الجامعة التكنولوجية

قسم الهندسة الكيمياوية

المرحلة الثانية

الكيمياء الفيزياوية وعلم العوالق

م.د. منال افهم

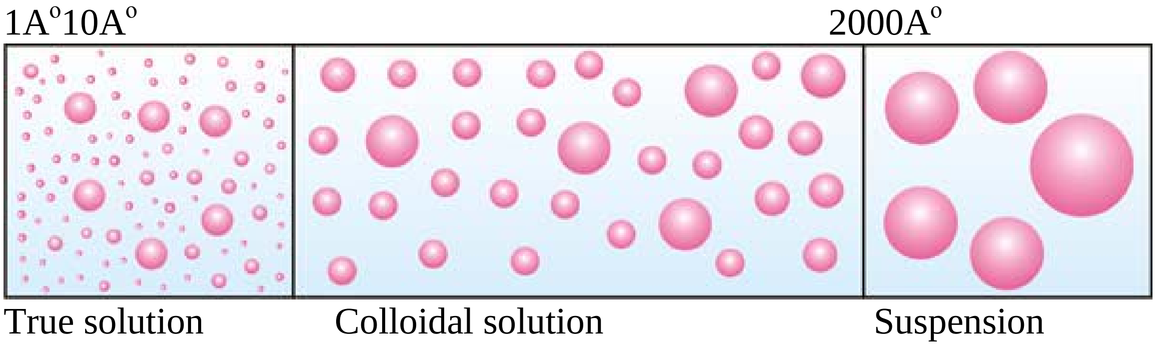
Colloid

Thomas Graham (1861) studied the ability of dissolved substances to diffuse into water across a permeable membrane. He observed that crystallinesubstances such as sugar, urea, and sodium chloride passed through themembrane, while others like glue, gelatin and gum arabic did not.

The former he called crystalloids and the latter colloids (Greek, kolla = glue ; eidos = like). Graham thought that the difference in the behavior of'crystalloids' and 'colloids' was due to the particle size. Later it was realised that any substance, regardless of its nature, could be converted into a colloid by subdividing it into particles of colloidal size.

In a true solution as sugar or salt in water, the solute particlesare dispersed in the solvent as single molecules or ions. Thusthe diameter of the dispersed particles ranges from 1Å to 10 Å.

On the other hand, in a suspension as sand stirred intowater, the dispersed particles are aggregates of millions ofmolecules. The diameter of these particles is of the order 2,000 Å or more.



Particle size (indicated by diameter) range of true solution, colloidal dispersion, and suspension

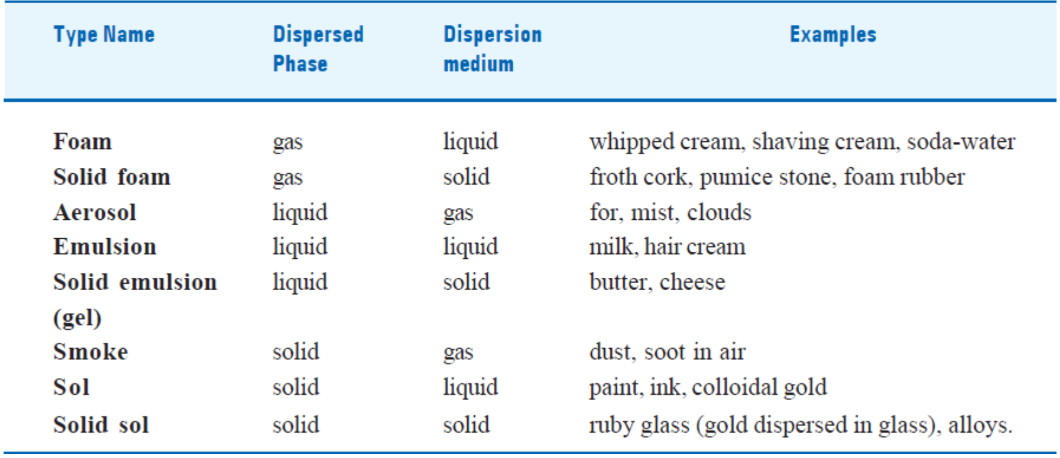
The colloidal solutions or colloidal dispersions are intermediate between true solutions andsuspensions.In other words, the diameter of the dispersed particles in a colloidal dispersion is morethan that of the solute particles in a true solution and smaller than that of a suspension.

When the diameter of the particles of a substance dispersed in a solvent ranges from about 10Å to 2,000 Å, the system is termed a colloidal solution, colloidal dispersion, or simply a colloid.The material with particle size in the colloidal range is said to be in the ***colloidal state.***

Types of colloidal systems

As we have seen above, a colloidal system is made of two phases. The substance distributed as the colloidalparticles is called the **Dispersed phase.** The second continuous phase in which the colloidal particles are dispersed is called the **Dispersion medium.** For example, for a colloidal solution of copper in water, copper particles constitute the dispersed phase and water the dispersion medium.

As stated above, a colloidal system is made of a dispersed phase and the dispersion medium. Because either the dispersed phase or the dispersion medium can be a gas, liquid or solid, there are eight types of colloidal systems possible. A colloidal dispersion of one gas in another is not possible since the two gases would give a homogeneous molecular mixture.



Type Name	Dispersed Phase	Dispersion medium	Examples
Foam	gas	liquid	whipped cream, shaving cream, soda-water
Solid foam	gas	solid	froth cork, pumice stone, foam rubber
Aerosol	liquid	gas	for, mist, clouds
Emulsion	liquid	liquid	milk, hair cream
Solid emulsion (gel)	liquid	solid	butter, cheese
Smoke	solid	gas	dust, soot in air
Sol	solid	liquid	paint, ink, colloidal gold
Solid sol	solid	solid	ruby glass (gold dispersed in glass), alloys.

