DEPARTMENT OF EDUCATION (S)
Government of Manipur

UNIT -5 Surface Chemistry

Surface chemistry is referred to as the study of the phenomena occurring on the surfaces of substances. These may be adsorption, catalysis, colloids formation etc.

Adsorption: The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed as adsorption.

Adsorbate: It is the substance which is being adsorbed on the surface of another substance.

Adsorbent: It is the substance present in bulk, on the surface of which adsorption is taking place.

Desorption: It is the process of removing an adsorbed substance from a surface on which it is adsorbed.

Difference Between Adsorption and Absorption:

Adsorption is accumulation of molecular species at the bottom instead of the liquid or solid. It is a surface phenomenon and is an exothermic process. On the other hand, absorption is the assimilation of the molecular system throughout the bulk of the solid or liquid medium. It is a bulk phenomenon and is endothermic.

Types of Adsorption: Based on the force of interaction between adsorbate and adsorbent, adsorption in surface chemistry is classified into two types.

1. Physical adsorption
2. Chemical adsorption

Physical adsorption or physisorption

1. If the adsorbate is held on a surface of adsorbent by weak van der Waals' forces, the adsorption is called physical adsorption or physisorption.
2. It is non-specific and reversible
3. The amount of gas depends upon nature of gas, i.e., easily liquefiable gases like NH_3, CO_2, gas adsorbed to greater extent than H_2 and He. Higher the critical temperature of gas, more will be the extent of adsorption.
4. The extent of adsorption increases with increase in surface area, e.g. porous and finely divided metals are good adsorbents.
5. It has low enthalpy of adsorption (20 – 40 kJ mol-1) and low temperature is favourable.

6. It forms multimolecular layers.

Chemical adsorption or chemisorption

1. If the forces holding the adsorbate are as strong as in chemical bonds, the adsorption process is known as chemical adsorption of chemisorption.
2. It is highly specific and is irreversible.
3. The amount of gas adsorbed is not related to critical temperature of the gas.
4. It also increases with increase in surface area.
5. It has enthalpy heat of adsorption (180 – 240 kJ mol-1) and high temperature is favourable.
6. It forms unimolecular layers.

Factors affecting adsorption of gases on solids

1. **Nature of adsorbate: In physisorption** easily liquefiable gases like NH_3,HCl, CO_2, etc. which have higher critical temperatures are absorbed to greater extent whereas H_2, O_2, N_2 etc. are adsorbed to lesser extent. In chemical adsorption, a gas gets adsorbed on specific solid only if it enters into chemical combination with it.
2. **Nature of adsorbent:** Activated carbon, metal oxides like aluminum oxide, silica gel and clay are commonly used adsorbents. They have their specific adsorption properties depending upon pores.
3. **Specific area of the adsorbent:** The greater the specific area, more will be the extent of adsorption. That is why porous or finely divided forms of adsorbents adsorb larger quantities of adsorbate. The pores should be large enough to allow the gas molecules to enter

Pressure of the gas: Physical adsorption increases with increase in pressure.

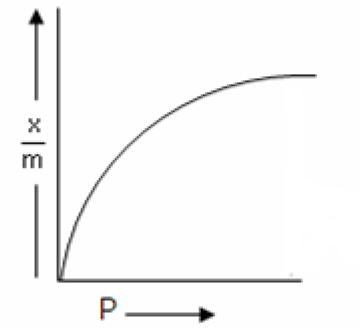
Adsorption isotherm: The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve is termed as adsorption isotherm.

Freundlich Adsorption isotherm: The relationship between $\frac{x}{m}$ and pressure of the gas at constant temperature is called adsorption isotherm and is given by

$$\frac{x}{m} = kp^{1/n} (n > 1)$$

Where x- mass of the gas adsorbed on mass m of the adsorbent and the gas at a particular temperature k and n depends upon the nature of gas

The slope first increases with increase in pressure at low pressure but become independent of pressure at high pressure.



