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.

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

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.

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

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.

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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.

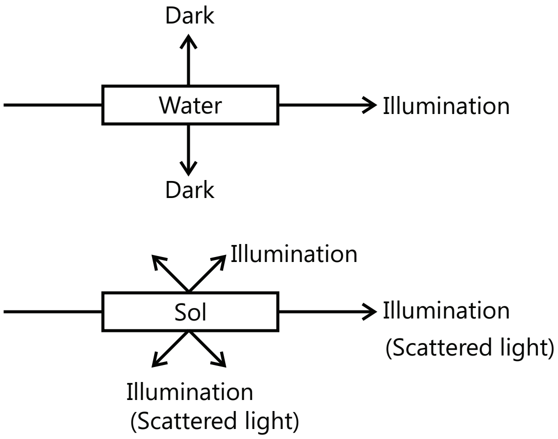

Figure 21.1: Scattering of light-Tyndall Effect

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.

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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.

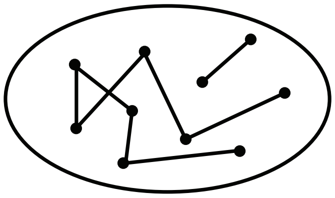

Figure 21.2: Brownian movement - zig-zag motion of a colloidal particle.

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.

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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.

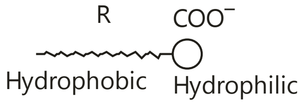
6.1 Origin of Charge

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

(b) Due to electron capture by sol particles.

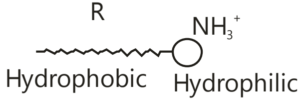
(c) Nature of dispersed phase: The nature of dispersed phase also contributes for the charge on sol particles.

(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.

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

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

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.

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

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

6.2 Distribution of Charge

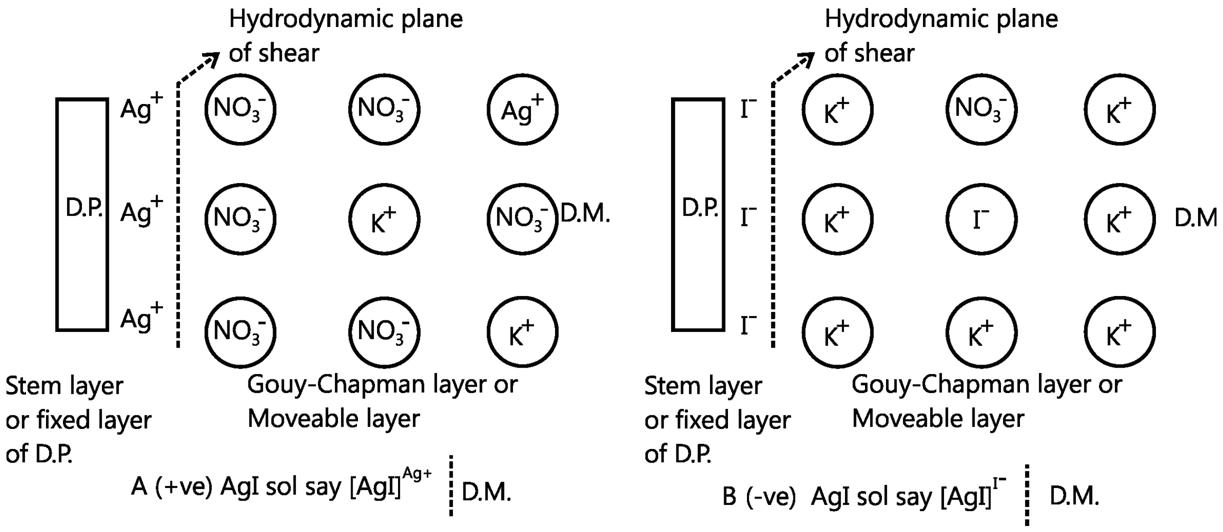


Figure 21.3: Distribution of charge

(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.