The name given to the colloid depends on the two phases involved. A **sol** is a dispersionof a solid in a liquid (such as clusters of gold atoms in water) or of a solid in a solid (such as ruby glass, which is a gold-in-glass sol, and achieves its colour by lightscattering). An **aerosol** is a dispersion of a liquid in a gas (like fog and many sprays) ora solid in a gas (such as smoke): the particles are often large enough to be seen with amicroscope. An **emulsion** is a dispersion of a liquid in a liquid (such as milk).

A further classification of colloids is as **lyophilic**, or solvent attracting, and **lyophobic**, solvent repelling. If the solvent is water, the terms **hydrophilic** and **hydrophobic**, respectively, are used instead. Lyophobic colloids include the metal sols.

Lyophilic colloids generally have some chemical similarity to the solvent, such as -OH groups able to form hydrogen bonds. A **gel** is a semirigid mass of a lyophilic sol in which all the dispersion medium has penetrated into the sol particles.

In this chapter we will restrict our study mainly to the colloidal systems which consist of a solidsubstance dispersed in a liquid. These are frequently referred to as **Sols** or **Colloidal solution.**

Thecolloidal solutions in water as the dispersion medium are termed **Hydrosols or Aquasols.** When thedispersions medium is alcohol or benzene, the sols are referred to as **Alcosols** and **Benzosols**respectively.

Sols are colloidal systems in which a solid is dispersed in a liquid.

These can be subdivided into two classes :

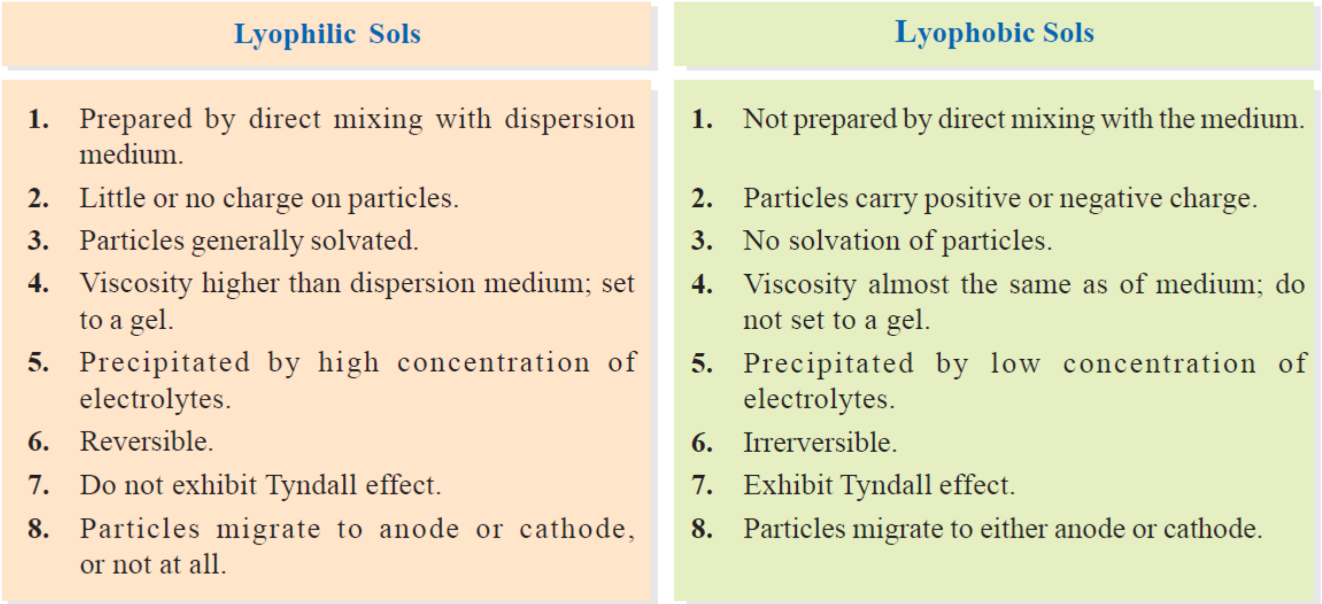
(*a*) Lyophilic sols (solvent-loving)

(*b*) Lyophobic sols (solvent-hating)

*Lyophilic sols are those in which the dispersed phase exhibits a definite affinity for the mediumor the solvent.*The examples of lyophilic sols are dispersions of starch, gum, and protein in water.

Lyophobic sols are those in which the dispersed phase has no attraction for the medium or thesolvent.The examples of lyophobic sols are dispersion of gold, iron (III) hydroxide and sulphur in water.

The affinity or attraction of the sol particles for the medium, in a lyophilic sol, is due to hydrogenbonding with water. If the dispersed phase is a protein (as in egg) hydrogen bonding takes placebetween water molecules and the amino groups (-NH-, $-NH_2$) of the protein molecule. In a dispersionof starch in water, hydrogen bonding occurs between water molecules and the -OH groups of thestarch molecule. ***There are no similar forces of attraction when sulphur or gold is dispersed inwater.***



Lyophilic Sols	Lyophobic Sols
1. Prepared by direct mixing with dispersion medium.	**1.** Not prepared by direct mixing with the medium.
2. Little or no charge on particles.	**2.** Particles carry positive or negative charge.
3. Particles generally solvated.	**3.** No solvation of particles.
4. Viscosity higher than dispersion medium; set to a gel.	**4.** Viscosity almost the same as of medium; do not set to a gel.
5. Precipitated by high concentration of electrolytes.	**5.** Precipitated by low concentration of electrolytes.
6. Reversible.	**6.** Irrerversible.
7. Do not exhibit Tyndall effect.	**7.** Exhibit Tyndall effect.
8. Particles migrate to anode or cathode, or not at all.	**8.** Particles migrate to either anode or cathode.

