

# Physical Chemistry

## "ASSIGNMENT"

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Semester - VII

To:

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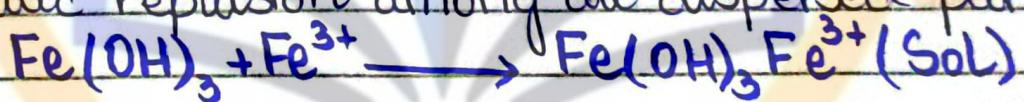
# Past Paper 2019

## Short Answers

-(i)-

**Peptization:-** The process of dispersing a precipitate into a colloidal solution by adding small quantity of an electrolyte is called peptization. The electrolyte added is called a peptizing agent.

**For Example:** Freshly precipitated  $\text{Fe(OH)}_3$  can be peptized by addition of dilute solution of ferric chloride into aqueous medium having  $\text{Fe(OH)}_3$  precipitates. The  $\text{Fe}^{+3}$  ions coming from  $\text{FeCl}_3$  are adsorbed on surface neutral  $\text{Fe(OH)}_3$  particles & convert them into positively charged  $\text{Fe(OH)}_3$  particles which dispersed in aqueous medium due to electrostatic repulsion among all dispersed particles:



-(ii)-

## Ultrafiltration:-

This is another important method for purifying sols. This process is similar to filtration of an ordinary precipitate except with difference that membrane used here is designed in such a way that it will permit the passage of only electrolytes and medium, not of colloidal particles.

Colloidal particles thus can be separated from

the medium containing electrolytes. Since ultrafiltration membranes are of delicate constitution and can be easily broken, they are generally supported on a wire screen. Ultrafiltration being a slow process can be quickened by using pressure.

### (iii) <sup>80</sup> Three Properties of Colloid:-

- 1- **Color:** Colloid solutions are invariably colored. The color of the sol depends on the size and shape of the colloid particles, the absorption power of dispersed phase and dispersion medium & wavelength of light falling on it.
- 2- **Heterogeneity:** Colloid particles being larger than molecules or ions, form heterogeneous mixtures consisting of particles of dispersed phase.
- 3- **Non-Settling:** Colloid solutions are quite stable systems and the suspended particles remain suspended indefinitely. Only some large particles may settle but very slowly.

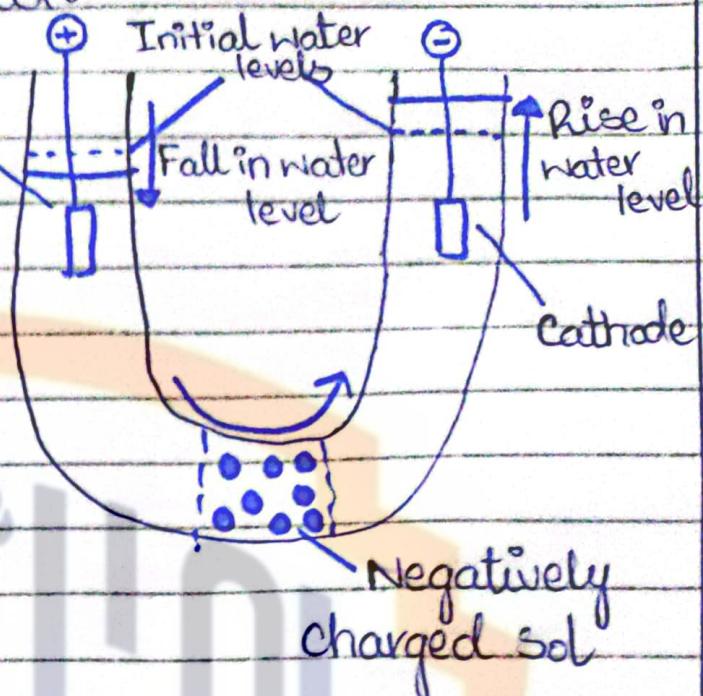
### (iv) <sup>80</sup> Electro-osmosis:-

The movement of dispersion medium under the influence of electric field when dispersed particles are prevented from moving is known as electro-osmosis.

In electro-osmosis, the liquid moves

through a porous material under influence of an applied electric field.

This apparatus is used for demonstrating the phenomenon of electro-osmosis in the laboratory.



## Persistent Dialysis:-

Stability of colloid is due to presence of traces of electrolytes invariably present. On prolonged dialysis, these traces of electrolytes are removed and the colloid becomes unstable and gets precipitated.

