: These are also lyophilic colloids but are formed by the aggregation of soap or detergent molecules in solution above CMC (these are micellar colloids).

11. SURFACTANTS AND DETERGENTS

Surfactants: Substances which possess surface activity i.e., the property to lower the surface tensions of liquids or the tendency to increase surface area. Surfactants are classified into three categories:

(a) Anionic surfactants: The anionic part of surfactant molecule possesses hydrophobic and hydrophilic particles and thus give rise to anionic micelles, e.g., sodium palmitate ($C_{15}H_{31}COONa$), sodium locate ($C_{17}H_{33}COONa$), sodium dodecyl sulphate ($C_{12}H_{25}SO_4Na$), etc.

(b) Cationic surfactants: The cationic part of surfactant molecule possesses hydrophilic and hydrophobic moieties and thus give rise to cationic micelles, e.g. octadecyl ammonium chloride ($C_{18}H_{37}NH_3^+Cl^-$), cetyl trimethyl ammonium chloride [$C_{16}H_{33}(CH_3)_3N^+Cl^-$], cetyl pyridinium chloride



(c) Non-ionic surfactant: The whole molecule of non-ionic surfactant possess non-dissociation nature and due to the presence of hydrophilic and hydrophobic moities in non-ionic surfactant undergoes micelle formation, e.g. poly oxy ethylene glycol derivatives, e.g., C_8H_{2n+1} $(OCH_2CH_2)m{\cdot}OH$.

Detergents: Substances which possess surface activity as well as detergency (i.e., cleansing action).

PLANCESS CONCEPTS

All detergents are surfactants but all surfactants are not detergents.

Rohit Kumar (JEE 2012, AIR 79)

Soaps: Metal salts (preferably alkali metals) of higher fatty acids. These belong to anionic class of detergents.

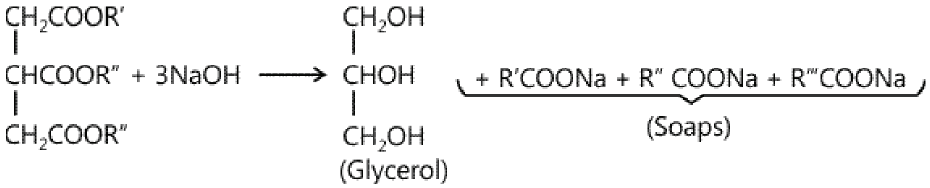
Illustration 11: Why hard water consumes more soap? **(JEE MAIN)**

Sol: Soap are metal salt of fatty acids, on dissolution in water it gives $RCOO^-$ ions, which undergoes to micelle formation, $RCOONa \rightarrow RCOO^- + Na^+$. This micelle formation is responsible for cleaning action. Hard water contains ions like Ca^{+2}, Mg^{+2}. Hence in hard water $RCOO^-$ ions are used up by Ca^{2+} or Mg^{2+} ions to form insoluble $(RCOO)_2Ca$ or $(RCOO)_2Mg$ and thus micelle formation starts only when whole of Ca^{2+} and Mg^{2+} ions are precipitated out by soap. Thus it consumes more soap.

Illustration 12: Which type of bonding occurs between greasy material and soap during detergency? **(JEE MAIN)**

Sol: Van der Waal's bonding.

Saponification: The action of alkalis over fats or oil is known as saponification.



$$\begin{array}{l} CH_2COOR' \\ | \\ CHCOOR'' + 3NaOH \\ | \\ CH_2COOR'' \end{array} \longrightarrow \underset{\text{(Glycerol)}}{\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}} \underbrace{+ R'COONa + R''COONa + R'''COONa}_{\text{(Soaps)}}$$

R', R" and R"' may be same or different.

ADSORPTION AND CATALYSIS

1. INTRODUCTION

There are many properties of substances, particularly of solids and liquids which depend upon the nature of the surface. The branch of chemistry which deals with the nature of surfaces and changes occurring on the surfaces is called surface chemistry. Adsorption of solid or on solution surfaces is an important surface effect which is useful to understand many physical and chemical properties of the substances.

(a) **Adsorption:** The phenomenon of attracting and retaining the molecules of a substances on the surface of a liquid or solid leading to a higher concentration on the surface in comparison to the bulk is called adsorption. Examples are (i) vapor on silica gel, (ii) $H_2O_2NH_3$ on activated charcoal.

(b) **Absorption:** It is the phenomenon in which a substance is uniformly distributed throughout the bulk, i.e. it is the penetration of the substance through the surface into the bulk of the solid.

Example: Water vapors are absorbed by anhydrous $CaCl_2$.

(i) **Adsorbent:** The solid substance on the surface of which adsorption occurs is known as adsorbent.

(ii) **Adsorbate:** The substances that get adsorbed on the solid surface due to intermolecular attraction are called adsorbate.

(c) **Sorption:** In some cases, both absorption and adsorption occur together and are not distinguishable. In such cases, the substance gets uniformly distributed into the bulk of the solid but at the same time, its concentration is higher at the surface than in the bulk. Such a phenomenon is called sorption.

2. TYPES OF ADSORPTION

Depending upon the nature of forces which hold the molecules of the adsorbate on the surface of the adsorbent, adsorption is classified into two types: Physical adsorption and Chemical adsorption.

(a) **Physical adsorption:** When the particles of the adsorbate are held to the surface of the adsorbent by physical forces, e.g. Van der Waals forces, the adsorption is called physical adsorption or physisorption.

(b) **Chemical adsorption:** When the molecules of the adsorbate are held to the surface of the adsorbent by the chemical forces, the adsorption is called chemical adsorption or chemisorption.

Table 21.3: Differences between physical adsorption and chemical adsorption

Physical Adsorption	Chemical Adsorption
The forces between the adsorbate molecules and the adsorbent are weak Van der Waals forces.	The forces between the adsorbate molecules and the adsorbent are strong chemical forces.
Low heat of adsorption of the order of 20-40kJ mol^{-1}.	High heat of adsorption of the order of 200-400 kJ mol^{-1}.
Usually occurs at low temperature and decreases with increasing temperature.	It occurs at high temperature.
It is reversible.	It is irreversible.
The extent of adsorption depends upon the ease of liquefication of the gas.	There is no correlation between extent of adsorption and the ease of liquefication of gas.
It is not specific in nature i.e., all gases are adsorbed on the surface of a solid to same extent.	It is highly specific in nature and occurs only when there is bond formation between adsorbent and adsorbate molecules.

The state of adsorbate is same as in the bulk from that in the bulk.	State of adsorbate molecules may be different.
It forms multimolecular layers.	It forms mono-molecular layer.
Rate of adsorption increases with increase in pressure of adsorbate.	Rate of adsorption usually remains almost same and does not change appreciably with change in pressure.

Illustration 13: Why are all adsorption exothermic? **(JEE ADVANCED)**

Sol: Adsorption process (be it physical or chemical) involves attractions between the molecules of adsorbate and adsorbent and thus, energy is given out.

3. ADSORPTION OF GASES ON SOLIDS

Gases are adsorbed on the finely divided metals such as Ni, Pt, Pd, Fe, etc. The extent of adsorption of a gas on a solid surface is affected by the following factors:

(a) Nature of the gas (b) Nature of adsorbent (c) Effect of pressure

(d) Effect of temperature (e) Activation of adsorbent.

(a) Nature of the gas: The higher the critical temperature, the more easily a gas is liquefied and hence more readily it will be adsorbed. For example.

Table 21.4: Critical temperature of some gases

Gas	H_2	N_2	CO	CH_4	CO_2	NH_3	SO_2
Critical temp. (K)	33	126	134	190	304	406	430
Amount of gas as adsorbed in mL	4.5	8.0	9.3	16.2	48	180	380

(b) Nature of adsorbent: Activated charcoal can adsorb which are easily liquefied. Many poisonous gases are adsorbed by charcoal.

(c) Effect of pressure: The extent of adsorption of a gas per unit mass of adsorbent depend upon the pressure of the gas. The variation of extent of adsorption (expressed as x/m where x is the mass of the adsorbate and m is the mass of the adsorbent) and the pressure is plotted. A graph between the amount of adsorption and gas pressure keeping the temperature constant is called an adsorption isotherm.

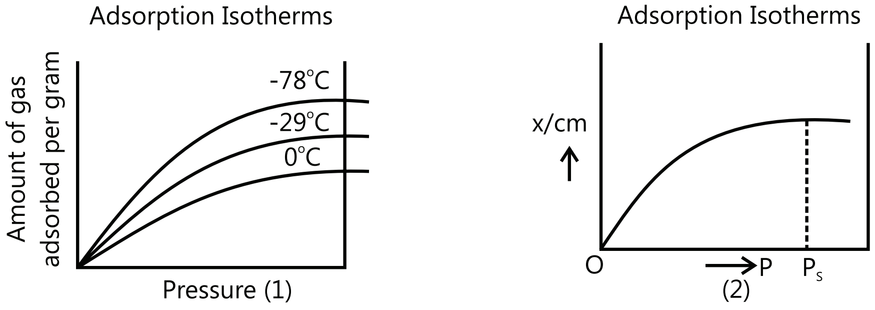


Figure 21.5: Effect of pressure on rate of adsorption

It is clear from the graph-2 that extent of adsorption (x/m) increases with pressure and becomes maximum corresponding to pressure P_s. called equilibrium pressure. Since adsorption is a reversible process, desorption also takes place simultaneously. At this pressure (P_s) the amount of gas adsorbed becomes equal to the amount of gas desorbed so that the extent of adsorption becomes constant even though the pressure is increased. This state is saturation state and P_s is called saturation pressure.

Freundlich Adsorption Isotherm: The variation on extent or adsorption (x/m) when pressure (p) was given mathematically by Freundlich. The following observations can be easily made:

(i) At low pressure, the graph is almost straight line which indicates the x/m is directly proportional to the pressure. This may be expressed as: $\frac{x}{m} \propto p$ or $\frac{x}{m} = kp$

(ii) At high pressure, the graph becomes almost constant which mean that x/m becomes independent of pressure. This may be expressed as: $\frac{x}{m} = \text{Constant}$ or $\frac{x}{m} \propto p^0$ $\quad (\because p^0 = 1)$

Or $\frac{x}{m} = pk^0 = k$ As $p^0 = 1$ (pressure raised to the power zero = 1)

(iii) This, in the intermediate range of pressure, x/m will depend upon the power of pressure which lies between 0 and 1 i.e., fractional power of pressure. This may be expressed as $\frac{x}{m} \propto p^{1/n}$; $\frac{x}{m} = kp^{1/n}$

Calculation of k and n of adsorption isotherm:

The constant k and n can be determined as explained below:

Taking logarithms on both sides of equation $\frac{x}{m} = kp^{1/n}$

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

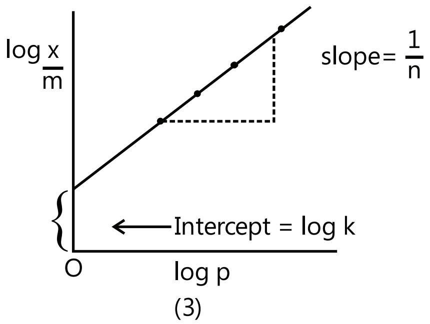


Figure 21.6: Plot of log (x/m) vs log p

Thus, if we plot a graph-3 between log (x/m) and log p, a straight line will be obtained. The slope of the line is equal to 1/n and the intercept is equal to log k.

Illustration 14: How much surface area of cube of edge length 1cm increases if it is broken into cube of edge length 1×10^{-3} cm? **(JEE ADVANCED)**

Sol: First calculate the surface area of one cube of edge length of (1×10^{-3}) now by calculating the volume of one cube, find out the number of cubes formed by a cube of 1 cm now by using volume and no of cubes calculate the new surface area**.**

Here It is given that the cube has an edge length if 1 cm.

So the surface are of the cube (by mathematical expression) = $6a^2$

Here a = 1

The surface area of cube of edge length 1 cm is 6 cm^2.

If edge length is reduced to 1×10^{-3} cm, The surface area of one cube becomes $6 \times 10^{-6}\ cm^2$

[n × volume of 1 cube $(1 \times 10^{-3})^3$ = Volume of 1 cube $(1)^3$]

$\therefore$ Number of cubes = $\frac{1}{1\times10^{-9}} = 10^9$

Number of cubes of edge length 1×10^{-3} cm formed by a cube of 1cm = 10^9

Thus total new surface area becomes

$= 6 \times 10^{-6} \times 10^9 = 6 \times 10^3\ cm^2$

Or increase in surface area is 10^3 times.

Illustration 15: 1.30 liter of O_2 gas 1 atm and 300 K is exposed to a solid surface of 3g in a container. After complete adsorption the pressure of O_2 is reduced to 0.7 atm. Calculate the value of $\frac{x}{m}$. **(JEE MAIN)**

Sol: By using ideal gas equation calculate x/m

$$w_{O_2} = \frac{PV_m}{RT} = \frac{1\times1.5\times32}{0.0821\times300} = 1.948\,g$$

$$w_{O_2}\ \text{Left after adsorption} = \frac{0.7\times1.5\times32}{0.0821\times300} = 1.364\,g$$

$$\therefore x_{O_2}\ \text{adsorbed} = 1.948 - 1.364 = 0.584\ g;$$

$$\frac{x}{m} = \frac{0.584}{3} = 0.194$$

Langmuir Adsorption Isotherm: Consider a solid surface of definite area in contact with gaseous molecules. Let fraction of the surface is occupied by the gaseous molecules to show adsorption at equilibrium, then rate of desorption $\propto \theta = K_d\theta$ (where K_d is desorption constant)

Rate of absorption $\propto P(1-\theta) = K_aP(1-\theta)$ (Where K_a is adsorption constant)

At equilibrium, $K_d\theta = K_aP(1-\theta)$

Or $$\theta = \frac{K_a\cdot P}{K_a\cdot P + K_d} = \frac{\frac{K_a}{K_d}\cdot P}{\frac{K_a}{K_d}\cdot P + 1} \qquad \text{... (i)}$$

$$\theta = \frac{K_1P}{1-K_1}\left(\text{where } K_1 = \frac{K_a}{K_d}\right) \qquad \text{... (ii)}$$

Also the amount of gas adsorbed per unit mass of adsorbent i.e. $\frac{x}{m}$ is directly proportional to θ i.e. $\frac{x}{m} \propto \theta = K_2\cdot\theta$

Or $$\frac{x}{m} = K_2\left[\frac{K_1P}{1+K_1P}\right] = \frac{K_1K_2P}{1+K_1P} \qquad \text{... (iii)}$$

$$\frac{x}{m} = \frac{aP}{1+bP} \qquad \text{... (iv)}$$

(Where $a = K_1K_2$ and $b = \frac{a}{K_2}$)

The Langmuir adsorption isotherm is thus, represented as $\frac{x}{m} = \frac{aP}{1+bP}$

(Where a and b are two Langmuir parameters)

At very high pressure, the above isotherm acquires the limiting form:

$$\frac{x}{m}=\frac{a}{b} \quad (K_1P >>> 1\ bP >>> 1) \qquad \text{... (v)}$$

And at very low pressure, it is reduced to

$$\frac{x}{m}=aP \quad (K_1P <<< 1bP <<< 1) \qquad \text{... (vi)}$$

The parameters a and b, can be determined by transforming the eq. (iv)

$$\frac{m}{x}=\frac{1+bP}{aP}=\frac{b}{a}+\frac{1}{aP} \qquad \text{... (vii)}$$

A plot of m/x against 1/P would give a straight line with slope and intercept equal to 1/a and b/a, respectively.

