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SURFACE CHEMISTRY

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Indroduction:

The branch of chemistry which deals with the nature of surfaces and changes occurring on the surfaces is called surface chemistry.

Adsorption

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

Desorption

The process of removal of an adsorbed substance from the surface on which it is adsorbed is called desorption.

Sorption

When both absorption and adsorption occur together and are not distinguisable, the substance gets uniformly distributed into the bulk of the solid but at the same time, its concentration is higher at the surface than in the bulk, the phenomenon is called sorption.

Example : Dyes get adsorbed as well as absorbed in the cotton fibres i.e. sorption takes place.

Positive adsorption:

When the concentration of adsorbate is more on the surface of adsorbent relative to its concentration in 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.

Factors affecting adsorption of gases by Solids

Almost all solids adsorb gases to some extent. The extent of adsorption of a gas on a solid surface depends on the following factors:

1. Nature of the gas (or adsorbate): Under given conditions of temperature and pressure, the easily liquefiable gases such as CO_2, HCl, NH_3, Cl_2 etc. are adsorbed more than the permanent gases such as H_2, N_2 and O_2.
2. Nature of adsorbent : The extent of adsorption of a gas depends upon the nature of adsorbent.
3. Specific area of the adsorbent : The specific area of the adsorbent is the surface area available for adsorption per gram of the adsorbent. The larger the surface area of the solid, the greater would be its adsorbing capcity.
4. Effect of pressure : The extent of adsorption of a gas per unit mass of adsorbent depends upon the pressure of the gas.
5. Effect of temperature : Adsorption is generally temperature dependent. Mostly adsorption processes are exothermic and therefore, extent of adsorption decreases with increasing temperature at constant pressure.

   Physical Adsorption : When the particles of the adsorbate are held to the surface of the adsorbent by the physical forces such as Van der Waal's forces, the adsorption is called physical adsorption or physisorption. The attractive forces are weak and therefore, these can be easily overcome either by increasing the temperature or by decreasing the pressure. In other words, physical adsorption can be easily reversed.

   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.

Adsorption Isotherms :

The variation of the amount of the gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve. This curve is termed as adsorption isotherm at the particular temperature.

Freundlich's adsorption isotherm:

Freundlich in 1909, gave an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature. The relationship can be expressed by the equation

$$\boxed{\frac{x}{m} = kp^{\frac{1}{n}}} \quad \ldots (1)$$

where 'x' is the mass of the gas adsorbed on a mass 'm' of the adsorbent at a pressure P. k and n are constants which depend on the nature of the adsorbent and the gas at a particular temperature.

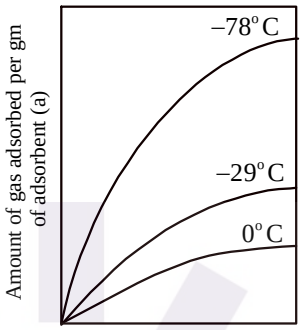


Fig (a) Adsorption isotherm

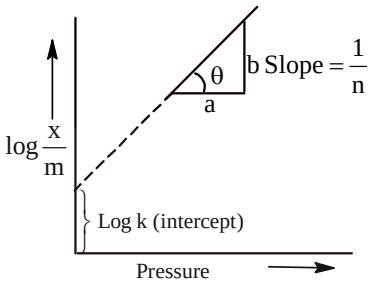


Fig (b) Freundlich isotherm

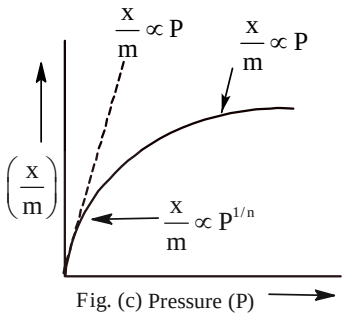


Fig. (c) Pressure (P)

Taking logarithm of equation .... (i)

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

$$\boxed{\log\frac{x}{m} = \frac{1}{n}\log P + \log k} \quad \ldots (ii)$$

$\Rightarrow$ The slope of the straight line gives the value of 1/n.

$\Rightarrow$ The intercept on the y-axis gives the value of log k.

In his derivation, Langmuir considered adsorption to consist of the following two opposing processes:

(i) Adsoprtion of the gas molecules on the surface of the solid.

(ii) Desorption of the adsorbed molecules from the surface of the solid.

Langmuir adsorption isotherm works particularly well for chemisorption.

The Langmuir adsorption isotherm is represented by the relation.

