SURFACE CHEMISTRY

Adsorption:

The tendency of accumulation of molecular species at the surface then in the bulk of a solid (or liquid) is termed adsorption.

Types of Adsorption

There are two types of adsorption of gases on solids.

(i) Physical Adsorption (ii) Chemical Adsorption

Characteristics of physical adsorption

(i) Lack of specificity: A given surface of an adsorbent does not show very strong attraction for a particular gas as the van der Waals forces are universal.

(ii) Nature of gas: The amount of gas adsorbed by a solid depends on the nature of gas. In general more easily liquefiable gases is adsorbed to a greater extent.

(iii) Reversible nature: Physical adsorption of a gas by a solid is generally reversible. The gas adsorbed can be removed by reversing the conditions temperature and pressure. Thus.

$$\text{Gas} \rightleftharpoons \text{Gas/Solid} + \text{Heat}$$

(iv) Surface area of adsorbent: The extent of adsorption increases with increase of surface area of the adsorbent. Thus, finely divided metals and porous substances having large surface areas as good adsorbents.

Characteristics of chemisorption

(i) High specificity: Chemi–sorption is highly specific and it will only occur if there is some possibility of chemical bonding. *For example*, oxygen is adsorbed on metals by virture of oxide formation and hydrogen is adsorbed by transition metals with unpaired d–orbitals leading to hydride formation.

(ii) Nature of gas: Chemisorption will occur if there is some possibility of chemical action between the gas and the solid adsorbent.

(iii) Irreversibility: As chemisorption involves compound formation, it is commonly irreversible in nature. Chemisorption is also an exothermic process but the process is very slow at low temperatures on account of high energy of activation. Like most chemical changes, it often increases with rise of temperature. A gas adsorbed at low temperature by physical adsorption may change into chemisorption at high temperature.

High pressure is favourable for chemisorption.

(iv) Surface area: Like physical adsorption, chemisorption also increases with increase of surface area of the adsorbent.

(v) Heat of adsorption: Heat of adsorption is high enough (80–240 kJ mol^{-1} or 20–60 kcal $mole^{-1}$) as chemisorption involves chemical bond formation.

Adsorption Isotherms

The relation between the quantity of gas adsorbed by a solid and the pressure of the gas over the solid when equilibrium has been reached is referred to as adsorption isotherm

Freundlich adsorption isotherm: Freundlich gave an empirical relationship between the quantity of gas absorbed by unit mass of solid adsorbent and pressure at a particular temperature called Freundlich adsorption isotherm which is expressed mathematically by the relation.

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

Where *x* is the mass of gas adsorbed, and m the mass of the adsorbent, and p is the pressure of the gas, where a and n are constants.

Types of Colloids

Dispersed phase	Dispersion medium	Name of Colloidal form	Some examples
1. Gas	Liquid	Foam or froth	Foam, whipped cream, beaten egg whites, froth, lemonade, soap sol, detergent solution etc.

2. Gas	Solid	Solid foam	Pumic stone (air in silicates) floating, soaps, rubber, biscuit, cake, breads dough, lava, volcanic ash, styrene foam, etc.
3. Liquid	Gas	Liquid aerosols	mist, fog, clouds, insecticide spray etc.
4. Liquid	Liquid	Emulsions	Milk, emulsified oils, medicine, cream, mayonnaise, etc.

5. Liquid	Solid	Gels	Cheese, jellies, gel, curd, butter, boot polish, pearl ($CaCO_3$ with water inclusions), etc.
6. Solid	Gas	Solid aerosols	Smoke, dust storm, fume, etc.
7. Solid	Liquid	Sols	Glue, Indian ink, some paints, starch dispersed in water, milk of magnesia, gold sol, sols of As_2O_3, S, Fe_2O_3 and AgCl in water, $Fe(OH)_3$ sol, white of an egg etc.
8. Solid	Solid	Solid sols	Black diamond, ruby glass, some alloys and minerals, and synthetic gem, etc.

Tyndall Effect

Although a colloid to be homogenous because the dispersed particles are tiny,
the ability to scatter light may differentiate it from a true solutio
n.
The Tyndall effect is defined as the scattering of light by colloid
al particles.

Electrical properties

(i) Electrophoresis: Colloidal particles (both lyophilic and lyophobic) are electrically charged either positive or negative. Such as

Positively charged	**Negatively charged**
(1). Hydroxides, e.g., $Al(OH)_3$, $Fe(OH)_3$, $Cr(OH)_3$, etc.	(1) Metallic sols, e.g., Pb, Ag. Au, Cu, etc.
(2) Protein in acid solution	(2) Sulphur, sulphides (e.g., CdS, As_2S_3), silicic acid, etc.
(3) Basic dyes, e.g., methylene blue.	(3) Organic sols, e.g. gelatin, starch etc. (4) Acid dyes, e.g., eosin.

Coagulation Of Sols

The colloidal solution's precipitation phenomenon is called "coagulation" And the solid separating under these conditions is called the "coagulum."

Emulsions

An emulsion is a colloidal typically a system of two or more liquid phases, one of which is spread as globules in the other. Known emulsion examples are milk (liquid fat), liver oil, etc. Emulsions can be classified into two groups.

(i) Water in oil type

(ii) Oil in water type

Characteristics of emulsions

(i) All emulsions exhibit typical colloid properties.

(ii) Emulsions usually carry negative charge

(iii) Stability of the emulsions is determined by the charge on the dispersed phase and the emulsifying agent film.

CATALYSIS

A catalyst is a substance which increases the rate at which a chemical reaction approaches equilibrium, without itself becoming permanently involved in the reaction.

Types of Homoegeneous Catalysis

Combination of phases	**Example**
Liquid + Liquid	Hydrolysis of ester catalysed by acids and bases
Gas + Gas	Oxidation of sulphur dioxide catalysed by nitric oxide
Liquid + Liquid + Solid	Hydrolysis of cellulose catalysed by acids.
Solid + Solid + Gas	Decomposition of potassium chlorate catalysed by manganese dioxide

Types of Heterogeneous Catalysis

Combination of phases	Example

Liquid + Gas	Polymerization of alkenes catalysed by phosphoric acid.
Solid + Liquid	Disproportionation of cyclohexane to benzene and cyclohexane catalysed by palladium.
Solid + Gas	Oxidation of carbon monoxide to carbon dioxide catalysed by zinc oxide.
Solid + Liquid + Gas	Hydrogenation of benzene to cyclohexane catalysed by nickel.