Taking logarithm on both sides, we get,

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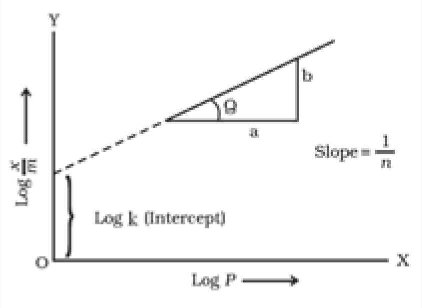
- If we plot a graph between log $\frac{x}{m}$ and log P, we get a straight line.



The slope of the line is $\frac{1}{n}$ and intercept will be equal to log k.

Catalysis: Substances, which accelerate the rate of a chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction, are known as catalysts, and the phenomenon is known as catalysis.

- Promoters: These are the substances which increase the activity of catalyst. Example – Mo is promoter whereas Fe is catalyst in Haber’s Process.
  $N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe(s)/Mo(s)} 2NH_{3(g)}$

- Catalytic poisons (Inhibitors): These are the substances which decrease the activity of catalyst. Example -Arsenic acts as catalytic poison in the manufacture of sulphuric acid by ‘contact process.

Types of catalysis:

There are two types of catalysis namely,

1. **Homogeneous catalysis:** When the catalyst and the reactants are in the same phase, this kind of catalytic process is known as homogeneous catalysis.

EXAMPLE:

Oxidation of sulphur dioxide into sulphur trioxide with dioxygen in the presence of oxides of nitrogen as the catalyst in the lead chamber process.

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

The reactants, sulphur dioxide and oxygen, and the catalyst, nitric oxide, are all in the same phase.

2. **Heterogeneous catalysis:** When the catalyst and the reactants are in different phases, the catalytic process is said to be heterogeneous catalysis.

EXAMPLE:

Oxidation of sulphur dioxide into sulphur trioxide in the presence of Pt.

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

The reactants are in gaseous state while the catalyst is in the solid state.

Adsorption Theory of Heterogeneous Catalysis

According to this theory, the reactant molecules are adsorbed on the surface of the catalystand the mechanism involves the following steps-

a. Diffusion of reactant molecules towards the surface of the catalyst.
b. Adsorption of the reactant molecules on the surface of the catalyst by forming loose bonds with catalyst due to free valencies.
c. Occurrence of chemical reaction between reactants and the catalyst forming an intermediate.
d. Desorption of the product molecule from the surface due to lack of its affinity for the catalyst surface.
e. Diffusion of product molecules away from the surface of the catalyst.

Activity and selectivity

1. **Activity of catalyst:** It is the ability of a catalyst to increase the rate of a chemical reaction.
2. **Selectivity of catalyst**: It is the ability of catalyst to direct a reaction to yield a particular product (excluding others).

Enzyme catalysis

Enzymes: These are complex nitrogenous organic compounds which are produced by living plants and animals. They are actually protein molecules of high molecular mass. They are biochemical catalysts.

Steps of enzyme catalysis
(i) Binding of enzyme to substrate to form an activated complex.
(ii) Decomposition of the activated complex to form product.

Characteristics of enzyme catalysis:

(i) They are highly efficient.
(ii) They are highly specific in nature
(iii) They are active at optimum temperature (298 – 310 K). The rate of enzyme catalysed reaction becomes maximum at a definite temperature called the optimum temperature.
(iv) They are highly active at a specific pH called optimum pH.
(v) Enzymatic activity can be increased in presence of coenzymes which can be called as promoters.
(vi) Activators are generally metal ions Na^+, Co^{2+} and Cu^{2+} etc. They weakly bind to enzyme and increase its activity.
(vii) Influence of inhibitors (poison): Enzymes can also be inhibited or poisoned by the presence of certain substances.

Colloidal state

A colloid is a heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance called dispersion medium.

Distinction among true solutions, colloidal solutions and suspensions

True solution:
(i) It is homogeneous.
(ii) The diameter of the particles is less than 1 nm.
(iii) It passes through filter paper.
(iv) Its particles cannot be seen under a microscope.