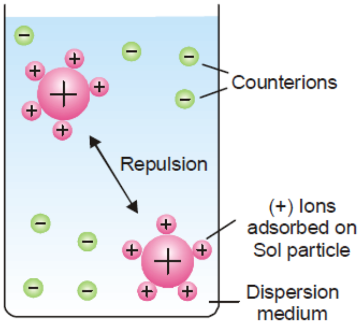
*****The phenomenon of the scattering of light by the sol particles is called Tyndall effect***

*****The continuous rapid zig-zag movement executed by a colloidal particle in the dispersion medium is called Brownian movement or motion.***

Electrical properties of Sols

I. The sol particles carry an electric charge

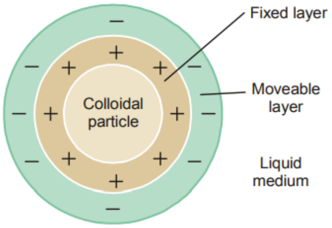
The most important property of colloidal dispersions is that all the suspended particles possess either a positive or a negative charge. The mutual forces of repulsion between similarly charged particles prevent them from aggregating and settling under the action of gravity (This gives stability to the sol). The sol particles acquire positive or negative charge by preferential adsorption of positive or negative ions from the dispersion medium. For example, a ferric hydroxide sol particles are positively charged because these adsorb Fe^{3+} ions from ferric chloride($FeCl_3$) used in the preparation of the sol. Since the sol as a whole is neutral, the charge on the particle is counterbalanced by oppositely charged ions termed **counterions** (in this case Cl^-) furnished by the electrolyte in medium.



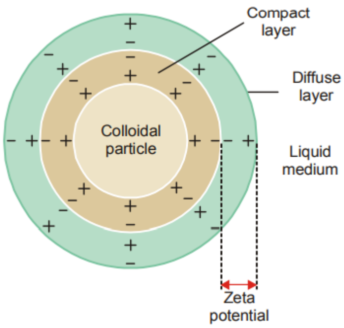
Adsorption of ions from dispersion medium gives charge to Sol particleswhich do not settle on account of mutual repulsions.

Electrical Double layer:

The surface of colloidal particle acquires a positive charge by selective adsorption of a layer of positive ions around it. This layer attracts counter ions from the medium which form a second layer of negative charges. The combination of the two layer of +ve and –ve charges around the sol particle was called Helmholtz Double layer. Helmholtz thought that positive charges next to the particle surface were fixed, while the layer of negative charges along with the medium were mobile.



Helmholtz double layer.



The electrical double layer (Stern).

More recent considerations have shown that the double layer is made of :

(a) a Compact layer of positive and negative charges which are fixed firmly on the particle surface.**(b)** a Diffuse layer of counter ions (negative ions) diffused into the medium containing positive ions. The combination of the compact and diffuse layer is referred to as the **Stern Double layer** after the colloid chemist who first realised its significance. The diffuse layer is only loosely attached to the particle surface and moves in the opposite direction under an applied electric field. Because of the distribution of the charge around the particle, there is a difference in potential between the compact layer and the bulk of solution across the diffuse layer. This is called Electrokinetic or **Zeta potential**.

The presence of the double layer accounts for the electrical properties :

(i) Cataphoresis; and (ii) Electro-osmosis of colloids. It has been made possible to estimate the magnitude of the zeta potential with the help of these properties. We have explained the theory of electrical double layer taking example of a positive sol. Our considerations could well be applied to a negative sol with the interchange of the disposition of positive and negative ions.

II. Electrophoresis:

If electric potential is applied across two platinum electrodes dipping in a hydrophilic sol, the dispersed particles move toward one or the other electrode.

The movement of sol particles under an applied electric potential is called electrophoresis or cataphoresis. If the sol particles migrate toward the positive electrode, they carry a negative charge. On the other hand, if they move toward the negative electrode, they are positively charged. Thus by noting the direction of movement of the sol particles, we can determine whether they carry a positive or negative charge.

The phenomenon of electrophoresis can be demonstrated by placing a layer of As_2S_3 sol under two limbs of a U-tube. When a potential difference of about 100 volts is applied across the two platinum electrodes dipping in deionised water, it is observed that the level of the sol drops on the negative electrode side and rises on the positive electrode side. This shows that As_2S_3 sol has migrated to the positive electrode, indicating that the particles are negatively charged. Similarly, a sol of ferric hydroxide will move to the negative electrode, showing that its particles carry positive charge.

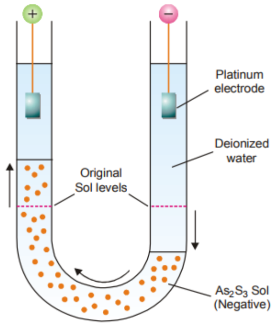


Illustration of Electro-osmosis.

Electrophoresis of a Sol.

Applications:

Some important applications of electrophoresis are:
(1) Removal of smoke from chimney gases;
(2) Removal of suspended impurities;
(3) Electro-plating of rubber on metal surfaces from latex (a sol);
(4) painting of metal parts of cars from colloidal pigments

III. Electro-osmosis

A sol is electrically neutral. Therefore the dispersion medium carries an equal but opposite charge to that of the dispersed particles. Thus the medium will move in opposite direction to the dispersed phase under the influence of applied electricpotential. When the dispersed phase is kept, stationary, the medium is actually found to move to the electrode of opposite sign that its own.

The movement of the dispersion medium under the influence of applied potential is known as electroosmosis.

Electro-osmosis is a direct consequence of the existence of zeta potential between the sol particles and the medium. When the applied pressure exceeds the zeta potential, that *diffuse layer* moves and causes electro-osmosis.

