Industrial Chemistry

Industrial Aspects of Chemistry

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Emulsions

Emulsions are intimate mixtures of two immiscible liquids, one of them being dispersed in the other in the form of the droplets. The phase present in the form of finally divided droplets is *called dispersed phase*. The phase in which there droplets are suspended is called *dispersion* medium or *continuous* phase. In emulsions, the size of particles lies in the range from 0.1 to 1 μ or more in diameter and so are larger than those found in sols. For example, milk is naturally occurring emulsion in which the particles (globules) of liquid fats are dispersed in water.

Properties of Emulsions: Emulsions have characteristic properties similar to those of lyopholic colloids. They show Tyndall effect and Brownion motion, provided the particles are not too large. Globules carry electrical charges and thus show electrophoretic motion under an electric field. Emulsion can be coagulated by electrolytes; particularly those containing polyvalent cations.

Emulsions can be broken (or converted) in to two separate layers by heating, freezing, centrifuging etc. This process is referred as demulsification. The conversion of cream in to butter by churning is an example of breaking of an emulsion of fats in water.

Preparation of Emulsion: Emulsions are generally prepared by vigorously shaking two liquids or by passing the mixture through a colloid mill, called the homogenizer. Since the two do not mix well, the emulsion is generally unstable and the two liquids may separate out on standing for some time. Therefore, to form stable emulsions, small quantities of certain other substances are added to their preparation. The substances, which are added to stabilize the emulsion, are called emulsifier or emulsifying agent. The substances that are commonly used as emulsifying agents are naturally occurring materials like gums, soaps of different form, gelatin or albumin, long chain molecules having polar groups viz. sulphonic acids, surface active agents, finely divided solids etc.
The main function of the emulsifier is to reduce the interfacial tension between the two liquids forming the emulsion.

The example of soap as an emulsifier can explain the role of emulsifier. Soaps are sodium or potassium salts of higher fatty acids such as sodium palmitate ($C_{15}H_{31}$ COONa) sodium stearate ($C_{17}H_{35}$ COONa). A molecule of soap consists of two parts: i) hydrocarbon (R) non-polar part etc. ($C_{15}H_{31}$, or $C_{17}H_{35}$ etc.) which is soluble in oil. ii) The polar part (group-COO-Na^+), which is soluble in water. When a drop of oil is surrounded by soap solution, R-part of the soap remains in oil and COO-Na^+ part remains in water, as a result, soap molecules get concentrated over the surface of the drop of oil and therefore form protective film around each oil drop, by which, interfacial tension between oil and water decreases. Hence, they are intermixed to form the emulsion.

Casein (a milk protein), a lyophobic colloid present in milk acts as an emulsifying agent as it forms a protective layer around fat molecules dispersed in water. Therefore, milk is a fairly stable emulsion.

Types of Emulsion: They are generally of two types:

(i) Oil-in-water (O/W) emulsion: In this case, oil acts as the dispersed phase (small amount) and water as the dispersion medium (excess). Milk is an example of oil in water emulsion in which an emulsion of soluble fats is in water having casein (protein) as an emulsifier. Vanishing cream is another example of this class. Such emulsions are called *aqueous* emulsions.

(ii) Water- in-oil (W/O) emulsion: When water acts as the dispersed phase (small amount) and oil behaves as the dispersed medium (excess). Butter, cod liver oil, cold cream etc. are examples. Such types of emulsions are called *oily emulsions*. Here, the term oil designates any liquid immiscible with water.

The type of emulsion that results on vigorous mixing of two liquids depends:

(a) On the relative proportions of the two, the one in excess acts as the outer phase and the other as the *inner phase* or *dispersoid*.

(b) On the nature of the emulsifying agent used.

The phase in which the emulsifier is more soluble forms the outer phase. Thus, when sodium oleate is added as an emulsifier, an oil in water emulsion results. But the addition of water insoluble emulsifier like calcium oleate, forms water oil type of emulsion.

(c) On the relative magnitude of the surface tension of two liquids.

Generally, the liquid with higher surface tension forms the inner phase due to its greater tendency to form spherical drops.

It may be stated that two types of emulsions can be interchanged by simply varying the ratio of the dispersed phase and dispersion medium. An oil-in water emulsion can be converted to water-in-oil emulsion by simply adding excess of oil in the first case.

Identification of Emulsion: The two types of emulsions can be identified by the following tests:

(i) Dye test: An oil soluble suitable dye is shaken with the emulsion. If colour is noticed on looking at a drop of the emulsion, it is oil in water type emulsion. If the entire background is coloured, it is an example of water in oil type.

(ii) Dilution test: It the emulsion can be diluted with the addition of water, then water acts as the dispersion medium and is an example of oil in water emulsion. If emulsion is not diluted with the addition of water, then oil acts as dispersion medium and is an example of water in oil emulsion.

Properties of Emulsions

(i) Emulsions show all the characteristics properties of colloidal solution such as Brownian movement, Tyndall effect electrophoresis etc.

(ii) The addition of electrolytes having polyvalent metal ions coagulates the emulsion indicating the presence of negative charge on the globules.
(iii)The size ($1000A^0$ to $10,000A^0$) of the dispersed particles in emulsions is larger than those in the sols, which is smaller than the size of particles in suspension.
(iv)Emulsion can be broken (or converted) in to two separate liquids by heating, centrifuging, freezing, filtration and chemical methods etc. This process is known as dimulsification.

Applications of Emulsions

1. Concentration of ores in metallurgy: The concentration of the sulphide ore of a metal by froth floatation process involves the use of some oil such as pine oil. The oil forms emulsion with ore particles. When air is passed through the emulsion, it rises to the surface as foam and is skimmed off.
2. In Medicine: The various pharmaceuticals and cosmetics available in liquid form are emulsions of water in oil type, viz. cod liver oil, B-complex, ointments etc. These are easily adsorbed in the intestine.
3. Cleansing action of soap: The cleansing action of soap is based upon the formation of oil-in water type emulsion and acts as micelle.
4. Milk: Milk, an important constituent of our diet, is an emulsion of fat in water.

Aerosols

Aerosols may be regarded as those systems having a *gas* as dispersion medium in which *liquid* as well as *solid* substances may be dispersed. When a *liquid* is dispersed in a gas, the resulting dispersion is called fog, *mist* or *cloud*. When a solid is dispersed in a gas, the resulting dispersion is called *dust, smoke, haze or fume*. It is however, not easy to distinguish these two kinds of *aerosols,* because there are systems, e.g., *smoke,* which consist of solid particles in the finest dispersion, along with some liquid, which might have condensed on these particles. Thus, we distinguish these three types of aerosols as, *dusts* and *smokes* of which the particles are non-*volatile*, and *fogs* including (mists) the particles of which are *volatile*.

Dusts are dispersions of solids (of comparatively large particles) in gases and are of poor stability. *Smokes* are formed by combustion of materials or as a part of the combustion process or from a chemical reaction, e.g. NH_3 and HCl vapour. Smokes consist of much fine particles. If simultaneously gases are formed in the combustion process as in the burning of organic compounds, the resulting gaseous suspension is known as fume. *Haze* may be regarded as a diluted fume and consists of solid particles with a liquid condensed on them.

A *fog* is formed by the condensation of a volatile material, such as water in droplets form. *Mists* consist of fine droplets of liquid which may or may not contain dissolved substances or solid particles in suspension, when the concentration of droplets is so high that the visibility range is much decreased, it may be regarded as a *fog. Sea fogs* are formed on nuclei of salt particles and are obtained from the evaporation of spray droplets.

Gels

A *gel* is a colloidal system in which a liquid is dispersed in a solid. Under certain conditions, the *lyophilic sols* may be coagulated to give a semi solid jelly like mass, which encloses all the liquid present in the sol. The process of gel formation is called *gelation* and the colloidal system formed is called *gel.* The common examples of *gel* are:

- (a) Gum arabic
- (b) Gelatin
- (c) Processed cheese
- (d) Silicic acid
- (e) Ferric hydroxide etc.

The gels may be classified in to two types:

1. **Elastic gels:** The gels, which possess the property of elasticity, are called *elastic gels*. They readily change their shape on applying force and return to original shape when the applied force in removed. Common examples are gelatin, agar-agar, starch etc. An elastic gel, say gum, on partial dehydration leads to the formation of an elastic solid from which the gel can be easily obtained by the addition of water.
2. **Non-Elastic gels**: These are the gels which are rigid and do not have the property of *elasticity*. Such as silica, on dehydration gives a glassy powder, which loses the elasticity. The sol cannot be obtained by adding water. Gels are generally prepared by cooling a not too dilute dispersion of these substances in hot water. On cooling, the particles in the sol associate to form chains, which then interlock in the form of loose framework where in the sorbed molecules of the medium, are accommodated.

Gels are characterized by

- (i) High viscosity and
- (ii) Swelling if placed in the dispersion medium.

This phenomena of swelling is known as *imbibition.* Gels, on standing, give out small quantities of liquid (e.g., water) which accumulates on the surface, this is known as *synersis* or weeping.

