

Chapter-2

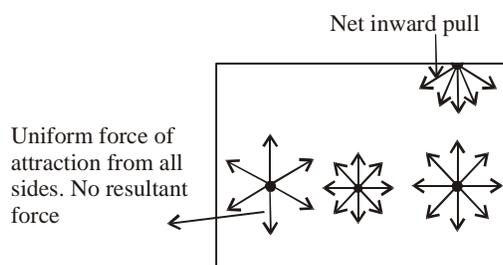
SURFACE AND CATALYSIS

Introduction

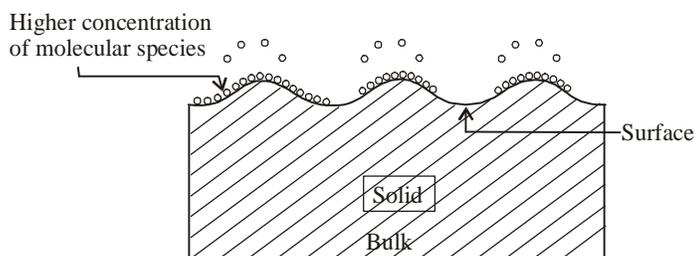
There are many properties of substances particularly of solids and liquids which depend upon the nature of the surface. The branch of chemistry which deals with the nature of surfaces and changes occurring on the surfaces is called surface chemistry. Adsorption on solid or on solution surfaces are important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

Adsorption

Adsorption is a surface phenomenon. It arises because of the unbalanced forces on the surface of the solids and liquids. If we consider a solid, it is observed that a molecule present in the bulk of the solid is being uniformly attracted from all sides by the neighbouring molecules. As a result, there is no net pull on this molecule. However, a molecule which lies near the surface (known as a surface molecule) is being attracted only by molecules below it. This is because there are no molecules above it. Therefore, surface molecules experience a resultant downward attractive force within the solid. In other words, the surface is under tension due to unbalanced forces.



Similarly inward forces of attraction exist on the surface of a liquid. As a result, the surface of the solid or liquid tends to satisfy their residual forces by attracting and retaining the molecules of other species when brought in contact with them. These molecules, however, remain only at the surface of the solid or liquid and do not penetrate into the bulk. For example, when a small amount of finely divided charcoal is put into a vessel containing a gas, it is observed that the pressure of the gas decreases rapidly at first, and then gradually. The decrease in pressure of the gas is due to the accumulation of the gas on the surface of charcoal. It has been observed that the gas molecules remain only on the surface and do not penetrate into the bulk of the solid. Thus, there is a high concentration of the species of gas on the surface and are said to be **adsorbed** on the surface.



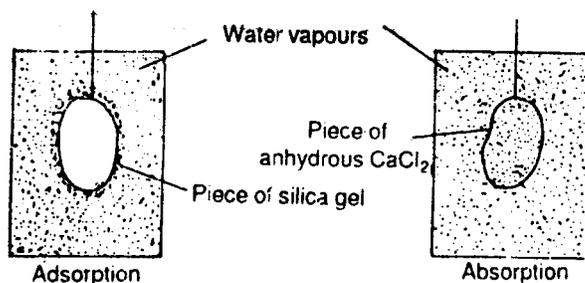
The phenomenon of higher concentration of molecular species (gases or liquids) on the surface of a solid than in the bulk is called adsorption.

- (a) *Adsorbent* : The solid substance on the surface of which adsorption occurs is known as adsorbent.
- (b) *Adsorbate* : The substances that get adsorbed on the solid surface due to intermolecular attractions are called adsorbate.

Examples of Adsorption

- Adsorption of a gas by charcoal:** Finely divided activated charcoal has a tendency to adsorb a number of gases like ammonia, sulphur dioxide, chlorine, phosgene, etc. In this case, charcoal acts as an adsorbent while gas molecules act as adsorbate.
- Adsorption of a dye by charcoal:** Animal charcoal is used for decolourising a number of organic substances in the form of their solutions. The discharge of the colour is due to the fact that the coloured component (generally an organic dye) gets adsorbed on the surface of the adsorbent i.e. animal charcoal.

Difference between Adsorption and Absorption	
Absorption	Adsorption
1. It is the phenomenon in which the particles of gas or liquid get uniformly distributed throughout the body of the solid.	1. It is the phenomenon of higher concentration particles of gas or liquid on the surface than in the bulk of the solid or liquid.
2. It is a bulk phenomenon.	2. It is a surface phenomenon.
3. Absorption occurs at uniform rate.	3. Adsorption is rapid in the beginning and its rate slowly decreases.
4. H ₂ O is absorbed in CaCl ₂ NH ₃ is absorbed in H ₂ O	4. H ₂ O is adsorbed over silica gel NH ₃ is adsorbed over charcoal



SORPTION : In some cases, both absorption and adsorption occur together and are not distinguishable. In such cases, the substances get uniformly distributed into the bulk of the solid but at the same time, its concentration is higher at the surface than in the bulk. Such a phenomenon is called sorption.

Positive and Negative Adsorption

Positive Adsorption: When the concentration of adsorbate is more on the surface of adsorbent relative to its concentration in the bulk, it is called positive adsorption.

Negative Adsorption: When the concentration of the adsorbate is less on the surface relative to its concentration in the bulk, it is called negative adsorption. For example, in case of some liquid solutions, it is observed that the concentration of the solute is less on the surface than in the bulk of the solution. This type of adsorption is called negative adsorption.

Type of Adsorption

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

(i) Physical adsorption and (ii) Chemical adsorption.

(i) *Physical adsorption* :

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

(ii) *Chemical adsorption* :

When the molecules of the adsorbate are held to the surface of the adsorbent by the chemical forces, the adsorption is called chemical adsorption or chemisorption.

Differences between Physical Adsorption and Chemical Adsorption.	
Physical Adsorption	Chemical Adsorption
1. The forces between the adsorbate molecules and the adsorbent are weak Van der Waals forces.	1. The forces between the adsorbate molecules and the adsorbent are strong chemical forces.
2. Low heat of adsorption of the order of 20-40 kJ mol ⁻¹ .	2. High heat of adsorption of the order of 200-400 kJ mol ⁻¹ .
3. Usually occurs at low temperature and decreases with increasing temperature.	3. It occurs at high temperature.
4. It is reversible.	4. It is irreversible.
5. The extent of adsorption depends upon the ease of liquefaction of the gas.	5. There is no correlation between extent of adsorption and the ease of liquefaction of gas.
6. It is not specific in nature, i.e, all gases are adsorbed on the surface of a solid to same extent.	6. It is highly specific in nature and occurs only when there is bond formation between adsorbent and adsorbate molecules.
7. The state of adsorbate is same as in the bulk.	7. State of adsorbate molecules may be different from that in the bulk.
8. It forms multimolecular layers.	8. It forms mono-molecular layer.
9. Rate of adsorption increases with increase in pressure of adsorbate.	9. Rate of adsorption usually remains almost same and does not change appreciably with change in pressure.

Adsorption of Gases on Solids

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

1. Nature of the gas
2. Nature of adsorbent
3. Effect of pressure
4. Effect of temperature
5. Activation of adsorbent.

1. Nature of the gas :

The adsorption depends upon the nature of the gas adsorbed. The easily liquefiable gases such as HCl, NH₃, Cl₂ etc. are adsorbed more than the permanent gases such as H₂, N₂ and O₂. The nature of

liquefaction of a gas depends upon its critical temperature. *The critical temperature of a gas is defined as the minimum temperature above which a gas cannot be liquefied however high the pressure may be applied. The higher the critical temperature, the more easily a gas is liquefied and hence more readily it will be adsorbed.* For example, 1g of activated charcoal can adsorb the following amounts of gases :

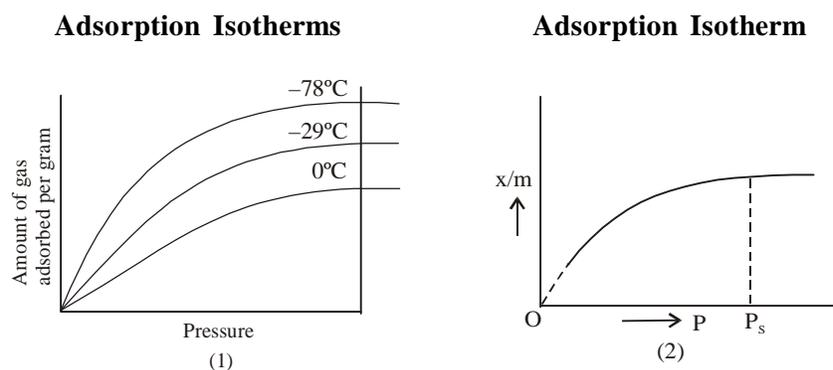
Gas	H ₂	N ₂	CO	CH ₄	CO ₂	NH ₃	SO ₂
Critical temp.(K)	33	126	134	190	304	406	430
Amount of gas as adsorbed in ml	4.5	8.0	9.3	16.2	48	180	380

2. Nature of adsorbent :

The extent of adsorption of a gas depends upon the nature of adsorbent. Activated charcoal can adsorb gases which are easily liquefied. Many poisonous gases are adsorbed by charcoal. Therefore, it is used in gas masks for adsorbing these poisonous gases. Gases such as H₂, N₂ and O₂ are generally adsorbed on finely divided transition metals e.g., Ni and Co. The extent of adsorption depends on the available surface.

3. Effect of pressure :

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



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

Freundlich Adsorption Isotherm

The variation of extent of adsorption (x/m) with pressure (P) was given mathematically by Freundlich. The following observations can be easily made:

- (i) **At low pressure**, the graph is almost straight line which indicates that x/m is directly proportional to the pressure. This may be expressed as :

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

- (ii) **At high pressure**, the graph becomes almost constant which means that x/m becomes independent of pressure. This may be expressed as :

$$\boxed{\frac{x}{m} = \text{constant or } \frac{x}{m} \propto p^0} \quad (\because p^0 = 1)$$

or $\boxed{\frac{x}{m} = kp^0 = k}$ As $p^0 = 1$ (Pressure raised to the power zero = 1)

- (iii) **Thus, in the intermediate range of pressure**, x/m will depend upon the power of pressure which lies between 0 to 1 *i.e.*, fractional power of pressure. This may be expressed as

$$\frac{x}{m} \propto p^{1/n}$$

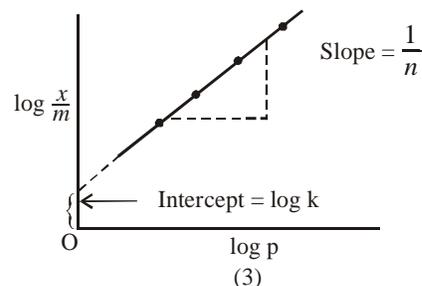
$$\frac{x}{m} = k p^{1/n}$$

Calculation of k and n of adsorption isotherm

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

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

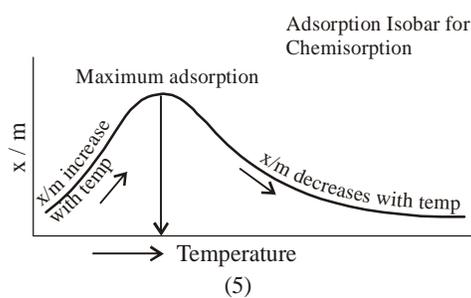
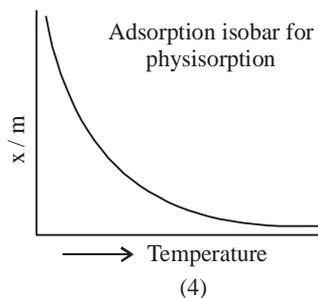
$$\boxed{\log \frac{x}{m} = \log k + \frac{1}{n} \log p}$$



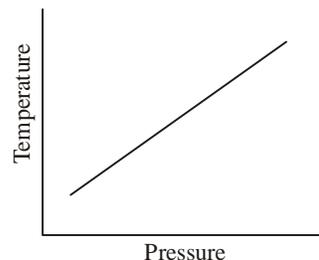
Thus, if we plot a graph-3 between $\log(x/m)$ and $\log p$, a straight line will be obtained. The slope of the line is equal to $1/n$ and the intercept is equal to $\log k$.