The phenomenon of electro-osmosis can be demonstrated by using a U-tube in which a plug of wet clay (a negative colloid) is fixed. The two limbs of the tube are filled with water to the same level. The platinum electrodes are immersed in water and potential applied across them. It will be observed that water level rises on the cathode side and falls on anode side. This movement of the medium towards the negative electrode, shows that the charge on the medium is positive. Similarly, for a positively charged colloid electro-osmosis will take place in the reverse direction.

Technically the phenomenon has been applied in the removal of water from peat, in dewatering of moist clay and in drying dye pastes.

IV. Coagulation or Precipitation

We know that the stability of a lyophobic sol is due to the adsorption of positive or negative ions by the dispersed particles. The repulsive forces between the charged particles do not allow them to settle. If, somehow, the charge is removed, there is nothing to keep the particles apart from each other. They aggregate (or flocculate) and settle down under the action of gravity.

The flocculation and settling down of the discharged sol particles is called coagulation orprecipitation of the sol.

How coagulation can be brought about?

The coagulation or precipitation of a given sol can be brought about in four ways :

(*a*) By addition of electrolytes
(*b*) By electrophoresis
(*c*) By mixing two oppositely charged sols
(*d*) By boiling

(*a*) **By addition of Electrolytes.** When excess of an electrolyte is added to a sol, the dispersedparticles are precipitated. The electrolyte furnishes both positive and negative ions in the medium.The sol particles adsorb the oppositely charged ions and get discharged. The electrically neutralparticles then aggregate and settle down as precipitateA negative ion (anion) causes the precipitation of a positively charged sol, and *vice versa*. Theeffectiveness of an anion or cation to precipitate a sol, will naturally depend on the magnitude of thecharge or valence of the effective ion. From a study of the precipitating action of various electrolyteson particular sol, Hardy and Schulze gave a general rule.Hardy-Schulze Rule states that **the precipitating effect of an ion on dispersed phase of oppositecharge increases with the valence of the ion.**

The higher the valency of the effective ion, the greater is its precipitating power. Thus forprecipitating an As_2S_3 sol (negative), the precipitating power of Al^{3+} , Ba^{2+}, Na^+ ions is in the order : $Al^{3+} > Ba^{2+} > Na^+$

Similarly, for precipitating $Fe(OH)_3$ sol (positive), the precipitating power of cations$[Fe(CN)_6]^{3-}$, SO_4^{-2} , Cl^- is in the order: $[Fe(CN)_6]^{3-} > SO4^{2-} > Cl^-$

The precipitation power of an electrolyte or ion is experimentally determined by finding theminimum concentration in millimoles per liter required to cause the precipitation of a sol in 2 hours.

This is called the **Flocculation value.** The smaller the flocculation value the higher the precipitatingpower of an ionratio for the mono-, di-, and trivalent anion or cation are approximately 1 : 40 : 90 for $Fe(OH)_3$ sol and1 : 70 : 500 for the As_2S_3 sol.

(*b*) **By Electrophoresis.** In electrophoresis the charged sol particles migrate to the electrode ofopposite sign. As they come in contact with the electrode, the particles are discharged and precipitated.

(*c*) **By mixing two oppositely charged sols.** The mutual coagulation of two sols of oppositecharge can be effected by mixing them. The positive particles of one sol are attracted by the negativeparticles of the second sol. This is followed by mutual adsorption and precipitation of both the sols.

Ferric hydroxide (+ve sol) and arsenious sulphide (–ve sol) form such a pair.

(*d*) **By boiling.** Sols such as sulphur and silver halides dispersed in water, may be coagulated byboiling. Increased collisions between the sol particles and water molecules remove the adsorbedelectrolyte. This takes away the charge from the particles which settle down.

V. Protective action of sols

Lyophobic sols are readily precipitated by small amounts of electrolytes. However these sols areoften stabilized by the addition of lyophilic sols.**The property of lyophilic sols to prevent the precipitation of a lyophobic sol is called *protection.***

The lyophilic sol used to protect a lyophobic sol from precipitation is referred to as a ***Protectivecolloid*.**

Example. If a little gelatin (hydrophilic colloid) is added to a gold sol (hydrophobic sol), the latteris protected. The 'protected gold sol' is no longer precipitated on the addition of sodium chloride.

Explanation. The particles of the hydrophobic sol adsorb the particles of the lyophilic sol. Thusthe lyophilic colloid forms a coating around the lyophobic sol particles. The hydrophobic colloid,therefore, behaves as a hydrophilic sol and is precipitated less easily by electrolytes.

Gold number

The lyophilic colloids differ widely in their powers of protection. The protective action of different colloids is measured in terms of the **'Gold number'** introduced by Zsigmondy. The gold number is defined as ***: the number of milligrams of a hydrophilic colloid that will just prevent the precipitation of 10 ml of a gold sol on the addition of 1 ml of 10 per cent sodium chloride solution.***

The onset of precipitation of the gold sol is indicated by a colour change from red to blue when the particle size just increases. The smaller the gold number of a hydrophilic colloid, the greater is its protective power. Gelatin has a small gold number and is aneffective protective colloid. Starch has a very high value, which shows that it is an ineffective protective colloid.

EMULSIONS

These are liquid-liquid colloidal systems. In other words, **an emulsion may be defined as adispersion of finely divided liquid droplets in another liquid.**

Generally one of the two liquids is *water* and the other, which is immiscible with water, isdesignated as *oil*. Either liquid can constitute the dispersed phase.

Types of Emulsions

There are two types of emulsions.

Oil-in-Water type (O/W type) ; (*b*) **Water-in-Oil type (W/O type)**

Examples of Emulsions

(1) Milk is an emulsion of O/W type. Tiny droplets of liquid fat are dispersed in water.

(2) Stiff greases are emulsions of W/O type, water being dispersed in lubricating oil.