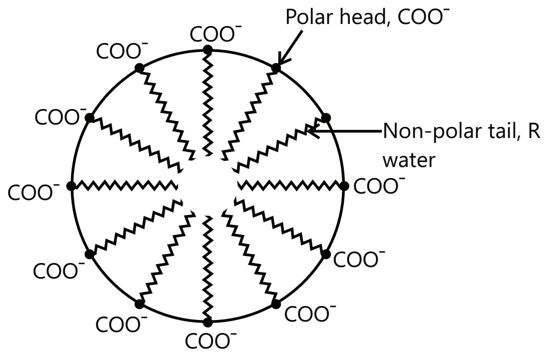
(c) **Thixotropy or melting by touch:** Outcome of internal liquid on applying shear to gels and thus, gel structure is also disturbed.

(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.



Aggregation of $RCOO^-$ ions to form anionic micelle

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).

MASTERJEE 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 $CH_3\left(CH_2\right)_{n_1}SO_4Na$ is lower than CMC of $CH_3\left(CH_2\right)_{n_2}SO_4Na$ 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

MASTERJEE 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

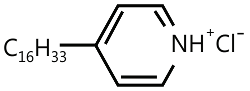
Association colloids: These are also lyophilic colloids but are formed by the aggregation of soap or detergent molecules in solution above CMC (these are micellar colloids).

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).

MASTERJEE 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.

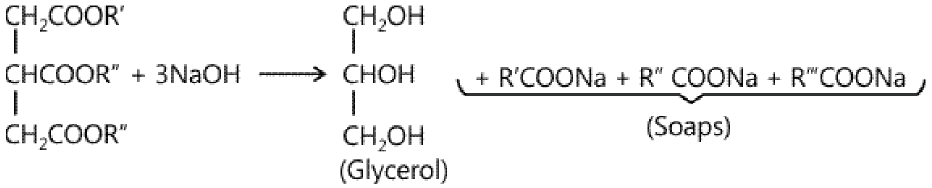
Illustration 11: Why hard water consumes more soap? **(JEE MAIN)**

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.



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

(Glycerol)

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.

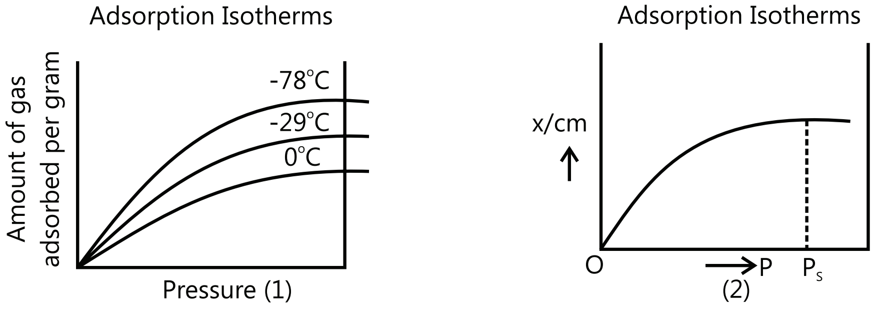


Figure 21.5: Effect of pressure on rate of adsorption

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 $\frac{x}{m} \propto p^0$ $\left(\because p^0 = 1\right)$

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

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

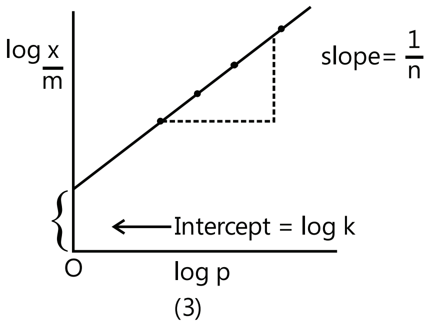


Figure 21.6: Plot of log (x/m) vs log p

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 6×10^{-6} cm^2

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

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

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 $\dfrac{x}{m}$. **(JEE MAIN)**

Sol: By using ideal gas equation calculate x/m

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

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

$\therefore x_{O_2}$ 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, $K_d\theta = K_aP(1-\theta)$

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

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

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

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

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

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

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

(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.