Such gels like ferric phosphate, ferric oxide etc. when vigorously agitated lose their semisolid gel character and acquire the behaviour of sol. They can again set to gel on standing. This reversible phenomenon of gel-sol transformation is called *thixotropy.* Some times thixotropic gels are obtained by adding electrolytes with in certain limits to ordinary sols.

Adsorption

The accumulation/retention of a substance on the surface of solid or liquid is called Adsorption.

Adsorbate: is the substance adsorbed on the surface.
Adsorbent: is the substance, to which substance is adsorbed or attached.

Adsorption is a surface phenomenon and it depends upon the surface area of adsorbent at a given temperature and pressure. Solids are good adsorbent due to large surface area because of presence in finely divided state. Adsorption is an exothermic process and increases with the decrease of temperature.

Adsorption is different from absorption, because in absorption substance goes to inside in to the bulk of a solid or liquid, where in adsorption, substance is retained only on surface. For example, acetic acid is adsorbed from its solution by charcoal whereas hydrogen gas is absorbed by metallic palladium.

Types of Adsorption: Adsorption can be of following two types depending upon the forces holding the gas molecules to the solid surface.
(i) Physical adsorption or Van der Waals adsorption and
(ii) Chemical adsorption or activated adsorption or chemisorption.

Generally gas molecules are held by physical or Van der Waals forces, when being adsorbed on the surface of a solid, whereas, in chemisorption, molecules on the surface are held by valence forces.

Distinction between physical adsorption and chemisorption

Physical		**Chemisorption**
Adsorption equilibrium is rapid and reversible	1.	Adsorption equilibrium is slow and irreversible
It has low enthalpy of adsorption (20 mol^{-1})	2.	It has high enthalpy of adsorption (80-200 mol^{-1})
Adsorption is more pronounced at temperature below the boiling point of the adsorbate.	3.	Chemisorptions usually occurs at high temperature.
No appreciable amount of activation energy is involved.	4.	High amount of activation energy is involved.
It is a function of the adsorbate than adsorbent.	5.	It depends on both adsorbate and adsorbent.
It increases with the pressure of adsorbate.	6.	It decreases with the increase of pressure of adsorbate.

Adsorption Isotherms : The relationship between the amount of the substance adsorbed and pressure or concentration of the adsorbate at constant temperature is called adsorption isotherm. Generally, the extent of adsorption on surface depends on the

1. Nature of the adsorbent
2. Pressure or concentration and nature of molecules of adsorbate
3. Temperature

Freundlich Isotherm: It represents empirically the variation of amount of adsorption per unit area or per unit mass of adsorbent with pressure and is given as

$$y = \frac{x}{m} = k(p)^n \qquad \text{(i)}$$

Where, x gm of the gas is adsorbed by m gm of adsorbent, so that x/m is the mass of the gas adsorbed per unit mass of adsorbent. p is the equilibrium pressure of the gas, k and n are the empirical constants depending upon the nature of the solid, gas and temperature.

Taking logarithm of both sides of equation (i)

$$\log y = \log x/m = \log k + n \log p \qquad \text{(ii)}$$

A linear plot of log y versus log p will give slope equal to n and the ordinate intercept equal to log k. However, at low temperature, the experimental data show deviation from linearity. This isotherm is applicable only in the limiting case of low concentration.

Langmuir Adsorption Isotherm: Langmuir in 1916 gave first quantitative theory of adsorption. It is based on a model that depends that there being a fixed number of adsorption sites on a catalyst surface, and each site is capable of holding one molecule of adsorbate and the solid surface is homogeneous. The energy of interaction of the adsorbate is assumed to be the same for each site, so that there is no interaction between adsorbed molecules. The adsorbed gas behaves ideally in the vapour phase. Langmuir adsorption is monomolecular. It does not consider the case that further adsorption may take place on the adsorbate already present on the surface.

Mathematical Derivation: Theta may be defined as:

$$\theta = \frac{\text{No. of adsoption sites occupied}}{\text{No. of adsoption sites available}}$$

If θ is the fraction of a catalyst surface that is occupied at a time t, the rate of desorption is proportional to the number of adsorbed species, $K_d \theta_t$:

$$\text{i.e. } d\theta_t/dt = K_d \theta_t \qquad (1)$$

where K_d is the rate constant for desorption

The rate of adsorption at a time t will be proportional to the unoccupied surface i.e. $(1-\theta_t)$ and to the rate at which the molecules stripe the surface, i.e. to the pressure p, so that we also have

i.e. Rate of adsorption $\alpha\,(1-\theta_t)$

$\alpha\,P$

$$\text{or} \quad \frac{d(1-\theta_t)}{dt} = k_a \quad p(1-\theta_t) \qquad (2)$$

After a period of time, a steady state is attained and the two rates are equal; hence

$$k_d\,\theta = k_a\,p\,(1-\theta) \qquad (3)$$

where θ is the equilibrium value of the fraction adsorbed at a given temperature and k_a is the rate constant for adsorption,

with $k_l = k_a/k_d$

hence equation (3) may be rearranged to give

$$\theta = k_L\,p\,/\,(1+k_L\,p) \qquad (4)$$

which is the Langmuir adsorption isotherm. k_L has the dimensions of $(\text{pressure})^{-1}$ and is dependent upon temperature and is known as adsorption coefficient.

The mass of the gas adsorbed per unit area or per unit mass of adsorbent y, will obviously proportional to be surface covered and hence.

$$y = \frac{x}{m} = k\theta$$

$$= k \times k_L\;p/(1+k_lp)$$

$$\text{or} \quad y = \frac{x}{m} = \frac{ap}{1+k_Lp} \qquad (5)$$

where the constant $a = k.\,k_L$

Equation (5) is known as Langmuir adsorption isotherm and gives the relation for the amount of gas adsorbed to the pressure of gas at constant temperature. Equation (5) can be written as

$$\frac{p}{y} = \frac{p}{p/(1+k_lp)} = \frac{p}{ap} = \frac{p(1+akl)}{ap}$$

$$= \frac{1}{a} + \frac{k_l}{a} \quad p$$

Hence plot of p/y [or p/(x/m)] versus p will be a straight line with intercept equal to 1/a and slope equal to k_L/a. Hence a and k_L in equation can be evaluated. Values of these constants have been found to be characteristics of the system under consideration. Two limiting cases of Langmuir adsorption isotherm are of interest. These are:

Case I :

When $k_L p << 1$, i.e. when pressure of the gas is very low, equation (5) changes to

$y = a\,p$

or

$y \alpha p$

This shows that the adsorption is directly proportional to the pressure of the gas.

Case II:

When $k_L\,p >> 1$ i.e., when pressure is very large or whole of the surface is covered, then equation (5) changes

$$y = \frac{a}{k_L}.$$

i.e. the adsorption reaches at its limiting value however, in the intermediate range of pressure, the adsorption will follow a relation

$y = k\,p^n$

where n lies between 0 and 1. This is the Freundlich isotherm

The assumption of the equivalence of all sites in Langmuir isotherm is an ideal, which may not always be realized. For example, adsorption at a particular site may depend upon the occupancy of neighboring sites, with the most energetically favourable sites being occupied first.

Experimental results from Langmuir isotherm for several substances have shown that the equation is less precise at high value of θ; that is at higher values of pressure, and that, for a given pressure p, θ increases with k_L; θ tends to unity only at very high pressures. The adsorption of carbon monoxide on a fixed amount of charcoal at 290 K proves the accuracy of Langmuir isotherm.

Catalysis

A catalyst is a foreign substance which can alter the rate of a chemical reaction, without itself being used up; and can be recovered unchanged chemically at the end of a chemical reaction. The term catalyst was first proposed by Berzelius in 1835. A catalyst increases the rate of reaction by lowering the activation energy of the rate determining step. A catalyst therefore provides an alternate path, or mechanism that involves usually of lower activation energy, for the reaction to proceed at an accelerated rate, compared with the activation energy for the uncatalyzed reaction. For example:

(1) Formation of oxygen by heating potassium chlorate in presence of small amount or manganese dioxide as catalyst.

$$2\,KClO_3 \xrightarrow[MnO_2]{Heating} 2KCl + 3O_2$$

(2) Iron acts as a catalyst, in the manufacture of ammonia by Haber's process,

$$N_2 + 3H_2o \xrightarrow{Fe} 2NH_3$$

(3) In the manufacture of sulfuric acid, platinum acts as a catalyst

$$250_2 + 0_2 \xrightarrow{Pt} 250_3$$

Catalysts, which accelerate the rate of chemical reaction, are called positive catalysts, and above reactions are examples of positive catalyst.

Negative catalyst or inhibitor is used to describe the retardation of a reaction by a catalyst. For example

(i) Retardation of oxidation of chloroform by adding small amount of alcohol.
(ii) Decrease in the decomposition of H_2O_2 in presence of small amount of glycerol or acetanilide.
(iii) Minimization of knocking effect by adding TEL or nickel carbonyl to petrol etc.
(iv) Traces of some sulphur compound inhibit auto oxidation of benzaldehyde
(v) Traces of propan – 1, 2, 3- triol (glycerol) retard the decomposition of Hydrogen peroxide.
(vi) Oxidation of chloroform is retarded by traces of alcohols.