Preparation of Emulsions

The dispersal of a liquid in the form of anemulsion is called **emulsification.** This can bedone by agitating a small proportion of oneliquid with the bulk of the other. It is betteraccomplished by passing a mixture of the twoliquid through a colloid mill known as**homogenizer.**

The emulsions obtained simply by shakingthe two liquids are unstable. The droplets ofthe dispersed phase coalesce and form aseparate layer. To have a stable emulsion, smallamount of a third substance called the**Emulsifier** or **Emulsifying agent** is addedduring the preparation. This is usually a soap,synthetic detergent, or a hydrophilic colloid.

Role of Emulsifier

The emulsifier concentrates at the interface and reduces surface tension on the side of one liquid which rolls into droplets. Soap, for example, is made of a long hydrocarbon tail (oil soluble) with a polar head —COO–Na+ (water soluble). In O/W type emulsion the tail is pegged into the oil droplet, while the head extends into water. Thus the soap acts as go-between and the emulsified droplets are not allowed to coalesce.

Properties of Emulsions

(1) ***Demulsification***: Emulsions can be broken or ‘demulsified’ to get the constituent liquids by heating, freezing, centrifuging, or by addition of appreciable amounts of electrolytes. They are also broken by destroying the emulsifying agent. For example, an oil-water emulsion stabilized by soap is broken by addition of a strong acid. The acid converts soap into insoluble free fatty acids.

(2) ***Dilution***: Emulsions can be diluted with any amount of the dispersion medium. On the other hand the dispersed liquid when mixed with it will at once form a separate layer. This property of emulsions is used to detect the type of a given emulsion.

Gels:

A gel is a jelly-like colloidal system in which a liquid is dispersed in a solid medium.

For example, when a warm sol of gelatin is cooled, it sets to a semisolid mass which is a gel. The process of a gel formation is known as **Gelation.**

Explanation. Gelation may be thought of as partial coagulation of a sol. The coagulating sol particles first unite to form long thread-like chains. These chains are then interlocked to form a solid framework. The liquid dispersion medium gets trapped in the cavities of this framework.

The resulting semisolid porous mass has a gel structure. A sponge soaked in water is anillustration of gel structure.

Two types of Gels

Gels may be classified into two types :

(*a*) **Elastic gels** are those which possess the property of elasticity. They change their shape on applying force and return to original shape when the force is removed. Gelatin, starch and soaps are examples of substances which form elastic gels.

Elastic gels are obtained by cooling fairly concentrated lyophilic sols. The linkages between the molecules (particles) are due to electrical attraction and are not rigid.

(*b*) **Non-elastic gels** are those which are rigid *e.g.*, silica gel. These are prepared by appropriate chemical action. Thus silica gel is produced by adding concentrated hydrochloric acid to sodium silicate solution of the correct concentration. The resulting molecules of silicic acid polymerize toform silica gel. It has a network linked by covalent bonds which give a strong and rigid structure.

Properties of Gels

(1) **Hydration:** A completely dehydrated elastic gel can be regenerated by addition of water. Butonce a nonelastic gel is freed from moisture, addition of water will not bring about gelation.

(2) **Swelling.** Partially dehydrate elastic gels imbibe water when immersed in the solvent. Thiscauses increase in the volume of the gel and process is called **Swelling.**

(3) **Syneresis:**Many inorganic gels on standing undergo shrinkage which is accompanied byexudation of solvent. This process is termed **Syneresis.**

(4) **Thixotropy:**Some gels are semisolid when at rest but revert to liquid sol on agitation. Thisreversible sol-gel transformation is referred to as **Thixotropy.** Iron oxide and silver oxide gels exhibitthis property. The modern thixotropic paints are also an example.

APPLICATIONS OF COLLOIDS

Colloids play an important role in our daily life and industry. A knowledge of colloid chemistry is essential to understand some of the various natural phenomena around us. Colloids make up someof our modern products. A few of the important applications of colloids are listed below.

(1) Foods

Many of our foods are colloidal in nature. Milk is an emulsion of butterfat in water protected bya protein, casein. Salad dressing, gelatin deserts, fruit jellies and whipped cream are other examples.Ice cream is a dispersion of ice in cream. Bread is a dispersion of air in baked dough.

(2) Medicines

Colloidal medicines being finely divided, are more effective and are easily absorbed in oursystem. Halibut-liver oil and cod-liver that we take are, in fact, the emulsions of the respective oils inwater. Many ointments for application to skin consist of physiologically active components dissolvedin oil and made into an emulsion with water. Antibiotics such as penicillin and streptomycin areproduced in colloidal form suitable for injections.

(3) Non-drip or thixotropic paints

All paints are colloidal dispersions of solid pigments in a liquid medium. The modern *nondrip orthixotropic paints* also contain long-chain polymers. At rest, the chains of molecules are coiled andentrap much dispersion medium. Thus the paint is a semisolid gel structure. When shearing stress isapplied with a paint brush, the coiled molecules straighten and the entrapped medium is released. Assoon as the brush is removed, the liquid paint reverts to the semisolid form. This renders the paint‘non-drip’.

(4) Electrical precipitation of smoke

The smoke coming from industrial plants is a colloidal dispersion of solid particles (carbon,arsenic compounds, cement dust) in air. It is a nuisance and pollutes the atmosphere. Therefore,before allowing the smoke to escape into air, it is treated by **Cottrell Precipitator**

The smoke is let past a series of sharp points charged to a high potential (20,000 to 70,000 V). Thepoints discharge high velocity electrons that ionise molecules in air. Smoke particles adsorb thesepositive ions and become charged. The charged particles are attracted to the oppositely chargedelectrodes and get precipitated. The gases that leave the *Cottrell precipitator* are thus freed fromsmoke. In addition, valuable materials may be recovered from the precipitated smoke. For example,arsenic oxide is mainly recovered from the smelter smoke by this method.