Precipitation of Hydrophilic Sols is most difficult than hydrophobic sols. This is because in such sols dispersed phase is heavily hydrated. The degree of hydration must be greatly decreased before coagulation. This is done by adding second solvent which is miscible with water. The solvent removes water from sol which changes into lyophobic colloid and is readily precipitated on adding small amount of an electrolyte.

## (vi) Hardy - Schulze:-

For given sol, the precipitation power of an electrolyte is determined by two factors:

- (i) Coagulation of sol is effective by ions carrying a charge opposite to that of colloidal particles and
- (ii) The precipitating power increases considerably with increasing valence of the coagulating ion.

These generalizations are often known as Hardy - Schulze rule.

## (vii) Surfactants:-

Surfactants are surface active substances which can be used as emulsifier due to their amphiphilic structure.

A conventional emulsifier has both hydrophilic & hydrophobic parts in its structure that is known as **amphiphilic structure**. Hydrophilic part has affinity towards water while hydrophobic part has affinity towards organic liquid.

## (viii) Autocatalysis:-

A type of catalysis in which one of the products formed act as catalyst is called auto catalysis.

The chemical reaction b/w acidified potassium permanganate ( $KMnO_4$ ) and oxalic acid is an example of autocatalysis.

(ix) *Ans*

## Adsorption isotherms:-

Adsorption isotherm represents the relationship b/w the adsorbate in the surrounding phase and adsorbate adsorbed on surface of adsorbent at equilibrium and constant temperature.

Freundlich and Langmuir isotherms are two primary methods utilized to predict capacity of adsorption of certain material.

(x) *Ans*

## Tyndall effect:-

Tyndall effect is the phenomenon of scattering of lights by particles.

A true solution does not show tyndall effect and is said to be optically void. This is because the size of solute particles in true solutions is so small that it cannot scatter a beam of light.

# Long Questions

(1) —

## Eiley-Rideal Mechanism:-

Eiley-Rideal mechanism involves following steps:

- i) One reactant gets adsorb on surface of catalyst.
- ii) Second reactant doesn't adsorb on catalyst surface. Instead it interacts with adsorbed reactant. In E-R mechanism, both reactants adsorb on catalyst surface.
- iii) After interaction products are formed. Later adsorbed product diffuses into reaction vessel after desorption.

However, product can remain in gaseous state and doesn't stay on catalyst surface in E-R mechanism.

## Scheme of E-R Mechanism

Reactant gases A and B are going to be converted into products C and D by following mechanism



According to E-R mechanism, rate of reaction is directly proportional to fraction of surface covered by gas A and pressure of gas B because adsorbed molecules of gas A interact with gas B

$$\text{Rate of reaction} \propto \theta_A$$

Rate of reaction  $\propto P_B$

Hence,

$$\text{Rate of reaction} = k_r \theta_A P_B \quad \text{---(1)}$$

Rate of reaction is independent of  $P_A$  as  $\theta_A$  depends upon  $P_A$ . For double system,

$$\theta_A = \frac{aP_A}{1+aP_A+bP_B}$$

Then eq (1) will become:

$$\text{Rate} = k_r \frac{aP_A P_B}{1+aP_A+bP_B} \quad \text{---(2)}$$

This is rate law expression for catalytic reaction of two gases on solid surface. Since, B is not adsorbing species so,  $b \approx 0$  then,

$$1 + aP_A + bP_B \approx 1 + aP_A$$

So eq (2) will be: Rate =  $k_r \frac{aP_A P_B}{1+aP_A}$

$$\text{Rate} = k_r \left( \frac{aP_A}{1+aP_A} \right) P_B$$

We reach at following results:

1- When partial pressure of gas A is very low,  $1+aP_A \approx 1$   
so, Rate =  $k_r aP_A P_B$

If partial pressure of gas A is low, reaction will be  $2^{\text{nd}}$  order.

2- When pressure of gas A is very high,  $1+aP_A \approx aP_A$   
so, Rate =  $k_r \frac{aP_A P_B}{aP_A}$

$$\text{Rate} = k_r P_B$$

When  $P_A$  is very high reaction will be  $1^{\text{st}}$  order.

If  $P_A$  is high then rate of reaction is independent of extent of adsorption of gas A.

