BRUSH UP

YOUR CONCEPTS

Class XII

This specially designed column will help you to brush up your concepts by practicing questions. You can mail us your queries and doubts related to this topic at editor@mtg.in. The queries will be entertained by the author.*

SURFACE CHEMISTRY

Physisorption or Physical Adsorption or van der Waals' Adsorption

Adsorbed molecules (of adsorbate) are held on the surface of adsorbent by weak van der Waals' forces, *e.g.*, adsorption of water vapours on silica gel.

It is a reversible general process with quite low enthalpy of adsorption of about 20 to 40 kJ mol^{-1}. Physisorption decreases by increasing temperature or by decreasing pressure. Multimolecular layers of adsorbent are formed.

Chemical Adsorption or Chemisorption or Langmuir Adsorption

Adsorbed molecules (of adsorbate) are held on the surface of adsorbent by strong forces of chemical nature, *e.g.*, adsorption of H_2 gas on Pd-surface.

It is specific and irreversible in nature with adsorption energy of 40 to 400 kJ mol^{-1}. It increases with increase in temperature upto certain limit after which it decreases. Layer formed is monomolecular.

Factors Affecting Adsorption of Gases on Solids

- **Nature of adsorbent and adsorbate:** Easily liquefiable or smelling or coloured gases are easily adsorbed on porous matter through physisorption while permanent gases are easily chemisorbed on metal surfaces.
- **Surface area of solid adsorbent :** Adsorption of a gas is directly proportional to the surface area of the adsorbent. Surface area of 1 g solid is called specific surface which can be increased by making it rough, vacuum cleaning, steam cleaning, etc.
- **Temperature:** The extent of adsorption $\frac{x}{m} = f(T)$ at constant pressure. From thermodynamic study $\Delta_{ads}H$ is negative, $\Delta_{ads}S$ is also negative. $\Delta_{ads}G$ will be negative only at low or moderate temperature $\Delta G = \Delta H - T\Delta S$, specially physisorption.
- For chemisorption, increase in temperature helps in achieving activation barrier and thereafter extent of adsorption decreases.
- **Pressure:** The extent of adsorption $\frac{x}{m}$ for physisorption is proportional to $p^{1/n}$. $\frac{1}{n}$ is the slope of the plot of $\log\frac{x}{m}$ vs $\log P$. It is known as Freundlich adsorption isotherm, after the name of the person who studied it the first.

Catalysis

It is the phenomenon of action of catalyst.

- **Autocatalysis :** A product of reaction acts as catalyst.
- **Induced catalysis :** Occurrence of a reaction is catalysed by some other reaction.
- **Homogeneous catalysis :** Catalyst and reactant(s) are in the same physical state.
- **Heterogeneous catalysis :** The catalyst and the reactant(s) are in different physical states. This phenomenon is explained by adsorption theory.
- **Shape selective catalysis :** Activity of some catalysts depends upon pore (cavity) size, *e.g.*, ZSM–5 converts CH_3OH to gasoline.
- A catalyst can not start a reaction. It cannot change the energy of reaction. Even a small quantity of a catalyst is sufficient enough. The extent of chemisorption decides the activity of catalyst. The ability of a catalyst for the production of specific product is called selectivity.

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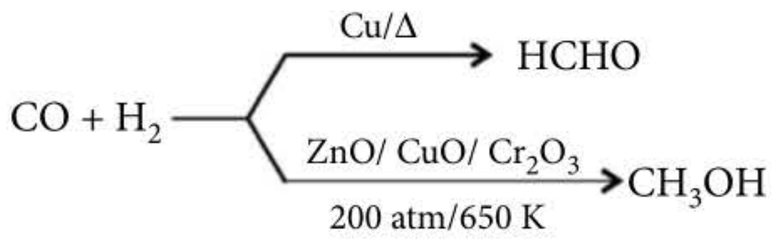

Enzyme catalysis : Enzymes are proteinous biocatalysts.

- They work in lock and key system with specific nature. These have extremely high efficiency to catalyse reactions to 10^6 times.
- In some cases an extra non-protein part called coenzyme also joins the enzyme. Now, the enzyme is called apoenzyme while after it is known combination as holoenzyme.
- Enzymes having two binding sites are called allosteric enzymes.