Negative catalyst acts in two ways:

(a) It may act as *poison* or *merely destroy* some catalyst, which already happens to be present in the reaction mixture. For example, decomposition of H_2O_2 is catalysed by traces of alkali dissolved from the glass container. But the addition of an acid would destroy the alkali and thus decomposition of H_2O_2 would also be prevented.

(b) It *dislocates* the mechanism by which the reaction would ordinarily proceed. For example, TEL or nickel carbonyl is added to petrol to retard the ignition of petrol vapour on compression in an internal combustion engine.

Characteristics of Catalyst:

1. The catalyst is unchanged in chemical constitution and the amount at the end of the reaction, although its physical appearance may have altered. Thus, granular manganese dioxide added to potassium chlorate to catalyse its decomposition is returned in a very finely divided form. It is evident that a catalyst takes part in a reaction.
2. Very small amounts of catalyst have a profound effect. For example, finely divided (colloidal) platinum at a concentration of 1mg dm^{-3} is a very effective catalyst for the decomposition of hydrogen peroxide.
3. A catalyst does not alter the position of equilibrium in a reaction. It follows that for a reaction symbolized by

$$A \rightleftharpoons B$$

The rate constants of both the forward and reverse reactions are increased to the same extent.

4. A catalyst does not initiate a reaction but only increases or decreases its speed generally. But few reactions are known to occur only in the presence of a catalyst.
5. The action of a catalyst is specific. A catalyst can catalyse only a specific reaction and cannot be used for every reaction. For example, manganese dioxide can catalyse the decomposition of potassium chlorate but not potassium nitrate or other substances.
6. Change of a catalyst also changes the nature of reaction.

$$CO = H_2 - \begin{cases} \underline{\text{Ni Catalyst}} \longrightarrow CH_4 + H_2O \\ \underline{\text{Zno Catalyst}} \longrightarrow CH_3OH \end{cases}$$

7. A catalyst has an optimum temperature at which the action of the catalyst is maximum.

Promoters: A substance which (though not a catalyst by itself) promotes the activity of the catalyst is called a *promoter* or *activator* and the process is known as Activation. For example, in Bosch's process of manufacturing hydrogen from water gas, finely divided iron acts more efficiently as a catalyst in presence of metallic copper as promoter. Similarly, molybdenum promotes the activity of iron catalyst in the manufacture of NH_3 by Haler's process

$$N_2 + 3H_2 \xrightarrow{Fe+Mo} 2NH_3$$

Anticatalyst: Those substances, which reduce or even completely destroy the activity of a catalyst are known as poison or anticatalyst. The poisoning of a catalyst may either be *temporary* or *permanent*. When the poison is adsorbed on the surface of the catalyst in preference to the reactions, the poisoning is called *temporary*. In *temporary poisoning*, the surface decreases its activity or loses it entirely only for the period for which poison is in contact with it due to a strong preferential adsorption of the poison on the surface of the catalyst. The activity is restored, as the poison is removed from the catalyst. Permanent poisoning involves a chemical combination between the surface and poison to form a new catalytic inert surface, volatile silicon, sulphur and arsenic cause permanent poisoning in many catalysis.

Some examples of anticatalyst are given below:

a. CO acts as an anticatalyst in the manufacture of NH_3 by Haber's process.
b. Traces of arsenic oxide poison the platinum catalyst in the oxidation of SO_2 to SO_3, in the manufacture of H_2SO_4 by contact process.
c. HCN poisons the platinum catalyst for the decomposition of H_2O_2.
d. The copper catalyst becomes inert in the presence of CO in action of hydrogen on ethylene.

Autocatalyst: There are certain reaction where one of the products of the reaction acts as a catalyst itself. Such reactions are called auto catalysed reactions.

(i) $CH_3\,COO\,C_2\,H_5 + H_2O \rightarrow CH_3\,COOH + C_2H_5OH$

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

The reaction is catalysed by NO_2 ion formed as a side reaction according to the reaction

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

(iii) $2\,KMnO_4 + 5\,\underset{\text{Oxalic acid}}{H_2C_2O_4} + 3H_2\,SO_4 \rightarrow 2\,MnSO_4 + 8H_2O + 10\,CO_2 + K_2SO_4$

Auto catalyst

$2AsH_3 \rightarrow \underset{\text{Auto catalyst}}{2As} + 3H_2$

Types of Catalysis: Generally, two classes of catalyst are recognized - homogeneous and heterogeneous.

Homogeneous catalysts, which are in the same phase as the reactants, as with the base**,** catalysed hydrolysis of an ester. Many homogeneous reactions have been studied in the gas phase and liquid phase.

Examples of Homogeneous Catalyst in gas phase:

1. A homogeneous gas-phase catalysed reaction is the arial oxidation of sulphur dioxide, in the presence of nitrogen monoxide.
   $NO + \frac{1}{2}\,O_2 \rightarrow NO_2$
   $NO_2 + SO_2 \rightarrow SO_3 + NO$
2. Decomposition of acetaldehyde is catalysed by iodine vapours.
   $$CH_3\,CHO \xrightarrow[\text{Vapours}]{I_2} CH_4 + CO$$
3. In the combination of carbon monoxide and oxygen, nitric oxide acts as a catalyst.
   $$2\,CO + O_2 \xrightarrow{NO} 2\,CO_2$$

Examples of Homogeneous Catalysis in liquid phase:

Important examples of homogeneous catalysis in liquid phase are acid-base catalysis. If an acid catalysis a reaction, the reactions said to be subject of acid catalysis in which generally hydronium ion is acid catalyst in water inversion of cane anger and hydrolysis of esters are some examples of acid catalysed reactions.

$$C_{12}\,H_{22}\,O_{11} + H_2\,O \xrightarrow{H_3O^+} C_{12}\,H_{12}\,O_6 + C_6\,H_{12}\,O_6$$

$$CH_3\,COO\,C_2\,H_5 + H_2O \xrightarrow{H_3O^+} CH_3\,COOH + C_2\,H_5\,OH$$

It has been observed that hydrochloric acid has a greater activity than acetic acid, showing that different acids have different catalytic activity. The rates of reaction are found to be proportional to the concentration of H^+ (or H_3O^+) ions being the actual catalysts in acid catalysed reactions and the concentration of the reacting molecules or ion.

Acid Base Catalysis: The reactions catalysed by acids and bases are called specifically acid base catalysed reactions. For example, the mutarotation of glucose in aqueous solutions is catalysed by acids and bases. The rate of reaction is proportional to H^+ ion concentration below pH 3 and proportional to OH^- ion concentration at a pH of about 6. The rate is independent between pH 3 and pH 6.

The acid catalysed hydrolysis of ethyldiazoethanoate at 298 K depends upon the pH of solution.

$$N_2\,CH\,CO_2\,C_2\,H_5 + H_2O \xrightarrow{H_3O^+} HO\,CH_2\,CO_2\,C_2\,H_5 + N_2$$

The reactions which are catalysed by certain acids (or H_3O^+ ions only) are said to be specific acid catalysis.

The reactions which are catalysed by base catalyst OH^- ions only, are said to be specific hydroxyl ion catalysis. Conversion of acetone in to diacetonyl alcohol or base hydrolysis of esters are examples of hydroxyl ion catalysis.

$$CH_3\,CO\,CH_3 + CH_3\,CO\,CH_3 \xrightarrow{OH^-} CH_3\,CO\,CH_2\,C\,(CH_3)_2\,OH$$

$$CH_3\,COO\,C_2H_5 + NaOH \rightarrow CH_3\,LOO\,Na + C_2\,H_5\,OH$$

The decomposition of aqueous solution of nitramide ($NH_2NO_2 \rightarrow NO_2 + H_2O$) is catalysed by OH^- ions in alkaline medium.

$$NH_2\,NO_2 + OH^- \rightarrow H_2O + NHNO_2^-$$

$$NHNO_2^- \rightarrow N_2O + OH^-$$

There are many reactions in which both H_3O^+ ions and OH^- ions simultaneously act as catalyst, probably along with water.

Mechanism of Homogeneous Catalytic Reactions: These reactions can be explained on the basis of intermediate compound formation. According to this theory, the catalyst combines with one of the reactants to form an intermediate. Intermediate compound being unstable combines with the other reactant to form the product. For example, the combination of SO_2 and O_2 to form SO_3 is a slow process. However, in the presence of NO (catalyst), the reaction becomes fast.

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

It is believed that in this reaction, nitric oxide combines with one of the reactants to form intermediate compound (NO_2). This intermediate (NO_2) combines readily with SO_2 to form SO_3 and the catalyst (NO) is regenerated in the last step:

(1) $\underset{\text{Catalyst}}{NO} + \frac{1}{2} O_2 \rightarrow \underset{\text{Intermediate}}{NO_2}$ (fast)

(2) $NO_2 + SO_2 \rightarrow SO_3 + \underset{\text{Regenerated catalyst}}{NO}$ (fast)

and

$SO_2 + \frac{1}{2} O_2 \rightarrow SO_3$ (fast)

Heterogeneous Catalysts, which are in a different phase from the reactants, as with the platinum, catalysed oxidation of ammonia to nitrogen monoxide. When the catalyst is in different phase than the reactants, it is called heterogeneous catalyst. Such reactions are called heterogenous catalytic reactions. In heterogeneous catalysis, catalyst is generally a solid and the reactants are generally gases. Sometimes liquid reactants are also used. This is also known as Surface Catalysis because the reaction starts at the surface of the solid catalyst.