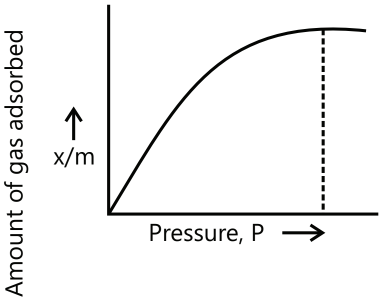


Figure 21.7: Plot of (x/m) vs pressure 1

MASTERJEE 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, $2.303\log\frac{r_2}{r_1}=\frac{Ea}{R}\frac{[T_2-T_1]}{T_1T_2}$;

$$2.303\log\frac{1.5a}{a}=\frac{Ea}{8.314}\left[\frac{1000-500}{1000\times500}\right]$$

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

$$\log 0.185=\frac{1}{n}\log 2\times10^{-2}+\log k \quad \text{... (i)}$$

$$\log 0.290=\frac{1}{n}\log 4\times10^{-2}+\log k \quad \text{... (ii)}$$

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

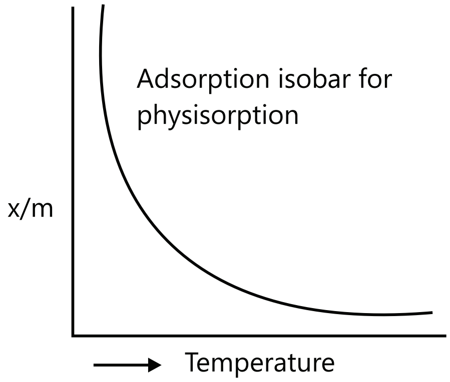


Figure 21.8: Effect of temperature on physisorption

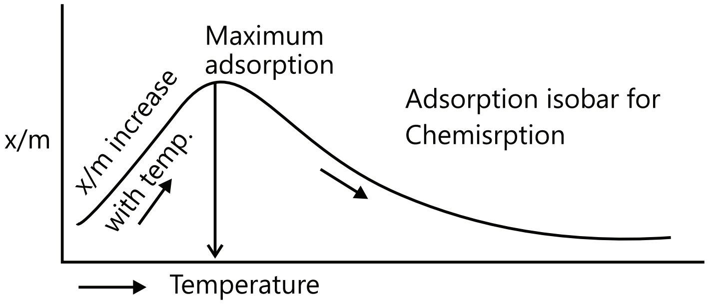


Figure 21.9: Effect of temperature on chemisorption

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.

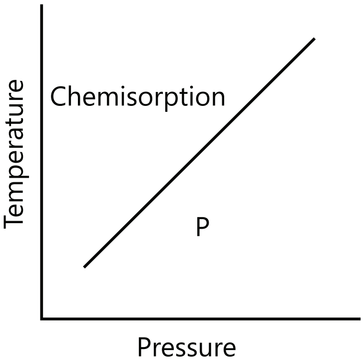


Figure 21.10: Effect of pressure on Chemisorption

(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.

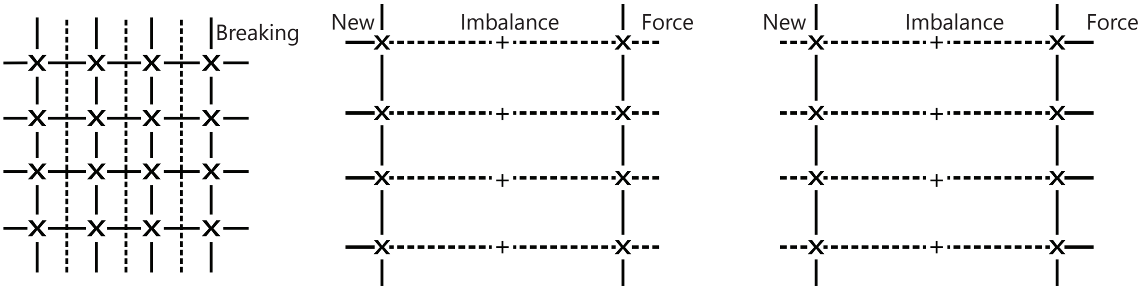


Figure 21.11: Adsorption power

- **(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.