The Langmuir isotherm, is preferred over the Freundlich isotherm when a monolayer is formed. A plot of x/m versus P is shown in Fig. 21.7. At low pressure, x/m increases linearly with P. At high pressure x/m becomes (eq. v) constant i.e., the surface is fully covered. Now change in pressure has no effect and non-further adsorption takes place.

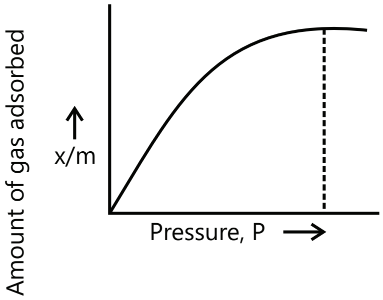


Figure 21.7: Plot of (x/m) vs pressure 1

PLANCESS CONCEPTS

The $\frac{x}{m}\propto$ surface covered $\propto\theta$. Also it increases with pressure and exothermic. At high pressure, $\frac{x}{m}=\frac{a}{b}$ = Constant, i.e. achieves the condition of equilibrium when rate of adsorption and rate of desorption becomes constant. Thus $\Delta G = 0$.

Krishan Mittal (JEE 2012, AIR 199)

$$\Delta G° = -2.303\ RT \log \frac{x}{m} \quad \text{or} \quad \frac{x}{m}=10^{\frac{-\Delta G°}{2.303RT}}=10^{-\left[\frac{\Delta H°-T\Delta S°}{2.303RT}\right]}$$

$$K_{eq.}=\frac{x}{m}=\left[10^{\frac{+\Delta S°}{2.303R}}\right]\times\left[10^{\frac{-\Delta H°}{2.303RT}}\right] \quad ; \quad K_{eq.}=\frac{x}{m}=\left[e^{\frac{\Delta S°}{R}}\right]\times\left[e^{\frac{-\Delta H°}{RT}}\right]$$

Illustration 16: The chemisorptions of H_2 on an activated surface becomes 40% faster if temperature is raised from 500 K to 1000K. Calculate the activation energy of chemisorptions. **(JEE ADVANCED)**

Sol: Here comparative rates are given hence by using the following equation calculate the activation energy.

Formula to be used = $2.303\log\frac{r_2}{r_1}=\frac{Ea}{R}\frac{[T_2-T_1]}{T_1T_2}$

Rate of chemisorption at 500K = a

Rate of chemisorption at 1000K = $50 \times \frac{a}{100} + a = 1.5a$

Now, $2.303 \log \frac{r_2}{r_1} = \frac{Ea}{R} \frac{[T_2 - T_1]}{T_1 T_2}$;

$$2.303 \log \frac{1.5a}{a} = \frac{Ea}{8.314} \left[\frac{1000 - 500}{1000 \times 500} \right]$$

E_a = 3371 J = 3 kJ

Competing adsorption: Adsorption is competitive for different adsorbates. A strong adsorbate adsorbs more efficiently than weak adsorbate. Even a strong adsorbate can adsorb by displacing pre-adsorbed weak adsorbate. This is called competing adsorption or preferential adsorption.

Illustration 17: Different concentrations of aqueous solution placed with charcoal which adsorbs a part of solute from solution as reported below at equilibrium.

Conc. of solution × 10^2	2.0	4.0
$\frac{x}{m}$	0.185	0.290

Calculate the values of log k and n. **(JEE MAIN)**

Sol: By using Freundlich equation $\log \frac{X}{m} = \frac{1}{n} \log C + \log k$ calculate the values of n and k

$$\log 0.185 = \frac{1}{n} \log 2 \times 10^{-2} + \log k \quad \text{... (i)}$$

$$\log 0.290 = \frac{1}{n} \log 4 \times 10^{-2} + \log k \quad \text{... (ii)}$$

By Eq. (i) – 0.7328 = $\frac{1}{n}$ × [– 6989] + log k

By Eqs. (ii) – 0.5376 = $\frac{1}{n}$ × [– 1.3979] + log k

By Eqs. (i) and (ii) n = 0.64, k = 83.5 and log k= 1.92

(d) Effect of temperature

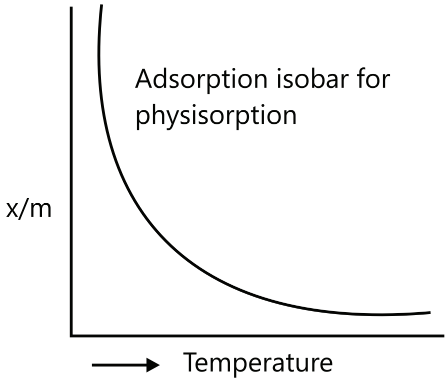


Figure 21.8: Effect of temperature on physisorption

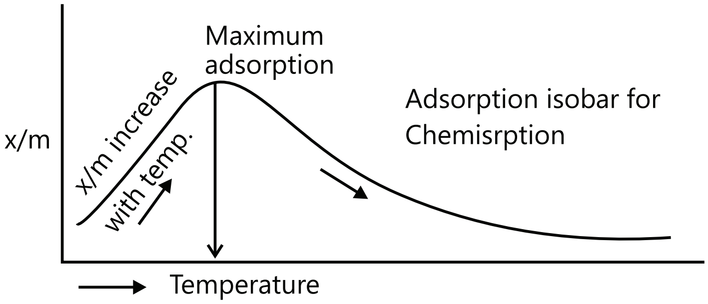


Figure 21.9: Effect of temperature on chemisorption

At low temperature, x/m is small. As temperature is increased, the molecules of the adsorbate gain energy and become equal to activation energy so that proper bonds are formed with the adsorbent molecules.

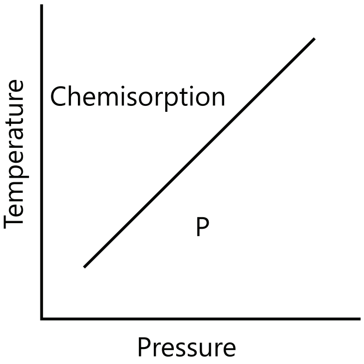


Figure 21.10: Effect of pressure on Chemisorption

(e) **Activation of adsorbent:** Activation of adsorbent means increasing the adsorbing power of the adsorbent. It is very necessary to increase the rate of adsorption. This can be done by the following methods.

- **(i)** Metallic adsorbents are activated by mechanical rubbing or by subjecting them to some chemical reactions.
- **(ii)** To increase the adsorbing power of adsorbents, they are sub-divided into smaller pieces. As a result, the surface area of imbalanced forces increases and therefore, the adsorbing power increases.

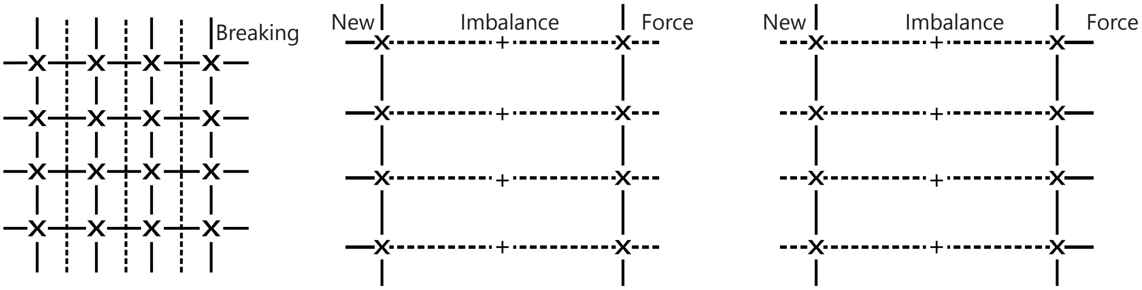


Figure 21.11: Adsorption power

- **(iii)** Some adsorbents are activated by strong heating in contact with superheated steam. For example, charcoal is activated by subjecting it in to the action of superheated steam.

Applications of Adsorption: Some of the important applications of adsorption are given below:

(a) **In gas masks:** Activated charcoal is generally used in gas masks to adsorb poisonous and toxic gases from air. These masks are commonly used by the miners because there are poisonous gases like CO, CH_4 etc. in the atmosphere in the coal mines. Therefore, these masks help to purify the air for breathing.

(b) **In dyeing cloth:** Mordants such as alums are used in dyeing cloth. They adsorb the dye particles which, otherwise, do not stick to the cloth.

(c) **In dehumidizers:** Silica gel is commonly used to adsorb humidity or moisture from air. This is necessary for storage of delicate instruments which might otherwise be damaged by moisture.

(d) **Removal of coloring matter:** Many substances such as sugar, juice and vegetable oils are colored due to the presence of impurities. They can be recolored by placing in contact with adsorbents like activated charcoal or fuller's earth. This method is commonly used in the manufacture of sugar. The colored sugar solution is treated with animal charcoal or activated charcoal.

(e) **Heterogeneous catalysis:** The phenomenon of adsorption is useful in the heterogeneous catalysis. The metals such as Fe, Ni, Pt, Pd, etc are used in the manufacturing process such as Contact process, Haber process and the hydrogenation of oils. Its use is based upon the phenomenon of adsorption.

(f) **In ion-exchange resins:** The organic polymers containing groups like – COOH, – SO_3H etc possess the property of selective adsorption of ions from solution. These are quite useful in the softening of water.

(g) **In adsorption indicators:** Many adsorption indicators are being used in volumetric analysis, e.g. dyes such as eosin and fluorescein are used as adsorption indicators.

(h) **In qualitative analysis:** Certain qualitative tests such as the lake test for the confirmation of Al^{3+} ions are based upon adsorption i.e. $Al(OH)_3$ has the capacity to adsorb the color of blue litmus from the solution.

(i) **Production of high vacuum:** The adsorption of air in liquid air helps to create high vacuum in a vessel. This process is used in high vacuum instruments as Dewar flask for storage of liquid air or liquid hydrogen.

4. CATALYSIS

Berzelius used the term catalyst for the first time for the substances which accelerate the rate of chemical reaction. Now, the term catalyst has been used for the foreign substances which influence the rate of reaction and the phenomenon is known as catalysis. Usually, two terms are used for catalysis.

(a) **Positive catalysis:** The phenomenon in which presence of catalyst accelerates the rate of reaction.

(b) **Negative catalysis:** The phenomenon in which presence of catalyst retards the rate of reaction. Such substances are also known as inhibitors or negative catalyst.

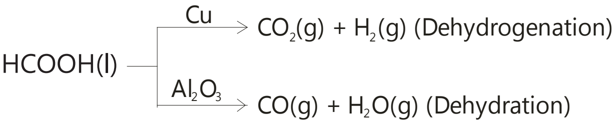
PLANCESS CONCEPTS

Substances that accelerates a reaction are called catalysts whereas those which decreases the rate of a reaction are called inhibitors.

T P Varun (JEE 2012, AIR 64)

4.1 Characteristics of Catalysts

The catalyst is generally specific in nature. Different catalysts for the same reactants may form different products. For example



$$HCOOH(l) \xrightarrow{Cu} CO_2(g) + H_2(g) \text{ (Dehydrogenation)}$$

$$HCOOH(l) \xrightarrow{Al_2O_3} CO(g) + H_2O(g) \text{ (Dehydration)}$$

(a) A catalyst can never initiate a chemical reaction. It simply influences the rate of reaction. However, combination of H_2 and Cl_2 takes place only when moisture (catalyst) is present.

(b) A small quantity of catalyst is sufficient to influence the rate of reaction, e.g. 1 g-atom of Pt (i.e. 195 g) is sufficient to catalyze decomposition of 108 liter H_2O_2.

(c) A catalyst does not influence the equilibrium constant or reaction. It simply helps in attaining equilibrium earlier. It alters the rate of forward and backward reactions equally.

Illustration 18: What role a catalyst plays in establishing the equilibrium in reversible process? **(JEE ADVANCED)**

Sol: Catalyst is a substance that increases the rate of forward reaction thus increases concentration of products which in turn favors backward reaction faster and ultimately helps in attaining the equilibrium earlier.

4.2 Types of Catalysis

(a) **Homogenous Catalysis:** In this, both the catalysts and the reactants are in the same phase.

Example,

(i) Catalytic oxidation of SO_2 into SO_3 in the presence of NO as catalyst in the lead chamber process. In this case all the reactant and the catalyst are in the gaseous phase.

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

(ii) Hydrolysis of ethyl acetate in the presence of acid

$$CH_3COOC_2H_5(l) + HOH(l) \xrightarrow{H^+(aq)} CH_3COOH(l) + C_2H_5OH(l)$$

(b) **Heterogeneous Catalysis:** In this, both the catalysts and the reactant are in different phase.