These catalysts have very large surface area of the order of 1 to 500 m^2 per gram for contact. Many reactions, which occur on a metal surface such as decomposition of HI on gold or the decomposition of N2O on platinum, are zero order reactions, because the rate-determining step occurs on the surface itself. Thus, despite an enormous surface area, once the reactant gas molecules cover the surface, the rate does not increase on increasing the reactant concentrations.

The most important example of heterogeneous catalysis is: addition of H_2 to carbon-carbon double bonds (C=C) of organic compounds to form C-C bonds. This is known as catalytic hydrogenation. This reaction is frequently used in petroleum, plastics and food industries. e.g., conversion of vegetable oil in margarine.

The simplest hydrogenation reaction is conversion of ethylene in to ethane as:

$$\underset{\text{Ethene}}{CH_2 = CH_2\ (g)} + H_2\ (g) \longrightarrow \underset{\text{Ethane}}{CH_3 - CH_3\ (g)}$$

In the absence of catalyst, the reaction occurs very slowly. However, the reaction becomes fast even at ordinary temperature in the presence of finely divided nickel, platinum or palladium as catalyst. The catalysed reactions proceed probably through the following steps.

(a) H_2 and ethane molecules approach the metal surface and get adsorbed on the metal surface.

(b) H_2 molecules get split up in to H-atoms, which get chemically bound to the platinum catalyst LP metal atoms forming M-H bonds as:

$H - H\ (g) + 2\ M\ (S) \rightleftharpoons 2\ M - H$

This step is the rate-determining step in the overall process.

(c) The H-atoms move over the surface of platinum metal and one of them combine with ethene molecule to form C_2H_5 which remain attached to the platinum surface.

(d) Finally, another H atom moves over the surface and combines with C_2H_5 forming C_2H_6 molecule, which leaves the surface. The reaction occurs as:

$$C_2H_4\,(g) + 2\,M - H \rightleftharpoons C_2H_6\,(g) + 2\,M\,(S)$$

Some other examples of industrial interest are:

(i) Combination of hydrogen and oxygen is catalysed by the presence of finely divided platinum:

$$2H_2\,(g) + O_2\,(g) \xrightarrow[\text{divided Pt.}]{\text{Finely}} 2H_2O\,(g)$$

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

$$3H_2\,(g) + N_2\,(g) \xrightarrow{\text{Fe}} 2NH_3\,(g)$$

(iii) Using a mixture of copper, zinc oxide as catalyst and Cr_2O_3 as promoter, methanol is prepared from CO and H_2

$$CO\,(g) + 2H_2\,(g) \xrightarrow{\text{Ch, ZnO/Cr}_3\text{O}_3} CH_3OH\,(l)$$

(iv) In the contact process, using V_2O_5 as catalyst, SO_2 is converted in to SO_3

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

(v) Using Nickel as catalyst, ethanol is dehydrogenated to aldehyde.

$$CH_3CH_2OH \xrightarrow{\text{Ni}} CH_3CHO + H_2$$

Mechanism of Heterogeneous Catalytic Reactions: The heterogeneous catalysis is a surface phenomena. It involves the following steps:

(i) Diffusion of the reactants at the surface of the catalyst.
(ii) Adsorption of the molecules of the reactant at the active sites.
(iii) Occurrence of the chemical reactions on the surface of the catalyst.
(iv) Desorption of product molecules from the surface.
(v) Diffusion of products away from the surface of the catalyst.

The role of heterogeneous catalysts can be explained in terms of adsorption of reactants on the surface of the catalyst. The adsorption helps the reaction in the following ways:

1. Adsorption increases the concentration of reactants on the surface of the catalyst, by which reactions proceed rapidly.

2. Adsorbed molecules get dissociated to form active species like free radicals, which react faster than molecules.
3. The adsorbed molecules are not free to move about and therefore, they collide with other molecules on the surface.
4. The heat of adsorption evolved acts as energy of activation for the reaction (chemisorption).

The above steps have been explained earlier with the example of hydrogenation of ethene in to ethane.

Some important industrial processes catalysed by different catalysts are given below:

1.	Haber process for the manufacture of NH_3	Fe, Mo, Fe_2O_3.
2.	Contact process for the manufacture of H_2SO_4	Platinum, V_2O_5.
3.	Lead chamber process for manufacture of H_2SO_4	NO,
4.	Manufacture of vanaspati ghee from oils i.e. hydrogenation of oils	Nickel
5.	Bosch process for the manufacture of H_2	$Fe_2O_3 + Cr_2O_3$.
6.	Ostwald process for the manufacture of HNO_3	Platinum guaze.
7.	Deacon's process for the manufacture of Cl_2 gas	$CuCl_2$.
8.	Manufacture of methyl alcohol from water gas ($CO + H_2$)	$ZnO + Cr_2O_3$.

Nature of solid catalyst: The solid catalysts may be metals, alloys, metal oxides or metal sulphides. The two important aspects viz. activity and selectivity determine the effectiveness of a catalyst.

(1) Activity: It is the ability of a catalyst to increase the rate of a reaction. This depends upon the strength of adsorption (chemisorption) in such a way that it allows the adsorption of other reactants and desorption of product molecules. Generally, activity increases from group 5 metals to group 11 metals with maximum activity shown by elements of groups 7-9 of the periodic table. A catalyst may increase the rate of reaction by a factor of 10^{10}. In presence of platinum, reaction between H_2 and O_2 occurs with high speed, though it is very slow in absence of catalyst.

(2) Selectivity: When a reaction is directed to obtain a particular product by a catalyst, then it is called selectivity of that particular catalyst.

(A) For examples, different products are obtained for the reaction between CO and H_2 using different catalysts

(i) $$CO\,(g) + H_2\,(g) \xrightarrow{Ni} CH_4\,(g) + H_2\,O\,(g)$$

(ii) $$CO\,(g) + 2H_2\,(g) \xrightarrow[Cr_2O_3]{C_1\ Zno} CH_3\,OH\,(g)$$

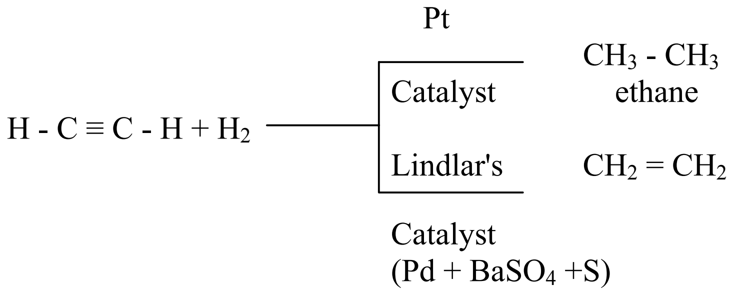
(iii) $CO\,(g) + H_2\,(g) \xrightarrow{Cu} HC\,HO\,(g)$

(B) Similarly Pt catalyst gives selectively toluene from n-leptane.

$$\underset{\text{n-heptane}}{n\text{–}C_7\,H_{16}} \xrightarrow{Pt} \underset{\text{Toluene}}{C_6\,H_5\,CH_3}$$

(C) Acrolern ($CH_2 = CH\,CHO$) is obtained selectively from the reaction between propylene and O_2 in the presence of bismuth molybedate catalyst.

Also, different products are obtained from the reaction between H_2 and acetylene using different catalysts.



Thus, the action of catalyst is highly specific. A given catalyst can act as catalyst only in particular reaction and not in all reactions. Thus, catalyst is highly selective in nature.

Enzyme Catalysts (Biological catalysts)

Many slow chemical reactions in living organisms are catalysed by complex substances called enzymes or natural catalysts produced by living cells in bodies of animals and plants. Thus, enzymes are biological catalysts produced by living cells, which catalyse the biochemical reactions in living organisms. They are proteins in nature. The catalytic activity of enzyme is greatest of all the catalysts and catalytic activity is due to their capacity to lower the energy of activation. Proteins have molar mass ranging from 15,000 to 1,000,000 g/mol. Some enzymes increase the rate of reaction by factors of 10^{12} to 10^{13}.

Enzyme catalysts have some peculiar characteristics. For example:

1. They act catalytically without taking part in chemical reaction.
2. They do not disturb the final state of equilibrium.
3. The rate of enzyme reaction is proportional to the concentration of the reactant (substrate), provided the concentration is small.
   At high concentrations, the rate of reaction is independent of the concentration (e.g. kinetics is of zero order).

4. A small quantity of enzyme can bring about the decomposition of large amount of the substrate. As small as millionth of a mole can increase the rate of reaction by a factor of 10^3 to 10^6.