Colloidal state : This is the state of dispersed phase particles when their size is 1 – 1000 nm and cannot pass through animal membrane or parchment paper. Based on states of dispersed phase (DP) and dispersion medium (DM), colloids are of eight types. A gas-gas mixture is always a solution.

- **Lyophilic colloids :** These colloids are reversible, have high stability and work as stabilizers for lyophobic colloids. These have surface tension lower than dispersion medium but have viscosity higher than dispersion medium. These generally, do not show electrophoresis, *e.g.*, starch sol, gelatin sol, etc.
- **Lyophobic colloids :** These are irreversible colloids which need a small quantity of lyophilic colloid or electrolyte for stability. Their surface tension and viscosity are equal to that of dispersion medium, *e.g.*, sulphur sol, As_2S_3 sol, etc.
- **Macromolecular colloids:** These are colloids of substances (DP) of high molecular masses, *e.g.*, starch, rubber, etc.
- **Multimolecular colloids :** These colloids have aggregates of DP particles of less than 1 nm size, *e.g.*, gold sol, sulphur sol, etc.
- **Micelles or Associated colloids :** Some strong electrolytes at some higher concentration called as Critical Micelle Concentration (CMC) and a specific temperature called as Kraft temperature form colloids known as associated colloids or micelles.

– CMC for soap is 10^{-4} to 10^{-3} mol L^{-1}. One micelle of soap has 100 or more $R-\overset{\overset{O}{\|}}{C}-O^-$ ions.

Preparation of Lyophilic Sols

- **Condensation methods :** These are chemical methods oxidation, reduction, double decomposition, hydrolysis, excessive cooling, exchange of solvent, etc.
- **Disintegration methods:** These are Bredig's electro disintegration, mechanical disintegration method (colloidal mill method), peptisation etc.

Origin of charge on colloidal particles : Charge on colloidal particles may appear because of electron capture, frictional electrification, preferential adsorption of ions, etc.

- Examples of negative colloids : Albuminoids in blood, metal sulphides, metals, macromolecular colloids, etc.,
- Examples of positive colloids : Metal hydroxides, proteins in acidic medium, etc.
- **Purification of sols:** Ions present in colloidal solutions can be removed by centrifugation, ultracentrifugation, dialysis and electrodialysis.
- **Properties of colloidal solutions :** Heterogeneous nature. Show osmotic pressure as the only colligative property. Visibility of particles under Zsigmondy's ultramicroscope. Colour depends upon the wavelength of scattered light. Brownian movement. Tyndall effect (originally studied by Faraday) is shown when refractive indices of DM and DP differ much but the size of DP particles is not much smaller than wavelength of light. Movement under electric field (Electrophoresis), etc.,

Coagulation or Flocculation or Precipitation

- It can be achieved by :

(a) Adding oppositely charged colloid
(b) Prolonged electrophoresis or dialysis
(c) Addition of suitable electrolyte which is governed by Hardy Schulze Rules:
(i) The ion of electrolyte having charge opposite to that of colloidal particle, coagulates it.
(ii) Higher the charge of the coagulating ion, higher is its coagulation power.
(iii) Coagulation power of ion is directly proportional to the 6^{th} power of the charge.

The order of flocculating powers of some ions are:
For $Fe(OH)_3$ positive sol :
$[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$
For As_2S_3 negative sol : $Sn^{4+} > Al^{3+} > Ca^{2+} > Na^+$
The minimum amount of electrolyte in millimole per litre of mixed solution needed to coagulate a colloidal solution is called the coagulation value of the electrolyte for the sol. Lower the coagulation value greater is the coagulating power.

Emulsions

This colloidal solution is obtained by shaking two partly miscible or immiscible liquids.

- Oil in water (O/W) type : Water is DM. It is generally unstable.
- Water in oil (W/O) type : Oil is DM.