## — (2) —

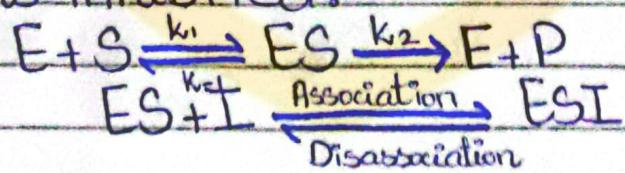
# Enzyme Catalysis:-

Enzymes are bio organic catalysts which catalyze the chemical reactions occurring in the human body. Enzymes are macromolecules and proteins in nature, because they have origin in living organisms so they are called biopolymers. Amino acids are building blocks of enzymes.

Enzymes are specific in nature and functioning. Stereo specificity is basic character of enzymes. Enzymes only work on specific temperature and specific pH.

## Uncompetitive Inhibition:-

In such type of inhibition, enzyme doesn't make a complex with inhibition directly but enzyme-substrate from a complex with inhibitor and stabilize it. As result of this process product formation is inhibited.



Dissociation constant of  $[ESI]$  will be

$$K_3 = \frac{[ES][I]}{[ESI]}$$
$$[ESI] = \frac{[ES][I]}{K_3}$$

$$u \propto [ES]$$

$$u = k_1 [ES]$$

Net rate of formation of  $[ES]$  complex

$$\frac{d[ES]}{dt} = k_1 [E][S] - k_{-1} [ES] - k_2 [ES]$$

Applying steady state approximation to it

$$0 = k_1 [E][S] - k_{-1} [ES] - k_2 [ES]$$

$$k_1 [E][S] = k_{-1} [ES] + k_2 [ES]$$

$$k_1 [E][S] = (k_2 + k_{-1}) [ES]$$

$$[ES] = \frac{k_1 [E][S]}{k_2 + k_{-1}}$$

$$[ES] = \frac{[E][S]}{\frac{k_2 + k_{-1}}{k_1}}$$

$$[ES] = \frac{[E][S]}{K_M}$$

$$[E]_0 = [E] + [ES] + [EST]$$

$$[E] = [E]_0 - [ES] - [EST]$$

By putting value of  $[EST]$

$$[E] = [E]_0 - [ES] - \frac{[ES][T]}{K_1}$$

Putting value of  $[E]$  in equation

$$[ES] = \frac{([E]_0 - [ES] - [ES][I])[S]}{K_1}$$

$$[ES]_{K_M} = \frac{([E]_0 - [ES] - [ES][I])[S]}{K_1}$$

$$[ES]_{K_M} = \frac{([E]_0 - [ES] \left\{ 1 + \frac{[I]}{K_1} \right\})[S]}{K_1}$$

$$[ES]K_m = [E]_0[S] - [ES][S] \left\{ 1 + \frac{[I]}{K_i} \right\}$$

$$[ES]K_m + [ES][S] \left\{ 1 + \frac{[I]}{K_i} \right\} = [E]_0[S]$$

$$[ES] \left( K_m + [S] \left\{ 1 + \frac{[I]}{K_i} \right\} \right) = [E]_0[S]$$

Putting value of  $[ES]$

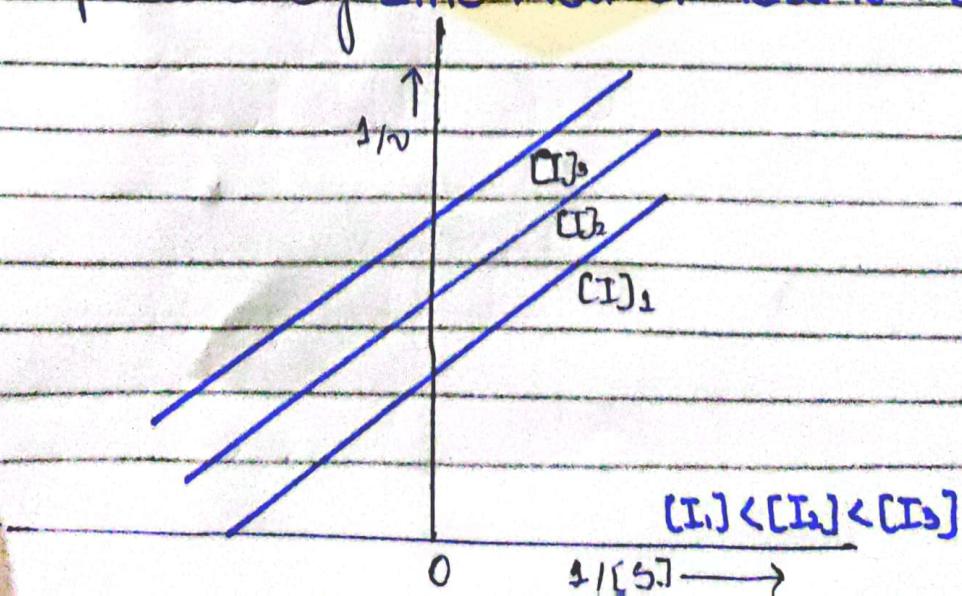
$$v = k_2 \frac{[E]_0[S]}{K_m + [S] \left\{ 1 + \frac{[I]}{K_i} \right\}}$$