MASTERJEE 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

$$\text{HCOOH(l)} \begin{cases} \xrightarrow{\text{Cu}} \text{CO}_2\text{(g)} + \text{H}_2\text{(g)} \text{ (Dehydrogenation)} \\ \xrightarrow{\text{Al}_2\text{O}_3} \text{CO(g)} + \text{H}_2\text{O(g)} \text{ (Dehydration)} \end{cases}$$

(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.

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

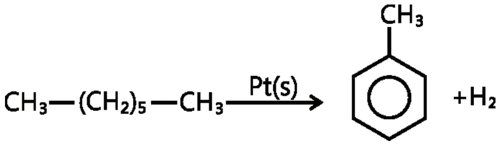
Important Characteristic of Heterogeneous Catalyst

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

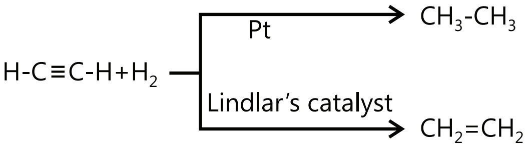
(a) **Activity:** It implies the ability of catalyst to accelerate a chemical reaction. The degree of acceleration can be sometimes as high as 10^{10}. For example, the reaction between H_2 and O_2 gases in the presence of platinum catalyst to form water occur with an explosive violence, whereas a mixture 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:

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

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

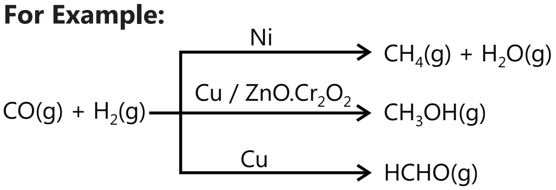
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Gulcose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

MASTERJEE 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.

$$CCl_2F_2 \xrightarrow{h\upsilon} CClF_2 + \dot{C}l$$

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

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

(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.

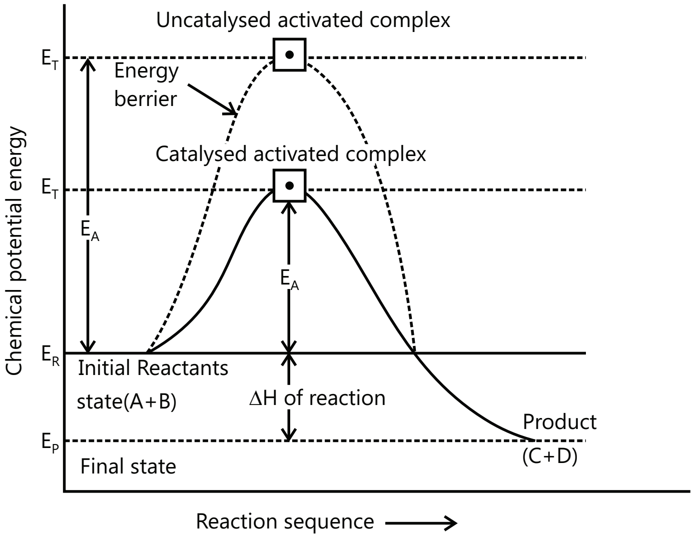


Figure 21.12: Catalytic Reaction Pathway

(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.

MASTERJEE 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.

MASTERJEE 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.