(5) Clarification of Municipal water

The municipal water obtained from natural sources often contains colloidal particles. The processof coagulation is used to remove these. The sol particles carry a negative charge. When aluminiumsulphate (*alum*) is added to water, a gelatinous precipitate of hydrated aluminium hydroxide (*floc*) isformed,

$Al^{3+} + 3H_2O \longrightarrow Al(OH)_3 + 3H^+$

$Al(OH)^{3+} + 4H_2O + H^+ \longrightarrow Al(OH)_3(H_2O)_4$

The positively charged *floc* attracts to it negative sol particles which are coagulated. The *floc*along with the suspended matter comes down, leaving the water clear.

(6) Formation of Delta

The river water contains colloidal particles of sand and clay which carry negative charge. Thesea water, on the other hand, contains positive ions such as Na^+, Mg^{2+}, Ca^{2+}. As the river water meetssea water, these ions discharge the sand or clay particles which are precipitated as **delta.**

(7) Artificial Kidney machine

The human kidneys purify the blood by dialysis through natural membranes. The toxic wasteproducts such as urea and uric acid pass through the membranes, while colloidal-sized particles ofblood proteins (haemoglobin) are retained. Kidney failure, therefore, leads to death due to accumulationof poisonous waste products in blood . Now-a-days, the patient's blood can be cleansed by shuntingit into an 'artificial kidney machine'. Here the impure blood is made to pass through a series of*cellophane tubes* surrounded by a washing solution in water. The toxic waste chemicals (urea, uricacid) diffuse across the tube walls into the washing solution. The purified blood is returned to thepatient. The use of artificial kidney machine saves the life of thousands of persons each year.

(8) Adsorption indicators

These indicators function by preferentialadsorption of ions onto sol particles. Fluorescein(Na^+Fl) is an example of adsorption indicatorwhich is used for the titration of sodium chloridesolution against silver nitrate solution.When silver nitrate solution is run into asolution of sodium chloride containing a littlefluorescein, a white precipitate of silver chlorideis first formed. At the end-point, the whiteprecipitate turns sharply pink.

Explanation. The indicator fluorescein is adye (Na^+Fl^-) which gives coloured anion Fl^- inaqueous solution. The white precipitate of silverchloride formed by running $AgNO_3$ solution intoNaCl solution is partially colloidal in nature.

(*a*) *Before the end-point,* Cl^- ions are inexcess. The AgCl sol particles adsorb these ionsand become negatively charged. The negative$AgCl/Cl^-$ particles cannot adsorb the colouredfluorescein anions (Fl^-) due to electrostaticrepulsion. Thus the precipitate remains white.

(*b*) *After the end-point,* Ag+ ions become in excess. AgCl sol particles adsorb these andacquire positive charge. The positive AgCl/Ag+ particles now attract the coloured fluorescein anions(Fl^-) and turn rose-red.

Thus the end-point is marked by white precipitate changing to pink.

(9) Blue colour of the sky

This is an application of Tyndall effect. The upper atmosphere contains colloidal dust or iceparticles dispersed in air. As the sun rays enter the atmosphere, these strike the colloidalparticles. The particles absorb sunlight and scatter light of blue colour (4600–

5100Å). The light thatis incident at earth's surface is considerably reddened due to the removal of most of the blue light inthe upper atmosphere.

Catalysis

Catalysts are chemical compounds that increase the rate of a reaction by lowering the activation energy required to reach the transition state and doesn't appear in the chemical equation. This term was coined in 1836 by Berzelius from the Greek words "kata" (wholly) and "lyein" (to loosen). Unlike reactants, a catalyst is not consumed as part of the reaction process. ***The process of speeding up a reaction by using a catalyst is known as catalysis***.

Classification of catalysis:

Catalysts can be divided into three main types - heterogeneous and homogeneous and enzyme catalysis. In a heterogeneous the catalyze reaction occur at the boundary between two phases (the catalysis is usually a solid), the catalyst is in a different phase from the reactants. In a homogeneous reaction, the catalyst is in the same phase as the all reactants, in enzyme catalysis can considered to be a separate class. A catalyst generally provides an alternative mechanism that competes with the uncatalyzed mechanism. If the catalyzed mechanism is faster than the uncatalyzed mechanism the observed rate of reaction is due mostly to the catalyzed mechanism, although the reaction is also still proceeding by uncatalyzed mechanism.

Enzyme catalysis:

In general, enzymes are proteins produced by living cells, they act as catalysts in biochemical reactions. One consequence of enzyme activity is that cells can carry out complex chemical activities at relative low temperatures. In an enzyme-catalyzed reaction, the substance to be acted upon (the substrate = S) binds reversibly to the active site of the enzyme (E). One result of this temporary union is a reduction in the energy required to activate the reaction of the substrate molecule so that the products (P) of the reaction are formed.

$$E + S \leftrightarrow ES$$

$$ES \longrightarrow E + P$$

the enzyme is not changed in the reaction and can even be recycled to break down additional substrate molecules. Each enzyme is specific for a particular reaction because its amino acid sequence is unique and causes it top have a unique three-dimensional structure. The active site is the portion of the enzyme that interacts with the substrate, so that any substance that blocks or changes the shape of the active site affects the activity of the enzyme. A description of several ways enzyme action may be affected follows:

1. **Salt Concentration**: If the salt concentration is close to zero, the charged amino acid side chains of the enzyme molecules will attract to each other. The enzyme will denature and form an inactive precipitate. If, on the other hand, the salt concentration is too high, normal interaction of charged groups will be blocked, new interactions will occur, and again the enzyme will precipitate. An intermediate salt concentration such as that of human blood (0.9%) or cytoplasm ins the optimum for many enzymes.