Example: Some common examples of heterogeneous catalysis are as follows.

(i) Oxidation of HCl into Cl_2 by Deason's process in the presence of $CuCl_2$.

$$4HCl(g) + O_2(g) \xrightarrow[450°C]{CuCl_2(s)} 2Cl_2(g) + 2H_2O(g)$$

(ii) Manufacture of NH_3 from N_2 and H_2 by Haber's process using finely divided iron as catalyst.

$$N_2(g) + 3H_2(g) \xrightleftharpoons[+Mo\ (Promoter)]{Fe(s)} 2NH_3(l)$$

(iii) Oxidation of sulphur dioxide (SO_2) into sulphur trioxide (SO_3) in the presence of vanadium pentoxide as catalyst.

$$2SO_2(g) + O_2(g) \xrightleftharpoons{V_2O_5(s)} SO_3(g) \quad (Contact\ Process)$$

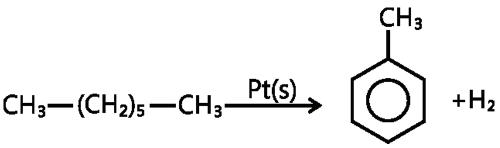
Important Characteristic of Heterogeneous Catalyst

The two important aspects of heterogeneous catalysis are activity and selectivity.

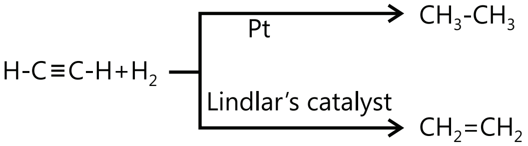
(a) **Activity:** It implies the ability of catalyst to accelerate a chemical reaction. The degree of acceleration can be sometimes as high as 10^{10}. For example, the reaction between H_2 and O_2 gases in the presence of platinum catalyst to form water occur with an explosive violence, whereas a mixture of pure H_2 and O_2 gases can be stored indefinitely without any reaction.

(b) **Selectivity:** Selectivity of a catalyst is its ability to direct the reaction in such a way so as to yield particular products excluding others. For example.

(i) n-Heptane selectivity give toluene in the presence of platinum catalyst.



(ii) Acetylene on reaction with H_2 in the presence of platinum catalyst gives ethane while in the presence of Lindlar's catalyst (Pd supported over $BaSO_4$ partially deactivated by sulphur or quinoline) gives ethene as the main product.



(iii) Enzyme catalysis: Enzymes are complex nitrogenous organic compounds present in living begins inside the human body like digestion therefore enzymes are also called biocatalyst.

Example:

$$\underset{\text{Urea}}{NH_2CONH_2} + H_2O \xrightarrow{\text{Uresse}} 2NH_3 + CO_2$$

$$C_6H_{12}O_6 + H_2O \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

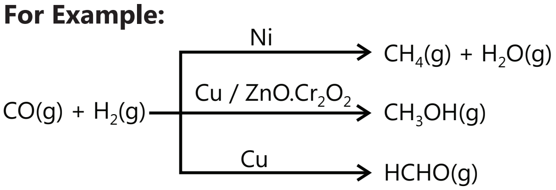
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Gulcose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

PLANCESS CONCEPTS

Substances that accelerates a reaction are called catalysts whereas those which decreases the rate of a reaction are called inhibitors.

T P Varun (JEE 2012, AIR 64)

For Example:



Note: Thus action of a catalyst is highly specific or selective in nature i.e., a substance can act as a catalyst for a particular reaction and not for all the reactions.

5. THEORIES OF CATALYSIS

(a) **Intermediate compound formation theory:** According to this theory catalyst combines with one or more of the reactants to give an intermediate product which either decomposes or reacts with other reactants to give product and regenerates the catalyst.

(i) Catalytic decomposition of $KClO_3$: $2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$

The mechanism of this reaction according to intermediate compound formation theory is given below:

$$2KClO_3 + 2MnO_2 \longrightarrow \underset{1-\text{intermediate}}{2KMnO_4} + Cl_2 + O_2$$

$$2KMnO_4 \longrightarrow \underset{\text{II}-\text{intermediate}}{K_2MnO_4} + MnO_2 + O_2$$

$$K_2MnO_4 + Cl_2 \longrightarrow 2KCl + MnO_2 + O_2$$

Illustration 19: Which acts as catalyst for the destruction of ozone layer in presence of Freon or chlorofluoro carbons? **(JEE MAIN)**

$$O_3 \xrightarrow{\text{UV rays}} O_2 + O$$

Sol: The destruction of ozone takes place by a free radical mechanism. Presence of chlorofluoro carbon forms free radicals which catalyzes the decomposition of ozone.

$$CCl_2F_2 \xrightarrow{h\upsilon} CClF_2 + \dot{Cl}$$

$$\dot{Cl} + O \longrightarrow O_2 + Cl\dot{O}$$

$$Cl\dot{O} + \dot{O} \longrightarrow Cl + O$$

(b) Adsorption Theory: According to this theory gas molecules are adsorbed on the surface of catalyst giving rise to higher concentration of reacting species at the surface which results in faster rate of reaction.

(c) The Modern Theory: It is a combination of previous two theories.

(i) The catalyst enters into loose chemical or physical combination (i.e. chemisorptions or physic adsorption) with reactants to form and adsorbed activated complex, having its energy level somewhat lower than the complex which would have been formed in absence of catalyst.

Thus, the catalyst provides new pathway involving lower threshold energy level due to large number of effective collisions occurring in the presence of a catalyst in comparison to effective collisions at the same temperature in absence of a catalyst. Hence, the presence of a catalyst makes the reaction to go faster. Fig. 21.12, shows threshold energy level E_T and activation energy E_A, in absence of a catalyst. These values are higher than the corresponding threshold energy level $E_{T'}$ and activation energy $E_{A'}$ in presence of a catalyst, E_R and E_P represent the average energies of reactants and products. The difference $(E_P - E_R)$ gives the value of ΔH.

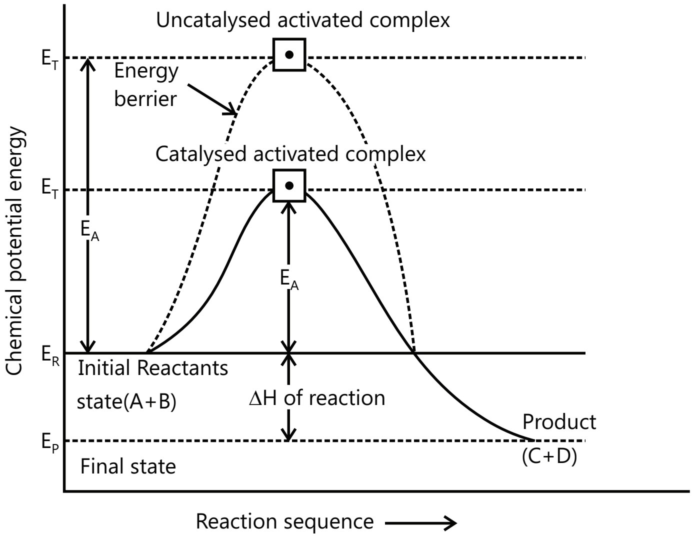


Figure 21.12: Catalytic Reaction Pathway

(ii) It is thus, evident that catalyst lowers the threshold energy barrier (E_T to E'_T) and thereby lowers the energy of activation of reaction, threshold energy level is the minimum energy level which the reactant molecules must possess in order to show a chemical change whereas energy of activation is the additional, i.e., the minimum amount of energy provided to reactant molecules to form activated complex. It is thus evident that catalyst provides another path way for a reaction which has lower values of threshold energy level.

6. SOME OTHER TYPES OF CATALYSIS

(a) **Negative Catalysis or Inhibitors:** The phenomenon in which presence of foreign substance retards the rate of the reaction.e.g.

(i) Acetanilide or glycerin or H_3PO_4 acts as negative catalyst for decomposition of H_2O_2.

(ii) Aldehydes and alcohols act as negative catalyst for oxidation of Na_2SO_4.

(b) **Autocatalysis:** The phenomenon in which either of the product formed during reaction acts as catalyst for the reaction.e.g.

(i) The color of $KMnO_4$ disappears slowly on treating it with oxalic acid but becomes faster after sometime due to formation of M_n^{2+} ions which acts as autocatalyst for the reaction.

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

(c) **Acid-Base Catalysis:** The phenomenon in which a reaction is catalysed by acid and base simultaneously.

(i) An acid donates proton to substrate or reactant to form an intermediate, which then loses proton to a base to give product.

(d) **Mutarotation of glucose:** The phenomenon in which optical activity of a freshly prepared α-glucose solution in water rapidly decreases with time till equilibrium is reached between α and β form and similarly, rotation of β-glucose in solution increases with time.

$$\underset{\alpha-\text{glucose}}{HG} \xrightarrow[\text{Acid}]{H^+} \underset{\text{Intermediate}}{HGH^+} \xrightarrow[-H^+]{\text{Base}} \underset{\beta-\text{glucose}}{HG}$$

(i) The mechanism of specific catalysis by H_3O^+ or OH^- involves formation of an ionized intermediate, which then yields products.

(ii) Ester hydrolysis in aqueous solution is catalysed only by H_3O^+ and OH^- and other acids or base (Lewis acid or Lewis base which do not furnish H_3O^+ or OH^-) are ineffective.

PLANCESS CONCEPTS

The acid hydrolysis of an ester is reversible while alkaline hydrolysis of ester (also called saponification) is irreversible.

Saurabh Chatterjee (JEE 2013, AIR)

(e) **Enzyme Catalysis:** The phenomenon in which reactions are catalysed by enzymes.

Enzymes are complex, biological, and nitrogenous, macromolecules (i.e. proteins) derived from living organisms and thus, phenomenon is also named as biological or biochemical catalysis.

Characteristics of enzyme catalysis

(i) Enzyme catalysed reactions are highly specific, i.e., one enzyme for one reaction.

(ii) Enzyme catalysed reactions are normally hydrolytic in nature.

(iii) Enzyme catalysed reactions take place with evolution of gases.

(iv) The rate of reaction depends upon enzyme concentration.

PLANCESS CONCEPTS

Enzyme catalysed reactions are highly susceptible to pH of medium. Favorable range of pH is 5 to 7. The optimum temperature for enzyme catalysed reaction is nearly 30°C. Enzymes being colloidal in nature and thus, their action is ruined by electrolytes.

Mredul Sharda (JEE 2013, AIR)

(f) **Induced Catalysis:** The phenomenon in which one reaction influences the rate of other reaction which does not occur under ordinary condition. e.g. Sodium arsenite solution is not oxidized by air. However, if air is passed through a mixture of solution of sodium arsenite and sodium sulphite, both of them undergo simultaneous oxidation. Oxidation of Na_2SO_3 induces the oxidation of Na_3AsO_3.

(g) **Shape Selective Catalysis by Zeolites:** Zeolites are microporous alumino-silicates of the general formula $Mn[(AlO_2)_x(SiO_2)_y].mH_2O$

Where n is the valency of cation M^{n+}. They may be considered as open structures of silica in which a fraction x/(x + y) of the tetrahedral sites have been substituted by aluminum. The net negative charge on the aluminosilicate framework is neutralized by exchangeable cations M of valency n. Zeolites have high porosity due to the presence of one, two or three dimensional network of interconnected channels and cavities of molecular dimensions. Other elements such as Ba, Mg, B, Ga and P can take the place of Si and Al in the zeolitic frame work. Shape selectivity of a catalyst depend upon the pore structure of the catalyst. The pore size of zeolites generally varies between 260 pm and 740 pm. Depending on the size of the reactant and product molecules when compound to the size of cages or pores of the zeolite, reactions proceed in a specific manner.

PROBLEM-SOLVING TACTICS

When free energy change is given and extent of adsorbent has to find out, use the following equation.

$$G° = -2.303\ RT\ \log\frac{x}{m} \quad \text{or}$$

It can be written as in terms of enthalpy and Entropy.

$$\frac{x}{m} = 10^{\frac{-\Delta G°}{2.303RT}} = 10^{-\left[\frac{\Delta H° - T\Delta S°}{2.303RT}\right]}$$

$$K_{eq.} = \frac{x}{m} = \left[10^{\frac{+\Delta S°}{2.303R}}\right] \times \left[10^{\frac{-\Delta H°}{2.303RT}}\right]; \quad K_{eq.} = \frac{x}{m} = \left[e^{\frac{\Delta S°}{R}}\right] \times \left[e^{\frac{-\Delta H°}{RT}}\right]$$

Also we can have $\ln\frac{K_{eq1}}{K_{eq2}} = \frac{\Delta H}{R} x \frac{(T_2 - T_1)}{T_1 T_2}$

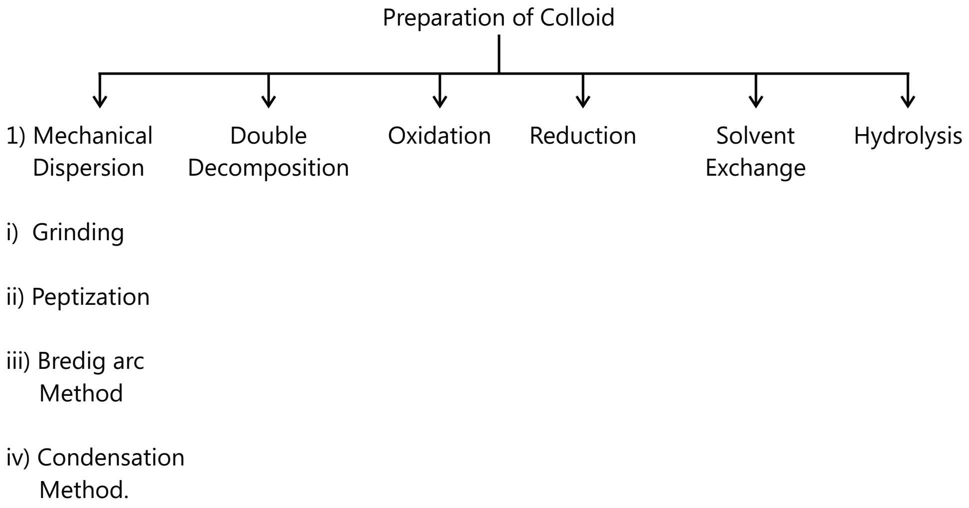
When rate of adsorption or desorption is given use the following equation, $2.303\log\frac{r_2}{r_1} = \frac{Ea}{R}\frac{[T_2 - T_1]}{T_1 T_2}$