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

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

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

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

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

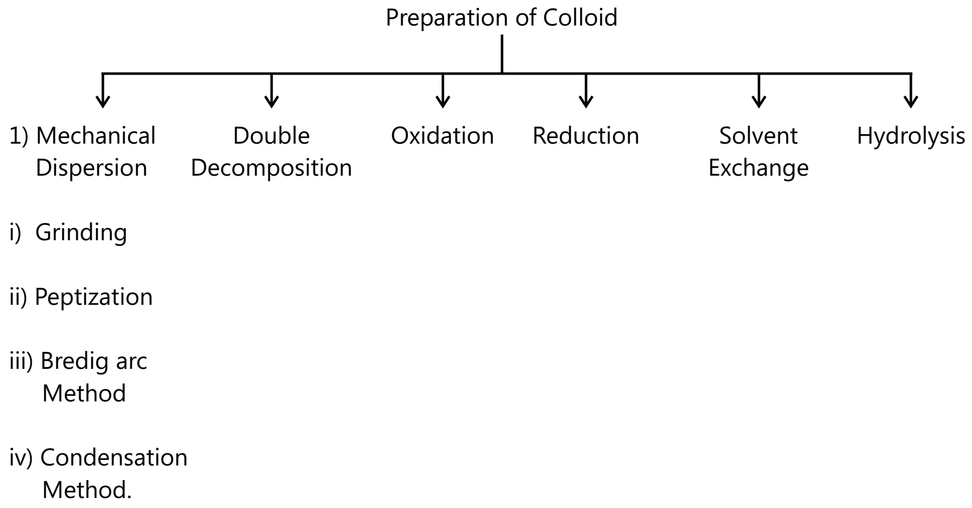
When rate of adsorption or desorption is given use the following equation, $2.303 \log \frac{r_2}{r_1} = \frac{Ea}{R} \frac{[T_2 - T_1]}{T_1 T_2}$