5. Their action is specific e.g. a particular enzyme can bring about a particular reaction. For example, urease catalyses the hydrolysis of urea but it has no effect on the hydrolysis of methyl urea. None of the several thousand other enzymes present in the cell catalyses that reaction. Similarly, maltase catalyses the hydrolysis of maltose. No other enzyme can catalyse its hydrolysis.

6. An enzyme is the most reactive at a particular temperature, called optimum temperature; in many cases it is $35\text{-}40^0$C. The rate is maximum at certain temperature. Above this temperature, the enzyme is denatured and hence, the rate decreases.

7. Enzymes like other catalysts are influenced by other substances. Some enzymes, called co-enzymes act as promoters. Co-enzymes are some non-protein components like small organic molecules or metal ions (Na+, Mn^{+2}, Cu^{+2}) etc. associated with enzyme by weakly bonded to them to promote the activity of catalyst. The activity of catalyst (enzyme) can be reduced or inhibited by the presence of certain compounds known as enzyme inhibitors like HiN etc., which poison the enzyme.

8. They are destroyed by u .v. light and heat.

9. They are most inactive at low temperatures (0°C) or at too high temperatures (70-80° C).

10. They bring about many complex reactions, e.g. oxidation, reduction, hydrolysis etc.

11. The enzyme catalysed reaction is faster than metal catalysed reaction because its activation energy is lower than that of metal catalysed reactions.

12. Enzyme catalysts increase the speed of reactions by 10^8 to 10^{20} times as compared to the uncatalysed reactions.

13. An enzyme reaction has an optimum pH value at which the catalytic activity of the enzyme is maximum. The rate of reaction decreases as the pH is lowered or raised from the optimum value. At extreme pH they are irreversibly denatured.

14. The activity of most enzymes is closely regulated.

15. The action of enzyme-catalysed reactions is controlled by various mechanisms and is accelerated/inhibited by various organic and inorganic molecules/metal/ions etc.

Some important reactions catalysed by enzymes are given below:

1.	Conversion of starch in to maltose $2(C_6H_{10}O_5)_n + nH_2O \rightarrow n\,C_{12}\,H_{22}\,O_{11}$	Diastase	from malt or liver
2.	Decomposition of H_2O_2 $2H_2O_2 \rightarrow 2H_2O + O_2$	Catalase	Blood, plant, juice
3.	Conversion of glucose in to ethanol $C_6H_{12}O_6 \rightarrow 2C_2H_5on + 2CO_2$	Zymase	Yeast
4.	Hydrolysis of urea $H_2CO\ NH_2 + H_2O \rightarrow 2NH_3 + CO_2$	Urease	
5.	Hydrolysis of sugar $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$	Invertase	Small intestine yeast
6.	Conversion of maltose in to glucose $C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_2H_{12}O_6$	Maltase	
7.	Oxidation of alcohol to acetic acid $C_2H_5OH + O_2 \rightarrow CH_3COOH + H_2o$	Microderma aceti	

All enzymes can be classified in to:

(i) Hydrolytic Enzymes: These enzymes appear to be complex acid base catalysis in which accelerate the ionic reactions mainly due to the transfer of hydrogen ions.

(ii) The Oxidation-Reduction Enzymes: These enzymes catalyse electron transfer perhaps through the formation of an intermediate radical.

Applications of Enzymes

1. Industrial Applications: The enzymes are widely used in industrial processes:
   - (i) In breweries, fermentation of carbohydrates using enzymes, the bear and wine are manufactured.
   - (ii) Enzymes are used for coagulation of milk for the production of cheese.
   - (iii) Sweet syrup, etc. are prepared in food processing industries with the help of enzyme catalysts.

2. Prevention of Diseases and Enzyme Deficiencies: The deficiencies of certain enzymes in living systems cause many diseases, which can be prevented by the supply of suitable enzyme through diet etc.
   - (i) A congenital disease called phenylketone urea is caused due to deficiency of phenylalanine hydroxylase enzyme, which results

retardation in children and severe brain damage. This can be prevented by a diet with low phenylalanine content.

(ii) Albinism is caused by the deficiency of enzyme tyrosinase.

3. Curing Diseases : Certain enzymes namely streptokinase used to dissolve blood clot useful for treatment of heart disease, are used for curing diseases.

Mechanism of Enzyme Catalysed Reactions: The exact molecular mechanism of enzyme catalysis is not known.The various steps involved in the enzyme-catalysed reactions are given below:

(i) Binding of the enzyme (E) to substrate (S) to form an enzyme substrate complex.

$E + S \longrightarrow ES$

(ii) Formation of product in the complex itself

$ES \longrightarrow EP$

where EP is an another complex of enzyme and product.

(iii) Release of product from the enzyme – product complex

$EP \longrightarrow E + P$

The active sites or catalytic sites are specific regions on the surface of catalyst responsible for catalytic action of enzyme. The active sites have characteristic shape to fit suitable shaped specific substance molecules. The high specificity of enzyme catalysed reactions can be accounted for specific handing of substrate molecules on the active sites on surfaces of enzyme catalysts. The specificity of fit or binding can be explained on the basis of models:

1. Lock and key model
2. Induced fit model or hand-in glove fit model

According to lock and key model, the substrate, the molecule on which the enzyme acts, fits into the slot as key fits in to a lock. The shape of the active site of any given enzyme is such that only a specific substrate can fit in to it, in the same way as one key can open a particular lock.

Modern x-ray crystallographic and spectroscopic methods have shown that in many cases unlike the ordinary lock, the protein molecule (enzyme) slightly changes the shape when the substrate lands at the active site. The ability of the enzyme to undergo the correct distortion also determines whether the "key" will fit or not. This refinement of the original lock and key model is known as induced fit model. According to this model, the substrate induces the active site to adopt a perfect fit rather than a rigidly shaped lock and key. Therefore, we can picture this model as hand in glove model, in which the glove (active site) does not attain its functional shape until the hand (substrate) moves in to place.

Zeolites as Catalyst

The shape selective catalysed reaction depends upon the pore structure of the catalyst, and size of the reactant and product molecules. Because of honey comb like structure, zeolites are good shaped selective catalysts. These are microporous alumino silicates with general formula $M_{x/y}$ $[(AlO_2)x\ (S_1O_2)y]\ mH_2O$

These are silicates having three dimensional network structure, in which some silicon atoms are replaced by aluminum atoms. The internal structure of zeolite is a network of tunnels and cavities having molecular dimensions. The zeolites have an enormous surface area lying inside of the solid. The entry and exit of molecules of a certain size can penetrate in to the active regions within the holes. The reactions in zeolites depend upon the structure and size of the cavities (cages) and pores (tunnels) present in them. Shape selectivity is the main feature of zeolite. Hence, the specificity of reaction in a particular manner depends upon the size of the molecules, products and pores of the zeolites.

These are used in petrochemical industries for cracking of hydrocarbons and isomerization. For example, zeolite catalyst, known as ZSM-5 converts alcohols to gasoline. The alcohol is dehydrated in the cavities and the hydrocarbons are formed. The shape selectivity in the reaction can be judged from the conversion of methanol and 1-heptanol to hydrocarbon mixtures. The composition of the product mixture depends on the ability of the pores to accommodate linear and iso-alkanes as well as benzene derivatives.

Micelles

There are certain substances, which behave as normal strong electrolytes at low concentrations but behave as colloids at higher concentrations. The colloidal behaviour is due to the formation of the aggregates of small particles. Such substances are called *micelles,* which are also known as associated colloids.

Surface acting agents such as soaps and detergents belong to the class of micelles. The formation of a micelle depends upon (i) concentration of the dispersed phase and (ii) temperature. It can occur only above a particular concentration called *critical micelle concentration* (CMC) and have a particular temperature known as *Kraft temperature* (T_k). For example, for soap solution, CMC lies between a range of 10^{-4} to 10^{-3} mol L^{-1}. Below CMC, soap behaves as a strong electrolyte, while above this, it is aggregated to form a micelle. Micelle again behaves as normal electrolyte upon dilution, as the ions are dissociated. Some examples of micelle systems are:

(i) Sodium stearate ($CH_3\ (CH_2)_{16}\ COONa^+$) which is soap.
(ii) Sodium lauryl sulphate $(CH_3\ (CH_2)_{11}\ SO_4^-\ Na^+)$ which is detergent.

The substances capable of behaving as micelles have both lyophilic and lyophobic parts, for example, alkyl portion consisting of long chain is lyophobic and polar group is of lyophilic nature in soaps and detergents.

Surfactants self associate in aqueous solution to form micelles and accumulate or adsorb in large excess at the air-water, oil-water and solid-water interfaces to lower interfacial tension. The phenomenon of association of the surfactants in the bulk aqueous phase is called micellization.

Mechanism of micelle formation: A micelle, when dissolved in water, generally dissociates to give ions. The anion consists of two parts. The polar group such as COO^- or SO_4^{2-} ion is lyophilic i.e. water loving in nature, and is called the head of the species. The hydrocarbon chain which is quite big in size is lyophobic (hydrophobic) i.e. water repelling (hating) in nature, and is known as the tail of the species. The hydrocarbon chain aggregates in to a micelle above the critical micelle concentration (CMC).