Dispersed phase of emulsion is generally negatively charged. Emulsion can be diluted, by the DM. Gums, proteins, soaps etc., are used as emulsifiers for O/W type emulsions, metal salts of fatty acids, etc., are used as emulsifiers for W/O type emulsions. W/O emulsion gives homogeneous mixture (colour) by adding oil soluble dye. Separation of components of an emulsion is called demulsification.

MULTIPLE CHOICE QUESTIONS

1. The energy released during physisorption is
(a) 10 – 20 kJ mol^{-1} (b) 20 – 40 kJ mol^{-1}
(c) less than 10 kJ mol^{-1} (d) more than 40 kJ mol^{-1}

2. Chemisorption is also known as
(a) van der Waals' adsorption
(b) Langmuir adsorption
(c) Lewis Kossel adsorption
(d) Faraday adsorption.

3. The surface of 1 g of adsorbate is maximum when the particles are in
(a) cubic form (b) powder form
(c) colloidal form (d) vapour form.

4. Physisorption is generally high at
(a) high temperature (b) low temperature
(c) low pressure
(d) equal in all these conditions.

5. When $\log\frac{x}{m}$ is plotted against log P, the slope is $\frac{1}{2}$ and the intercept is 0.301. What will be the extent of adsorption when pressure is 9 units?
(a) 2 (b) 3 (c) 6 (d) 9

6. The following volumetric analysis reaction of oxalic acid against $KMnO_4$/ H^+ is catalysed by the product $MnSO_4$. The catalysis is an example of

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

(a) homogeneous catalysis
(b) autocatalysis
(c) induced catalysis (d) both (a) and (b).

7. $Na_3AsO_3 + O_2(air) \xrightarrow{\Delta}$ No reaction ...(i)

$$Na_2SO_3 + \frac{1}{2}O_2(air) \xrightarrow{\Delta} Na_2SO_4 \quad ...(ii)$$

$$Na_2SO_3 + Na_3AsO_3 + O_2(air) \xrightarrow{\Delta} Na_2SO_4 + Na_3AsO_4 \quad ...(iii)$$

The reaction (iii) is an example of
(a) autocatalysis (b) induced catalysis
(c) negative catalysis (d) heterogeneous catalysis.

8. $CH_3OH \xrightarrow{ZSM\text{-}5} CH_2 \xrightarrow{Polymerisation}$ gasoline

Here, ZSM-5 works as
(a) autocatalyst (b) induced catalyst
(c) homogeneous catalyst (d) shape selective catalyst.

9. Which of the following is not correct w.r.t. catalysis?
(a) It may undergo physical changes only.
(b) Its quantity used in a reaction depends upon the quantity of reactants.
(c) It does not alter the enthalpies of reactants, products and the reaction.
(d) It gives new mechanism to the reaction.

10. For the hypothetical reaction

$$2A + B \longrightarrow C + D$$

E_{af} = 100 kJ mol^{-1}, E_{ab} = 100 kJ mol^{-1}
The enthalpy of reaction $\Delta_r H$ would be
(a) 300 kJ mol^{-1} (b) 100 kJ mol^{-1}
(c) $\frac{300}{5}$ kJ mol^{-1} (d) 0 kJ mol^{-1}

11. Sometime a non-protein part is joined with an enzyme for its working. The combination is called as
(a) coenzyme (b) apoenzyme
(c) holoenzyme (d) allosteric enzyme.

12. Which of the following is an example of sol?
(a) Blood (b) Milk
(c) Butter (d) Coloured glass

13. Which of the following is not correct for Lyophilic colloid?
(a) Affinity for medium is very high.
(b) Need lyophobic sols as stabilizers.
(c) Viscosity is higher and surface tension is lower than DM.
(d) Electrophoresis is generally not shown.

14. The temperature required to be achieved for the formation of a micelle is called as
(a) critical temperature
(b) critical micelle temperature
(c) Kraft temperature (d) Boyle's temperature.

15. Which of the following has colloidal particles positively charged?
(a) Albuminoids in blood
(b) Au sol prepared by Bredig's method
(c) $Fe(OH)_3$ sol prepared by hydrolysis of $FeCl_3$
(d) As_2S_3 sol prepared by passing H_2S through suspension of As_2O_3