POINTS TO REMEMBER

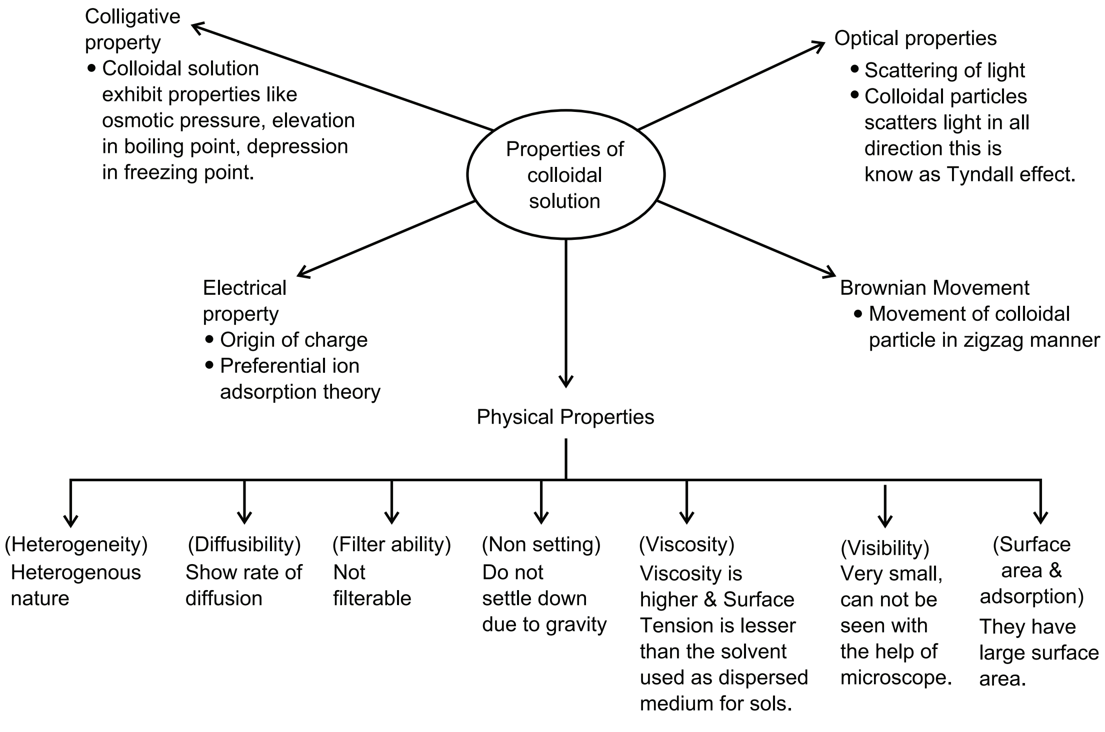
COLLOIDS

Characteristics of Colloidal State

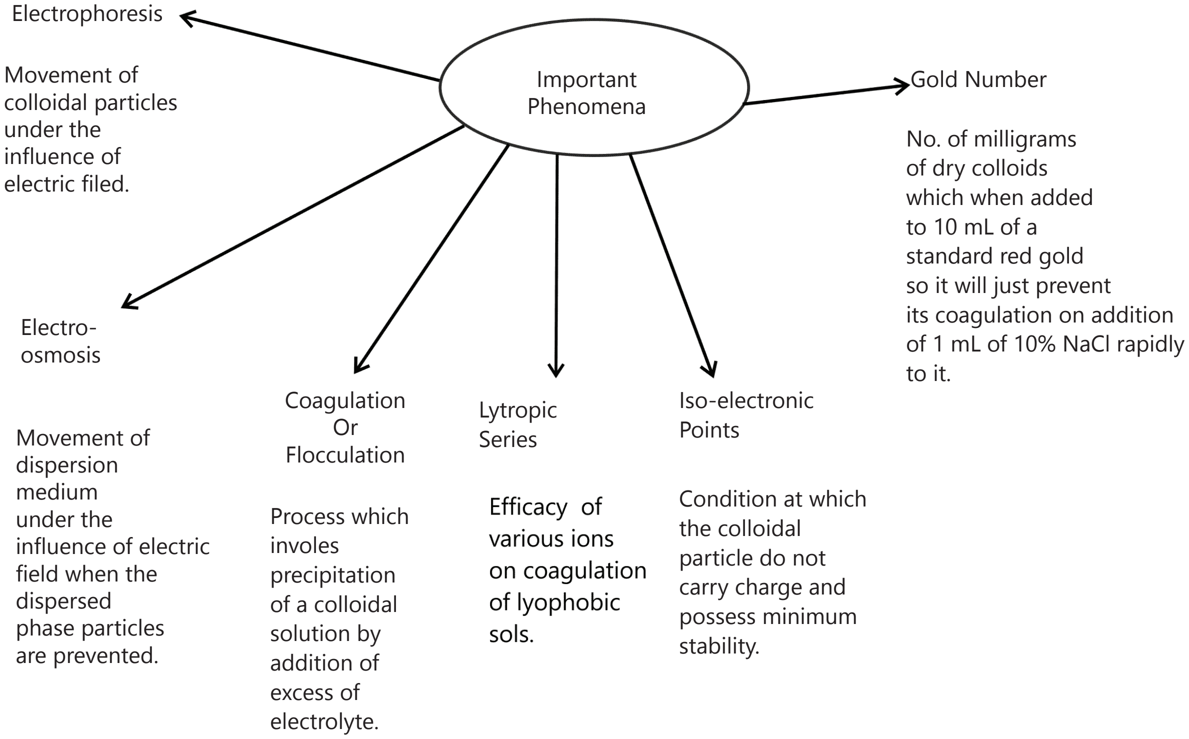
- It is a particular state, Heterogeneous in nature, number of phases = 2. i.e Dispersed phase and Dispersion medium.
- The one phase dispersed in other is known as dispersed phase (or D.P.) or internal phase or discontinuous phase whereas, the other in which dispersions are made is known as dispersion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

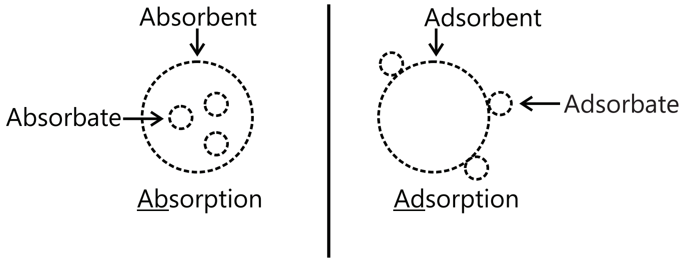
Condition at which the colloidal particle do not carry charge and possess minimum stability.