Properties of micelle: The low conductance of micelle is due to the non-availability of the ions associated with the micelles, to conduct the current. As the concentration increases, the number and size of micelles increase, and a few cations associated with the micelles are released, and conductance increases. Many physico-chemical properties such as surface tension, equivalent conductivity, turbidity, osmotic pressure etc. show an abrupt change around the CMC. CMC is an important characteristic of any surfactant. CMC usually decreases with increase in hydrocarbon chain length of the surfactant; change of counter ions can also alter the CMC of surfactants.

Addition of foreign electrolyte has a pronounced effect in reducing the CMC of ionic surfactants, while it has no effect on the CMC of non-ionic surfactant. In general, the addition of non-electrolytes causes a decrease in CMC of the surfactant. The effect of the variation of temperature and pressure on CMC of surfactants is usually small.

Micelle and Kraft point: Solubility of surfactant increases with temperature. The temperature at which the large change in surfactant solubility takes place is known as *Kraft point*. Below Kraft temperature, surfactant exits as monomer and monomer concentration increases with increase of temperature.

But when the monomer concentration exceeds CMC, the surfactants are dissolved as micelles, and since micelle solubility is much higher than the monomer solubility, the dramatic change occurs around the point of micellization. Thus, it is necessary to experiment all studies of micellization above the Kraft temperature.

Micelle Size and Shape: The size of micelle is related to the micelle aggregation number (n) given by

$$nA \rightleftharpoons A_n$$

The most commonly known method to determine 'n' is fluorescence quenching which gives an aggregation number of 70 for SDS micelles at room temperature. Micelles are polydisperse in size and shape, so when size changes, there is possibility of change of shape. Micelles are mostly spherical at CMC, and changes shape from sphere to cylinder with the increase of concentration.

Hydration Number: Surfactants form micelle in order to reduce unfavourable contact between water and hydrophobic group, however water is associated with micelle. Hydration number is the number of water molecules moving with micelle as a kinetic entity. Viscosity, conductance, self-diffusion methods give hydration number of approximately 8-10 per amphiphile for most ionic surfactants.

Structure of Micelle: Micelle are highly dynamic and flexible, and even the hydrocarbon chain segments undergo very rapid internal motion. It has been found that the interior of the micelle is "liquid like, close to that of oil".

Interactions among Miceller aggregates : In miceller solutions, different interactions viz, hydrophobic interactions among surfactants, interactions arising from the high charges in case of ionic micelles, steric interaction because of excluded volume effect and micelle-salt interactions are present.

Application - Cleansing action of Soap: The cleansing action of a soap is based upon its tendency to act as micelles. The soap has the capacity to clean a dirty piece of cloth while ordinary water fails to do so. The cloth gets dirty and becomes oily due to organic matter dispersed in the atmosphere, and perspiration coming out of skin of body of human. For washing the cloth, soap is applied to it after dipping the cloth in water. In water solution, soap dissociates to give cation (Na^+) and anion carboxylate ($RCOO^-$). The alkyl portion containing long chain of hydrocarbons in the carboxylate ion is the tail, points towards the oil drops, whereas the COO^- portion, is the head, directed towards water.

Soap, acting as an emulsifier, helps in forming a stable emulsion of oil and water by acting as a bridge between the two i.e. oil and water. The oil droplets along with the dust particles get detached from the fibers of the cloth and pass in to the emulsion. In this manner, the cloth becomes free from dust, and is, thus, washed by the soap.

Surfactants

Surface – active Substances: All such substances which when added to a solvent (particularly water) decrease its surface tension are called surface-active agents or surfactants. Examples are soap and alcohol, which decrease the surface tension of water on addition to it. These substances produce a marked reduction in surface tension of a solvent. The limiting value of the decrease of surface tension with concentration at infinite dilution ($C \rightarrow 0$) is called the surface activity.

Most of the organic compounds decrease the surface tension of water thereby meaning that they are present in excess at surface of water. The tendency of surface-active substances, having more concentration at the surface of water can be explained on the weaker nature of interactions between surface-active solute than those existing between solvent-solvent molecular interactions. The solute molecules are pushed up to the surface from the bulk of solution due to stronger solvent-solvent interactions. Surface tension of solvent is decreased due to the presence of these substances at the surface, which decrease the molecular interactions in the surface layers. Hence, a sharp decrease in the surface tension is observed as more and more of solute is added to the solvent.

Any substance, which shows positive deviation from Raoult’s law, is expected to have excess concentration of solute per unit area of surface, at the surface of a solution. The surface excessive concentration attains a constant value and is independent of the length of the hydrocarbon chain of the fatty acid. The surface-active materials such as fatty acids and alcohols have highly specific orientations in nature, especially when their concentration is very large. The carboxylic group or –OH group points towards the surface of water and the hydrocarbon chain points vertically away from the solution, forming a single layer of fatty acid. The concentration of the surface adsorbed fatty acid increases as the concentration of the latter is increased until a complete unimolecular layer is formed.

Surface inactive substances: If an increase in the concentration of substance in a solution causes an increase in the surface tension of the solution, those substances are called surface inactive substances. This means that the substance has larger concentration in the bulk in comparison to that present at the surface. This type of behaviour is known as negative adsorption. Examples include most of inorganic salts, sugars etc. The concentration of solvent in the surface layer changes very slightly due to the addition of surface inactive substances, hence, the increase in surface tension is very small. For these substances, interaction between solute and solvent molecules are of stronger in nature than those existing between solvent-solvent molecules, These substances have negative deviations from Raoult's law.

Surfactants are also called amphiphiles because all these compounds are usually composed of a fairly long hydrocarbon chain (hydrophobic tail) and a polar or hydrophilic head group. The polar head group may be cationic, anionic, amphoteric or even non-ionic, and the surfactants are called accordingly cationic, anionic, amphoteric or nonionic surfactants. Table lists some common surfactants of various types.

Table: Name and structure of some common surfactants

Name of surfactant	**Structure**	**Classification**	**Remark**
Potassium laurate	$CH_3 - (CH_2)_{10} - COO^-K^+$	Anionic	Single chain
Sodium dodecyl sulphate or lauryl sulphate	$CH_3 - (CH_2)_{11} - SO_4^- Na^+$	Anionic	-do-
Dodecylamine hydrochloride	$CH_{.3} - (CH_{.2})_{11} N^+H_{.3}Cl^-$	Cationic	-do-
Dodecylamine dimethylamnonium bromide	$CH_3 - (CH_2)_{11} N(CH_3)_2 Br^-$	Cationic	Double chain
N-dodecyl-N, N[1] dimethyl betaine	$C_{12}H_{25}N^+(CH_3)_2CH_2(COO^-)$	Zwitterion	Single chain

Cationic surfactants are mostly based on quaternary ammonium group although phosphonium surfactants are also known. The common types of anionic surfactants are the sulphates, sulphonates or carboxylates of sodium or potassium. Amphoteric or Zwitterionic surfactants contain both cationic and anionic head groups, a common example being dipalmitoyl lecithin, a biological surfactant which contains both quaternary ammonium and sulphate groups. Proteins may also be regarded as Zwitterionic (ammonium + carboxylates) surfactants.The head group in nonionic surfactants is usually derived from an uncharged group polyoxyethylene.

The surfactant plays many roles, one of which is lowering of interfacial tension, hence the stress needed to deform and break up a droplet. It is essential that the surfactant prevent coalescence of newly formed drops. An important distinction for surfactant on the basis of size is that small molecule surfactants is regarded as, "soaps" and large molecules as polymers. Another differentiation of surfactant is based on solubility. In emulsification, surfactants have to be soluble, unless they are rendered insoluble, by chemical modification, after adsorption to the 0-W (oil-water) interface.

The difference between soap and a polymer is that the polymer is far more surface active than soap. Soap tend to give lower surface tension (y) value, if present at high concentration than polymer, consequently, they can displace polymer from the interface.

Surfactant's another characteristic is the surface activity; how much surfactant is needed, or more precisely, how large should the surfactant activity be, to reach a certain value of surface tension. Generally mixtures of surfactants, often containing several different components in practice are used as emulsifiers. The properties of such mixtures are widely variable as various components vary in surface activity and hence surface tension. In principle, those giving the lowest surface tension y value at the prevailing conditions tend to predominate at the interface though may be present in a very low concentration. Some specific mixtures of surfactants give much smaller y-values than each one separately. So-called co-surfactants can further decrease (y), and so can salt for some surfactants.

Practical applications of surfactants :

1. The most primitive use of surfactants is in the form of soaps, washing powders, liquid detergents for various uses including washing clothes and household utensils.
2. Surfactants find important application in pharmaceuticals like skin cleansers and medicated shampoos, cosmetic creams, ointments, sprays etc.
3. Another important application of surfactant is to make emulsion. Emulsion finds applications in a wide range of products used in all spheres of life. Milk, butter, shaving cream, paints, foods, and synthetic resins are examples of emulsion.
4. A recent industrial application of surfactant is in tertiary oil recovery from underground reservoirs.
5. Surfactants are also used as phase transfer catalysts and miceller catalysts for controlling reactivity in many complex reactions.