2. **pH:** Amino acid side chains contain groups such as – COOH and NH_2 that readily gain or lose H+ ions. As the pH is lowered an enzyme will tend to gain H+ ions, and eventually enough side chains will be affected so the enzyme's shape is disrupted. Likewise, as the pH is raised, the enzymes will lose H+ ions and eventually lose its active shape. Many of the enzymes function properly in the neutral pH range and are denatured at either an

extremely high or low pH. Some enzymes, such as pepsin, which acts in the human stomach where the pH is very low, have a low pH optimum.

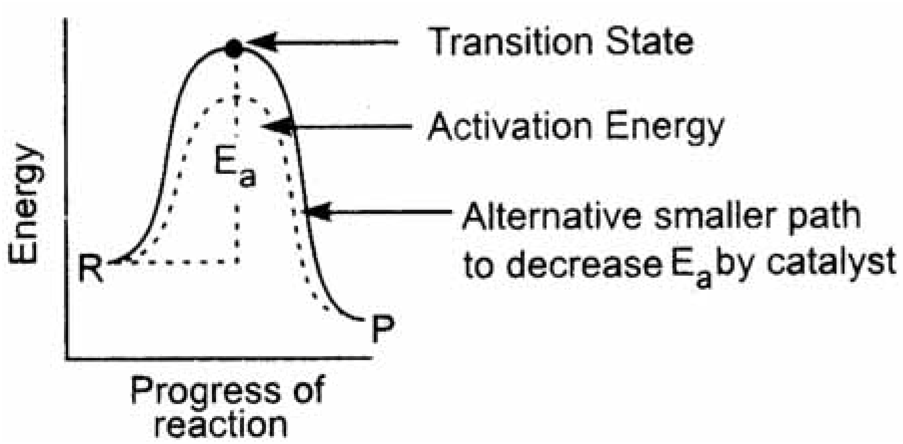
3. **Temperature**: Generally, chemical reactions speed up as the temperature is raised. As the temperature increases, more of the reacting molecules have enough kinetic energy to undergo the reaction. Since enzymes are catalysts for chemical reactions, enzyme reactions also tend to go faster with increase temperature. However, if the temperature of an enzyme-catalyzed reaction is raised still further, a temperature optimum is reached; above this value the kinetic energy of the enzyme and water molecules is so great that the conformation of the enzyme molecules is disrupted. The positive effect of speeding up the reaction is now more than offset by the negative effect of changing the conformation of more and more enzyme molecules. Many proteins are denatured by temperatures around 40-50 degrees C, but some are still active at 70-80 degrees C, and a few even withstand boiling.

4. **Activation's and Inhibitors**: Many molecules other than the substrate may interact with an enzyme. If such a molecule increases the rate of the reaction it is an activator, or if it decreases the reaction rate it is an inhibitor. These molecules can regulate how fast the enzymes acts. Any substance that tends to unfold the enzyme, such as an organic solvent or detergent, will act as an inhibitor. Some inhibitors act by reducing the -S-S- bridges that stabilize the enzyme's structure. Many inhibitors act by reacting with the side chains in or near the active site to change its shape or block it. Many well-known poisons such as potassium-cyanide and curare are enzyme inhibitors that interfere with the active site of critical enzymes

And also can be classified to :

(i) Positive catalysts:

A catalyst which increases the rate of reaction is called positive catalyst. Such catalyst decreases activation energy by accepting a smaller path, so rate of reaction is increased.



Positive Catalyst

E.g.

$$2SO_2(g) + O_2(g) \overset{Pt(s)}{\rightarrow} 2SO_3(g)$$

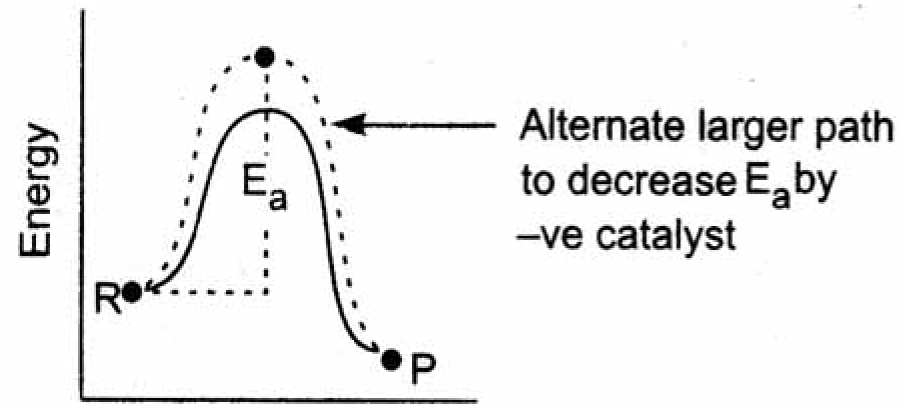
$$2KClO_3(s) \overset{MnO_2(s)}{\rightarrow} 2KCl(s) + 3O_2(g)$$

$$N_2(s) + 3H_2(g) \overset{Fe(s)}{\rightarrow} 2NH_3(g)$$

$$CH_2 = CH_2(g) + H_2(g) \overset{Ni(s)}{\rightarrow} CH_3 - CH_3(g)$$

(ii) Negative catalysts (Inhibitors):

A catalyst which decreases or retards the rate of reaction is called negative catalysts.



It is because a -ve catalyst increase activation energy by taking a longer alternative path.

(1) $2H_2O_2 \underset{orGlycerine}{\overset{H_3PO_4(s)}{\rightarrow}} 2H_2O + O_2$

(2) T.E.L (Tetra Ethyl Lead) an ant knocking substance is added to petrol to decrease the ignition of petrol vapours.

(3) $Na_2SO_3 \underset{Atmospheric}{\overset{C_2H_5OH}{\rightarrow}} Na_2SO_4$ Here C_2H_5OH acts as -ve catalyst to slow the oxidation .

(4) Acetanilide also acts as —ve catalyst in decomposition of H_2O_2

(iii) auto-catalysts:

When one of the products formed in the reaction acts as a catalyst is known as auto-catalyst.