Gold Number

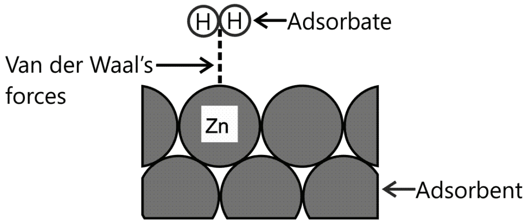
No. of milligrams of dry colloids which when added to 10 mL of a standard red gold so it will just prevent its coagulation on addition of 1 mL of 10% NaCl rapidly to it.

ADSORPTION

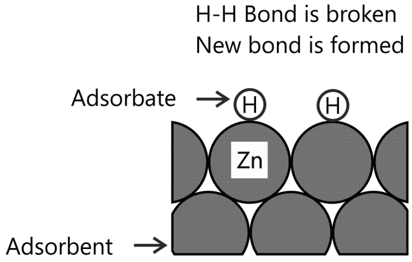
Absorption and Adsorption process:



Physical Adsorption and Chemical Adsorption



Physical Adsorption



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.

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

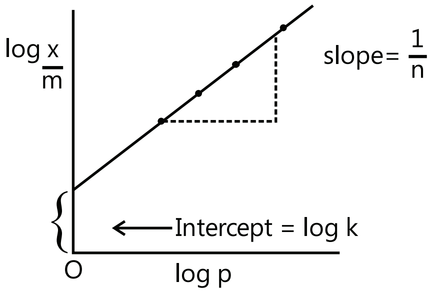
2. At high pressure extent of adsorption is independent of pressure.

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

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

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

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

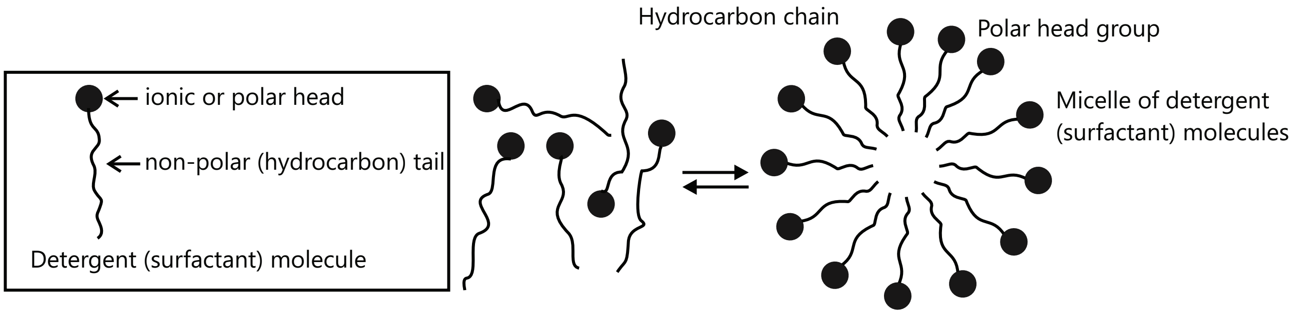
$$\frac{x}{m} = aP \quad (K_1P <<< 1 \therefore bP <<< 1)$$

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.