4. Effect of temperature :

The process of adsorption is exothermic. Therefore, the reverse process *i.e.* desorption is endothermic. Then according to Le-Chatelier's principle, the rate of adsorption will not be favoured by the increase in temperature. With the increase in temperature at constant pressure, the extent of adsorption (x/m), will be decreased. The graph between extent of adsorption and temperature at constant pressure is called adsorption isobar.



However, this is true for physical adsorption as shown in graph-4. In case of chemisorption, the adsorption initially increases with rise in temperature and then decreases as shown in graph-5. This behaviour is expected because like all chemical reactions, some activation energy is required for chemisorption. **At low temperature, x/m is small. As temperature is increased, the molecules of the adsorbate gain energy and become equal to activation energy so that proper bonds are formed with the adsorbent molecules.**

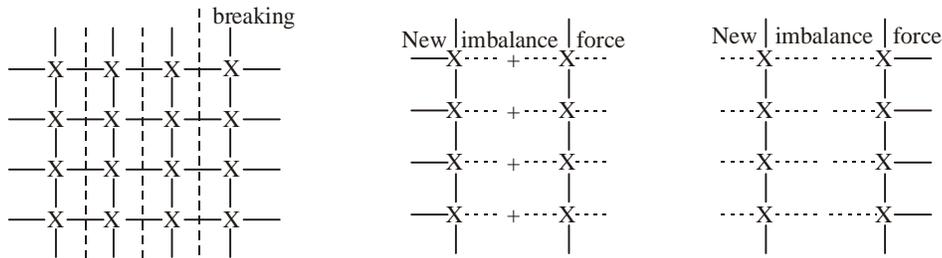


Therefore, initially amount of gas adsorbed is less which then increases with rise in temperature. Further increase of temperature will increase the energy of molecules which have already been adsorbed. This would increase the rate of desorption and therefore, decrease the extent of adsorption. An adsorption isosters is the graph of the variation of pressure with temperature for a given amount of adsorption.

5. Activation of adsorbent :

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

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



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

Adsorption from Solutions

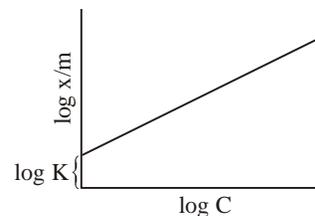
The process of adsorption can take place from solutions also. It is observed that solid adsorbents adsorb certain solutes from solution in preference to other solutes and solvents. For example, animal charcoal decolourises impure sugar solution by adsorbing colouring dye in preference to sugar molecules. The Freundlich's adsorption isotherms obtained for the adsorption of gases on the surface of solid adsorbents have also been found to be applicable to the adsorption of solutes from the solutions. The adsorption isotherm may be represented as :

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

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

From the graph, the values of $1/n$ and $\log k$ can be calculated as slope and intercept respectively.

$$\text{Slope} = \frac{1}{n} \text{ and intercept on y axis} = \log K$$



Application of Adsorption

Some of the important applications of adsorption are given below :

1. **In Gas Masks:** Activated charcoal is generally used in gas masks to adsorb poisonous and toxic gases from air. These masks are commonly used by the miners because there are poisonous gases like CO, CH₄ etc. in the atmosphere in the coal mines. Therefore, these masks help to purify the air for breathing.
2. **In Dyeing Cloth:** Mordants such as alums are used in dyeing cloth. They adsorb the dye particles which, otherwise, do not stick to the cloth.
3. **In dehumidizers:** Silica gel is commonly used to adsorb humidity or moisture from air. This is necessary for storage of delicate instruments which might otherwise be damaged by moisture.
4. **Removal of colouring matter:** Many substances such as sugar, juice and vegetable oils are coloured due to the presence of impurities. They can be decolourised by placing in contact with adsorbents like activated charcoal or fuller's earth. This method is commonly used in the manufacture of sugar. The coloured sugar solution is treated with animal charcoal or activated charcoal.
5. **Heterogeneous catalysis:** The phenomenon of adsorption is useful in the heterogeneous catalysis. The metals such as Fe, Ni, Pt, Pd, etc. are used in the manufacturing process such as Contact process, Haber process and the hydrogenation of oils. Its use is based upon the phenomenon of adsorption.
6. **In ion-exchange resins:** The organic polymers containing groups like -COOH, -SO₃H etc. possess the property of selective adsorption of ions from solutions. These are quite useful in the softening of water.
7. **In adsorption indicators:** Many adsorption indicators are being used in volumetric analysis, e.g. dyes such as eosin and fluorescein are used as adsorption indicators.
8. **In qualitative analysis:** Certain qualitative tests such as the lake test for the confirmation of Al³⁺ ions are based upon adsorption. *i.e.* Al(OH)₃ has the capacity to adsorb the colour of blue litmus from the solution.
9. **Production of high vacuum:** The adsorption of air in liquid air helps to create high vacuum in a vessel. This process is used in high vacuum instruments as Dewar flask for storage of liquid air or liquid hydrogen.

The Colloidal State

Thomas Graham, in 1861, during his work on diffusion, found that while certain substances, such as sugars, salts, acids and bases diffused readily through a parchment membrane, others, such as gelatin, albumen, glue and silicic acid, diffused at a very slow rate. The substances belonging to the former category which generally exist in crystalline state, were called crystalloids while the substances belonging to the second category were given the name colloids. These observations led to the development of a new branch of knowledge, known as colloidal science.

It was soon realized by many investigators, including Thomas Graham himself, that the distinction between crystalloids and colloids was not rigid since many crystalline substances, like sulphur, carbon and salts, can be converted into colloidal forms by suitable means.

True Solutions, Colloidal Solutions and Suspensions: When a few crystals of a water-soluble substance, like sugar or sodium chloride, are added to water, they dissolve to give a homogeneous solution. The particles of a solute are now of molecular size. They are invisible and do not settle down on standing. Such mixtures are termed as true solutions or molecular solutions. If an insoluble substance like barium sulphate or clay is added to water, the particles are large enough to be visible, if not to a

naked eye, at least under a microscope. They settle down on standing for some time. Such mixtures are called suspensions. In between these two extremes, lie particles which are bigger than molecules but are too small to be visible even under a most powerful microscope. When suspended in a liquid, they have a tendency to settle down, though extremely slowly. These particles are said to belong to the colloidal state and their solutions are referred to as colloidal solutions.

Table-1

Property	Suspension	Colloid Solution	True Solution
	(Coarse dispersion)	(Colloidal dispersion)	(Molecular Solutions)
1. Nature	Heterogeneous	Heterogeneous	Homogeneous
2. Particle size*	> 100 nm	1 nm-100 nm	< 1 nm
3. Separation by			
(i) Ordinary filtration	Possible	Not possible	Not possible
(ii) Ultra-filtration	Possible	Possible	Not possible
4. Settling of particles	Settle under gravity	Settle only on	Do not settle
	centrifugation	ultracentrifugation	
5. Appearance	Opaque	Generally transparent	Transparent
6. Tyndall effect	Shows	Shows	Do not show
7. Diffusion of particles	Does not diffuse	Diffuses slowly	Diffuses rapidly
8. Brownian movement	May show	Show	Negligible

Classification of Colloids

Types of Colloidal Systems: Finely divided particles of any substance with diameters lying with 10–1000 Å (1nm – 100nm) range dispersed in any medium constitute the colloidal system.

The dispersed phase may not necessarily be a solid always. It may be a liquid or even a gas. Similarly, the dispersion medium may be a gas or a liquid or even a solid. Thus, several different types of colloidal system depending upon the states of aggregation of the dispersed phase and the dispersion medium, are possible, as shown in Table 2.

Table-2

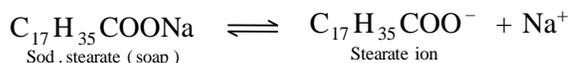
Different Colloidal Systems		
Dispersion Medium	Dispersed Phase	Examples
Gas	Liquid	Clouds, mists, fogs
Gas	Solid	Smoke, volcanic dust
Liquid	Gas	Foams, whipped cream
Liquid	Liquid	Emulsions (milk, cod-liver oil)
Liquid	Solid	Starch, proteins, arsenic sulphide, gold
Solid	Gas	Adsorbed or occluded gases
Solid	Liquid	Jellies, gels, cheese
Solid	Solid	Coloured precious stones, rock-salt

Multimolecular Macromolecular and Associated Colloids

Depending upon the molecular size, the colloids can be classified as :

- (i) *Multimolecular colloids* : In this type, the particles consist of an aggregate of atoms or small molecules. For example, sols of gold atoms and sulphur (S₈) molecules. In these colloids, the particles are held together by van der Waals forces.

- (ii) *Macromolecular colloids* : In this type, the particles of the dispersed phase are sufficiently big in size (macro) to be of colloidal dimensions. These macromolecules forming the dispersed phase are generally polymers having very high molecular masses. Naturally occurring macromolecules are starch, cellulose, proteins, enzymes, gelatin, etc. Artificial macromolecules are synthetic polymers such as nylon, polythene, plastics, polystyrene, etc. Since these macromolecules have large sizes, the solutions of such molecules are called macromolecular colloidal solutions. Their solutions are quite stable and resemble true solution in many respects. Thus, the common examples of macromolecular colloids are starch, cellulose, proteins, plastics, etc.
- (iii) *Associated colloids* : These are the substances which behave as normal electrolytes at low concentration but behave as colloidal particles at higher concentration. These associated particles are also called micelles. For example, in aqueous solution, soap (sodium stearate) ionises as :



In concentrated solution, these ions get associated to form an aggregate of colloidal size.

When the dispersion medium is a gas, the colloidal system is called aerosol. The systems with solids as dispersed phase and a liquid as dispersion medium are known as sols. When the liquid medium is water, the system is called hydrosol or aquasol. When this is alcohol or benzene or any other organic liquid, the system is referred to as alcisol, benzosol or organosol, respectively.

Classification based upon interaction forces between the dispersed phase and dispersion medium.

- (a) If strong interactive force exist between the dispersed phase and dispersion medium then such colloids are called Lyophilic colloids e.g., starch, gum, etc.
- (b) If no interactive forces exist between the dispersed phase and dispersion medium, such colloids are called Lyophobic colloids.

Table-3

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

Preparation of Colloidal Solutions

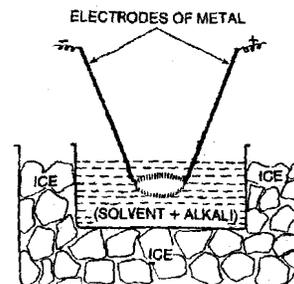
The primary consideration in the preparation of colloidal solutions is that the dispersed particles should be within the size range of 1 nm –100 nm. The lyophilic sols can be readily prepared since colloidal materials such as starch, gelatin, acacia, etc., when added to water swell up and spontaneously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

1. *Breaking down the coarser aggregates into particles of colloidal size or*
2. *Grouping molecules into larger aggregates of colloidal size.*

The methods belonging to these two categories are known as dispersion and condensation methods, respectively.

1. **Mechanical Dispersion:** The most obvious dispersion method consists in breaking down the coarser solid particles by mechanical grinding. This is done in the so-called ‘colloid mill’ which generally consists of two metal discs held at a very small distance apart from one another which are capable of revolving at a high speed (of the order of 7000 rpm) in opposite direction. The material to be ground is fed in between the two discs in the form of a wet slurry. The particles get broken to colloidal dimensions by the operating shearing force. However, it is doubtful if this method produces particles uniformly of colloidal dimensions. Some sols can alternatively be prepared by mechanical dispersion in a high intensity ultrasonic generators operating at a frequency of 20 kHz(not audible to human ear) and above. This technique is effective only if the substance being dispersed has low mechanical strength such as sulphur, graphite, resins and gypsum. Ultrasonic vibrations are usually obtained by piezoelectric oscillations which convert electric vibrations of high frequency into mechanical vibrations.

2. **Electrical Dispersion:** In this method an arc is struck between two electrodes of a metal like platinum, gold, silver or copper, in water containing traces of an alkali, when the metal passes into colloidal solution of a reasonable, though not high, concentration. The metal first changes into vapours (molecular state) on account of the heat of the spark and the vapours then condense in water to give aggregates of colloidal range.