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH(auto-catalyst) + C_2H_2OH$$

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \overset{80^0c}{\rightarrow} K_2SO_4 + 2MnSO_4(\text{autocatalyst}) + 10CO_2 + 8H_2O$$

$$2AsH_3 \rightarrow 2As + 3H_2(\text{autocatalst})$$

$$3Cu + 8HNO_3(dil.) \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$$

In this reaction NO_2^- acts as auto catalyst which is formed as a side reaction :

$$2NO + H_2O + O \rightarrow 2H^+ + 2NO_2^-$$

Auto catalysis reaction starts slowly in the beginning but as auto catalyst is formed rate of reaction starts increasing.

(iv) Induced catalyst:

The substance which influences the speed of other reaction, which is not possible under ordinary conditions, is known as induced catalyst.

Sodium sulphite solution readily oxidizes in air, but sodium arsenite solution does not oxidise by passing air in the solution. When both these solutions are mixed and air is passed then both the substances get oxidized.

$$Na_2SO_3 \overset{Air}{\rightarrow} Na_2SO_4$$

$$Na_2AsO_3 \overset{Air}{\rightarrow} \text{No reaction}$$

$Na_3AsO_3 + Na_2SO_3(\text{Induced catalyst}) \rightarrow Na_3AsO_4(\text{Sodium Arsenate}) + Na_2SO_4$

Characteristics of Catalysis

The following are the characteristics which are common to most of catalytic reactions.

(1) A catalyst remains unchanged in mass and chemical composition at the end of the reaction.

(2) A small quantity of the catalyst is generally sufficient to catalysis almost unlimited reactions

(i) For example, in the decomposition of hydrogen peroxide, one gram of colloidal platinum can catalysis 108 liters of hydrogen peroxide.

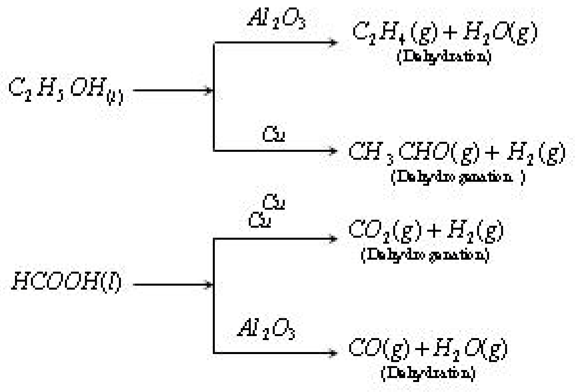
(ii) In Friedel craft's reaction, anhydrous aluminium chloride is required in relatively large amount to the extent of 30% of the mass of benzene,

$C_6H_6 + C_2H_5Cl \xrightarrow{AlCl_3} C_6H_5C_2H_5 + HCl$

(3) The catalyst cannot initiate the reaction: The function of the catalyst is to alter the speed of the reaction rather than to start it.

(4) The catalyst is generally specific in nature: A substance, which acts as a catalyst for a particular reaction , fails to catalyze the other reaction , different catalysts for the same reactant may for different products.

Examples :



(5) The catalyst cannot change the position of equilibrium : The catalyst catalyze both forward and backward reactions to the same extent in a reversible reaction and thus have no effect on the equilibrium constant.

(6) Catalytic promoters : Substances which themselves are not catalysts, but when mixed in small quantities with the catalysts increase their efficiency are called as promoters or activators.

(i) For example, in Haber's process for the synthesis of ammonia, traces of molybdenum increases the activity of finely divided iron which acts as a catalyst.

(ii) In the manufacture of methyl alcohol from water gas (CO + H2), chromic oxide (Cr2O3) is used as a promoter with the catalyst zinc oxide (ZnO).

(7) Catalytic poisons : Substances which destroy the activity of the catalyst by their presence are known as catalytic poisons.

(i) For example, the presence of traces of arsenious oxide (As_2O_3) in the reacting gases reduces the activity of platinized asbestos which is used as catalyst in contact process for the manufacture of sulphuric acid.

(ii) The activity of iron catalyst is destroyed by the presence of H_2S or CO in the synthesis of ammonia by Haber's process.

(iii) The platinum catalyst used in the oxidation of hydrogen is poisoned by CO.

(8) Change of temperature alters the rate of catalytic reaction as it does for the same reaction in absence of catalyst : By increasing the temperature, there is an increase in the catalytic power of a catalyst but after a certain temperature its power begins to decrease. A catalyst has thus, a particular temperature at which its catalytic activity is maximum. This temperature is termed as optimum temperature.

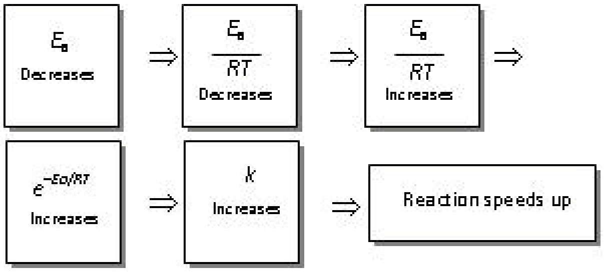
(9) A positive catalyst lowers the activation energy

(i) According to the collision theory, a reaction occurs on account of effective collisions between the reacting molecules.

(ii) For effective collision, it is necessary that the molecules must possess a minimum amount of energy known as activation energy (Ea).

(iii) After the collision molecules form an activated complex which dissociate to yield the product molecules.

(iv) The catalyst provides a new pathway involving lower amount of activation energy. Thus,



larger number of effective collisions occur 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.

(v) Figure shows taht activation energy Ea, in absence of a catalyst is higher than the activation energy Ea, in presence of a catalyst.

(vi) E_R and E_P represent the average energies of reactants and products. The difference gives the value of ΔG, i.e., $\Delta G = E_R - E_P$