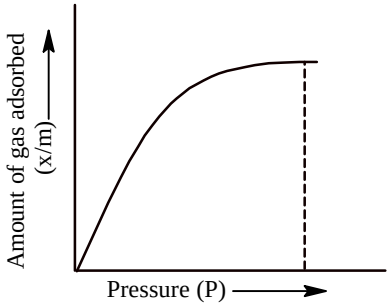
$$\boxed{\frac{x}{m} = \frac{ap}{1+bp}} \quad \ldots (i)$$

where a and b are two Langmuir parameters.

Case I: i.e., at very high pressure:

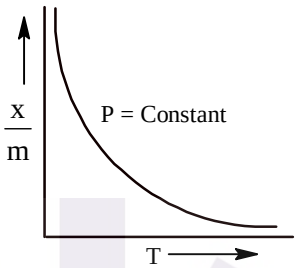
$$\boxed{\frac{x}{m} = \frac{a}{b}} \quad \ldots (ii)$$

Case II: i.e., at very low pressure:

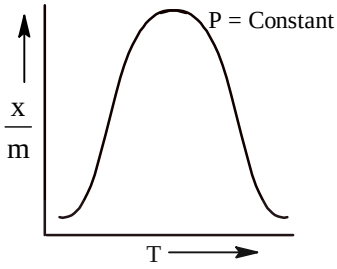


Adsorption Isobars

A graph drawn between degree of adsorption (x/m) and temperature 'T' at a constant pressure of adsorbate gas is known as adsorption isobar.



(Physi-sorption isobars)



(Chemi-sorption isobars)

Adsorption isobars of physical and chemical adsorption shows an important difference and this difference is helpful in distinguishing these two adsorptions.

CATALYSIS

Substance which alter the velocity of a reaction, without undergoing any change in mass and composition, are termed as catalysts and the phenomenon is known as catalysis.

Classification of Catalysis

Catalysis can be broadly classified into two main groups as:

(i) Homogeneous catalysis and

(ii) Heterogeneous catalysis

Homogeneous catalysis : When the catalyst is in the same phase as the reactants and products, then the catalyst is said to be homogeneous catalyst and such catalytic reaction is said to be homogeneous catalysis.

$$C_{12}H_{22}O_{11}(l) + H_2O(l) \xrightarrow{H_2SO_4(l)} C_6H_{12}O_6(l) + C_6H_{12}O_6(l)$$

Heterogeneous catalysis : When the catalyst is in the different phase as the reactants and products, then the catalyst is said to be heterogeneous catalyst and such catalytic reaction is said to be Heterogeneous catalysis

Examples: $2SO_2(g) + O_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$

Positive catalysis : When the rate of reaction is accelerated by a foreign substance, it is said to be a positive catalyst and the phenomenon is positive catalysis.

e.g., Oxidation of sulphur dioxide in presence of nitric oxide.

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

Negative catalysis : The substance which when added to the reaction mixture, retards the reaction rate is termed negative catalyst and the phenomenon is known as negative catalysis.

The oxidation of chloroform by air is retarded if some alcohol is added to it.

$$2CHCl_3(l) + O_2(g) \xrightarrow{Alchol(l)} 2COCl_2(g) + 2HCl(g)$$

ENZYME CATALYSIS

The enzymes are also termed as bio-chemical catalysts and the phenomenon is known as bio-chmeical catalysis. Enzymes are highly specific in nature.

e.g., (i) Normal conversion of glucose into ethanol by zymase (enzyme) present in yeast.

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

(ii) Oxidation of alcohol to acetic acid by mycoderma aceti.

$$C_2H_5OH + O_2 \xrightarrow[\text{aceti}]{\text{Mycoderma}} CH_3COOH + H_2O$$

(iii) Hydrolysis of urea (NH_2CONH_2) by urease (enzyme) present in soyabean.

$$\underset{\text{Urea}}{H_2N-\overset{\overset{O}{\|}}{C}-NH_2} + H_2O \xrightarrow{\text{Urease}} 2NH_3 + CO_2$$

On the basis of particle size of the substance, solutions are divided into three classes as:

1. True solution
2. Suspension
3. Colloidal solution

True solution is a homogeneous solution in which molecules or ions are uniformly dispersed in the solvent (dispersion phase). A suspension is heterogeneous solution in which particle of the solute do not dissolve completely. A colloidal solution is a heterogeneous solution in which particle size is bigger than that of true solution but smaller than that of suspension.

Classification of Colloids

On the basis of nature of interaction between dispersed phase and dispersion medium, colloids may be of two types, viz. lyophilic and lyophobic. If water is the dispersion medium, the terms used are hydrophilic and hydrophobic.