POINTS TO REMEMBER

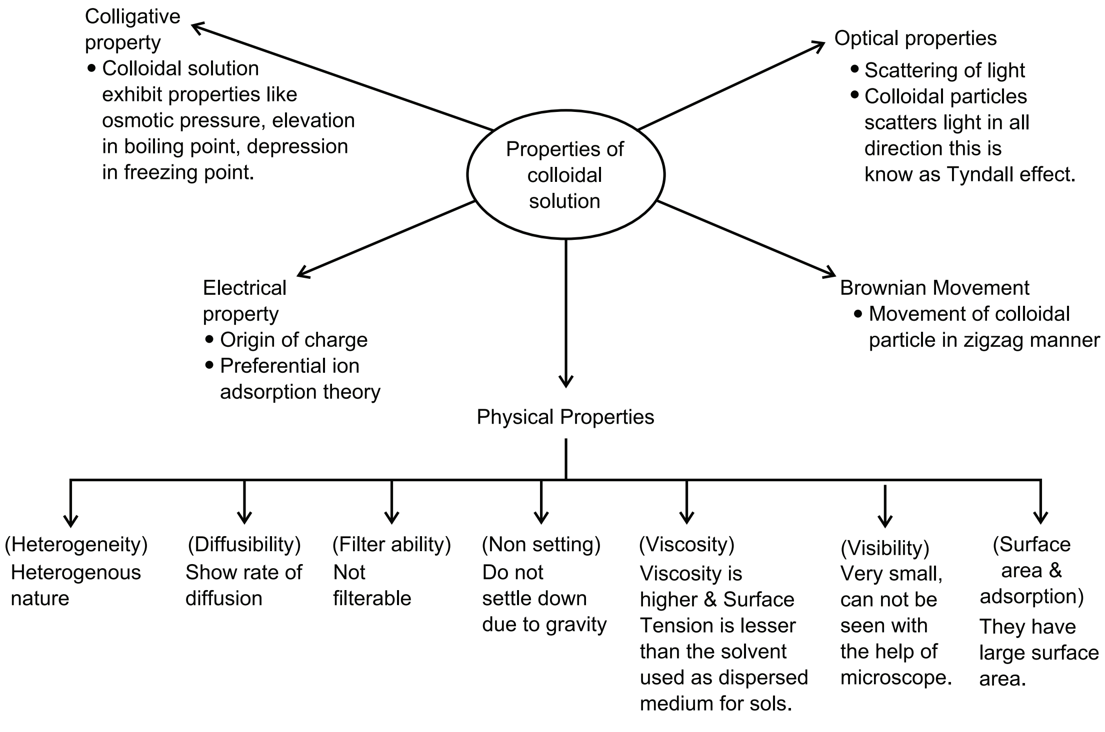
COLLOIDS

Characteristics of Colloidal State

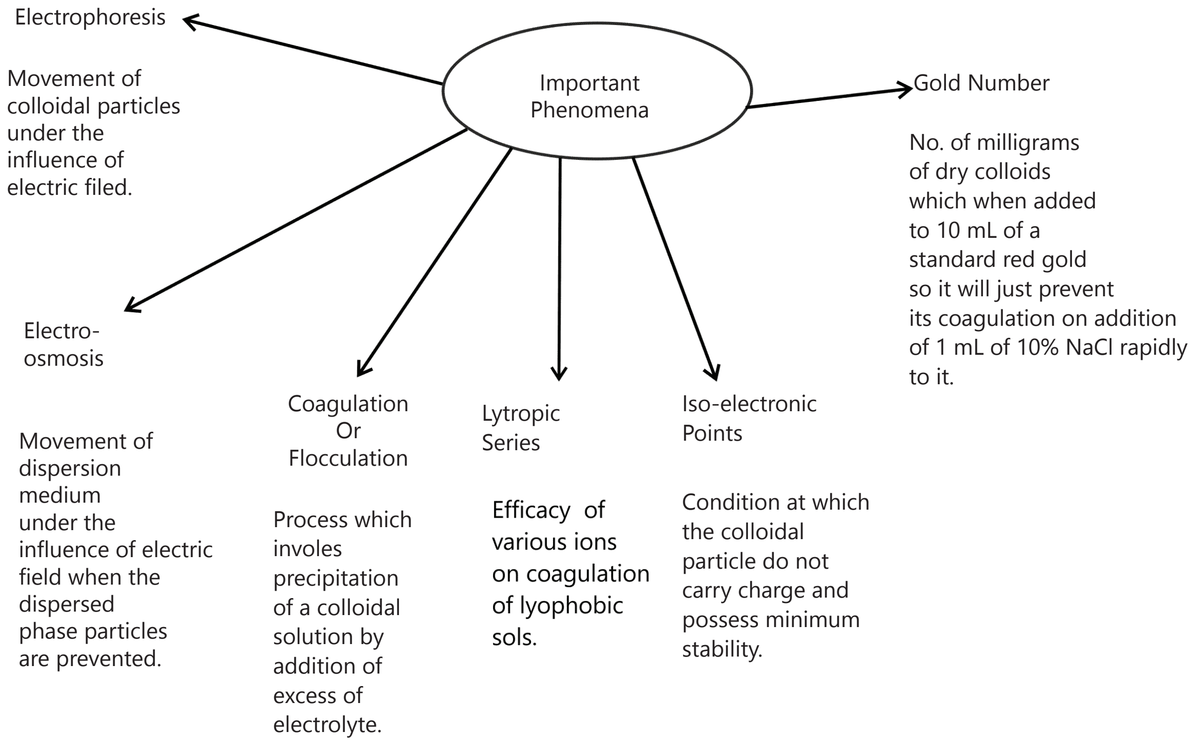
- It is a particular state, Heterogeneous in nature, number of phases = 2. i.e Dispersed phase and Dispersion medium.
- The one phase dispersed in other is known as dispersed phase (or D.P.) or internal phase or discontinuous phase whereas, the other in which dispersions are made is known as dispersion medium (D.M) or external phase or continuous phase.



Properties of Colloids



Important Phenomena:



Important Phenomena

Electrophoresis: Movement of colloidal particles under the influence of electric filed.

Electro-osmosis: Movement of dispersion medium under the influence of electric field when the dispersed phase particles are prevented.

Coagulation Or Flocculation: Process which involes precipitation of a colloidal solution by addition of excess of electrolyte.

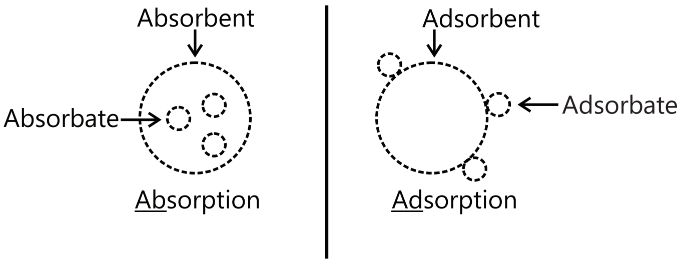
Lytropic Series: Efficacy of various ions on coagulation of lyophobic sols.

Iso-electronic Points: Condition at which the colloidal particle do not carry charge and possess minimum stability.

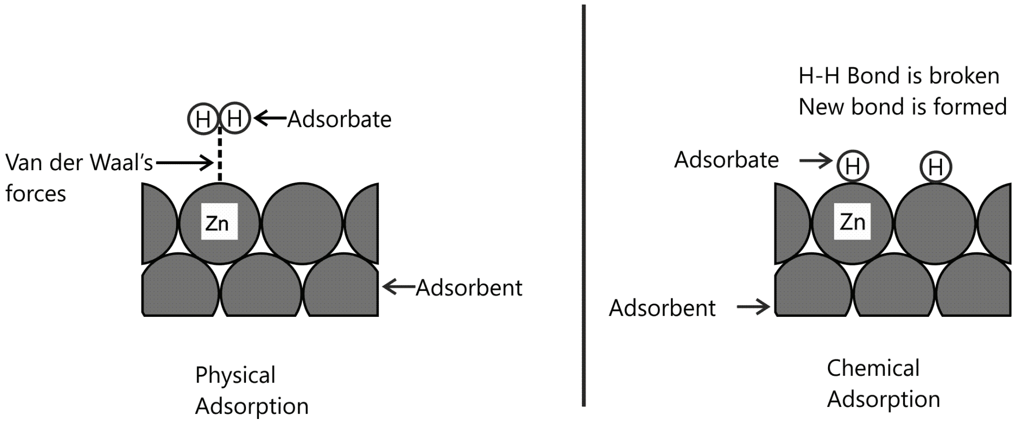
Gold Number: No. of milligrams of dry colloids which when added to 10 mL of a standard red gold so it will just prevent its coagulation on addition of 1 mL of 10% NaCl rapidly to it.

ADSORPTION

Absorption and Adsorption process:



Physical Adsorption and Chemical Adsorption



Freundlich Adsorption Isotherm

Extent of adsorption (x/m) increases with pressure.

1. At low pressure extent of pressure is directly proportional to pressure.

$$\frac{x}{m} \propto p \text{ or } \frac{x}{m} = kp$$

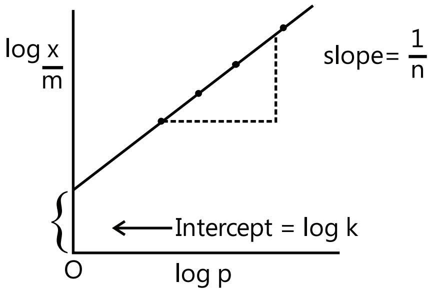
2. At high pressure extent of adsorption is independent of pressure.

$$\frac{x}{m} = \text{constant} \text{ or } \frac{x}{m} \propto p^0$$

3. In the intermediate range of pressure, x/m will depend upon the power of pressure which lies between 0 and 1 i.e., fractional power of pressure.

This may be expressed as $\frac{x}{m} \propto p^{1/n}$; $\frac{x}{m} = kp^{1/n}$ Calculation of k and n of adsorption isotherm:

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



(3)

Langmuir Adsorption Isotherm

$$\theta = \frac{K_1 P}{1 - K_1}\left(\text{where } K_1 = \frac{K_a}{K_d}\right)$$

θ= Fraction of area occupied.

K_a= Rate of adsorption

K_b= Rate of desorption.

The Langmuir adsorption isotherm is thus, represented as

$$\frac{x}{m} = \frac{aP}{1+bP}$$ (Where a and b are two Langmuir parameters)

At very high pressure, the above isotherm acquires the limiting form:

$$\frac{x}{m} = \frac{a}{b} \quad (K_1P >>> 1 \ bP >>> 1) \qquad \text{... (v)}$$

And at very low pressure, it is reduced to

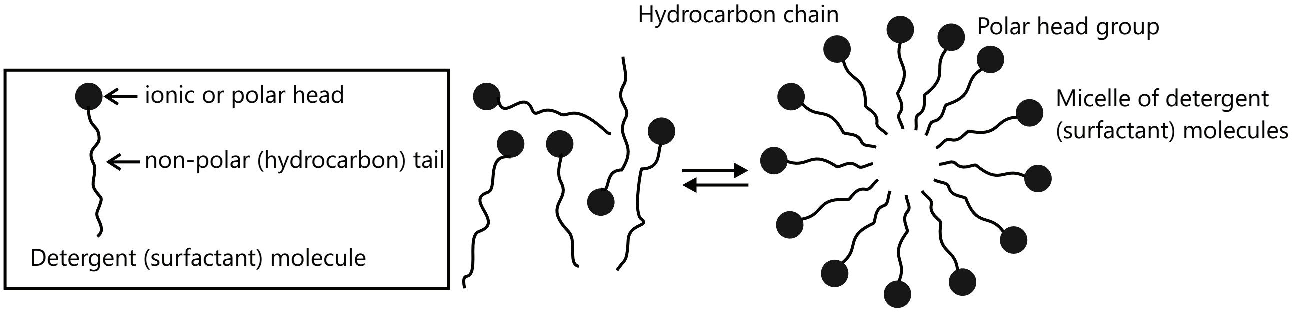
$$\frac{x}{m} = aP \quad (K_1P <<< 1 \therefore bP <<< 1)$$

Soap and Detergent:

- Saponification of fats and oil yields soap and glycerol as a byproduct.
- Detergents are surface active agents having cleaning properties they are also known as surfactants (Surface active agents).This cleaning properties is due to their characteristic structure.

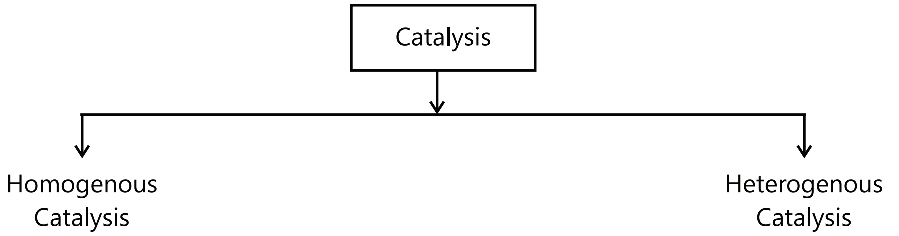
- They have polar head group and long hydrocarbon chain tail which is apolar.
- The concentration at which the surfactants molecule aggregates and micelle formation takes place is known as critical micellar concentration.
- Though their hydrocarbon chain they interact with the dirt particle (say oil or grease)
- Forming and emulsion and imparting cleansing property.