T. Syedberg improved this method to obtain organosols of metals and non-metals. In syedberg’s method, the electrodes are usually of iron or aluminium and alternating current (instead of the direct current used in the Bredig method) is employed. The material to be dispersed is taken in the form of granules and pasted on the electrodes (immersed in the organic medium) through which the electric arc is passed. Electroputtering occurs as the electric spark gets through the granules of the material pasted on the electrode. Electroputtering technique is used for obtaining organosols of several metals and non-metals. Organosols of metals are used (i) in the hydrogenation and reduction of organic compounds, (ii) as catalysts for combustion of liquid fuels in rockets, (iii) as fillers of plastics, glues, anticorrosive lacuers and paints and (iv) in medicine.

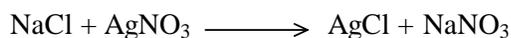
3. **Peptization:** Certain freshly prepared precipitates, such as silver chloride, ferric hydroxide, aluminium hydroxide, can be converted into colloidal solutions by the addition of a small amount of a suitable electrolyte. An electrolyte having an ion in common with the material to be dispersed is required for sol formation. The peptization action is due to the preferential adsorption of one of the ions of the electrolyte by the particles of the material. As would be illustrated a little later in this chapter, as a result of the preferential adsorption of the ion which is more closely related chemically to the precipitate, the particles

acquire a positive or a negative charge depending upon the charge on the ion adsorbed. Because of the presence of the same type of charge, the particles of the precipitate are pushed apart. The precipitate thus gets dispersed resulting in the formation of a stable sol.

Condensation Methods

Colloidal solutions can be obtained by various chemical reactions such as double decomposition, oxidation, reduction, hydrolysis, etc

1. **Double Decomposition** : A sol of arsenious sulphide is prepared by passing H₂S gas through a dilute solution of arsenious oxide and removing the excess H₂S by boiling.



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



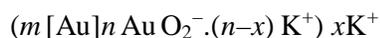
3. **Reduction** : Sols of metals such as silver, copper, gold and platinum are obtained by reducing the aqueous solutions of their salts by non-electrolytes such as formaldehyde, tannin, phenyl hydrazine, carbon monoxide and phosphorus. Zsigmondy prepared the gold hydrosol by reducing potassium aurate with formaldehyde. In this reaction, chloroauric acid, H[AuCl₄]. 4H₂O, first formed, is made to react with potassium carbonate in an aqueous solution to yield potassium aurate :



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



Potassium aurate, KAuO₂, acts as the stabilizer of the red gold sol obtained. The miscelle of the gold sol is represented by the formula



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



Boiling promotes the reactions because HCl formed is removed with water vapours from the system. In this reaction, ironoxychloride, (FeOCl), formed as a result of incomplete hydrolysis of FeCl₃, is believed to act as the stabilizer :



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

Purification of Colloidal Solutions

The presence of impurities, particularly the electrolytes, renders the sols unstable. The cause of this instability will be discussed later.

1. **Dialysis:** It has already been stated that while particles in the true solution can easily diffuse through parchment and other fine membranes, the colloidal particles, being much larger, cannot do so readily. The process of separating substances in colloidal state from those present in true solution with the help of fine membranes, is known as dialysis and the membrane used for the purpose is known as dialyser. Ordinarily, the process of dialysis is quite slow but it can be quickened by applying an electric field if the substance in true solution is an electrolyte. The process is then called electro-dialysis.
2. **Ultra-filtration:** The separation of solutes from colloidal systems can also be carried out by the process known as ultra-filtration. Ordinarily, filter papers have larger pores hence the colloidal particles can readily pass through along with the ions or molecules in solutions. But the pores can be made smaller by soaking the filter papers in a solution of gelatin or collodion $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ and subsequently hardening them by soaking in formaldehyde. Other semipermeable membranes are (i) animal or vegetable membranes (ii) parchment membrane, cellophane membranes (iii) Inorganic gelatinous membranes like silicates of iron, cobalt, nickel. The pores thus become very small and the colloidal particles may be retained on the treated filter paper. The treated filters are known as ultra-filters. This process of separating colloids from solutes is known as ultra-filtration.

Properties of Colloidal System

1. **Heterogeneous Character :** As already stated, colloidal systems, unlike true solutions, are heterogeneous in character. They consist of two phases – the dispersed phase and the dispersion medium.
2. **Diffusibility :** The colloidal particles constituting the dispersed phase do not readily diffuse through parchment or other fine membranes. In fact, it was this property which led Thomas Graham to lay the foundation of colloid science, as already mentioned.
3. **Filtrability :** The colloidal particles readily pass through ordinary filter papers along with any dissolved material. This is because even the finest filter paper has pores bigger than the colloidal dimensions.
4. **Visibility :** It is not possible to see colloidal particles even with the help of a powerful microscope. A gold sol, for instance, appears to be as clear as a true solution of gold chloride in water. The reason for the invisibility of colloidal particles has already been discussed.

Attempts have been made in recent times to use ultraviolet rays or cathode rays for seeing the colloidal particles. But, these rays make no impression on the retina of the eye. However, the images formed by them can be photographed. The electron microscope, for instance, makes use of a beam of cathode rays and by combination of special types of lenses, images of colloidal particles can be obtained on photographic plates.

5. **Colligative Properties:** The magnitude of osmotic pressure, lowering of vapour pressure, depression in freezing point and elevation in boiling point, depend upon the number of solute particles present in a given mass of the solvent. Now, colloidal particles are not simple molecules. These are physical aggregations of molecules. In arsenic sulphide sol, for instance, each particle is composed of about 1000 molecules. Thus, for a given mass of arsenic sulphide, the number of particles in the sol will be only $\frac{1}{1000}$ th of the number present in true solution. Hence, all colloidal dispersions (unlike true solutions) give very low osmotic pressure and show very small freezing point depression or boiling point elevation.

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6. **Optical Properties :** It was observed by Tyndall, in 1869, that when a beam of light is passed through a true solution, it cannot be seen unless the eye is placed directly in the path. However, when the same beam of light is passed through a colloidal dispersion, it becomes visible as a bright streak. This phenomenon is known as the Tyndall effect and the illuminated path (streak of light) is known as Tyndall cone. This phenomenon is due to the scattering of light from the surface of colloidal particles. In a true solution, there are no particles of sufficiently large diameter to scatter light and hence the beam is invisible.

The visibility of dust particles in a semi-darkened room when a sun beam enters or when a light is thrown from a light projector.

The intensity of the scattered light depends on the difference between the refractive indices of the dispersed phase and the dispersion medium.

7. **The Brownian Movement :** It was found that particles of lyophobic sols were also in a state of ceaseless erratic and random motion similar to pollen grains. This kinetic activity of particles suspended in a liquid is called Brownian movement. The Brownian movement is due to the bombardment on colloidal particles by molecules of dispersion medium which are in constant motion e.g. molecules in a gas.

Some Specific Properties of Hydrophobic Colloidal Systems

I. **Electrical Properties of Colloids:**

Electro kinetic effect : It is now established that colloidal particles carry an electric charge. When colloid particles are placed in an electrical field, they exhibit some specific properties known as electro kinetic effect. Such effects are of four types:

- (i) Electro phoresis or Cataphoresis
- (ii) Electro osmosis or electroendosmosis
- (iii) Streaming potential
- (iv) Sedimentation potential

Charge on Colloidal Particles : The presence of similar charges on colloidal particles is largely responsible in giving stability to colloidal systems because the mutual forces of repulsion between similarly charged particles, prevent them from coalescing and coagulating or aggregating when they come closer to one another. Metallic hydroxides, some metals such as bismuth, lead, iron, methyl violet and methylene blue, are electropositive colloids while metallic sulphides, prussian blue, many metals (such as silver, gold, platinum), silicic acid, tannic acid are electronegative colloids.

The Origin of Charge on Colloidal Particles : The origin of charge on colloidal particles has not been completely understood. However, it has been observed that sols are invariably associated with minute quantities of electrolytes and that if the latter are completely removed by persistent dialysis, the sols become unstable. It is believed, therefore, that the charge on the colloidal particles is due to preferential adsorption of either positive or negative ions on their surface. According to this view, positive charge on ferric hydroxide sol prepared by hydrolysis of ferric chloride is largely due to preferential adsorption of Fe^{3+} ions on the surface of particles ferric of hydroxide. The ferric ions come from the ionisation of ferric chloride which is always present in traces in the sol.

The negative charge on arsenic sulphide sol is due to preferential adsorption of sulphide ions on the surface of arsenic sulphide particles. The sulphide ions are furnished by ionisation of hydrogen sulphide which is present in traces. Likewise, the negative charge on metal sols prepared by the Bredig's arc method is due to adsorption of hydroxyl ions furnished by traces of the alkali added. It should be remembered that the ion which is more nearly related chemically to the colloidal particle is preferentially adsorbed by it.

Precipitate of stannic oxide is peptised by a small amount of hydrochloric acid, the sol carries a positive charge but if peptised by a small amount of sodium hydroxide, the sol carries a negative charge. In the former case, a small amount of stannic chloride, SnCl_4 , is formed and the positively charged Sn^{4+} ion is preferred and the sol is positively charged. In the latter case, a small amount of sodium stannate, Na_2SnO_3 , is formed and now the negatively charged SnO_3^{2-} ion is preferred and accordingly the sol is negatively charged.

Another interesting case is furnished by the formation of positively as well as negatively charged sols of silver iodide. If a dilute solution of silver nitrate is added to a slight excess of a dilute solution of sodium iodide, a negatively charged sol of silver iodide is formed. This is due to the adsorption of iodide ions. [Fig.-1(a)]

On the other hand if excess of AgNO_3 is added to a solution of NaI then a positively charged AgI is formed due to the preferential adsorption of Ag^+ ions. [Fig-1(b)]

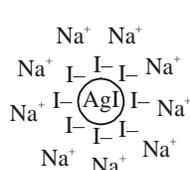


Figure -1 (a)

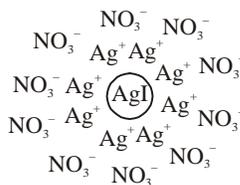


Figure -1 (b)

Another possible way in which colloidal particles may acquire charge is by direct ionisation of the material constituting the particles. This phenomenon is observed mostly in the case of acidic and basic dyestuffs. An acidic dyestuff, for example, ionises yielding hydrogen ions in solution and thereby leaving an equivalent amount of negative charge on the particles. The structure of the colloidal particles of the dye may be represented as shown in Figure 2.

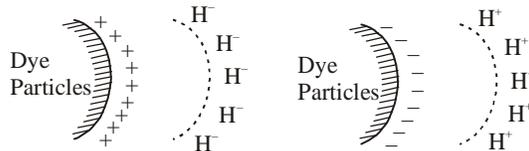


Fig. 2

An Electrical Double Layer:

The governing factor to the understanding of the electrical properties of colloids is the concept of electrical double layer. Consider once again the formation of silver iodide sol from the double decomposition reaction



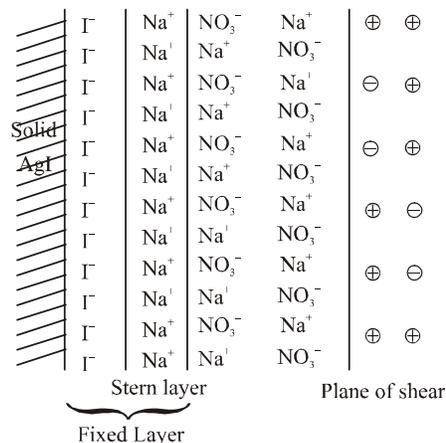
Let us suppose that the electrolyte used in excess of sodium iodide. This would result in preferential adsorption of I^- ions giving a negatively charged sol of silver iodide.

The ions preferentially adsorbed on the surface of a particle of a colloidal system are called potential-determining ions. A sheath of tightly bound solvent molecules lies immediately adjacent to this potential determining ion layer.

The Electrical Double Layer

The negatively charged surface of AgI particle attracts the positive ions (Na^+) and repels the negative ions (NO_3^-). As a result the positive Na^+ ion tend to form a compact layer in the vicinity of the potential-determining ion layer. This is called the Stern layer. The ions present in the Stern layer are called the counter ions.

The influence of the surface charge decreases with distance and so does the number of ions with the result that at a certain distance from the surface of the particle, the concentration of Na^+ ions equals the concentration of (NO_3^-) ions and a state of electroneutrality prevails.