Colloids

Colloid solutions have properties between true solutions and coarse suspensions. A colloidal solution, therefore, consists of solute particles, which are larger than the normal molecules but not large enough to be seen by a microscope. Generally particle size in a colloidal solution lies in the range 1 mμ to 1 μ (0.001 to 1 μm). Colloidal state is not a state of matter but rather a system composed of very small solid or liquid particles, 10nm to 100 nm in size, known as a disperse phase, in a suspensory phase, the dispersion medium, which itself may be in either the liquid or the gaseous state.

Classification of colloids

(i) Physical appearance: A colloidal solution is defined as a heterogeneous system consisting of two phases. (i) A dispersed phase, which consists of the colloidal particles and (ii) dispersion medium. For example, a colloidal solution is formed when As_2S_3, gold or oil is dispersed in water. Colloids have been classified in to eight different classes on the basis of state of aggregation of the dispersed phase and the dispersion medium.

For example, gas being dispersion medium and liquid/solid being dispersed phase, colloid is known as Aerosol having clouds, mist, smoke, haze as examples. The colloids having rigid structures are called gels e.g. butter, cheese, jelly etc. Here, rigidity varies from substance to substance. Gelatin like colloid may behave both as a sol and gel. At low temperature and high gelatin concentration, the hydrosol may change in to gel. At high temperature and low concentration, the gelatin colloid is a hydrosol in which water acts as the dispersion medium. Colloidal solutions are generally known as sols especially solid as dispersed phase in liquid dispersion medium e.g., AgCl, As_2S_3 in water. If the dispersion medium is water then they are called hydrosols or aqua sols, while those containing alcohol as dispersion medium are termed as alcosol.

(ii) Affinity of Phase: Colloids can also be classified on the basis of affinity of the two phases i.e. lyophilic sols and lyophobic colloids:

Lyophilic colloids : The colloidal solution in which the particles of the dispersed phase have a great affinity (or love) for the dispersion medium are called lyophilic colloids. As soon as dispersed phase and dispersion medium come in contact, lyophilic colloids are formed. Lyophilic colloid is also known as hydrophilic colloid when water acts as the dispersion medium. (Hence, lyophilic sols are easily formed, are more stable and reversible, e.g. gums, starch, gelatin, glue, proteins and rubber etc.).

Lyophobic colloids : The colloidal solutions in which the particles of the dispersed phase have hatred, but no love or affinity for dispersion medium, are called lyophobic colloids. They are irreversible in nature, unstable in nature, and are stabilized by the addition of small amount of electrolyte, called stabilizer. They are made with difficulty e.g. gold, $As_2 S_3$ in water.

Some important distinguishing points between lyophilic and lyophobic colloids are given below in table.

S. No.	**Lyopholic sols**	**Lyophobic sols**
1.	Direct mixing forms them easily	Special indirect methods are employed for their preparation
2.	They are reversible	They are irreversible
3.	The particles are not easily seen even under ultra microscope	The particles are easily detected under ultra microscope
4.	These are self stabilized	These can be stabilized due to traces of stabilizer electrolyte
5.	Colloidal solutions can be precipitated/coagulated with large amounts of electrolyte	Small amount of electrolyte can cause precipitation or coagulation of the colloidal solution.
6.	Viscosity of lyophilic sols are higher than the dispersion medium	Viscosity of lyophobic sol is same as that of the dispersion medium
7.	Surface tension is lower than that of the dispersion medium	Surface tension is nearly the same as that of dispersion medium.
8.	Tyndall effect is not shown	Tyndall effect is exhibited.
9.	Due to the attraction of solvent, these are highly hydrated	Due to repulsion for the solvent, no appreciable hydration is observed.
10.	The particles may or may not migrate in an electric field	Due to electric charge, migrate towards the electrode in an electric field.

(iii) Molecular size basis: The colloids can also be classified on the basis of molecular size as follows:

(a) Multimolecular colloids: In these colloids, the molecular size of individual particles consisting of an aggregate of atoms or small molecules is less them 10^3 pm. Gold sol consisting of several atoms has particles of various sizes. Similarly, a sulphur sol consists of particles each having eight sulphur atoms (S_8). In these colloids, particles are held by Van der Waal forces

(b) Macromolecular colloids: The particles of dispersed phase are sufficiently big in size (macro), to be of colloidal dimensions normally polymers. For example, naturally occurring starch, cellulose and proteins are macromolecules in nature. Polythene, nylon, plastics etc. are examples of artificial macromolecules.

(c) Associated colloids or micelles:These are substances which behave as normal electrolytes at low concentration, but get associated at higher concentration and behave as colloidal solutions. These associated particles are also called micelles.

Preparation of colloidal solutions : Generally, two methods are employed to prepare colloidal solutions.

(i) Condensation or aggregation method: In this method, particles in the true solutions as ions or molecules are allowed to grow in size to particles of colloidal dimensions. The substance which is to dispersed in the dispersion medium is obtained by chemical reactions, or by the physical changes under controlled conditions of temperature, concentrations, by exchange of solvent or by excessive cooling or heating methods etc. Chemical reactions can be achieved by various methods namely, reduction, oxidation, hydrolysis and double decomposition etc.

(ii) Dispersion method: When bigger particles are disintegrated in to particles of colloidal dimensions, which remain in the dispersion medium, the method is called dispersion method.

Various techniques viz. mechanical disintegration, peptization and electrical dispersion or Bredig's arc methods are employed. Peptization may be defined as the process of converting a freshly prepared precipitate in to colloidal form by addition of suitable electrolyte named as peptizing agent.

Purification of Colloidal Solution : The sols/colloids prepared by any one of methods contain some soluble impurities and excess of electrolytes, and hence need purification to remove these impurities to have pure sols.

Dialysis and ultrafilteration are two main methods for this purpose. The process of separating the substances in the colloidal state from those present in true solution by means of diffusion through parchment or a suitable cellophane membrane though which ions of electrolyte can pass while colloidal particles cannot pass, is called dialysis. Ordinary dialysis process is slow. Electrodialysis process involving the application of electric field, is quite fast.

Electrodialysis in ultrafilteration, the ultra filters retain the pure particles and allow the passage of the electrolyte and other soluble impurities whereas ordinary filter allow the passage of both. The size of pores for the ultrafilter is reduced and hardened by soaking the ordinary filter paper in solution of gelatin or colloidal ion and then soaking in formaldehyde.

Properties of Colloids: Colloids have following main characteristic properties:

(i) Colour: The sols are generally coloured. The size, shape and nature of the particles determine the colour of colloid. Actually, the colour of the colloidal solution depends upon the wavelength scattered by the dispersed phase particles and it changes with the change of particle's size. The colour of sol also depends upon the manner in which the observer receives the light. For example, in a reflected light, aqueous solution of milk appears blue, where as it is seen as red in the transmitted light.

(ii) Optical Properties: Due to large size of particles of colloids, light rays are scattered and the phenomenon is called Tyndall effect. When a beam of light is passed through a colloidal solution in a dark room, solution becomes luminescent when viewed through a microscope at right angle to the path of the incident beam. The intensity of the scattered polarized beam depends upon the nature of system, wavelength of light and position of observer etc. This effect has helped to confirm the size of colloidal particles as well as heterogeneous nature of the colloidal solutions.

(iii) Kinetic property: Brownian movement: An English Botanist Brown in 1828 observed that pollen grains suspended in water execute a continuous zig-zag motion. The ceaseless chaotic and random motion of colloidal particles in a liquid, seen under a microscope is called Brownian movement. It was later found that the particles of the dispersed phase of all colloidal solutions also show zig-zag motion. The smoke particles continue to move ceaselessly in a zig-zag motion, seen in the beam of light in a dark room. The movement increases with increase of temperature, decrease in size of suspended particles and decrease in the viscosity of the medium.

(iv) Electrical Properties

(a) Charge on colloidal particles:The negative or positive charge on the colloidal particles is of the same type in a colloidal solution. This may be due to preferential adsorption of ions, due to presence of acidic and basic groups, due to ionization of molecules on the surface (negative charge on As_2S_3), and due to dissociation of the surface molecules (charge on the particles in soap).

(b) Electrophoresis: The phenomenon of migration of colloidal particles in an electric field is called electrophoresis or cataphoresis. The speed of colloidal particles when the applied field strength is 1 volt m^{-1}, is known as the electrophoretic or cataphoretic mobility. The electrophoretic mobility depends upon the size of molecules of the colloidal particles. The difference in the electrophoretic mobility is used in the separation of mixtures.

If the colloidal particles are prevented from moving, then the dispersion medium moves in the electric field, then the phenomenon is known as electro osmosis. The presence of the charge on the sol particles and determination of the nature of the charge whether positive or negative can be done with the help of electrophoresis phenomenon. It involves the migration of colloidal particles towards appositively charged electrodes under the influence of applied electric current.

(v) Heterogeneous nature: The colloidal solutions are heterogeneous in nature consisting of dispersed phase and dispersion medium. The colloidal solutions generally appear homogeneous to the naked eye because of small particle size. However, under an ultra microscope heterogeneity can be seen.