Micelle Formation:



CATALYSIS

Type of Catalysis



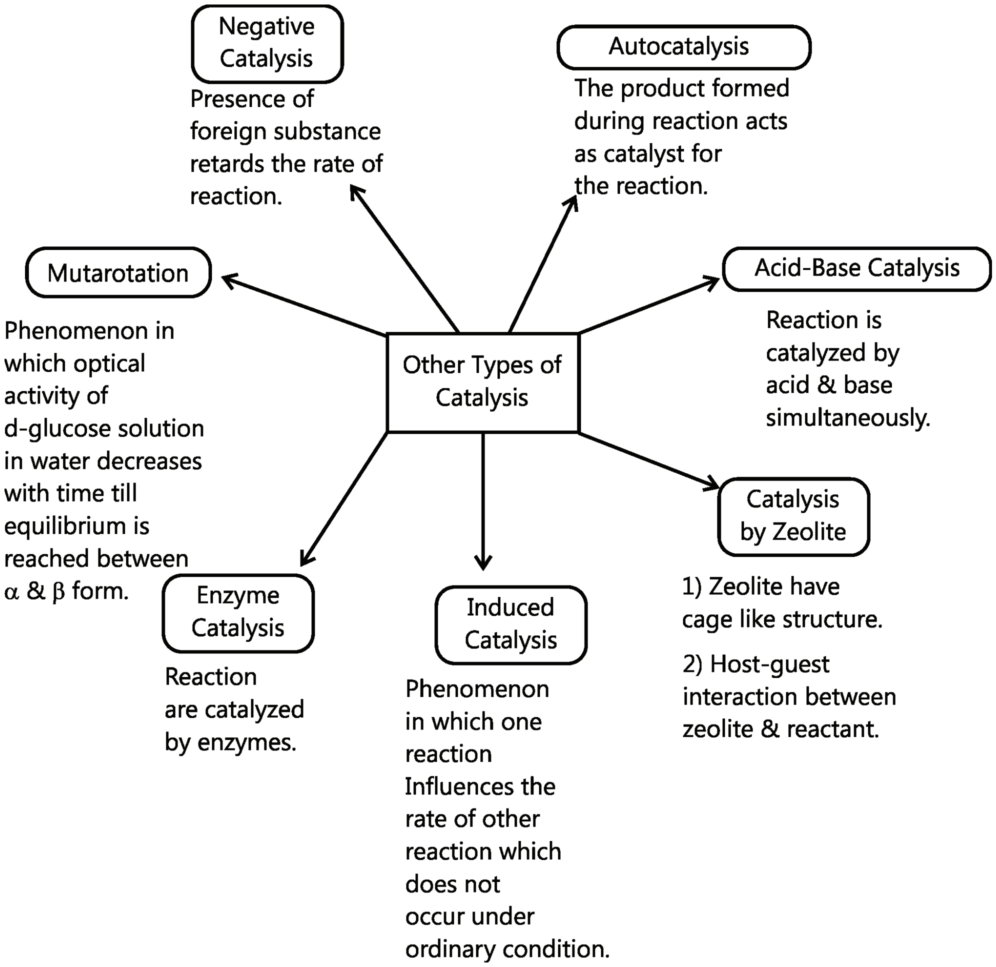
Catalyst & reactants are in the same phase.

Both the catalyst & the reactants are in different phases.

Theories of Catalysis

1. Intermediate Compound Formation theory.
2. Adsorption Theory.
3. The Modern Theory.

Other Catalysis



Negative Catalysis: Presence of foreign substance retards the rate of reaction.

Autocatalysis: The product formed during reaction acts as catalyst for the reaction.

Mutarotation: Phenomenon in which optical activity of d-glucose solution in water decreases with time till equilibrium is reached between α & β form.

Acid-Base Catalysis: Reaction is catalyzed by acid & base simultaneously.

Enzyme Catalysis: Reaction are catalyzed by enzymes.

Induced Catalysis: Phenomenon in which one reaction Influences the rate of other reaction which does not occur under ordinary condition.

Catalysis by Zeolite:

1) Zeolite have cage like structure.

2) Host-guest interaction between zeolite & reactant.

Solved Examples

JEE Main/Boards

Example1: What are the physical states of dispersed phase and dispersion medium of froth?

Sol: Froth is a small mass of bubbles in liquid**.**

Dispersed phase : Gas
Dispersion medium : Liquid

Example 2: Define the term ‘Tyndall effect’.

Sol: The scattering of light by colloidal particles is known as Tyndall effect.

Example 3: What is meant by the term peptization?

Sol: The process of conversion of a freshly prepared precipitate into a colloidal solution by adding a suitable electrolyte is called peptization.

Example 4: Explain the following terms with suitable example (i) Alcohol (ii) Serosol and (iii) Hydrosol.

Sol: (i) Alcohol: It is a colloidal dispersion having alcohol as the dispersion medium e.g. collodion (a colloidal sol of cellulose nitre in ethyl alcohol.)

(ii) Serosol: It is a colloidal dispersion of a liquid in a gas e.g. fog.

(iii) Hydrosol: It is a colloidal sol of a solid in water as the dispersion medium e.g. starch sol or gold sol.

Example 5: The movement of sol particles under an applied electric field is called:

(A) Electro deposition (B) Electrodialysis

(C) Electro-osmosis (D) Electrophoresiss

Sol: (D) Colloidal Particles carry charge (positive or negative) and thus on application of electric field they move towards opposite electrodes and the phenomenon is known as cataphores is or electrophoresis.

Example 6: At CMC, the surfactant molecules undergoes:

(A) Association (B) Aggregation

(C) Micelle formation (D) All of these

Sol: (D) All are same processes.

Example 7: A catalyst:

(A) Alter the state of equilibrium

(B) Decreases the activation energy

(C) Increases collision frequency

(D) Increases the average kinetic energy of reacting species.

Sol: (B) Catalyst shows exothermic adsorption of reactant molecules and thus energy of activation is lowered.

Example 8: Plots of $\log\left(\frac{x}{m}\right)$ vs. log C showing a straight line parallel to X-axis reveals that:

(A) $n = 0$ (B) $\frac{1}{n} = 0$

(C) $C = 0$ (D) $\log C = \text{constant}$

Sol: (B) $\frac{x}{m} = K \cdot C^{1/n}$

Example 9: Which characteristic is not correct for physical adsorption?

(A) Adsorption is spontaneous

(B) Both enthalpy and entropy change of adsorption are negative

(C) Adsorption on solid is reversible

(D) Adsorption increases with increase in temperature

Sol: (D) Physical adsorption is non-directional, reversible, multilayers exothermic process where adsorbent are held by physical forces such as van der waal forces.

Example 10: The minimum energy level necessary to permit a reaction to occur is:

(A) Internal energy (B) Threshold energy

(C) Activation energy (D) Free energy

Sol: (B) The minimum energy required to permit a reaction to occur is called as Activation Energy.

JEE Advanced/Boards

Example 1: A negatively charged yellow sol of As_2S_3 on mixing with a +vely charged $Fe(OH)_3$ red sol in equivalent amount give rise to colorless solution. Why?

Sol: Mutual coagulation leaves behind colorless Liquid which is water. The negative charge on As_2S_3 and positive charge on $Fe(OH)_3$ neutralizes each other causes mutual coagulation and thus dispersed particles of As_2S_3 and $Fe(OH)_3$ are settled down leaving water, which is colorless.

Example 2: 0.1 M $AlCl_3$ solution is more effective than 0.1 M NaCl solution in coagulating As_2S_3 sol while 0.1 M $AlCl_3$ is less effective than 0.1 M Na_3PO_4 solution in coagulating ferric oxide

Sol: As_2S_3 is a negatively charged sol and thus effective ions are Al^{3+} and Na^+ whereas Fe_2O_3 is a positively charged sol and the effective ions and Cl^- and PO_4^{3-}. More is the valence of effective ion, more is its coagulating power. Thus, Al^{3+} is more effective than Na^+ and PO_4^{3-} is more effective than Cl^-

Example 3: Action of soap is due to emulsification and micelle formation. Comment.

Sol: Soap molecule has water soluble head and oil soluble tail. The soap molecules get adsorbed on the dirty (oily) surface through the tail and try to emulsify it. Soap micelles do solubilize the insoluble dirt/greasy material.

Example 4: The average molecular weight of colloidal particles is determined by:

(A) Tyndall effect

(B) Osmotic pressure measurement

(C) Victor Meyer's method

(D) None of the above

Sol: (B) The osmotic pressure measurements gives average molecular weight of colloidal particles.

Example 5: Acid deposits on pans can be removed by boiling pans with washing soda. Explain.

Sol: The basic reaction behind this process is saponification.

Na_2CO_3 (washing soda) on hydrolysis forms NaOH which on boiling with fat give rise to saponification.

$RCOOR + NaOH \rightarrow RCOONa + ROH$

A part of fat is thus used and rest fat is removed by the soap so formed.

Example 6: Which of the following is not correct about colloids?

(A) The $[H^+]$ at which colloids particles do not carry charge is called isoelectric point of colloid

(B) At isoelectric point of colloidal state possess minimum stability

(C) At isoelectric point sol particles possess no electrophoretic motion

(D) Silicic acid sol have minimum stability at its isoelectric point.

Sol: (D) It is an exception and the silicic acid sol possess maximum stability.

Example 7: Why a finely divided substance is more effective as an adsorbent?

Sol: Finely divided substances have very large specific surface area and therefore provide more sites for adsorption.

Example 8: Show that if a cube of 1 cm^3 is broken into smaller cubes such that each side is divided just in the middle. How many cubes will be formed? Also calculate the total surface area of such cubes.

Sol: First calculate the surface area of one cube of edge length of (0.5 cm) now by calculating the volume of one cube find out the number of cubes formed by a cube of 1 cm now by using volume and no of cubes calculate the new surface area**.**

Surface area of cube = $6a^2$

a = 1

Total surface area of cube of $1cm^2 = 6 \times 1^2 = 6\ cm^2$

Total surface are of one cube of 1/2 cm edge

$$= 6 \times \frac{1}{2} \times \frac{1}{2} = 1.5$$

No of cubes x Volume of 1 cube of ½ edge length $(1/2)^3$cm = Volume of 1 cube of 1 cm edge length $(1)^3$

n x 0.125 = 1

n = 1/0.125

n = 8

Let each side be halved, than total number of cubes formed of edge length of each cube $\frac{1}{2}$ cm are 8.

Thus surface area of 8 cubes $= 8 \times 6 \times \frac{1}{2} \times \frac{1}{2}$ = 12 cm^2.

Example 9: Why it is advantageous to use a catalyst for a reaction having endothermic nature?

Sol: For an endothermic reaction (ΔH = +ve) and thus heat is required to get better yield which raises the cost appreciably. In presence of catalyst, less heat is required to start a reaction.

Example 10: What role does adsorption play in heterogeneous catalysis?

Sol: Heterogeneous catalysis generally employs a solid adsorbent and the reactants are mostly gases. The reactions occurs at the surface of the catalyst where the reactant molecules (adsorbates) get chemisorbed. Due to adsorption, chances of effective collisions in reactant molecule increases.

JEE Main/Boards

Exercise 1

Q.1 Why is ferric chloride preferred over Potassium chloride in case of a cut leading to Bleeding?

Q.2 What causes Brownian movement in a colloidal solution?

Q.3 Which has a higher enthalpy of adsorption, physisorption or chemisorptions?

Q.4 Mention two ways by which lyophilic colloids can be coagulated.

Q.5 What is an emulsion?

Q.6 What is physical adsorption?

Q.7 What is meant by chemical adsorption?

Q.8 What is desorption?

Q.9 How is adsorption of a gas related to its critical temperature?

Q.10 Why is a colloidal sol stable?

Q.11 Write two difference between sols and emulsions.

Q.12 Define ultrafiltration?

Q.13 Why do colloidal solutions exhibit Tyndall effect?

Q.14 Why artificial rain can be caused by throwing common salt on the clouds?

Q.15 What happens when an electric field is applied to a colloidal dispersion?

Q.16 Account for the following:

(i) Ferric hydroxide sol is positively charged.

(ii) The extent of physical adsorption decreases with rise in temperature.

(iii) A delta is formed at the point where the river enters the sea.

Q.17 Explain the following terms:

(i) Electro-dialysis

(ii) Phases of a colloidal solution

Q.18 What is meant by 'shape selective' catalysis?

Q.19 What is adsorption? How does adsorption of a gas on a solid surface very with (a) temperature and (b) pressure? Illustrate with the help of appropriate graphs.

Q.20 Explain what is observed when

(i) An electrolyte is added to ferric hydroxide Sol

(ii) An emulsion is subjected to centrifugation.

(iii) Direct current is passed through a colloidal Sol

Q.21 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.22 (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? Give an example of shape-selective catalysis.

Q.23 (i) What are micelles? How do they differ from ordinary colloidal particles? Give two examples of micelles forming substances.

(ii) State Hardy-Schulze rule.

Q.24 Describe the following types of colloids, giving an example for each:

(i) Multimolecular colloids

(ii) Macromolecular colloids

Q.25 Of physisorption and chemisorption which type of adsorption has a higher enthalpy of adsorption?

Q.26 Explain what is observed when

(i) KCl, an electrolyte, is added to hydrated ferric oxide sol

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

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

Q.27 Describe the following:

(i) Tyndall effect

(ii) Shape-selective catalysis

Q.28 Coagulations of lyophobic sols can be carried out by?

Q.29 Describe a conspicuous change observed when

(i) A solution of NaCl is added to a sol of hydrated ferric oxide.

(ii) A beam of light is passed through a solution of NaCl and then through a sol

Q.30 What is meant by coagulation of a colloidal solution? Describe briefly any three methods by which coagulation of lyophobic sols can be carried out.

Exercise 2

Single Correct Choice Type

Q.1 Which gas will be adsorbed on a solid to greater extent?

(A) A gas having non polar molecule

(B) A gas having highest critical temperature

(C) A gas having lowest critical temperature

(D) A gas having highest critical pressure

Q.2 Which of the following factors affects the adsorption of a gas on solid?

(A) T_c (critical temp.) (B) Temperature of gas

(C) Pressure of gas (D) All of them

Q.3 The volume of gases NH_3, CO_2 and CH_4 adsorbed by one gram of charcoal at 298 K are in

(A) $CH_4 > CO_2 > NH_3$ (B) $NH_3 > CH_4 > CO_2$

(C) $NH_3 > CO_2 > CH_4$ (D) $CO_2 > NH_3 > CH_4$

Q.4 Platinum is not used as a catalyst in the

(A) Oxidation of CH_3OH to HCHO

(B) Oxidation of SO_2 to SO_3

(C) Combination of H_2 and I_2 to form HI

(D) Synthesis of NH_3 from N_2

Q.5 Which type of metals form effective catalysts?