It must be borne in mind that the system as a whole is electrically neutral even though there exist regions of unequal distribution of anions and cations. The diffuse layer between the Stern layer and the electrically neutral part of the system is referred to as the Gouy-Champman layer.

The presence of charge gives rise to potential at the surface of the particle. The region in which the influence of the charge is appreciable is known as the electrical double layer. The double layer consists of two parts : the Stern layer, the thickness of which is of the order of ionic dimensions and the diffusion through double layer, the thickness of which is given as

$$d = \left(\frac{RT}{2\rho F^2 I} \right)^{1/2} \quad (\text{where } d \text{ is thickness of double layer}).$$

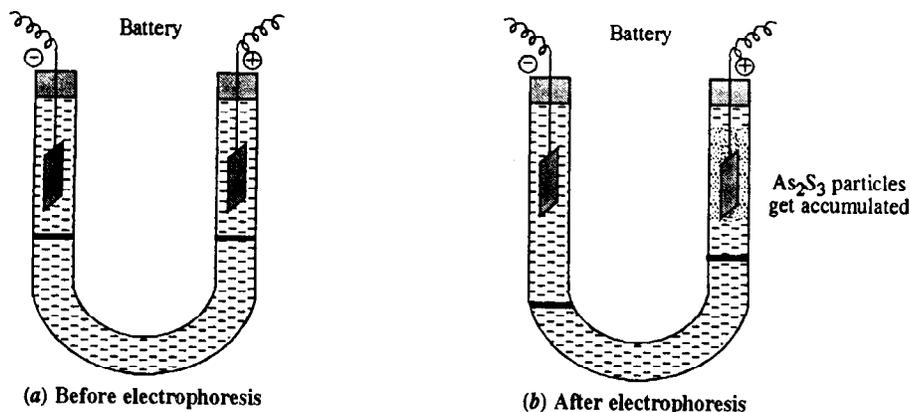
A very important quantity in the present context is the so-called zeta potential (ξ) defined as the difference in potential between the surface of the tightly bound layer (called the plane of shear) and the electroneutral region of the solution. The zeta potential is located at the shear plane. It determines the stability of colloidal systems.

Electrophoresis

The particles of colloidal solution possesses electrical charges. Positive or negative while the dispersion medium has opposite charge.

- Ex.** Positively charged solutions $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, etc.
 Negatively charged solutions Au , Pt , Ag , As_2S_3 , etc.

The presence of the charge on a solution particle can be determined with the help of a phenomenon known as electrophoresis in which colloidal particles move towards oppositely charged electrodes under the influence of electrical field.



Application :

1. It is used to bring about coagulation of colloidal solution if carried out for a prolonged times.
2. It is used to find charge on colloidal particle.
3. Due to difference in mobilities of different colloidal particles in a mixture it is possible to separate different proteins, carbohydrates, nucleic acids.

Isoelectric Point

The hydrogen ion concentration at which colloidal particles are neither positively charged nor negatively charged (*i.e.* uncharged) is known as isoelectric point of colloid.

At this point, the lyophilic colloid is expected to have minimum stability because at this point particles have no charge or equal proportions of -ve and +ve charges. At isoelectric point no electrophoretic motion takes place.

Coagulation or Flocculation

When an electrolyte is added to colloidal solution, the particles of the solution take up oppositely charged ions and thus, get neutralized. The neutral particles then comes closer and get accumulated to form bigger particles which settle down.

Hence coagulation is defined as a process which involves precipitation of a colloidal solution by addition of excess of electrolyte.

Hardy Schulze Rule

The greater the valency of oppositely charged ions of the electrolyte being added, more would be its coagulation power, e.g., For the coagulation of negatively charged solution the coagulating power of $Al^{3+} > Ca^{2+} > Na^{+}$. For the coagulation of positively charged solutions the coagulating power is $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{-}$.

Flocculation Value

The minimum amount of an electrolyte which must be added to one litre of a colloidal solution so as to bring about complete coagulation in two hours is called precipitating power or coagulation value, or flocculation value. Lower the flocculation value greater the coagulating power.

Coagulation can also be caused by

1. Electrophoresis
2. By prolonged dialysis
3. By mutual precipitation in which opposite charged solutions are mixed in proper proportions to neutralize the charges of each other causing coagulations of both solutions.

Protective Action of Lyophobic Colloids And Gold Number

We know that lyophobic sols (like metal sols) are unstable and are easily coagulated by addition of electrolytes. However, it is observed that if a lyophilic colloid is added to lyophobic one, the latter is not coagulated easily by the addition of electrolytes. The process is called protection and the lyophilic sols used for protection are known as protective colloids. The protective action is generally so strong that the resulting sol is reversible *i.e.*, it can be evaporated to dryness and then peptized simply by shaking with water to get the sol. Protargol and Argyrol used as eye drops are protected forms of colloidal silver. Gelatin is added in the preparation of ice cream as protective agent to the colloidal particles of ice. It is believed that the protective action of lyophilic colloids is due to the smaller particles which are absorbed over the bigger particles. The layer so formed protects the colloid. Zsigmondy introduced the

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

S.No.	Protective colloid	Gold number	Reciprocal of gold number (Protecting Power)
1.	Casein	0.01 – 0.02	100 – 50
2.	Gum arabic	0.15 – 0.25	7 – 4
3.	Wheat starch	4 – 5	0.2 – 0.25
4.	Potato starch	20 – 25	0.5 – 0.4
5.	Sodium oleate	0.4 – 1.0	1 – 2.5

The protective power is also measured in terms of Congo Rubin number, which may be defined as :
“The amount of a protective colloid in milligrams which prevents colour change in 100 ml of 0.01% congo rubin dye solution to which 0.15 gram equivalent of KCl is added when observed after 10 - 16 minutes.”

EMULSIONS

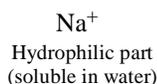
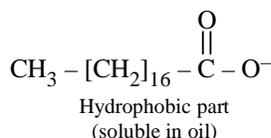
An emulsion can be defined as a colloidal dispersion in which both the dispersed phase and dispersion medium are liquids. Common examples of emulsions in our everyday life are milk, butter (molten), milk cream, cold cream, vanishing cream and other cosmetics like hair creams, lotions.

Methods of preparation

Emulsions may be produced by vigorously shaking or churning a mixture of relevant liquids in a homogenizer or by subjecting a coarse mixture thereof to ultrasonic vibrations. The emulsions are generally unstable unless a third stabilising substance, known as emulsifying agent is present. Thus, the substance which stabilises the emulsion is called an emulsifier or emulsifying agent.

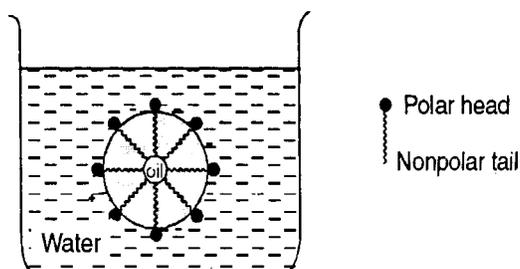
Role of emulsifying agent

The emulsifying agents are generally long chain compounds with polar groups. Their function is to lower the interfacial tension between oil and water so as to facilitate the mixing of the two liquids. This can be explained by taking the example of common soap (say sodium stearate) as an emulsifier. A molecule of soap consists of two parts, the long chain hydrocarbon part, which is non-polar, hydrophobic and soluble in oil. The other part is polar, hydrophilic and soluble in water.



(Sodium stearate)

The soap molecules gets concentrated at the interface between oil and water in such a way that their polar ends are dipping in water and hydrocarbon non-polar chains are dipping in oil. This helps in bringing the two liquid phases in more intimate contact with each other. An additional stability is provided to the emulsion by the presence of negative charge on the oil droplets.



This negative charge on droplets do not allow them to come near to each other due to electrostatic repulsions. This obstruct their aggregation and increase the stability of such emulsions.

Type of Emulsions

As the two immiscible liquids encountered in emulsions are mostly oil and water, emulsions are classified into two types :

(i) Oil in water type Emulsions

In this type of emulsions, oil acts as the dispersed phase and water act as the dispersion medium. Some examples of this type of emulsions are milk, vanishing cream, hair cream and most of the ointments. These are easily washable with water and are called aqueous emulsions.

(ii) Water in oil type Emulsions

In this type of emulsions, water acts as the dispersed phase and oil acts as the dispersion medium. Common examples of this type of emulsions are cold cream, milk cream, butter, etc. These are also called oily emulsions.

Properties of Emulsions :

- (i) The size of the dispersed particles in emulsions are much bigger than in sols (solid in liquid type). It lies in the range of 100 nm to 1000 nm. This is due to much less difference in densities of the two phases namely oil and water.
- (ii) Emulsions exhibit all the general properties of colloidal solutions such as Tyndal effect, Brownian motion, electrophoresis etc.
- (iii) The process of breaking an emulsion to give the constituent liquids is called de-emulsification. It can be brought about by
 - (a) suitable centrifugal action – milk cream is separated from milk by centrifugation
 - (b) freezing
 - (c) addition of large bulk of inner phase or dispersed phase
 - (d) chemical destruction of stabiliser
 - (e) application of electric field – electrophoresis
 - (f) distilling off of one of the component – usually water
 - (g) addition of de-emulsifiers like alcohol, phenol etc.

Applications of Emulsions :

- (i) The cleansing action of soaps and synthetic detergents for washing clothes, crockery and bathing is based upon the formation of oil in water type emulsion.
- (ii) Milk which is an important constituent of our food is an emulsion of fat (milk fat) in water. Butter obtained from milk is also an emulsion.
- (iii) Various cosmetics such as cold cream, vanishing cream, hand and body lotions are all emulsions.
- (iv) Various oily drugs such as cod liver oil are also administered in the form of emulsions for their better and faster assimilation. Similarly, various ointments are also administered in the form of emulsions for their better absorption from the skin. Milk of magnesia (an emulsion) is used for stomach disorders.
- (v) The digestion of fats in the intestine occurs by the process of emulsification. A little of the fat forms a sodium soap with alkaline solution of the intestine, and this soap emulsifies the rest of the fat, thus making it easier for the digestive enzymes to carry out their functions.
- (vi) Emulsions are used for concentrating the ores, especially the sulphide ores. Finely pulverised ore is treated with an oil emulsion, and the mixture is vigorously shaken by blowing compressed air through it. The particles of the sulphide ore are carried to the surface with the froth and is skimmed off (froth floatation process).

(vii) Asphalt emulsified in water can be used for boiling roads without the necessity of melting the asphalt.

Harmful effects of emulsions

The formation of emulsions is sometimes harmful. For example, petroleum forms emulsion with water. Some oil wells yield emulsified petroleum instead of petroleum alone. This emulsion when broken down or de-emulsified yield the petroleum.

GELS

Colloidal systems in which liquids are the dispersed phase and solids act as dispersion medium are known as gels. The most common examples are table jelly and boot polishes. It is characteristic of several hydrophilic sols that under suitable conditions, a fairly dilute solution of them 'set' as elastic semisolid masses. For example, a 5% solution of gelatin in water on cooling form the jelly block in which gelatin particles seem to be forming interlocking threads with the whole water being held between them, possibly by capillary action.

Solidified alcohol fuel is a gel of alcohol in calcium acetate. Ordinary milk curd is also a gel of water in casein. Soap made with sodium silicate may hold a very high percentage of water as silicate gel.

Application of Colloid Chemistry

Colloids play a very vital role in our daily life as well as in industry, agriculture, medicine and technology. Some of the important application of colloids are discussed below.