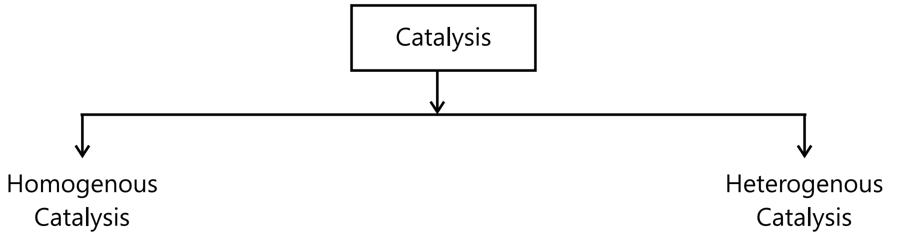
- They have polar head group and long hydrocarbon chain tail which is apolar.
- The concentration at which the surfactants molecule aggregates and micelle formation takes place is known as critical micellar concentration.
- Though their hydrocarbon chain they interact with the dirt particle (say oil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

Micelle Formation:



CATALYSIS

Type of Catalysis



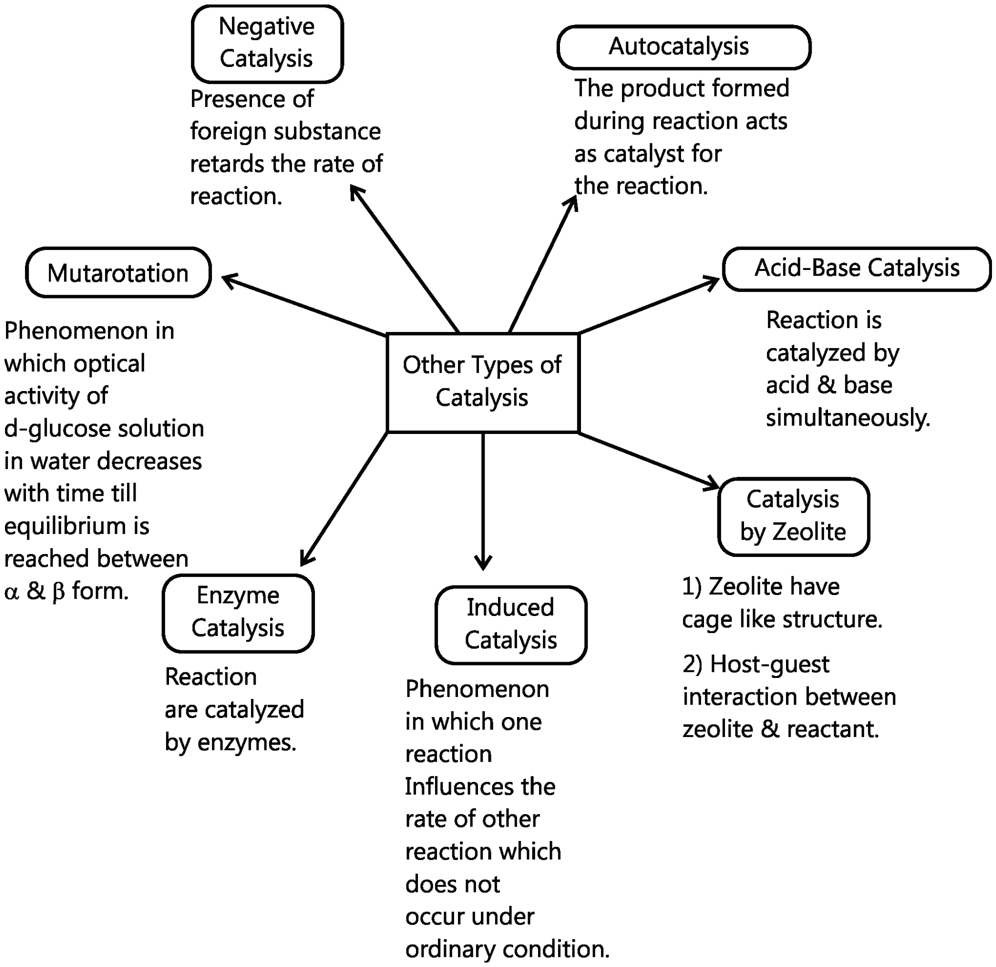
Catalyst & reactants are in the same phase.

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



Other Types of Catalysis

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

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

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

Catalysis by Zeolite
1) Zeolite have cage like structure.
2) Host-guest interaction between zeolite & reactant.

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

Enzyme Catalysis
Reaction are catalyzed by enzymes.

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