(A) Alkali metals

(B) Transition metals

(C) Alkaline earth metals

(D) Radioactive metals

Q.6 The heat of physisorption lie in the range of

(A) 1 – 10 kJ mol^{-1} (B) 20 to 40 kJ mol^{-1}

(C) 40 to 200 kJ mol^{-1} (D) 200 to 400 kJ mol^{-1}

Q.7 Adsorption is multilayer in case of

(A) Physical adsorption (B) Chemisorptions

(C) In both (D) None of these

Q.8 Reversible adsorption is

(A) Chemical adsorption

(B) Physical adsorption

(C) Both (A) and (B)

(D) None of these

Q.9 Which of the following is not a gel?

(A) Cheese (B) Jellies

(C) Curd (D) Milk

Q.10 The amount of gas adsorbed physically on charcoal increases with increase of

(A) Temperature and pressure

(B) Temperature and decreases of pressure

(C) Pressure and decreases of temperature

(D) None of these

Q.11 An emulsion is a colloidal system of

(A) Two solids

(B) Two liquids

(C) One gas and one solid

(D) One gas and one liquid

Q.12 Which of the following is a lyophobic colloid?

(A) Gelatin (B) Sulphur

(C) Starch (D) Gum

Q.13 The nature of bonding forces in adsorption

(A) Purely physical such as Van Dar Waal's forces

(B) Purely chemical

(C) Both chemical and physical always

(D) None of these

Q.14 Which can adsorb larger volume of hydrogen gas?

(A) Colloidal solution of palladium

(B) Finely divided nickel

(C) Finely divided platinum

(D) Colloidal $Fe(OH)_3$

Q.15 Which statement is correct?

(A) A catalyst increases the rate of a reaction by decreasing the rate of backward reaction

(B) The reaction is fast if the activation energy of a reaction is low

(C) The activation energy of a forward reaction can never be smaller than that of the back ward reaction

(D) Reaction rate increases with temperature because the activation energy decreases at high temperature

Q.16 The Tyndall effect associated with colloidal particles is due to

(A) Presence of electrical charges

(B) Scattering of light

(C) Absorption of light

(D) Reflection of light

Q.17 Which one of the following is not applicable to chemisorptions?

(A) Its heat of adsorption is high

(B) It takes place at high temperature

(C) It is reversible

(D) It forms mono-molecular layers

Q.18 In the colloidal state the particle size ranges

(A) Below 1 nm

(B) Between 1 m to 100 nm

(C) More than 100 nm

(D) None of the above

Q.19 All colloids

(A) Are suspensions of one phase in another

(B) Are two-phase systems

(C) Contain only water-soluble particles

(D) Are true solutions

Q.20 Which is an example of auto-catalysis?

(A) Decomposition of $KClO_3$ + MnO_2 mixture

(B) The decomposition of nitroglycerine

(C) Breakdown of ${}_6C^{14}$

(D) Hydrogenation of vegetable oils using catalyst

Q.21 Colloids can be purified by

(A) Condensation (B) Peptization

(C) Coagulation (D) Dialysis

Q.22 Milk is an example of

(A) Emulsion (B) Suspension

(C) Foam (D) Sol

Q.23 Colloidal particles in a sol can be coagulated by

(A) Heating

(B) Adding an electrolyte

(C) Adding oppositely charged sol

(D) Any of the above methods

Q.24 Enzymes are

(A) Substances made by chemists to activate washing powder

(B) Very active vegetable catalysts

(C) Catalysts found in organisms

(D) Synthetic catalysts

Q.25 Fog is a colloidal system of

(A) Gas in liquid (B) Liquid in gas

(C) Gas in gas (D) Gas in solid

Q.26 Given below are a few electrolytes, indicate which one among them will bring about the coagulation of a gold sol quickest and in the least of molar concentration?

(A) NaCl (B) $MgSO_4$

(C) $Al_2(SO_4)_3$ (D) $K_4[Fe(CN)_6]$

Q.27 When a lyophobic colloidal solution is observed, we can see

(A) Light scattered by colloidal particle

(B) Size of the colloidal particle

(C) Shape of the colloidal particle

(D) Relative size of the colloidal particle

Q.28 The process which is catalysed by one of the products formed during the reaction is known

(A) Auto-catalysis (B) Anti-catalysis

(C) Negative catalysis (D) Acid catalysis

Q.29 Colloidal solutions are classified on the basis of

(A) Molecular size

(B) Organic or inorganic

(C) Surface tension value

(D) pH value

Q.30 The minimum concentration of an electrolyte required to cause coagulation of a sol is called

(A) Flocculation value (B) Gold number

(C) Protective value (D) None of these

Q.31 Smoke precipitator works on the principle of

(A) Distribution law

(B) Neutralization of charge on colloids

(C) Le-Chaterlier's principle

(D) Addition of electrolytes

Q.32 The disperse phase in colloidal iron (III) hydroxide and colloidal gold is positively and negatively charged respectively. Which of the following is not correct?

(A) Magnesium chloride solution coagulates the gold more readily than iron (III) hydroxide Sol

(B) Sodium sulphate solution cause coagulation in both sols

(C) Mixing of the sols has no effect

(D) Coagulation in both sols can be brought about by electrophoresis.

Previous Years' Questions

Q.1 Which of the following statements is incorrect regarding physisorption ***(2009)***

(A) It occur because of Van der Waals forces

(B) More easily liquefiable gases are adsorbed readily

(C) Under high pressure it results into multi molecular layer on adsorbent surface.

(D) Enthalpy of adsorption (ΔH-adsorption) is known and positive

Q.2 Which one of the following characteristics is not correct for physical adsorption ***(2003)***

(A) Adsorption on solid is reversible

(B) Adsorption increases with increase in temperature

(C) Adsorption is spontaneous

(D) Both enthalpy and entropy of adsorption are negative

Q.3 The equation for Freundlich adsorption isotherm is ***(2012)***

(A) $\frac{x}{m} = kp^{1/n}$ (B) $x = mkp^{1/n}$

(C) $\frac{x}{m} = kp^{-n}$ (D) All of these

Q.4 Which one of the following is not a colloid? ***(1992)***

(A) Milk (B) Blood

(C) Solution of urea (D) Ice cream

Q.5 Choose the correct reason(s) for the stability of the lyophobic colloidal particles ***(2012)***

(A) Preferential adsorption of ions of their surface from the solution

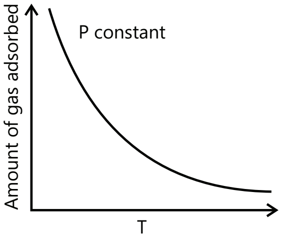
(B) Preferential adsorption of solvent on their surface from the solution

(C) Attraction between different particles having opposite charge on their surface

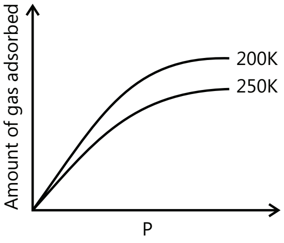
(D) Potential difference between the fixed layer and the diffused layer of opposite charges around the colloidal particles

Q.6 The given graphs/data I, II, III and IV represent general trends observed for different physisorption and chemisorptions processes under mild conditions of temperature and pressure. Which of the following choice(s) about I, II, III and IV is (are) correct. ***(2012)***

(I)



(III)



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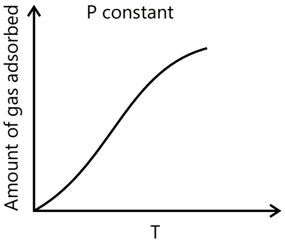
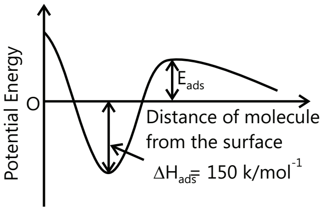


(IV)



(A) I is Physisorption and II is chemisorption

(B) I is Physisorption and III is chemisorption

(C) IV is chemisorption and II is chemisorption

(D) IV is chemisorption and III is chemisorption

Q.7 Gold numbers of protective colloids A, B, C and D are 0.50, 0.01, 0.10 and 0.005, respectively. The correct order of their protective powers is ***(2008)***

(A) D < A < C < B (B) C < B < D < A

(C) A < C < B < D (D) B < D < A < C

Q.8 Which of the following statements is incorrect regarding physisorption? ***(2009)***

(A) It occurs because of Vander Waal's forces.

(B) More easily liquefiable gases are adsorbed readily.

(C) Under high pressure it results into multi molecular layer on adsorbent surface.

(D) Enthalpy of adsorption $\left(\Delta H_{\text{adsorption}}\right)$ is low and positive.

Q.9 According to Freundlich adsorption isotherm, which of the following is correct? ***(2012)***

(A) $\frac{x}{m} \propto P^0$

(B) $\frac{x}{m} \propto P^1$

(C) $\frac{x}{m} \propto P^{1/n}$

(D) All the above are correct for different ranges of pressure

Q.10 The coagulating power of electrolytes having ions Na^+, Al^{3+} and Ba^{2+} for arsenic sulphide sol increases in the order: ***(2013)***

(A) $Al^{3+} < Ba^{2+} < Na^+$ (B) $Na^+ < Ba^{2+} < Al^{3+}$

(C) $Ba^{2+} < Na^+ < Al^{3+}$ (D) $Al^{3+} < Na^+ < Ba^{2+}$

Q.11 3 g of activated charocoal was added to 50 mL of acetic acid solution (0.06N) in a flask. After an hour it was filtered and the strength of the fitrate was found to be 0.042 N. The amount of acetic acid adsorbed (per gram of charcoal) is: ***(2015)***

(A) 18 mg (B) 36 mg (C) 42 mg (D) 54 mg

Q.12 For a linear plot of log(x/m) versus log p in a Freundlich adsorption isotherm, which of the following statements is correct? (k and n are constants) ***(2016)***

(A) 1/n appears as the intercept

(B) Only 1/n appears as the slope.

(C) log (1/n) appears as the intercept.

(D) Both k and 1/n appear in the slope term.

JEE Advanced/Boards

Exercise 1

Q.1 Give reason why a finely divided substance is more effective as an adsorbent.

Q.2 What are enzymes? Write in brief the mechanism of enzyme catalysis.

Q.3 What are emulsion? What are their different types? Give example of each type.

Q.4 Why are substances like platinum and palladium often used for carrying out electrolysis of aqueous solutions?

Q.5 Why are powdered substance more effective adsorbent that their crystalline forms?

Q.6 Why is it necessary to remove CO when ammonia is obtained by Haber's process?

Q.7 What is the role of desorption in the process of catalysis?

Q.8 Why is ferric chloride preferred over potatassium chloride in case of a cut leading to bleeding?

Q.9 What is the 'coagulation' process?

Q.10 Which will be adsorbed more readily on the surface of charcoal and why-NH_3 or CO_2?

Q.11 How is adsorption of a gas related to its critical temperature?

Q.12 What does you mean by activity of catalysis?

Q.13 What happens when gelatin is added to gold sol?

Exercise 2

Single Correct Choice Type

Q.1 Which equation represents Freundlich adsorption isotherm (physical adsorption is basis of this theory)?

(A) $\frac{x}{m} = K(P)^{1/n}$ Where x is amount of gas adsorbed on mass 'm' at pressure P

(B) $\log\frac{x}{m} = \log K + \frac{1}{n}\log P$

(C) $\frac{x}{m} = KP$ at low pressure and $\frac{x}{m} = K$ at high pressure

(D) All of these

Q.2 Emulsifier is an agent which

(A) Accelerates the dispersion

(B) Homogenizes an emulsion

(C) Stabilizes an emulsion

(D) Aids the flocculation of an emulsion

Q.3 The process which is catalysed by one of the products formed during the reaction is known

(A) Auto-catalysis (B) Anti-catalysis

(C) Negative catalysis (D) Acid catalysis

Q.4 The electrical charge on a colloidal particle is indicated by

(A) Brownian movement (B) Electrophoresis

(C) Ultra microscope (D) Molecular sieves

Q.5 Among the following, the surfactant that which will from micelles in aqueous solution at the lower molar concentration at ambient conditions is

(A) $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$

(B) $CH_3(CH_2)_{11}OSO_3^-Na^+$

(C) $CH_3(CH_2)_6COO^-Na^+$

(D) $CH_3(CH_2)_{11}N^+(CH_3)_3Br^-$

Comprehension Type

Paragraph 1: In macromolecular type of colloids, the dispersed particles are themselves large molecules (usually polymers) . Since these molecules have dimensions comparable to those of colloidal particles, their dispersions are called macromolecular colloids. Most lyophilic sols belong to this category. There are certain colloids which behave as normal strong electrolytes at low concentrations, but exhibit colloidal properties at higher concentrations due to the formation of aggregated particles. These are known as micelles or associated colloids. Surface active agents like soaps and synthetic detergents belong to this class.

Critical micelle concentration (CMC) is the lowest concentration at which micelle formation appear. CMC increases with the total surfactant concentrations. At concentration higher than CMC, they from extended parallel sheets known as lamellar micelles which resemble biological membranes. With two molecules thick, the individual molecule is perpendicular to the sheets such that hydrophilic groups are on the outside in aqueous solution and on the inside is a non-polar medium.

In concentrated solutions, micelles take the form of long cylinders packed in hexagonal arrays and are called lytotropic mesomorphs.

In an aqueous solution (polar medium), the polar group points towards the periphery and the hydrophobic hydrocarbon chain point towards the center forming the core of the micelle.

Micelles from the ionic surfactants can be formed only above a certain temperature called the Kraft temperature. They are capable of forming ions. Molecules of soaps and detergents consist of lyophilic as well as lyophilic parts which associate together to form micelles. Micelles may contain as many as 100 molecules or more.