- (i) **Medicines :** Argyrol is a silver sol used as an eye lotion. Colloidal gold is used for intramuscular injections to raise the low vitality of human system. Colloidal antimony is used in curing kalazar. Due to smaller particle size in colloidal state, they are better assimilated and thus are quicker in their action.
- (ii) **Food :** Milk is an emulsion of fat dispersed in water. It is stabilised by casein which itself is a lyophilic colloid. Gelatin is added to ice cream as a protective agent so as to preserve its 'smoothness'. Whipped cream, fruit jellies, eggs, *halwa*, *dahi* or custard pudding, *kheer* etc. used as food are colloidal in nature.
- (iii) **Industry :**
 - (a) In chrome tanning of leather
 - (b) Latex, the milky secretion obtained from rubber tree is a colloidal solution of negatively charged rubber particles in water. As such rubber can be electro-deposited on metal parts or moulds by making them anode in a bath of latex and passing an electric current.
- (iv) **Cottrell precipitator :** Smoke and dust are one of the biggest air pollutants and as such create health problems in industrial areas. The removal of these particles from air or waste gases from furnaces involve the principle of electrophoresis. The suspended particles are discharged and settle down.
- (v) **Sewage disposal :** Sewage water consists of particles of dirt, rubbish, mud etc., which are of colloidal dimensions and carry electrical charge. On creating an electric field in a sewage tank, these particles migrate to the oppositely charged electrodes, get neutralised and settle down at the bottom thus clarifying the water for further treatment.
- (vi) **Purification of drinking water :** Water from rivers or lakes are sometimes used for domestic and industrial purposes after purification. The water from lake or rivers are turbid due to the presence of fine clay particles which are negatively charged. These can be removed by adding potash alum or aluminium sulphate. Al^{3+} ions from potash alum or aluminium sulphate neutralises the negative charge on clay particles.

-
- (vii) The cleaning action of soaps and synthetic detergents.
- (viii) **Artificial rain** : Tiny water droplets in clouds are electrically charged. In any cloud all such water particles carry the same charge. As we know, electrical discharge between two oppositely charged clouds or a cloud and ground result in electric discharge resulting in thunder. Artificial rain can be caused by spraying oppositely charged dust or fine sand or precipitates like AgI (which has a crystal structure similar to ice and as such particles of AgI can act as nuclei for precipitation) on to a cloud.
- (ix) **Photography** : Light sensitive layer over film or paper used in photography consists mainly of a semisolid colloidal suspension of silver bromide in a gel of gelatin in water.
- (x) **Formation of river delta** : River water contains charged colloidal particles of sand, clay etc. As soon as this river water come in contact with saline sea water, the electrolytes present in sea water coagulate the suspended colloidal particles.
- (xi) Blue colour of the sky is due to the scattering of light by colloidal dust particles suspended in air (Tyndal effect). If there were no scattering, the sky would appear totally black. Similarly waters of the seas and lakes appear blue.
- (xii) Blood is a colloidal solution of albuminoid substance. The separating action of ferric chloride solution and alum is due to coagulation of blood forming a clot which stops further bleeding.
- (xiii) **Smoke screens** : Smoke screens are used in warfare for the purpose of concealment and camouflage. These consist of titanium dioxide dispersed in air.

CATALYSIS

A substance which can alter the speed of a reaction without being used up in the reaction (i.e. it remains chemically and quantitatively unchanged after the reaction) is known as **catalyst** and the phenomenon is known as **catalysis**.

Types of Catalytic Reactions

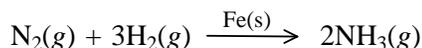
(a) Positive catalyst

When a catalyst increases the rate of a reaction, it is called a positive catalyst and the phenomenon as positive catalysis. For example,

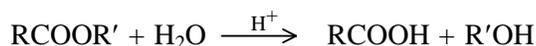
(i) Decomposition of H_2O_2 in presence of colloidal platinum.

(ii) Hydrogenation of alkenes $\text{CH}_2 = \text{CH}_2 + \text{H}_2 \xrightarrow[\Delta]{\text{Ni}} \text{CH}_3 - \text{CH}_3$

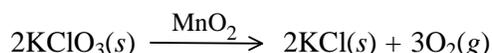
(iii) Synthesis of NH_3 by Haber's process using finely divided iron as catalyst.



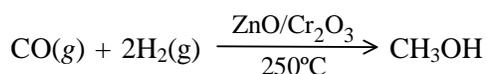
(iv) Hydrolysis of esters in the presence of H^+ ions as catalyst.



(v) Decomposition of KClO_3 using MnO_2 catalyst.



(vi) Synthesis of methyl alcohol using $\text{ZnO}/\text{Cr}_2\text{O}_3$ catalyst.



(b) Negative catalysis

When a catalyst which decreases the rate of a reaction, it is called a negative catalyst or inhibitors and the phenomenon is known as negative catalysis. For example,

- (i) Decomposition of H_2O_2 is retarded by adding acetanilide or phosphoric acid or glycerine which act as a negative catalyst.



- (ii) Oxidation of chloroform by air is retarded by adding ethyl alcohol.

- (iii) Oxidation of sodium sulphite by air is retarded by adding alcohol.

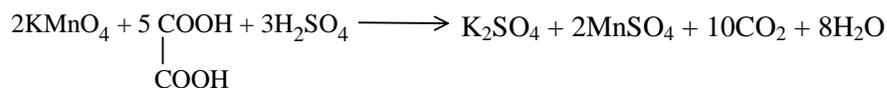
- (iv) Tetraethyl lead (TEL) acts as an antiknock compound in case of gasoline (or petrol). It decreases knocking of petrol and acts as a negative catalyst.

(c) Autocatalysis

When one of the product of the reaction start catalysing the reaction, it is called Autocatalysis.

Examples :

- (i) In the reaction of KMnO_4 with oxalic acid and H_2SO_4 , the product Mn^{+2} ion acts as autocatalyst and increases the rate of reaction.



- (ii) In the hydrolysis of ethyl acetate, to produce acetic acid and ethyl alcohol. The reaction is slow initially but its rate increases gradually. This is due to the formation of acetic acid which acts as autocatalyst in this reaction.

(d) Induced catalysis :

When one reaction influences the speed of other reaction which does not take place under ordinary conditions, the phenomenon is known as induced catalysis. For example,

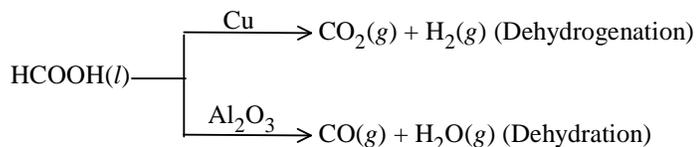
- (i) Sodium arsenite (Na_3AsO_3) solution is not oxidised by air but sodium sulphite (Na_2SO_3) is readily oxidised by air. If air is passed through a mixture of solution of sodium arsenite and sodium sulphite, both of them undergo simultaneous oxidation. The oxidation of sodium sulphate, thus induces the oxidation of sodium arsenite.

- (ii) The reduction of mercuric chloride with oxalic acid is very slow but potassium permanganate is readily oxidised with oxalic acid. If oxalic acid is added to a mixture of potassium permanganate and mercuric chloride, both are reduced simultaneously. The reduction of KMnO_4 , thus, induces the reduction of HgCl_2 .

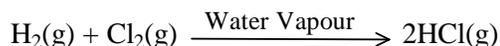
Characteristics of Catalysts

- (i) A catalyst remains unchanged in mass and chemical composition after the reaction, however a physical change may take place. For example, MnO_2 is used in the granular form as catalyst in the decomposition of KClO_3 but after the reaction, it is left as fine powder.
- (ii) A catalyst is required in small amount. For example, 1 g of colloidal platinum can catalyse the decomposition of 10^8 litres of hydrogen peroxide.
- (iii) A catalyst does not change the value of ΔH or ΔG .
- (iv) A catalyst cannot affect the final state of equilibrium, however in the presence of a catalyst, equilibrium is attained earlier.

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



- (vi) 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 is most active at a particular temperature known as **optimum temperature**.
- (vii) The catalyst generally cannot initiate a reaction, however, there are certain reactions which cannot start in the absence of catalyst. For example, combination of dry H_2 and dry Cl_2 is not possible in the absence of water vapour, which acts as catalyst for the reaction. Water vapour is thought to start the reaction.



- (viii) A catalyst lowers the activation energy needed for a reaction, by providing an alternate mechanism.
- (ix) There are certain substances which itself are not catalysts but when mixed in small quantities with the catalyst increases their efficiency. Such substances are called **catalytic promotors** or **activators**. For example,
- Molybdenum act as promotor for the iron catalyst in Haber's process.
 - Asbestos act as promotor for platinum catalyst in the contact process for H_2SO_4 manufacture.
 - In Bosch's process for manufacture of H_2 from water gas, copper act as promotor for the Fe_2O_3 catalyst.
 - Chromic oxide (Cr_2O_3) act as promotor for ZnO catalyst in the manufacture of methyl alcohol from water gas.
- (x) There are certain substances which destroy the catalytic activity. Such substances are called inhibitors or catalytic poisons or Anticatalysts. For example,
- Arsenious oxide (As_2O_3) inhibits the catalytic activity of platinised asbestos catalyst in the manufacture of H_2SO_4 by contact process.
 - The activity of Fe catalyst in Haber's process is destroyed by H_2S or CO .

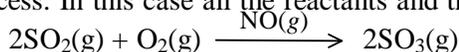
Homogeneous, Heterogeneous and Enzyme Catalysis

(A) Homogeneous Catalysis

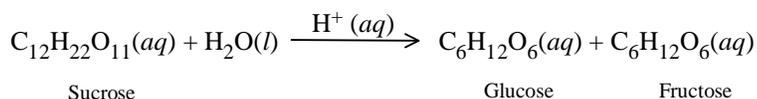
In this, both the catalysts and the reactants are in the same phase.

Example,

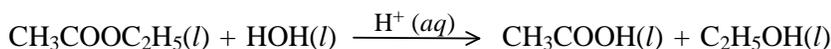
- (i) Catalytic oxidation of SO_2 into SO_3 in the presence of NO as catalyst in the lead chamber process. In this case all the reactants and the catalyst are in the gaseous phase.



- (ii) Acidic hydrolysis of sugar.



- (iii) Hydrolysis of ethyl acetate in the presence of acid.

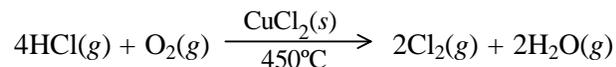


(B) Heterogeneous Catalysis :

In this, both the catalysts and the reactants are in different phase.

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

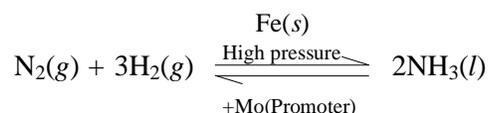
- (i) Oxidation of HCl into Cl₂ by Deacon's process in the presence of CuCl₂.



- (ii) Oxidation of carbon monoxide (CO) to carbon dioxide (CO₂) in automobile exhaust by finely divided platinum (Pt) as catalyst.



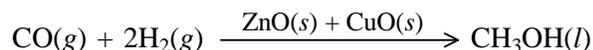
- (iii) Manufacture of NH₃ from N₂ and H₂ by Haber's process using finely divided iron as catalyst.



- (iv) Oxidation of sulphur dioxide (SO₂) into sulphur trioxide (SO₃) in the presence of vanadium pentoxide as catalyst.



- (v) Synthesis of methanol (CH₃OH) from carbon monoxide (CO) and hydrogen (H₂) using zinc oxide (ZnO) + cupric oxide (CuO) as catalysts.



In this way extremely poisonous CO is converted into relatively harmless CO₂.

- (vi) Stereo specific polymerisation of ethylene on titanium (IV) chloride, TiCl₄ and trialkyl aluminium (Zeigler Natta catalyst).

- (vii) Hydrogenation of vegetable oils (*l*) in the presence of finely divided nickel (*s*) as catalyst to form vegetable ghee.

- (viii) Synthesis of hydrocarbons from carbon monoxide (CO) and hydrogen (H₂) using iron or cobalt as catalyst.

Important Characteristic of Heterogeneous Catalyst.

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

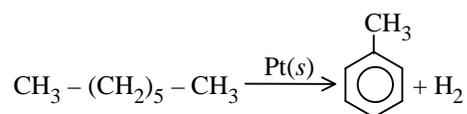
(i) Activity

It implies the ability of catalyst to accelerate a chemical reaction. The degree of acceleration can be sometimes as high as 10¹⁰. For example, the reaction between H₂ and O₂ gases in the presence of platinum catalyst to form water occur with an explosive violence, whereas a mixture of pure H₂ and O₂ gases can be stored indefinitely without any reaction.