1. Lyophilic colloids : The colloidal solution in which the particle of the dispersed phase have a great affinity (or love) for the disperion medium are called lyophilic colloids.
2. Lyophobic colloids : The colloidal solution in which there is no affinity (or love rather they have hatred tendency) between particles of the dispersed phase and dispersion medium are called lyophobic colloids.

PREPARATION OF COLLOIDAL SOLUTIONS

1. By dispersion : By breaking up suspension particles into colloidal size, the goal is achieved.

   (a) By Grinding : Freshly precipitated mass + medium $\xrightarrow[\text{ingrinder}]{\text{Grind}}$ sols

   (b) Peptization : The phenomenon of converting freshly prepared precipitate into colloidal sol by the action of solute or solvent is known as peptization. The solute or solvent used are known as peptizing agent.

   Freshly precipitated $Fe(OH)_3$ is passed in colloidal sol by the action of $FeCl_{3(aq).}$

Bredig's arc method:

Two metal electrodes are immersed in a liquid medium. Both of them are connected to a high tension battery by which an electric arc is produced between the electrodes. High temperature of the arc vaporizes some of the metal which condenses on cooling to form sols. The heat generated during process is removed by putting system under ice cold water. The method in general used for preparation of metal sols in water.

2. By condensation : By aggregating true solution particles into colloidal size. The goal is achieved by

A. Physical method:

1. By exchange of solvent : Sulphur, phenolphthalein, indigo … sols are prepared by adding their solutions in suitable solvent drop by drop in water. Liquid indigo marketing is based on this aspect.
2. By excessive cooling : Water + chloroform mixture on sudden cooling leads to formation of ice in chloroform sol.

B. Chemical Methods:

1. Double decomposition : On passing H_2S through cold and dilute solution of some metal salts e.g. As and Cd (Yellow) sols are formed. $As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O$
2. Hydrolysis : Addition of $FeCl_3$ drop by drop to boiling water forms red coloured, positively charged $Fe(OH)_3$ sol. $FeCl_3 + 3H_2O \xrightarrow[\text{Water}]{\text{Boiling}} \underset{\text{sol}}{Fe(OH)_3} + 3HCl$
3. Oxidation : During II group analysis by passing H_2S in cold solution having an oxidizing agent, reduction of H_2S leads to the formation of white, grey turbidity of sulphur sol instead of precipitate of 2^{nd} group radicals. $2H_2S + SO_2 \longrightarrow 2H_2O + \underset{(Sol.)}{3S}$
4. Reduction : Metal salts in water on reduction with non electrolytic reducing agents such as HCHO, HCOOH, $SnCl_2$, NH_2NH_2 leads to metalsols.

$$2AuCl_3 + 3SnCl_2 \longrightarrow \underset{(Sol.)}{2Au} + 3SnCl_4$$

PURIFICATION OF SOLS

Sols so obtained are contained with two types of impurities and need purification.

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

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

1. Dialysis: The separation of soluble impurities from sols on the basis of their different rates of diffusion through parchment membrane is known as dialysis. This principle is based upon the fact that colloidal particles cannot pass through a parchment or cellophane membrane while the ions of the electrolyte can pass through it.

Electrodialsysis: The ordinary process of dialysis is slow. To increase the process of purification, the dialysis is carried out by applying electric field. This process is called electro dialysis.

2. Ultra filtration: It is the process of removing the impurities from the colloidal solution by passing it through graded filter papers called ultra-filter papers.
3. Ultra-centrifugation : In this method, the colloidal sol is taken in a tube which is placed in an ultra centrifuge. On rotation of the tube at high speeds, the colloidal particles settle down at the bottom of the tube and the impurities remain down in the solution called centrifugate.

PROPERTY OF COLLOIDS

1. Colligative properties:

Like true solutions, colloidal solutions also exhibit colligative properties such as osmotic pressure, elevation in b.pt, depression in freezing point, lowering in vapour pressure.

2. Optical Properties :

When a strong beam of light is passed through a true solution placed in a beaker, in a dark room,the parth of the light does not become visible. However, if the light is passed through a sol, placed in the same room, the path of the light becomes visible when viewed from a direction at right angle to that of the incident beam.

3. Electrical Properties:

(i) Sol particles carry +ve or –ve charge.

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

(iii) Origin of charge : The origin of charge on sol particle have been explained in terms of following concepts.

(1) Frictional electricity: Due to friction between dispersed phase & dispersion medium.

(2) Due to electron capture by sol particles.

4. Electrophoresis or Cataphoresis

The presence of the charge on the sol particles and its nature whether positive or negative can be determined with the help of phenomenon known as electrophoresis. In this phenomenon, the colloidal particles move towards positive or negative electrodes depending upon their chage under the influence of electrical field.