Q.6 Select incorrect statement(s):

(A) Surface active agent like soaps and synthetic detergents are micelles

(B) Soaps are emulsifying agents

(C) $C_{17}H_{35}$ (hydrocarbon part) and –COO– (carboxylate) part of stearate ion ($C_{17}H_{35}COO$–) both are hydrophobic

(D) All are incorrect statements

Q.7 Which part of the soap (RCOO–) dissolves grease and forms micelle?

(A) R part (called tail of the anion)

(B) – COO – part (called head of the anion)

(C) Both (A) and (B)

(D) None of these

Q.8 In multimolecular colloidal sols, atoms or molecules are held together by:

(A) H-bonding (B) Van der Waals forces

(C) Ionic bonding (D) Polar covalent boding

Q.9 Cleansing action of soap occurs because:

(A) Oil and grease can be absorbed into the hydrophobic centers of soap micelles and washed away

(B) Oil and grease can be absorbed into hydrophilic centers of soap micelles acid washed away

(C) Oil and grease can be absorbed into both hydrophilic and hydrophobic centers but not washed away

(D) Cleansing action is not related to micelles

Paragraph 2: The protective power of the lyophilic colloids is expressed in terms of gold number a term introduced by Zsigmondy. Gold number is the number of milligram of the protective colloid which prevent the coagulation of 10 mL of red gold sol. When 1 mL of a 10 percent solution of sodium chloride is added to it. Thus, smaller the gold number of lyophilic colloid, the greater is the protective power.

Q.10 On addition of one mL of solution of 10% NaCl to 10 mL of red gold sol in presence of 0.025 g of starch, the coagulation is just prevented. The gold number of starch is

(A) 0.025 (B) 0.25 (C) 2.5 (D) 25

Q.11 Which of the following statement(s) is/are correct

(A) Higher the gold number, more protective power of colloid

(B) Lower the gold number, more the protective power

(C) Higher the coagulation value, more the coagulation power

(D) Lower the coagulation value, higher the coagulation power

Q.12 Gold number gives an indication of

(A) Protective nature of colloids

(B) Purity of gold in suspension

(C) The charge on a colloidal solution of gold

(D) g-mole of gold per liter

Paragraph 3: Whenever a mixture of gases is allowed to come in contact with a particular adsorbent under the same conditions, the stronger adsorbate is adsorbed to greater extent irrespective of its amount present, e.g. H_2O is adsorbed to more extent on silica gel than N_2 and O_2. This shows that some adsorbates are preferentially adsorbed. It is also observed that preferentially adsorbable adsorbents can displace a weakly adsorbed substance from the surface of an adsorbent.

Q.13 Which of the following gases is adsorbed to maximum extent:

(A) He (B) Ne (C) Ar (D) Xe

Q.14 Which of the gas can displace remaining all the gases.

(A) O_2 (B) N_2 (C) CO (D) H_2

Q.15 When temperature is increased

(A) Extent of adsorption increases

(B) Extent of adsorption decreases

(C) No effect on adsorption

(D) Extent of adsorption first decreases, then increases

Assertion Reasoning Type

These questions consist of two statements each, printed as assertion and reason, while answering these questions you are required to choose any one of the following responses.

(A) If assertion is true but the reason is false

(B) If assertion is false but the reason is true

(C) If both assertion and reason are true and the reason is a correct explanation of assertion

(D) If both assertion and reason are true but reason is not a correct explanation of assertion.

Q16 Assertion: For adsorption ΔG, ΔH, ΔS all have –ve values

Reason: Adsorption is a spontaneous exothermic process in which randomness decreases due to force of attraction between adsorbent and adsorbate.

Q.17 Assertion: A gas with higher critical temperature gets adsorbed to more extent than a gas with lower critical temperature.

Reason: The easily liquefiable gases get adsorbed to more extent.

Q.18 Assertion: The micelle formed by sodium stearate in water has – COO– groups at the surface.

Reason: Surface tension of water is reduced by the addition of stearate.

Q.19 Assertion: Isoelectric point is pH at which colloidal can move towards either of electrode.

Reason: At isoelectric point, colloidal particles become electrically neutral.

Previous Years' Questions

Q.1 When the temperature is increased, surface tension of water ***(2002)***

(A) Increases (B) Decreases

(C) Remains constant (D) Shows irregular behavior

Q.2 Rate of physisorption increases with ***(2003)***

(A) Decrease in temperature

(B) Increase in temperature

(C) Decrease in pressure

(D) Decrease in surface area

Q.3 Spontaneous adsorption of a gas on solid surface is an exothermic process because ***(2004)***

(A) ΔH increases for system (B) ΔS increases for gas

(C) ΔS decreases for gas (D) ΔG increases for gas

Q.4 As gas is adsorbed on surface of solid, entropy decreases, i.e. $\Delta S < 0$. Therefore, for $\Delta G < 0$, ΔH must be negative. Lyophilic sols are ***(2005)***

(A) Irreversible sols

(B) Prepared from inorganic compounds

(C) Coagulated adding electrolytes

(D) Self-stabilizing

Q.5 Among the following, the surfactant that will form micelles in aqueous solution at the lowest molar concentration at ambient condition, is ***(2008)***

(A) $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$ (B) $CH_3(CH_2)_{11}OSO_3^-N^+$

(C) $CH_3(CH_2)_6COO^-N^+$ (D) $CH_3(CH_2)_{11}N^+(CH_3)_3Br^-$

Q.6 Among the electrolytes Na_2SO_4, $CaCl_2$, $Al_2(SO_4)_3$ and NH_4Cl, and NH_4Cl, the most effective coagulating agent for Sb_2S_3 sol is ***(2009)***

(A) Na_2SO_4 (B) $CaCl_2$ (C) $Al_2(SO_4)_3$ (D) NH_4Cl

Q.7 The correct statement(s) pertaining to the adsorption of a gas on a solid surface is (are) ***(2011)***

(A) Adsorption is always exothermic

(B) Physisorption many transform into chemisorption at high temperature

(C) Physisorption increases with increasing temperature but chemisorption decreases with increasing temperature

(D) Chemisorption is more exothermic than physisorption, however it is very slow due to higher energy of activation.

Assertion and Reasoning Type

Read the following questions and answer as per the direction given below:

(A) Statement-I is true: statement-II is a correct explanation of statement-I.

(B) Statement-I is true; statement-II is true; statement-II is not the correct explanation of statement-I

(C) Statement-I is true; statement-II is false.

(D) Statement-I is false, statement-II is true

Q.8 Statement-I: Micelles are formed by surfactant molecules above the critical micelle concentration (CMC).

Statement-II: The conductivity of a solution having surfactant molecules decreases sharply at the CMC. ***(2007)***

Q.9 Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at 250C. For this process, the correct statement is ***(2013)***

(A) The adsorption requires activation at 25°C.

(B) The adsorption is accompanied by a decrease in enthalpy.

(C) The adsorption increases with increase of temperature.

(D) The adsorption is irreversible

Q.10 When O_2 is adsorbed on a metallic surface, electron transfer occurs from the metal to O_2. The true statement(s) regarding this adsorption is(are) ***(2015)***

(A) O_2 is physisorbed

(B) Heat is released

(C) Occupancy of k π^*_{2p} of O_2 is increased

(D) Bond length of O_2 is increased

Q.11 Choose the correct reason(s) for the stability of the **lyophobic** colloidal particles. ***(2012)***

(A) Preferential adsorption of ions on their surface from the solution

(B) Preferential adsorption of solvent on their surface from the solution

(C) Attraction between different particles having opposite charges on their surface

(D) Potential difference between the fixed layer and the diffused layer of opposite charges around the colloidal particles

PlancEssential Questions

JEE Main/Boards

Exercise 1

Q.3 Q.9 Q.13 Q.17
Q.19 Q.24 Q.31

Exercise 2

Q.3 Q.12 Q.15 Q.26
Q.31

Previous Years' Questions

Q.6

JEE Advanced/Boards

Exercise 1

Q.2 Q.4 Q.13

Exercise 2

Q.1 Q.5 Q.7 Q.10-12

Previous Years' Questions

Q.2 Q.6 Q.19

Answer Key

JEE Main/Boards

Exercise 2

Single Correct Choice Type

Q.1 B **Q.2** D **Q.3** C **Q.4** D **Q.5** B **Q.6** B
Q.7 A **Q.8** B **Q.9** D **Q.10** C **Q.11** B **Q.12** B
Q.13 B **Q.14** A **Q.15** B **Q.16** B **Q.17** C **Q.18** B
Q.19 B **Q.20** B **Q.21** D **Q.22** A **Q.23** D **Q.24** C
Q.25 B **Q.26** C **Q.27** A **Q.28** A **Q.29** A **Q.30** A
Q.31 B **Q.32** C

Previous Years' Querstions

Q.1 D **Q.2** B **Q.3** D **Q.4** C **Q.5** A, D **Q.6** A, C
Q.7 C **Q.8** D **Q.9** D **Q.10** B **Q.11**A **Q.12** B

JEE Advanced/Boards

Exercise 2

Single Correct Choice Type

Q.1 D **Q.2** C **Q.3** A **Q.4** B **Q.5** A

Comprehension Type

Q.6 A, D **Q.7** A **Q.8** B **Q.9** A **Q.10** D
Q.11 B, D **Q.12** A **Q.13** D **Q.14** C **Q.15** B

Assertion Reasoning Type

Q.16 C **Q.17** C **Q.18** A **Q.19** B

Previous Years’ Questions

Q.1 B **Q.2** A **Q.3** C **Q.4** D **Q.5** A **Q.6** C
Q.7 A,B,D **Q.8** B **Q.9** B **Q.10** B,C,D **Q.11** A, D

Solutions

JEE Main/Boards

Exercise 1

Sol 1: As the charge of Fe^{3+} is high, it's coagulation power will be high. So, it can stop bleeding.

Sol 2: The Brownian movement is due to the collision between the particles of colloid & the medium of the solution.

Sol 3: Chemisorption because it involves breaking & forming of bonds. Physisorption just depends on weak Vander Waals forces.

Sol 4: We can coagulate lyophilic colloids by

- adding on electrolyte. (it reacts with colloids)
- adding a suitable solvent.

Sol 5: Emulsion is a mixture of two or more liquids which are normally immiscible. Ex. Milk.

It's a colloid of a liquid in another liquid.

Sol 6: It's a kind of adsorption in which adsorbate is held by weak Vander Waal's forces to the medium (adsorbent) .

Sol 7: If there is bond formation (chemical reaction) between adsorbate & the medium, then it's chemical adsorption.

Sol 8: Desorption is the reverse of adsorption. It's a process of removing an adsorption from some medium.

Sol 9: If T_C of a gas is high, then it can be liquified easily, so greater is the extent of adsorption (because of high Van der Waals force) . If T_C is low, the given gas is a bad adsorbate.

Sol 10: Colloidal sol is stable because of the like charged particles. So, they do not form large particles. Sol is solids dispersed in liquid.

Sol 11: (i) Sols are solids in liquids, where as emulsions are liquids in liquids.

(ii) Sols are more stable compared to emulsions.

Sol 12: Ultra filtration is a type of filtration in which purification is carried out through special filters or semipermeable membranes. Generally, they allow passage of electrolyte but not colloid particles.

Sol 13: The size of particles is greater than the wavelength of visible light. So, colloid particles scatter light which is Tyndall effect.

Sol 14: Clouds are colloids of water droplet in air. Adding salt coagulates the water droplets. So they form bigger drops. So, it comes down as rain.

Sol 15: The oppositely charged go to separate electrodes and get coagulated there.

Sol 16: (i) Fe^{+3} is the preferential adsorbate. So, it's positively charged Sol

(ii) Physical adsorption decreases with increase in T due to increase in the energy of particles, they escape Van der Waals forces.

(iii) It's due to possible formation of colloid at the point of mixing.

Sol 17: (i) Electro-dialysis : It's the process of transporting salt ions from one solution to other through ion-exchange membrane under a potential difference.

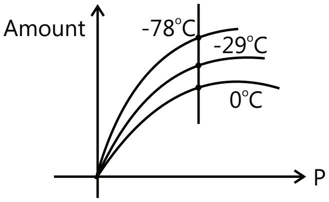
(ii) (a) Dispersal phase : - It's the component present in small proportions and is just like a solute in a solution. It's also called the 'Internal phase'.

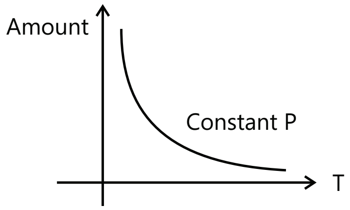
(b) Dispersion medium : - It's generally the component present in excess and is just like a solvent in a solution. It's also called the 'External phase'.

Sol 18: Shape selectivity of a catalyst depends upon the pore structure of the catalyst.

Depending on the size of the reactant and product molecules when compared to the size of cages or pores of the zeolite, reactions proceed in a specific manner.

Sol 19:



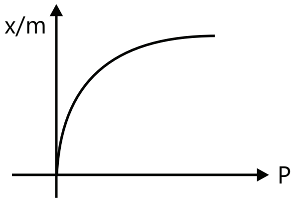


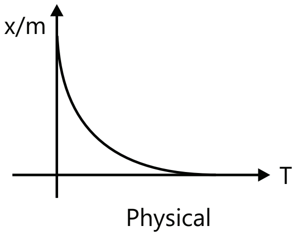
Sol 20: (i) It leads to coagulation as oppositely charged electrolyte particles get attracted to the sol particles.

(ii) It leads to separation of dispersed phase & dispersion medium.

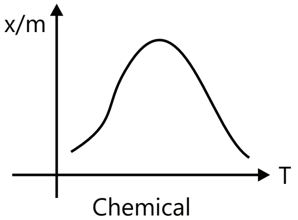
(iii) Colloid particles will be accumulated at electrodes.

Sol 21: In physisorption, the size is an important factor because it determines Van der Waals forces.





Physical



Chemical

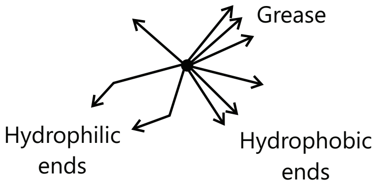
Sol 22: (a) (i) Silica gel – adsorption

(ii) Anhydrous $CaCl_2$ – Absorption

(b) Due to the presence of empty orbital in B.