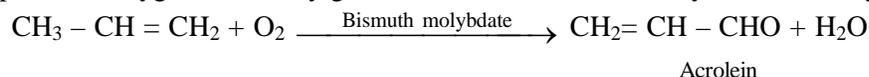
(ii) Selectivity

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

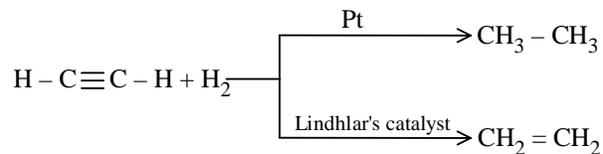
- (a) *n*-Heptane selectivity give toluene in the presence of platinum catalyst.



(b) Propene and oxygen selectively give acrolein over bismuth molybdate as catalyst.

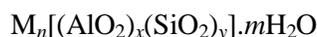


(c) Acetylene on reaction with H_2 in the presence of platinum catalyst gives ethane while in the presence of Lindlar's catalyst (Pd supported over BaSO_4 partially deactivated by sulphur or quinoline) gives ethene as the main product.



Shape Selective Catalysis by Zeolites.

Zeolites are microporous aluminosilicates of the general formula



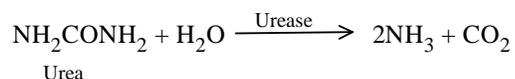
where n is the valency of cation M^{n+} . They may be considered as open structures of silica in which a fraction $x/(x+y)$ of the tetrahedral sites have been substituted by aluminium. The net negative charge on the aluminosilicate framework is neutralised by exchangeable cations M of valency n . Zeolites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

(C) Enzyme catalysis

Enzymes are complex nitrogenous organic compounds present in living beings. Enzymes catalyse many biochemical reactions taking place inside the human body like digestion therefore enzymes are also called biocatalysts.

Example,

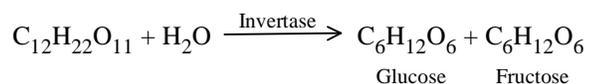
(i) Decomposition of urea into NH_3 and CO_2 is catalysed by urease.



(ii) Conversion of glucose to ethyl alcohol and CO_2 is catalysed by Zymase.



(iii) Inversion of cane sugar is catalysed by invertase.



Mechanism of enzyme catalysis

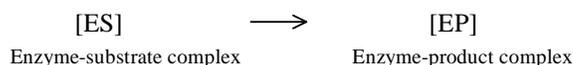
A number of cavities of characteristic shape are present on the surface of enzymes. The molecules of the reactant (substrate) which have complementary shape, fit into these cavities just as a key fits into a lock. An activated Enzyme-substrate complex is formed which then decomposes to

yield the products. It involves the following steps :

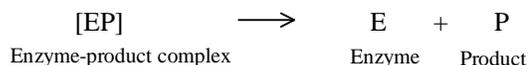
Step-1 : Binding enzyme to substrate (reactant) to form a complex :



Step-2 : Product formation from the complex :



Step-3 : Release of the product from the enzyme-product complex :



Characteristics of Enzyme catalysts

- (i) *Most efficient catalysts* : Enzymes form a colloidal solution in water, hence they behave as very active catalysts. The activation energy of the reaction in presence of enzyme is low, thus enzyme catalysed reaction are very fast in comparison to the reactions catalysed by inorganic substances.
- (ii) *Highly specific in nature* : Enzymes are highly specific in nature, i.e., one enzyme cannot catalyse more than one reaction. e.g., urease can catalyse hydrolysis of urea but not of N-Methyl urea.
- (iii) *Temperature dependence* : The enzymatic activity rises rapidly with temperature, becomes maximum at a definite temperature known as optimum temperature. The favourable range for enzymatic activity is 25 - 37°C. At higher temperatures (fever), the enzyme activity becomes less.
- (iv) *pH dependence* : The favourable pH range for enzymatic activity is 5-7 while the optimum pH (at which enzymatic activity is maximum) for enzymatic reactions in human body is 7.4.
- (v) *Inhibitors and poisons* : The inhibitors or poisons interact with the active groups on the enzyme surface and often reduce the catalytic activity of the enzymes.

The use of many drugs is related to their action as enzyme inhibitors in the body. Cyanide poisoning is due to the inhibition of respiratory enzyme-cytochrome by cyanide ion.

- (vi) Enzymes cannot disturb the final state of equilibrium of a reversible reaction like inorganic catalysts.
- (vii) *Activators or Coenzymes* : Some enzymes are also associated with non-protein component called prosthetic group for their activity. These prosthetic group can either be metal ions called cofactors (e.g., Na, K, Zn, Mg, Fe, Cu, Mn etc.) or some inorganic molecule called coenzymes (Coenzymes are derived from vitamins like thiamine, riboflavin etc.).
- (viii) Their efficiency is decreased in the presence of large quantities of electrolytes.
- (ix) Enzymes are destroyed by U.V. rays.

Inorganic Catalysts and Enzymes :

Inorganic catalysts and enzyme resembles and differ in many respects.

Similarities

- (i) Both are needed in small quantities as compared to reactants.
- (ii) They do not start a reaction, but only change its rate.
- (iii) They accelerate a given chemical reaction by lowering the energy of activation.
- (iv) They only temporarily combine with the reactant molecules.
- (v) The reactions speeded up by both are reversible.
- (vi) They do not change the nature and amount of the end products of the reaction.
- (vii) They do not undergo any change in their composition and quantity and thus can be used again and again.

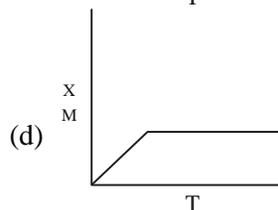
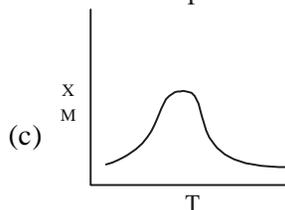
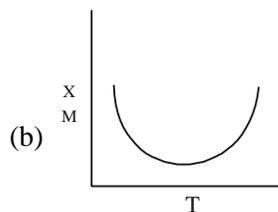
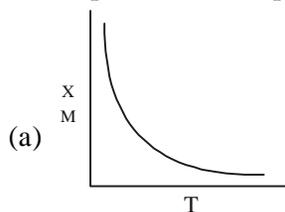
Difference between Enzymes and Inorganic Catalysts

S.No.	Enzymes	Inorganic Catalysts
1.	Enzymes are complex proteins with a three dimensional structure and have a high molecular mass.	Inorganic catalysts are simple ions or small molecules with low molecular mass.
2.	Enzymes catalyse biological reactions.	Inorganic catalyst catalyses non-biological reactions.
3.	Enzymes are highly specific in their action.	Inorganic catalysts are not so specific in action.
4.	Their efficiency is very high.	Their efficiency is generally not very high.
5.	Enzymes are greatly affected by changes in temperatures or <i>pH</i> .	These are not much affected by a change in temperature or <i>pH</i> .
6.	The activity of the enzyme is generally regulated by specific prosthetic group.	Activity of an inorganic catalyst is not controlled by any regulator molecule.

OBJECTIVE QUESTIONS

1. Platinum is not used as a catalyst in the
- (a) Oxidation of CH_3OH to HCHO (b) Oxidation of SO_2 to SO_3
(c) Combination of H_2 and I_2 to form HI (d) Synthesis of NH_3 from N_2 and H_2
2. Which type of metals form effective catalysts?
- (a) Alkali metals (b) Transition metals
(c) Alkaline earth metals (d) Radioactive metals

3. Which plot is the adsorption isobar for chemisorption?



4. Which equation represents Freundlich adsorption isotherm (physical adsorption is basis of this theory)?
- (a) $\frac{x}{m} = K(P)^{1/n}$ where x is amount of gas adsorbed on mass 'm' at pressure P
(b) $\log \frac{x}{m} = \log K + \frac{1}{n} \log P$
(c) $\frac{x}{m} = KP$ at low pressure and $\frac{x}{m} = K$ at high pressure
(d) All of these
5. The amount of gas adsorbed physically on charcoal increases with increase of
- (a) temperature and pressure (b) temperature and decreases of pressure
(c) pressure and decreases of temperature (d) none of these
6. Which can adsorb larger volume of hydrogen gas?
- (a) Colloidal solution of palladium (b) Finely divided nickel
(c) Finely divided platinum (d) Colloidal $\text{Fe}(\text{OH})_3$
7. Which statement is correct?
- (a) A catalyst increases the rate of a reaction by decreasing the rate of backward reaction.
(b) The reaction is fast if the activation energy of a reaction is low.
(c) The activation energy of a forward reaction can never be smaller than that of the backward reaction.
(d) Reaction rate increases with temperature because the activation energy decreases at high temperature.
-

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8. Which is an example of auto-catalysis?
(a) Decomposition of $\text{KClO}_3 + \text{MnO}_2$ mixture (b) The decomposition of nitroglycerine
(c) Breakdown of ${}^6\text{C}^{14}$ (d) Hydrogenation of vegetable oils using catalyst
9. Enzymes are
(a) substances made by chemists to activate washing powder
(b) very active vegetable catalysts
(c) catalysts found in organisms
(d) synthetic catalysts
10. The process which is catalysed by one of the products formed during the reaction is known as
(a) Auto-catalysis (b) Anti-catalysis (c) Negative catalysis (d) Acid catalysis
11. A catalyst in the finely divided form is most effective because
(a) less surface area is available (b) more active centres are formed
(c) more energy gets stored in the catalyst (d) none of these
12. The effect of a catalyst on a chemical reaction is to change the
(a) activation energy (b) equilibrium concentration
(c) heat of the reaction (d) final products
13. AlCl_3 in Friedel-Craft reaction acts as
(a) Oxidizing agent (b) Reducing agent (c) Acid catalyst (d) None of these
14. The phenomenon in which adsorption and absorption takes place simultaneously is called
(a) Desorption (b) Sorption (c) Both (a) and (b) (d) None of these
15. Which is correct in case of Van der Waals' adsorption?
(a) High temperature, low pressure (b) Low temperature, high pressure
(c) Low temperature, low pressure (d) High temperature, high pressure
16. Which gas is adsorbed strongly by charcoal?
(a) CO (b) N_2 (c) H_2 (d) NH_3
17. When white light is passed through a colloidal solution containing fine suspended particles of gold, then the scattered light seen in a direction different from that of the incident light is
(a) Yellow coloured (b) Blue coloured (c) Green coloured (d) Red coloured
18. Which is not correct?
(a) Every solid substance can be brought in colloidal state
(b) Every solid substance can be made to behave like a lyophobic colloid
(c) Addition of electrolyte coagulates the sol
(d) Colloidal particles carry charges
19. Which ion has least flocculation value for a +ve sol ?
(a) $[\text{Fe}(\text{CN})_6]^{4-}$ (b) Cl^- (c) SO_4^{2-} (d) PO_4^{3-}
20. Hydrophilic sols are
(a) reversible (b) irreversible (c) permanent (d) unstable
-

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21. Colloidal solution of arsenious sulphide can be prepared by
(a) Electrodispersion method (b) Peptization
(c) Double decomposition (d) Hydrolysis
22. $\text{Fe}(\text{OH})_3$ when treated with FeCl_3 solution a reddish-brown colloidal solution is formed. The process is known as
(a) Dispersion (b) Exchange of solvent (c) Peptization (d) Cataphoresis
23. Dialysis is process of
(a) precipitating colloids by addition of electrolytes
(b) separating suspensions from solution
(c) removing soluble impurities from colloidal solution
(d) dispersion of freshly precipitated substances into colloids
24. A freshly prepared $\text{Fe}(\text{OH})_3$ precipitate is peptized by adding FeCl_3 solution. The charge on the colloidal particle is due to preferential adsorption of
(a) Cl^- ions (b) Fe^{3+} ions (c) OH^- ions (d) None of these
25. Which reaction gives colloidal solution?
(a) $\text{Cu} + \text{HgCl}_2 \rightarrow \text{CuCl}_2 + \text{Hg}$ (b) $2\text{HNO}_3 + 3\text{H}_2\text{S} \rightarrow 3\text{S} + 4\text{H}_2\text{O} + 2\text{NO}$
(c) $2\text{Mg} + \text{CO}_2 \rightarrow 2\text{MgO} + \text{C}$ (d) $\text{Cu} + \text{CuCl}_2 \rightarrow \text{Cu}_2\text{Cl}_2$
26. The correct statement in case of milk
(a) milk is an emulsion of fat in water (b) milk is an emulsion of protein in water
(c) milk is stabilized by protein (d) milk is stabilized by fat
27. The potential difference between the fixed charged layer and the diffused layer having opposite charge is called
(a) Zeeta potential (b) Streaming potential (c) Dorn potential (d) Colloidal potential
28. An emulsifier is a substance which
(a) Homogenises the emulsion (b) Stabilizes the emulsion
(c) Retards the dispersion of liquids in liquid (d) Coagulates the emulsion
29. On adding 1 mL solution of 10% NaCl to 10 mL gold solution in the presence of 0.25 g of starch, the coagulation is just prevented. Starch has the gold number equal to
(a) 0.25 (b) 2.5 (c) 250 (d) 0.025
30. The colloidal solutions of gold prepared by different methods have different colours due to
(a) Difference in the size of colloidal particles (b) The fact that gold exhibits variable valency
(c) Different concentration of gold (d) Presence of different types of foreign particles
31. The magnitude of colligative properties in all colloidal dispersions is than true solution
(a) higher (b) lower (c) both (a) and (b) (d) none of these
32. Alum purifies muddy water by
(a) Dialysis (b) Absorption
(c) Coagulation (d) Forming a true solution
-