The phenomenon of movement of colloidal particles under an applied electric field is called electrophoresis.

5. Coagulation

A small amount of an electrolyte is necessary for the stability of the colloidal sol. The ions of the electrolytes are adsorbed on the sol particles and impart them some charge; positive or negative. The charged colloidal particles repel one another and are prevented from coming close together to unite into bigger particles. However, in the presence of a large excess of the electrolyte, the charge on the particles of the dispersed phase is neutralized and as a result, they come closer, grow in size and ultimately form precipitates. This is called precipitation or coagulation. Thus, The phenomenon of the precipitation of a colloidal solution by the addition of the excess of an electrolyte is called coagulation or flocculation.

Hardy Schulze Rule:

Thus, according to Hardy Schulze rule :

(i) The ions carrying the charge opposite to that of sol particles are effective in causing coagulation of the sol.

(ii) Coagulating power of an electrolyte is directly proportional to the valence of the active ions (ions causing coagulation). For example, to coagulate negative sol of As_2S_3, the coagulating power of different cations has been found to decrease in the order as:

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

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

$$[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{-}$$

The minimum concentration of an electrolyte which is required to cause the coagulation or flocculation of a sol is known as flocculation value. It is usually expressed as millimoles per litre.

POINTS TO REMEMBER:

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

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

Protection

(i) Lyophobic sols are relatively less stable than lyophilic sols, however their stability may be increased on addition of lyophilic sols. This phenomenon of stabilizing lyophobic sols by the addition of lyophilic colloids is known as protection. The lyophilic colloids which are used for this purpose are known as protective colloids.

(ii) The protective character of various lyophilic substances has been expressed in terms of gold number.

(iii) Gold number of a lyophilic colloid is defined as the minimum amount of lyophilic colloid in milligrams which prevents the coagulation of 10 ml gold sol against 1 ml of 10% NaCl solution.

Emulsions

If a mixture of two immiscible or partially miscible liquid is shaken, a coarse dispersion of one liquid in the other is obtained which is called emulsion.

Classification of colloids based on type of particles of dispersed phase

Depending upon the type of the particles of the dispersed phase, the colloids are classified as:

(i) Multimolecular colloids (ii) Macromolecular colloids (iii) Associated colloids.

Mechanism of Micelle Formation

Micelles are generally formed by the aggregation of several ions or molecules with lyophobic as well as lyophilic parts. For example, sodium stearate ($C_{17}H_{35}COONa$) is a typical example of such type of molecule. The micelle many cotain as many as 100 molecules or more. When sodium stearate is dissolved in water, it gives Na^+ and $C_{17}H_{35}COO^-$ ions.

$$\underset{\text{Sod. sterate}}{C_{17}H_{35}COONa} \rightleftharpoons \underset{\text{Stearate ion}}{C_{17}H_{35}COO^-} + Na^+$$

The stearate ions associate to form ionic micelles of colloidal size (in fig). It has long hydrocarbon part of $C_{17}H_{35}$ radical which is lyophobic end and COO^- part which is lyophilic. In the figure, the chain corresponds to stearate ion, $C_{17}H_{35}COO^-$. When the concentration of the solution is below its critical micelle concentration (10^{-3} mol L^{-1}), it behaves as normal electrolyte. But above this concentration, it is aggregated to behave as micelles.

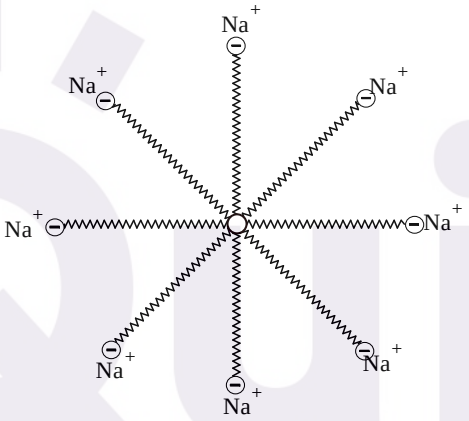


Fig. Aggregation of several ions to form ionic micelle

Emulsion

The colloids in which both the dispersed phase and dispersion medium are liquid.

Types of Emulsion:

(i) Oil in water emulsion: Oil is dispersed as dispersion medium e.g. milk

(ii) Water in oil emulsion: Water acts as disperesed phase and oil acts as dispersion medium e.g. cold cream, butter

Emulfication

The process of making an emulsion is known as emulsification. Soap and detergens are most frequently used as emulsifier.