Ba, Mg, B, Ga, P in zeolites.

Sol 23: (i) A micelle is an aggregate of surfactant molecules dispersed in a liquid colloid. The hydrophobic end dissolves in the grease where as hydrophilic end dissolves in H_2O.



(ii) Hardy-Schulze Rule – Greater is the valency of the coagulating ion, greater is its power to bring coagulation.

And the effective ions of the electrolyte in bringing about coagulation are those which carry opposite charge to that of colloid particles.

Sol 24: (i) Multimolecular colloids: - They are formed by aggregates of a large number of atoms or molecules. E.g. Sols of Gold, Sulphur etc.

(ii) Macromolecular colloids: - They are molecules of very large size. E.g. Polymers like rubber, starch etc.

Sol 25: Chemisorption have higher activation energy and enthalpy of adsorption.

Sol 26: (i) The sol coagulates due to addition of electrolyte.

(ii) The positive and negative sol particles deposit at respective electrodes.

(iii) We observe Tyndall effect i.e. light gets scattered.

Sol 27: (i) Tyndall effect: - Tyndall scattering, is light scattering by particles in a colloids or particles is a fine suspension. Individual particles of colloid reflect and scatter light of wavelength (in same order as particle sizes).

(ii) A catalytic reaction which depends upon the active site and pore structure of catalyst and not on the size of reactant and product is known as shape selective catalysis.

Sol 28: Coagulation of hydrophobic ions can be done by using method of neutralising ions.

Sol 29: (i) It will lead to coagulation as NaCl acts as electrolyte. and $FeCl_3$ comes as precipitate.

(ii) If beam of light is passed through NaCl solution. The intensity decreases as NaCl (aq) is a true solution.

It does not show Tyndall effect.

But when light is passed through sol, we observe scattering (Tyndall effect).

Sol 30: Coagulation is the process which involves precipitation of a colloidal solution by addition of excess of electrolyte.

It can be caused by

- Electrophoresis
- Prolonged dialysis
- Addition of two sols (Mutual precipitation)

Exercise 2

Single Correct Choice Type

Sol 1: (B) A gas with high critical temperature (T_C) can be liquefied easily. So, it's adsorbed on a solid to a greater extent.

Sol 2: (D) Adsorption of a gas depends on

- T_C of gas
- Temperature
- Pressure

Sol 3: (C) $NH_3 > CO_2 > CH_4$ (ease of liquefaction)

It's because of their T_C.

$T_{C_{NH_3}} > T_{C_{CO_2}} > T_{C_{CH_4}}$

Sol 4: (D) Pt is not use in synthesis of NH_3. N_2, H_2 are not easily liquifiable.

Sol 5: (B) Transition metals form effective catalyst due to high inter-atomic spaces.

Sol 6: (B) The heat of physisorption is quite low. It's in the range of 20-40 kJ/mole.

Sol 7: (A) Physical adsorption can be multi-layered because of Van der Waals forces.

Sol 8: (B) Physical adsorption is reversible but not chemical. It's because chemisorption has high activation energy.

Sol 9: (D) Gels – Solid in liquid (jelly type). Milk is an emulsion, rest all are gels.

Sol 10: (C) Increases with P, decreases with T.

Sol 11: (B) Emulsion is a colloidal system of 2 liquids.

Sol 12: (B) Sulphur does not dissolve in water. It's a lyophobic colloid.

Sol 13: (B) Physical – Van der Waals. Chemical – Chemical bonds.

Sol 14: (A) Colloidal solution of Pd because Pd has highly affinity towards H and colloid solution will have higher Pd surface.

Sol 15: (B) The reaction is fast, if activation energy is low. Catalyst reduces activation energy.

Activation energy need not be inversely proportion to temperature.

Sol 16: (B) Scattering of light.

Sol 17: (C) Chemisorption is not reversible. Other statements are true about chemisorption.

Sol 18: (B) In colloids, size of particles is nearly wavelength of visible light. i.e. 1 nm – 100 nm range.

Sol 19: (B) Colloids are 2 phase system. They are different from suspensions.

Sol 20: (B) Decomposition of nitro glycerine is auto-catalysis. So it's used in explosive, TNT.

Sol 21: (D) Colloids can be purified by dialysis.

Sol 22: (A) Milk–Emulsion. (Oil in water)

Sol 23: (D) Adding oppositely charged Sol. Heating and adding an electrolyte can coagulate sols.

Sol 24: (C) Enzymes are naturally occurring catalysts. (Present in organisms) .

Sol 25: (B) Fog – Liquid in gas (water vapour in atmosphere)

Sol 26: (C) Gold sol in negative. So Al^{3+} will be the best coagulating agent.

Sol 27: (A) We can observe scattering of light due to larger size of particles.

Sol 28: (A) Auto-catalysis as we need very less amount of catalyst but the reaction goes quickly.

Sol 29: (A) Colloids are classified on the basis of their particle size.

Sol 30: (A) Flocculation value is the minimum concentration of an electrolyte required to cause coagulation.

Sol 31: (B) Smoke precipitation works on neutralisation of charge on colloids. It uses the force of an induced electrostatic charges.

Sol 32: (C) Mixing of sols will lead to coagulation. Electrophoresis can coagulate both.

$MgCl_2$ will coagulate gold sol quickly because Mg^{2+} has higher charge than Cl^-. Mg^{+2} coagulates negatively charged Sol

Previous Years' Questions

Sol 1: (D) Since adsorption is exothermic process so ΔH of adsorption is always negative.

Sol 2: (B) Adsorption increases with increase in temperature

Sol 3: (D) $\frac{x}{m} = kp^{1/n}$ or $x = m.kp^{1/n}$

or $x / m = kp^{-n}$

All of these equation represent Freundlich adsorption isotherm.

Sol 4: (C) Solution of urea is not a colloid.

Sol 5: (A, D)

(A) Due to preferential adsorption of common ion

(B) Incorrect

(C) Incorrect (due to repulsion, not due to attraction)

(D) The layer of oppositely charged particles around any colloidal particles will decrease the potential energy of system.

Sol 6: (A, C) In Physisorption, on increasing temperature at constant pressure, adsorption decreases while in chemical adsorption on increasing temperature due to requirement of activation energy adsorption will increases at same pressure. So, I is physisorption while II is chemisorption.

III is physical adsorption as on increasing temperature, extent of adsorption is decreasing. IV is representing enthalpy charge (which is high) during chemical adsorption (due to bond formation) So, is valid for chemical adsorption. So, answer is (A) and (C).

Sol 7: (C) Higher the gold number lesser will be the protective power of colloid.

Sol 8: (D) Enthalpy of adsorption regarding physisorption is not positive and it is negative.

Sol 9: (D) $\frac{x}{m} \propto P^1$; $\frac{x}{m} \propto P^{1/n}$ are true at low and moderate pressures.

Sol 10: (B) According to Hardy Schulze rule, greater the charge on cation, greater is its coagulating power for negatively charged solution. So, order of coagulating power: $Na^+ < Ba^{2+} < Al^{3+}$.

Sol 11: (A)

Initial m moles of $CH_3COOH = 0.06 \times 50$

Final m moles of $CH_3COOH = 0.042 \times 50$

Hence, mass of CH_3COOH adsorbed per gram of charcoal $= \frac{(0.06 - 0.042) \times 50 \times 10^{-3} \times 60 \times 10^3}{3} = 18$ mg

Sol 12: (B) According to the Freundlich adsorption isotherm

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

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

JEE Advanced/Boards

Exercise 1

Sol 1: Finely divided substance has more surface area than normal crystals. So, adsorption will be more effective.

Sol 2: Enzyme:-They are complex organic compounds present in living beings inside the human body (or other organisms) and act as catalyst in many processes.

They are also called Bio-Catalyst. Its mechanism is similar to other catalysis. By providing an alternative reaction route, the enzyme reduces the energy required to reach the highest energy transition state of the reaction.

Sol 3: Emulsion are colloids of liquid in liquid.

- Oil in water type – Ex. Milk
- Water in oil type – Ex. Butter.

Sol 4: There are 2 main reasons:

- They are chemically inert.
- They are good catalyst due to high inter atomic spaces. Their affinity towards hydrogen is very high.

Sol 5: Powdered substances have very high surface area compared to crystals. So, adsorption on powdered substance is effective.

Sol 6: CO acts as poison in Haber's process. Poison is a negative catalyst i.e. it reduces the rate of reaction.

Sol 7: The products after reaction must be desorbed from the catalyst so that further reaction can take place.

Sol 8: Fe^{+3} has higher coagulating power compared to K^+, So, it can stop bleeding by coagulating blood around the wound.

Sol 9: It's the process of setting down of colloid particles.

Sol 10: NH_3 has a higher T_C than CO_2. So it is easily liquefiable.

$\therefore$ NH_3 will be adsorbed more readily.

Sol 11: More is the T_C of a gas, more is the easiness to liquefy the gas. So, more is the extent of adsorption.

Sol 12: Activity is the ability of a catalyst to drive the reaction in forward direction.

It depends on many factors like surface area, temperature etc.

Sol 13: Gelatin has a low gold number, so even adding small amounts of gelatin will stabilise it. It will act as a lyophilic colloid.

Exercise 2

Single Correct Choice Type

Sol 1: (D) $\frac{x}{m} = k(P)^{\frac{1}{n}} \Rightarrow \log\left(\frac{x}{m}\right) = \frac{1}{n}\log P + \log K.$

At high P

$\frac{x}{m} \approx K$

At low P

$\frac{x}{m} \approx KP'$

Sol 2: (C) Emulsifier is a substance used to stabilise emulsions.

Sol 3: (A) Auto-catalysis as we need very less amount of catalyst but the reaction goes quickly.

Sol 4: (B) Electrophoresis depends on electric charge. Rest, all methods depends on size of particles.

Sol 5: (A) To form micelle at very low concentration, it must be highly insoluble in water. $CH_3(CH_2)_{11}OSO_3^-$,$CH_3(CH_2)_6COO^-$has charged ends. N^+ in other 2 structure is crowded, so it's interaction with H_2O will be less. So $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$ will need minimum conc. as its H.C. length is high.

Comprehension Type

Sol 6: (A, D) COO^- is hydrophilic part. Soaps are emulsifying agents.

Sol 7: (A) R part is hydrocarbon part. It dissolves in grease and forms micelle.

Sol 8: (B) In multi-molecular colloids, atoms or molecules are held together by weak Van der Waals forces.

Sol 9: (A) Cleansing action of soap is due to attraction between hydrophobic part of soap & grease (oil) .

Sol 10: (D) 0.025 g – 25 mg

$\therefore$ Gold number = 25

Sol 11: (B, D) Lower the gold number, more is the protective power as lesser the amount of substance required to prevent coagulation. Similarly, lower is coagulation value, higher is coagulation power.

Sol 12: (A) Protective nature of colloids.

Sol 13: (D) Xe will be adsorbed to maximum extent because of its high T_C compared to other elements in it's group.

Sol 14: (C) CO. As its the most easily liquefiable gas.

Sol 15: (B) Adsorption is inversely proportional to temperature.

Assertion Reasoning Type

Sol 16: (C) In adsorption, ΔH is –ve (adsorption is exothermic) ΔS is also negative as freedom of adsorbent decrease.

Sol 17: (C) If T_C of a gas is high, its easily liquefiable. So, it can be adsorbed easily.

Sol 18: (A) Adding detergents reduces the surface tension of water. COO^- interacts with polar H_2O molecules.

Sol 19: (B) Assertion is false, isoelectric point is the pH at which particle is electrically neutral (may be Zwitter ions). A is false.

Previous Years' Questions

Sol 1: (B) As temperature increases, surface tension of liquid decreases.

Sol 2: (A) It is an exothermic process. According to Le-Chatelier's principle, lowering temperature drive the process in forward direction.

Sol 3: (C) $\Delta G = \Delta H - T\Delta S$

Sol 4: (D) Lyophilic sols are reversible, not easily coagulated because it is self-stabilizing.

Sol 5: (A) Larger the hydrophobic fragment of surfactant, easier will be the micellization, smaller the critical micelle concentration. Therefore, $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$ will have the lowest critical micelle concentration.

Sol 6: (C) Sb_2S_3 is a negative (anionic) Sol According to Hardy Schulze rule, greater the valency of cationic coagulating agent, higher its coagulating power. Therefore, $Al_2(SO_4)_3$ will be the most effective coagulating agent in the present case.

Sol 7: (A, B, D) (A) In the process of adsorption, a bond is formed between adsorbate and adsorbent, hence always exothermic.

(B) Physisorption required very low activation energy while chemisorption require high activation energy. Therefore, a physisorption may transform into chemisorption but only at high temperature.

(C) It is wrong statement as at higher temperature, physically adsorbed substance starts desorbing.

(D) In physical adsorption, van der Waal's force hold the adsorbate and adsorbent together which is a weak electrostatic attraction. In chemisorption, strong chemical bond binds the adsorbate to the adsorbent. Therefore, chemisorption is more exothermic than physical adsorption.

Sol 8: (B) Both statements are independently correct but statement-II does not explain statement-I. Critical micelle concentration is the minimum concentration of surfactant at which micelle formation commences first. At critical micelle concentration, several molecules of surfactant coalesce together to form one single micelle molecule. This decreases the apparent number of molecule suddenly lowering conductivity sharply.

Sol 9: (B) Adsorption of methylene blue on activated charcoal is physical adsorption hence it is characterised by decrease in enthalpy.

Sol 10: (B, C, D) Adsorption of O_2 on metal surface is exothermic. During electron transfer from metal to O_2 electron occupies π^*_{2p} orbital of O_2.

Due to electron transfer to O_2 the bond order of O_2 decreases hence bond length increases.

Sol 11: (A, D) Lyophobic colloids are stable due to preferential adsorption of ions on their surface from solution and potential difference between the fixed layer and the diffused layer of opposite charges around the colloidal particles that makes lyophobic sol stable.