33. Which statement is incorrect?
- Higher the gold number of lyophilic substance better is its protective action
 - Lower the gold number of a lyophilic substance better is its protective action
 - The Bredig's arc method is usually suitable for preparing sols of metals
 - The osmotic pressure method gives the average molar mass of a polymer
34. Crystalloids differ from colloids mainly in respect of
- Electrical behaviour
 - Particle size
 - Particle nature
 - Solubility
35. Which of the following reaction does not involve colloidal solution formation?
- $\text{AgNO}_3 + \text{Trannic acid (or HCHO)} \rightarrow \text{Silver sol}$
 - $$2 \begin{array}{l} \text{CH[OH]COOK} \\ | \\ \text{CH[OH]COO[Sbo]} \end{array} + 3\text{H}_2\text{S} \longrightarrow 2 \begin{array}{l} \text{CH[OH]COOK} \\ | \\ \text{CH[OH]COOH} \end{array} + \text{Sb}_2\text{S}_3 + 3\text{H}_2\text{S} \longrightarrow$$

Orange sol
 - $\text{H}_2\text{S} + [\text{O}] \longrightarrow \text{H}_2\text{O} + \text{S}$
 - $2\text{Mg} + \text{CO}_2 \longrightarrow 2\text{MgO} + \text{C}$
36. Which of the following does not contain a hydrophobic structure ?
- Linseed oil
 - Lanolin
 - Glycogen
 - Rubber
37. Rubin number which was proposed by Ostwald as an alternative to the Gold number in order to measure the protective efficiency of a lyophilic colloid may be defined as the
- mass in milligrams of a colloid per 100 cc. of solution which just prevents the colour change of sol. of dye Congo-Rubin from red to violet when 0.16 g equivalent KCl is added to it.
 - mass in grams of a colloid per 100 cc of solution which just prevents the colour change of standard sol of dye Congo-Rubin from red to violet when 0.1 M KCl is added to it.
 - mass in grams of a colloid per 100 cc of solution which just prevents the colour change of standard sol of dye Congo-Rubin from red to violet when 0.2 M KCl is added to it.
 - mass in grams of a colloid per 100 cc of solution which just prevents the colour change of standard sol of dye Congo-Rubin from red to violet when 1 M KCl is added to it.
38. For the congulation of 100 ml of arsenius sulphide sol 5 ml of 1 M NaCl is required. What is the coagulating value of NaCl ?
- 46.7
 - 47.6
 - 49.9
 - 42.0
39. 50 ml of 1 M oxalic acid is shaken with 0.5 g wood charcoal. The final conc. of the solution after adsorption is 0.5 M. What is the amount of oxalic acid adsorbed per gram of carbon ?
- 3.15 g
 - 3.45 g
 - 6.30 g
 - None of these
40. Peptization denoted ...
- Digestion of food
 - Hydrolysis of proteins
 - Breeding and dispersion into the colloidal state
 - Precipitation of solid from colloidal dispersion

-
41. The stability of lyophilic colloids is due to
- (a) charge on their particles
 - (b) a layer of medium of dispersion on their particles
 - (c) the smaller size of their particles
 - (d) the large size of their particles
42. Butter is a colloid formed when
- (a) fat is dispersed in water
 - (b) fat globules are dispersed in water
 - (c) water is dispersed in fat
 - (d) none of these
43. On adding few drops of dil. HCl to freshly precipitated ferric hydroxide, a red coloured colloidal solution is obtained. This phenomenon is known as
- (a) Peptization
 - (b) Dialysis
 - (c) Protective action
 - (d) Dissolution
44. Gold number is minimum in case of
- (a) Gelatin
 - (b) Egg albumin
 - (c) Gum arabic
 - (d) Starch
45. The ability of an ion to bring about coagulation of a given colloid depends upon
- (a) its size
 - (b) the magnitude of its charge only
 - (c) the sign of its charge alone
 - (d) both magnitude and sign of its charge.
46. If dispersed phase is a liquid and the dispersion medium is solid, the colloid is known as
- (a) a sol
 - (b) a gel
 - (c) an emulsion
 - (d) a foam
47. If in 100 ml colloidal solution of gold, 0.025g of starch is added first before mixing 10 ml of 10% solution of sodium chloride then coagulation of colloidal solution completely stops. Gold number of starch will be
- (a) 25
 - (b) 10
 - (c) 20
 - (d) 80
48. Tyndal effect in colloidal solution is due to
- (a) Scattering of light
 - (b) Reflection of light
 - (c) Absorption of light
 - (d) Presence of electrically charged particles
49. The sky looks blue due to
- (a) Dispersion effect
 - (b) Reflection
 - (c) Transmission
 - (d) Scattering
50. Point out the false statements
- (a) Brownian motion and Tyndall effect are shown by colloidal systems
 - (b) The colloidal solution of a liquid in liquid is called emulsion
 - (c) Hardy-Schulze law is related with coagulation of sol
 - (d) Higher is the gold number, greater will be the protective power of a lyophilic colloid.

MORE THAN ONE CORRECT ANSWER TYPE QUESTIONS

51. The coagulation of sol particles may be brought in by
- (a) heating
 - (b) adding oppositely charged sol
 - (c) adding electrolyte
 - (d) persistent dialysis

-
- 52.** Point out the correct statement(s) amongst the following
- (a) physisorption is favoured by low temperature owing to small value of activation energy and the process being exothermic
 - (b) Chemisorption is favoured by elevated temperature because the process is endothermic
 - (c) Chemisorption increases with increase in temperature owing to high activation energy
 - (d) Oxygen adsorbed by charcoal can be desorbed by lowering pressure and raising the temperature.
- 53.** When a hydrophilic sol like gelatin is subjected to electric field, the sol particles move
- (a) towards cathode at pH less than the iso-electric point
 - (b) towards anode at pH greater than the iso-electric point.
 - (c) in both directions at iso-electric pH
 - (d) in neither direction at iso-electric pH
- 54.** Amongst the following which is/are correct statements about the metal sulphide sols?
- (a) The sol particles are positively charged due to preferential adsorption of metal ions
 - (b) The sol particles are negatively charged due to preferential adsorption of sulphide ions
 - (c) The cations of added electrolytes are effective in causing the coagulation of the sol
 - (d) The sol is stabilized due to both the electric charge and hydration of the particles.
- 55.** Which of the following are macromolecular colloids?
- (a) Starch
 - (b) Egg albumen
 - (c) Detergent
 - (d) Cellulose
- 56.** The effect of temperature and pressure on adsorption are
- (a) The amount of gas adsorbed per gram of adsorbent does not vary linearly with pressure at constant temperature if the pressure is neither very low nor very high.
 - (b) Chemisorption decreases with increase of temperature at high temperatures.
 - (c) There is not effect of pressure on physisorption if temperature is kept constant.
 - (d) Higher the critical temperature of a gas, less is its adsorption.
- 57.** Which of the following plots related to adsorption will be linear?
- (a) $\log x/m$ versus pressure (P)
 - (b) $P/(x/m)$ versus pressure (P)
 - (c) $P/(x/m)$ versus $1/P$
 - (d) m/x versus $1/P$
- 58.** The correct characteristics of lyophilic and lyophobic colloids are
- (a) Lyophobic sols are highly hydrated while lyophilic sols are not.
 - (b) Lyophilic sols have lower surface tension and viscosity than that of the dispersion medium.
 - (c) Lyophobic sols can be easily coagulated but lyophilic sols are not.
 - (d) Gold sol is irreversible sol because gold cannot be obtained back.
-

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- 59.** The correct statement(s) pertaining to the adsorption of a gas on solid surface is (are)
- (a) Adsorption is always exothermic
 - (b) Physisorption may transform into chemisorption at high temperature.
 - (c) Physisorption increases with increasing temperature but chemisorption decreases with increasing temperature.
 - (d) Chemisorption is more exothermic than physisorption. However, it is very slow due to higher energy of activation.
- 60.** Choose the correct reason(s) for the stability of the lyophobic colloidal particles.
- (a) Preferential adsorption of ions on their surface from the solution
 - (b) Preferential adsorption of solvent on their surface from the solution
 - (c) Attraction between different particles having opposite charges on their surface
 - (d) Potential difference between the fixed layer and the diffused layer of opposite charges around the colloidal particles.

MISCELLANEOUS ASSIGNMENT

Comprehension

The clouds consist of charged particles of water dispersed in air. Some of them are positive charged, others are negatively charged. When positively charged clouds come closer they cause lightening and thundering whereas when positive and negative charged colloids come closer they cause heavy rain by aggregation of minute particles. It is possible to cause artificial rain by throwing electrified sand or silver iodide from an aeroplane and thus coagulating the mist hanging in air.

1. When excess of AgNO_3 is treated with KI solution, AgI forms
(a) +vely charged sol (b) -vely charged sol (c) neutral sol (d) true solution
2. Clouds are colloidal solution of
(a) liquid in gas (b) gas in liquid (c) liquid in liquid (d) solid in liquid
3. AgI helps in artificial rain because
(a) it helps in condensation process (b) it helps in dispersion process
(c) it helps in coagulation (d) all of these
4. Electrical chimneys are made on the principle of
(a) Electrosmosis (b) Electrophoresis (c) Coagulation (d) all of these
5. Smoke screens consist of
(a) fine particles of TiO_2 dispersed in air by aeroplanes
(b) fine particle of AgI dispersed in air by aeroplanes
(c) fine particle of Al_2O_3 dispersed in air by aeroplanes
(d) none of these

Comprehension-II

Different gases are adsorbed to different extent on the same adsorbent at the same temperature. Besides other factors, adsorption depends upon the nature of the gas which in turn is related to the critical temperature or the van der Waals constant ' a ' of the gas. Further, adsorption may be a physical process or a chemical process. The extent of adsorption of a gas on an adsorbent depends upon the pressure of the gas while that of a solute it depends upon the concentration of the solution. These studies were made by Freundlich and Langmuir. The mathematical expressions put forward by them are called Freundlich adsorption isotherm and Langmuir adsorption isotherm respectively.