(vi) Non-settling nature: The particles of colloidal solution do not settle at the bottom of the container due to being in a state of motion.

(vii) Filterability: Due to large size of pores of the ordinary filter papers, the colloidal particles can pass through them. However, animal and vegetable membranes and ultra filter papers where the pore size are fine, do not allow the colloidal particles to pass through them.

(viii) Visibility: The colloidal particles cannot he seen by naked eye and ordinary microscope. Only ultra-microscopes can visualize them.

(ix) Colligative properties: The colligative properties (namely osmotic pressure, elevation in boiling point, depression in freezing point, relative lowering in vapour pressure) depend upon the number and size of the solute particles in a solution. As the particles of the dispersed phase in a colloidal solution are quite big in size, and less in number per unit volume as compared to true solutions, all the above quoted colligative properties have smaller values. Determination of osmotic pressure for some of the colloidal solutions has evaluated average molecular masses of the colloidal particles.

Charge on colloidal particles i.e. stability of colloidal sols: The presence of charge on the particles of dispersed phase of colloidal sol brings stability to the colloidal sol. Generally, all particles of the dispersed phase carry the same charge either positive or negative in a particular colloidal sol. As these particles with similar charges repel one another, they do not come close together or do not coalesce to form particles of large size.

Some negatively and positively charged colloidal sols with water as the dispersion medium are given below in table

S. No.	Negatively charged sols	Positively charged sols
1.	Metal sulphides like CdS, $As_2 S_3$,	Oxides like TiO_2
2.	Metals like Ag, Au, Cu, Pt.	Metal hydroxides such as $Fe(OH)_3$, $Al(OH)_3$, $Ca(OH)_2$
3.	Starch, gelatin, Haemoglobin	Basic dyes like methylene dyes
4.	Silicic acid, Clay	
5.	Acid dyes such as Congo red, eosin etc.	

The origin of the charge on the colloidal particles can be accounted for due to different theories, based upon:
(i) Frictional electrification i.e. of the rubbing of the dispersed phase particles with those of dispersion medium.
(ii) Dissociation of the surface molecules: The electric charge on colloidal particles may be due to dissociation of the surface molecules. For example, dissociation of sodium palmitate soap in aqueous solution leads to formation of positive sodium cation and negative anion $C_{15} H_{31} COO^-$. These negative ions form aggregate due to weak attractive forces present in the hydrocarbon chains. Thus, the anions, which are of colloidal size, bear negative charge. The positive cations (Na^+) pass in to solution.
(iii) Selective adsorption of ions: The charge on the colloidal particles is generally acquired by preferentially absorbing positive or negative ions from the electrolyte present in solution to stabilize colloidal sols. If the colloidal particles have preference to positive ions, they get positive charge, and if they have liking for negative ions, they acquire negative charge.

Generally, the particles constituting the dispersed phase adsorb only those ions preferentially which are common with their lattice. For example, the $Fe(OH)_3$ solution prepared by the hydrolysis of $FeCl_3$ has positive charge because it preferentially adsorbs Fe^{3+} ions on its surface from solution.

If silver nitrate solution is added to an aqueous solution of potassium iodide, the silver iodide will adsorb negative ions (I^-) from the dispersion medium to form a negatively charged sol.

$$\underset{\text{(Dispersion medium)}}{AgI + I^-} \longrightarrow \underset{\text{(negative sol)}}{AgI.\ I^-}$$

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

AgI + Ag+ $\longrightarrow$ AgI. Ag^+
(Dispersion medium) (positive sol)

The presence and nature of charge on sol particles can be detected by electrophoresis phenomenon.

Precipitation of colloids : While traces of electrolytes are essential for the stability of a sol, the addition of a comparatively large amount of electrolytes make the sol unstable; the colloidal particles grow in size and are precipitated. This phenomenon of precipitation or coagulation of the sol particles with the addition of the excess amount of electrolyte is known as *flocculation*.The coagulation behaviour of different electrolytes can be explained on the basis of Hardy-Schulze law given as:

(i) Coagulation of the sol is effective by ions carrying a charge opposite to that of the colloidal particles. These ions are called *active ions*.
(ii) With increasing valency of the coagulating ion, the precipitating power of active ion increases.

The coagulating power of different cations to coagulate negative sol of As_2S_3 changes as

$Al^{3+} > Mg^{2+} > Na^+$

where as the coagulating power of different anions to coagulate positive sol such as $Fe(OH)_3$ has been found to decrease in the order:

$PO_4^{3-} > SO_4^{2-}\ Cl^-$

The minimum concentration of an electrolyte, which is able to bring about the flocculation of a sol, *is* called its *flocculation value*. It is usually expressed in *millimoles* of electrolyte per dm^3 of the sol. The flocculation values of some common electrolytes for a positively and a negatively charged sol are given in table.

Table: Effect of ions on coagulation of various sols.

As_2S_3 (negative sol)			**$Fe(OH)_3$ (positive sol)**		
Electrolyte	Valency and cation	Flocculation value	Electrolyte	Valency and cation	Flocculation value
NaCl	1 (Na^+)	51	KCl	1 (Cl^-)	103
KCl	1 (K^+)	50	KNO_3	$1(NO_3^-)$	131
$CaCl_2$	2 (Ca^{2+})	0.65	K_2SO_4	$2(SO_4^{-2})$	.219
$ZnCl_2$	2 (Zn^{+2})	0.68	$K_3Fe(CN)_6$	$3[Fe(CN)_6^{-3}]$	0.096
$AlCl_3$	3 (Al^{3+})	0.093			

It is clear from the table that on increasing the valency of the precipitating ion, the flocculation value decreases. The precipitating effect of a trivalent ion is about 600 to 1000 times more than that of a monovalent ion.

Apart from the addition of the electrolyte, the coagulation of a colloidal sol can also be brought by prolonged dialysis, electrophoresis and mixing of two colloids of opposite charge in equivalent proportions.

Protective action of colloids : A lyophobic sol is prevented from precipitation when a lyophilic sol is added to a lyophobic sol, thereby latter becoming more stable and less sensitive towards the electrolytes. The lyophilic sol thus plays a protective role, usually by forming an adsorbed layer completely covering the particles of the lyophobic sol, so that it virtually behaves like a lyophilic sol.

The protective capacity of various lyophilic colloids are expressed in terms of *Gold Number*. It is defined as the *mass* in milligrams of a dry lyophilic sol which when added to 10 ml of a standard gold sol to just prevent its coagulation (i.e., the change of colour from red to blue) on the addition of 1 ml of a 10 percent solution of sodium chloride. The change in colour indicates the initiation of a flocculation. Smaller the gold number, greater is the protective action of a lyophilic colloid.
Gelatin, agar, albumin, etc. have low gold numbers and thus have high protective powers. Values of gold numbers and their reciprocals for a few lyophilic colloids are given in the table.

Table: Gold number and their reciprocals of certain lyophilic sols

Protective colloid	**Gold Number**	**Reciprocal of Gold Number**
Gelatin	0.005-0.01	200-100
Haemoglobin	0.03-0.07	33-14
Albumin	0.1-0.2	10-5
Sodium oleate	0.4-1.0	2.5-1.0
Potato starch	25	0.04

The protective action of a lyophilic sol on a lyophobic colloid against coagulation may be due to association or united action of particles of the two sols.

Applications of coagulation: Based upon the neutralization of charge on the dispersed phase particles by suitable means, colloidal sols find many applications as given below.

1. Cottrell precipitator**:** Smoke and dust particles of air pollutants create health problems in industrial area. These are basically colloidal sol having dispersions of electrical charged particles. Involving the principle of electrophoresis, the smoke or dust particles from air or waste gases can be removed by discharging, depositing or setting down.
2. Sewerage disposal**:** Sewerage water has particles of colloidal sol with electrical charge in the form of dust, rubbish mud etc. suspending in water and do not settle down easily in the surface of tank. By applying electric field, these particles settle down due to neutralization of charges, and making water suitable for further purification.

3. Purification of river or lake water**:** After purification, river or lake water is used for domestic and industrial purposes. The lake or river water is turbid due to presence of negatively charged fine clay particles. By adding potash alum or aluminum sulphate these particles are removed.
4. Stoppage of bleeding from a fresh cut: By applying concentrated solution of ferric chloride or potash alum, bleeding from a fresh cut can be stopped. The negatively charged colloidal particles of colloidal sol of haemoglobin are neutralized and coagulated by the cations available from these substances in solution and the bleeding stops.
5. Artificial rain**:** Artificial rain can be caused by spraying oppositely charged dust or fine sand or precipitates like AgI on to a cloud which has tiny water droplets with electrical charge. The neutralization of charge results in coagulation of water droplets in the form of artificial rain.

A natural disaster of cloud bursts resulting in a very heavy down pour over a short time is believed to occur due to mutual discharge of oppositely charged clouds particles.

6. Formation of river delta : When river water containing charged particles of sand, clay, etc. come in contact with saline sea water, they get coagulated to settle down at the point of contact, resulting in a rise of the river bed. Hence, water adopts a different course and a delta is formed in due course of time.