Colloids:
(i) It appears to be homogeneous but is actually heterogeneous.
(ii) The diameter of the particles is 1 nm to 1000 nm.
(iii) It passes through ordinary filter paper but not through ultra-filters.
(iv) Its particles can be seen by a powerful microscope due to scattering of light.

Suspension:
(i) It is heterogeneous.
(ii) The diameter of the particles are larger than 1000 nm.
(iii) It does not pass through filter paper.
(iv) Its particles can be seen even with naked eye.

Classification of colloids:

Colloids are made up of two components- Dispersed phase which is the substance dispersed as very fine particles and Dispersion medium which is the substance in which the particles are dispersed.

On the basis of the physical state of dispersed phase and dispersion medium, colloids may be classified as:

Name	**Dispersed phase**	**Dispersed medium**	**Examples**
Solid sol	solid	Solid	Coloured gem stones
Sol	Solid	Liquid	Paints
Aerosol	Solid	Gas	Smoke, dust
Gel	Liquid	Solid	Cheese, jellies
Emulsion	Liquid	Liquid	Hair cream, milk
Aerosol	Liquid	Gas	Mist, fog, cloud

Solid sol	Gas	Solid	Foam rubber, pumice stone
Foam	Gas	Liquid	Whipped cream

Based on the nature of interaction between dispersed phase and dispersion medium, the colloids are classified into two types namely:

1. **Lyophobic sols:** In these colloids the particles of dispersed phase have no affinity for the dispersion medium and they are not stable.
2. **Lyophilic sols:** In these colloids, the particles of dispersed phase have great affinity for the dispersion medium and they are stable.

Based on the types of particles of the dispersed phase colloids may be:

1. **Multimolecular colloids**: In this the colloidal particles consist of aggregates of atoms or small molecules and has diameter less than 1 nm.
2. **Macromolecular colloids:** In this the dispersed particles are themselves large molecules (usually polymers) which have dimensions comparable to those of colloids particles.
3. **Associated colloids (Micelles):** These colloids behave as normal, strong electrolytes at low concentrations, but show colloidal properties at higher concentrations due to the formation of aggregated particles of colloidal dimensions.

***Kraft Temperature (Tk):**Micelles are formed only above a certain temperature called Kraft temperature.

* **Critical Micelle Concentration (CMC):** Micelles are formed only above a particular concentration called critical micelle concentration.

Properties of colloids:

1. **Tyndall effect:** The scattering of a beam of light by colloidal particles is called Tyndall effect. The bright cone of light is called the Tyndall cone.
2. **Brownian movement:** Colloidal particles move in zig – zag path. This type of motion is due to colliding molecules of dispersion medium constantly with colloidal particles.
3. **Electrophoresis:** The movement of colloidal particles under an applied electric potential is called electrophoresis.
4. **Coagulation or precipitation:** The process of settling of colloidal particles as precipitate is called coagulation.

Hardy – Schulze rules:

1. Oppositely charged ions are effective for coagulation.

2. The coagulating power of electrolyte increases with increase in charge on the ions used for coagulation.

   Examples –
   Al^{3+}> Ba^{2+}> Na^{+} for negatively charged colloids. Fe $(CN)_6]^{4-}$>PO_4^{3-} >SO_4^{2-} >Cl^{-} for positively charged colloids.

Emulsions: These are liquid-liquid colloidal systems, i.e., the dispersion of finely divided droplets in another liquid.

Types of emulsions:

1. Water dispersed in oil: When water is the dispersed phase and oil is the dispersion medium. E.g. butter
2. Oil dispersed in water: When oil is the dispersed phase and water is the dispersion medium. E.g. milk

Nano materials

A nanoparticle is defined as a particle of matter that is between 1 and 100 nanometres (nm) in diameter. The properties of nanoparticles often differ markedly from those of larger particles of the same substance. Nanotechnology is the study and application of such particles and can be used across all the science fields, such as chemistry, biology, physics, materials science, and engineering.