6. Which one of the following statements is true?
(a) Less is the critical temperature of gas, greater is its adsorption
(b) Higher is the critical temperature of a gas, greater is its adsorption
(c) Greater is the van der Waals constant ' a ' of a gas, less is its adsorption.
(d) A gas cannot be adsorbed above its critical temperature.
-

7. Which of the following is less than zero during adsorption?
 (a) ΔG (b) ΔS (c) ΔH (d) all of these
8. Which one of the following statements is correct?
 (a) Physisorption is unimolecular while chemisorption is multimolecular
 (b) Physisorption is multimolecular while chemisorption is unimolecular
 (c) Both physisorption and chemisorption are unimolecular
 (d) Both physisorption and chemical sorption are multimolecular.
9. The plot of m/x versus $1/P$ is linear with slope and intercept on m/x axis respectively as
 (a) $\frac{a}{b}, \frac{1}{a}$ (b) $\frac{1}{a}, \frac{b}{a}$ (c) $\frac{1}{b}, \frac{b}{a}$ (d) $\frac{1}{b}, \frac{a}{b}$

MATRIX MATCH TYPE QUESTIONS

- 10. Column-I**
- | | |
|---|---|
| <p>A. Smoke</p> <p>B. Butter</p> <p>C. Hair cream</p> <p>D. Whipped cream</p> <p>(a) A-(r); B-(s); C-(q); D-(p)</p> <p>(c) A-(p); B-(s); C-(q); D-(r)</p> | <p style="text-align: center;">Column-II</p> <p>(p) Foam</p> <p>(q) Emulsion</p> <p>(r) Aerosol</p> <p>(s) Gel</p> <p>(b) A-(r); B-(q); C-(s); D-(p)</p> <p>(d) A-(s); B-(p); C-(r); D-(q)</p> |
|---|---|
- 11. Column-I**
- | | |
|--|---|
| <p>A. Lead chamber process for manufacture of H_2SO_4</p> <p>B. Decomposition of H_2O_2 in presence of phosphoric acid</p> <p>C. Acid catalysed hydrolysis of esters</p> <p>D. Bosch process for manufacture of hydrogen</p> <p>(a) A-(p),(s); B-(r),(s); C-(q),(t); D-(p),(s)</p> <p>(c) A-(p),(r); B-(q),(r); C-(r),(t); D-(p),(s)</p> | <p style="text-align: center;">Column-II</p> <p>(p) Positive catalysis</p> <p>(q) Negative catalysis</p> <p>(r) Homogeneous catalysis</p> <p>(s) Heterogeneous catalysis</p> <p>(t) Autocatalysis</p> <p>(b) A-(p),(s); B-(q),(t); C-(p),(r); D-(r),(s)</p> <p>(d) none of these</p> |
|--|---|

INTEGER TYPE QUESTIONS

12. The number of free valencies available for adsorption if four Pt atoms are linked together by covalent bonds is
13. If 772 ml of SO_2 gas at STP is adsorbed on 2 g of charcoal at an equilibrium pressure of 16 atmospheres and the value of the constant k in the Freundlich equation is 0.48, the value of constant ' n ' will be

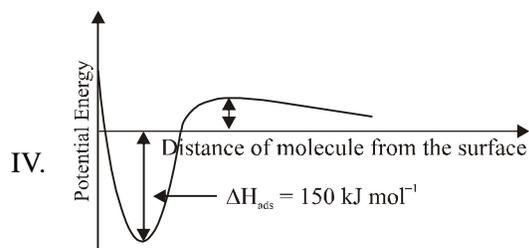
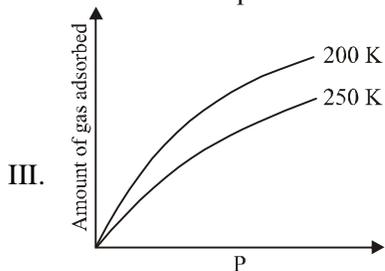
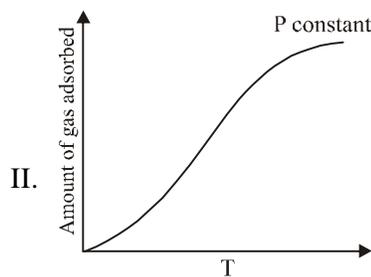
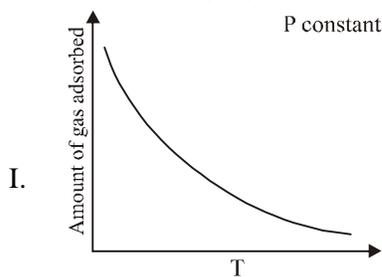
-
14. 50 mL of 1 M oxalic acid (molecular mass = 126) is shaken with 0.525 g of wood charcoal. The final concentration of the solution after adsorption is 0.5 M. The amount of oxalic acid in grams adsorbed per gram of charcoal is
15. The number of negatively charged sols among the following is
Gold sol, $\text{Fe}(\text{OH})_3$ sol, $\text{Al}_2\text{O}_3 \cdot x \text{H}_2\text{O}$ sol, As_2S_3 sol, starch sol, silicic acid sol, congo red sol, prussian blue sol, haemoglobin.
16. The coagulation of 100 mL of standard red gold sol is completely prevented by addition of 2 mg of gum arabic before adding 10 mL of 10% NaCl solution. The reciprocal value of gold number of gum arabic which directly compares the protective powers is
17. How many of the following are aerosols?
Paints, Milk, Smoke, Dust, Foam Rubber, Cheese, Fog, Clouds, Insecticide Sprays, Mist.
18. For coagulation of 100 mL of a colloidal sol, 5 mL of 0.16 M electrolyte solution is required. The flocculation value of the electrolyte is
19. In an adsorption experiment, a graph between $\log(x/m)$ versus $\log P$ is found to be linear with a slope of 45° . The intercept on the $\log(x/m)$ axis is found to be 0.3010. The amount of the gas adsorbed in grams per gram of the adsorbent under a pressure of 2 atm will be
20. Plot of $\log x/m$ against $\log P$ is a straight line inclined at an angle of 45° . When the pressure is 0.5 atm and Freundlich parameter, K is 10.0, the amount of the solute adsorbed per gram of adsorbent will be ($\log 5 = 0.6990$).

PREVIOUS YEAR QUESTIONS

IIT-JEE/JEE-ADVANCE QUESTIONS

- Spontaneous adsorption of a gas on solid surface is an exothermic process because
 - ΔH increases for system
 - ΔS increases for gas
 - ΔS decreases for gas
 - ΔG increases for gas
 - Which of the following is correct for lyophilic sols?
 - They are irreversible
 - They are formed by inorganic substances
 - They are readily coagulated by addition of electrolytes
 - They are self stabilized
 - A catalyst
 - Increases the average kinetic energy of reacting molecules.
 - Increases the activation energy
 - Alters the reaction mechanism
 - Increases the frequency of collisions of reacting species
 - STATEMENT-1:** Micelles are formed by surfactant molecules above the critical micellar concentration (CMC).
STATEMENT-2: The conductivity of a solution having surfactant molecules decreases sharply at the CMC.
 - Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1
 - Statement-1 and 2 is True; Statement-2 is not a correct explanation for Statement-1
 - Statement-1 is True, Statement-2 is False
 - Statement-1 is False, Statement-2 is True
 - Among the following, the surfactant that will form micelles in aqueous solution at the lowest molar concentration at ambient conditions is
 - $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$
 - $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$
 - $\text{CH}_3(\text{CH}_2)_6\text{COO}^-\text{Na}^+$
 - $\text{CH}_3(\text{CH}_2)_{11}\text{N}^+(\text{CH}_3)_3\text{Br}^-$
 - Among the electrolytes Na_2SO_4 , CaCl_2 , $\text{Al}_2(\text{SO}_4)_3$ and NH_4Cl , the most effective coagulating agent for Sb_2S_3 sol is
 - Na_2SO_4
 - CaCl_2
 - $\text{Al}_2(\text{SO}_4)_3$
 - NH_4Cl
 - The correct statement(s) pertaining to the adsorption of a gas on a solid surface is (are)
 - Physisorption may transform into chemisorption at high temperature
 - Physisorption increases with increasing temperature but chemisorption decreases with increasing temperature
 - Chemisorption is more exothermic than physisorption, however it is very slow due to higher energy of activation
 - The given graphs / data **I**, **II**, **III** and **IV** represent general trends observed for different physisorption
-

and chemisorption processes under mild conditions of temperature and pressure which of the following choice(s) about **I**, **II**, **III** and **IV** is (are) correct?



- (a) **I** is physisorption and **II** is chemisorption (b) **I** is physisorption and **III** is chemisorption
 (c) **IV** is chemisorption and **II** is chemisorption (d) **IV** is chemisorption and **III** is chemisorption

9. Choose the correct reason(s) for the stability of the **lyophobic** colloidal particles.

- (a) Preferential adsorption of ions on their surface from the solution
 (b) Preferential adsorption of solvent on their surface from the solution
 (c) Attraction between different particles having opposite charges on their surface
 (d) Potential difference between the fixed layer and the diffused layer of opposite charges around the colloidal particles.

10. Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at 25°C. For this process, the correct statement is

- (a) The adsorption requires activation at 25°C
 (b) The adsorption is accompanied by a decrease in enthalpy
 (c) The adsorption increases with increase of temperature
 (d) The adsorption is irreversible

DCE QUESTION

1. In Adsorption rate of physisorption increases when

- (a) temperature is decreased (b) temperature is increased
 (c) pressure is decreased (d) none of these

AIEEE/JEE-MAINS QUESTIONS

-
1. Identify the correct statement regarding enzymes:
 - (a) Enzymes are specific biological catalysts that cannot be poisoned
 - (b) Enzymes are normally heterogeneous catalysts that are very specific in their action
 - (c) Enzymes are specific biological catalysts that can normally function at very high temperatures ($T \sim 1000 \text{ K}$)
 - (d) Enzymes are specific biological catalysts that possess well-defined active sites
 2. In Langmuir's model of adsorption of a gas on a solid surface
 - (a) the mass of gas striking a given area of surface is independent of the pressure of the gas
 - (b) the rate of dissociation of adsorbed molecules from the surface does not depend on the surface covered.
 - (c) the adsorption at a single site on the surface may involve multiple molecules at the same time
 - (d) the mass of gas striking a given area of surface is proportional to the pressure of the gas
 3. Which of the following statements is *incorrect* regarding physisorptions?
 - (a) More easily liquefiable gases are adsorbed readily
 - (b) Under high pressure it results into multi molecular layer on adsorbent surface
 - (c) Enthalpy of adsorption ($\Delta H_{\text{adsorption}}$) is low and positive
 - (d) It occurs because of van der Waal's forces
 4. According to Freundlich adsorption isotherm, which of the following is correct?
 - (a) $\frac{x}{m} \propto p^0$
 - (b) $\frac{x}{m} \propto p^1$
 - (c) $\frac{x}{m} \propto p^{1/n}$
 - (d) All the above are correct for different ranges of pressure
 5. 3 g of activated charcoal was added to 50 mL of acetic acid solution (0.06N) in a flask. After an hour it was filtered and the strength of the filtrate was found to be 0.042 N. The amount of acetic acid adsorbed (per gram of charcoal) is :
 - (a) 18 mg
 - (b) 36 mg
 - (c) 42 mg
 - (d) 54 mg
-

ANSWERS

Objective Questions

- | | | | | |
|---------------|-----------|-------------|-------------|-------------|
| 1. (d) | 2. (b) | 3. (c) | 4. (d) | 5. (c) |
| 6. (a) | 7. (b) | 8. (b) | 9. (c) | 10. (a) |
| 11. (b) | 12. (a) | 13. (c) | 14. (b) | 15. (b) |
| 16. (d) | 17. (b) | 18. (b) | 19. (a) | 20. (a) |
| 21. (c) | 22. (c) | 23. (c) | 24. (b) | 25. (b) |
| 26. (a) | 27. (a) | 28. (b) | 29. (c) | 30. (a) |
| 31. (b) | 32. (c) | 33. (a) | 34. (b) | 35. (d) |
| 36. (d) | 37. (a) | 38. (b) | 39. (a) | 40. (c) |
| 41. (b) | 42. (c) | 43. (a) | 44. (a) | 45. (d) |
| 46. (d) | 47. (b) | 48. (a) | 49. (d) | 50. (d) |
| 51. (a,b,c,d) | 52. (a,c) | 53. (a,b,d) | 54. (b,c) | 55. (a,b,d) |
| 56. (a,b) | 57. (b,d) | 58. (a,c) | 59. (a,b,d) | 60. (a,d) |

Miscellaneous Assignment

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (a) | 2. (a) | 3. (a) | 4. (b) | 5. (a) |
| 6. (b) | 7. (d) | 8. (b) | 9. (b) | 10. (a) |
| 11. (c) | 12. (8) | 13. (4) | 14. (6) | 15. (5) |
| 16. (5) | 17. (6) | 18. (8) | 19. (4) | 20. (5) |

Previous Year Questions

IIT-JEE/JEE-ADVANCE QUESTIONS

- | | | | | |
|--------|------------|----------|----------|---------|
| 1. (a) | 2. (d) | 3. (c) | 4. (b) | 5. (a) |
| 6. (c) | 7. (a,b,d) | 8. (b,d) | 9. (a,d) | 10. (b) |

DCE QUESTIONS

1. (a)

MAINS QUESTIONS

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (d) | 2. (c) | 3. (c) | 4. (d) | 5. (a) |
|--------|--------|--------|--------|--------|