It is rate law expression of enzyme catalyzed reaction in presence of inhibitor due to uncompetitive inhibition. Taking inverse.

$$\frac{1}{v} = \frac{1}{k_2 [E]_0 [S]} + \frac{1}{K_m [S]} \left\{ 1 + \frac{[I]}{K_i} \right\}$$

$$\frac{1}{v} = \frac{1}{k_2 [E]_0 [S]} + \frac{1}{K_m [S]} \left\{ 1 + \frac{[I]}{K_i} \right\}$$

This is rate law expression for enzyme catalyzed reaction suffering uncompetitive inhibition. We can know that inhibition is competitive or uncompetitive by Line weaver Burk Plot.



(3)

## Molecular weight of macro-molecules:-

Molecular weight determination is a crucial aspect of characterizing macromolecules in solution. There are number of methods available for the determination of molecules weight of macromolecules.

### Osmotic Pressure Method

According to Vant Hoff's Law:

"This law states that the osmotic pressure of a solution is directly proportional to the concentration of solute particles in the solution. This means that as concentration of solute particles increases, the osmotic pressure also increase."

The Vant Hoff's equation for dilute solution may be written as;

$$P = \frac{C \times RT}{M}$$

$$\frac{P}{C} = \frac{RT}{M}$$

where,

R = Gas constant

T = Temperature in Kelvin

M = Molecular weight of solute

In actual determination of molecular weight of polymer, Osmotic pressure of a series of small concentration  $c$  is measured with help of special osmometer. The plot of  $P/c$  against  $c$  is straight line.

It is extrapolated to zero concentration

Thus  $\frac{RT}{M}$  as intercept from which the molecular

weight can be calculated.

## Fuoss-Mead Osmometer:

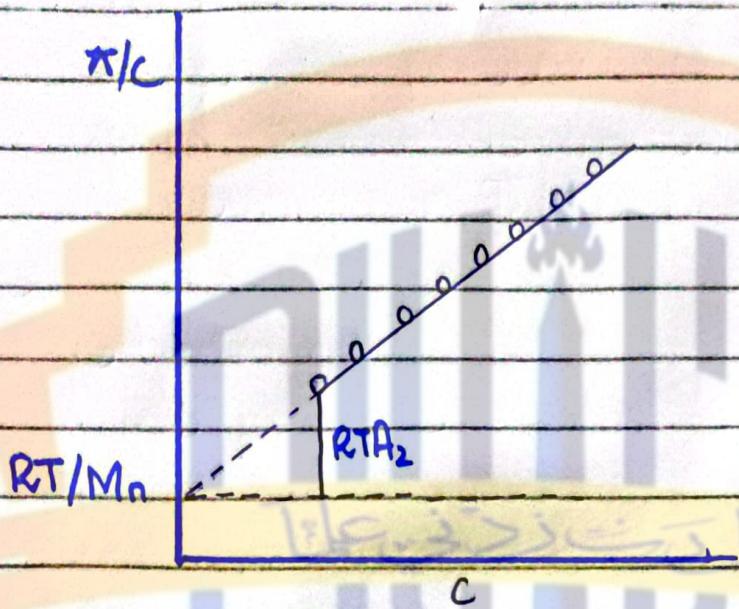
It is a modern device for measuring the osmotic pressure of polymer solution!

## Construction

It consists of two metal blocks holding a cellophane disc in between each block carrier a capillary tube. The hollow metal compartments are charged with solvent and solution through the side tubes. Osmosis occurs across the semipermeable membrane (cellophane disc). The height of solution

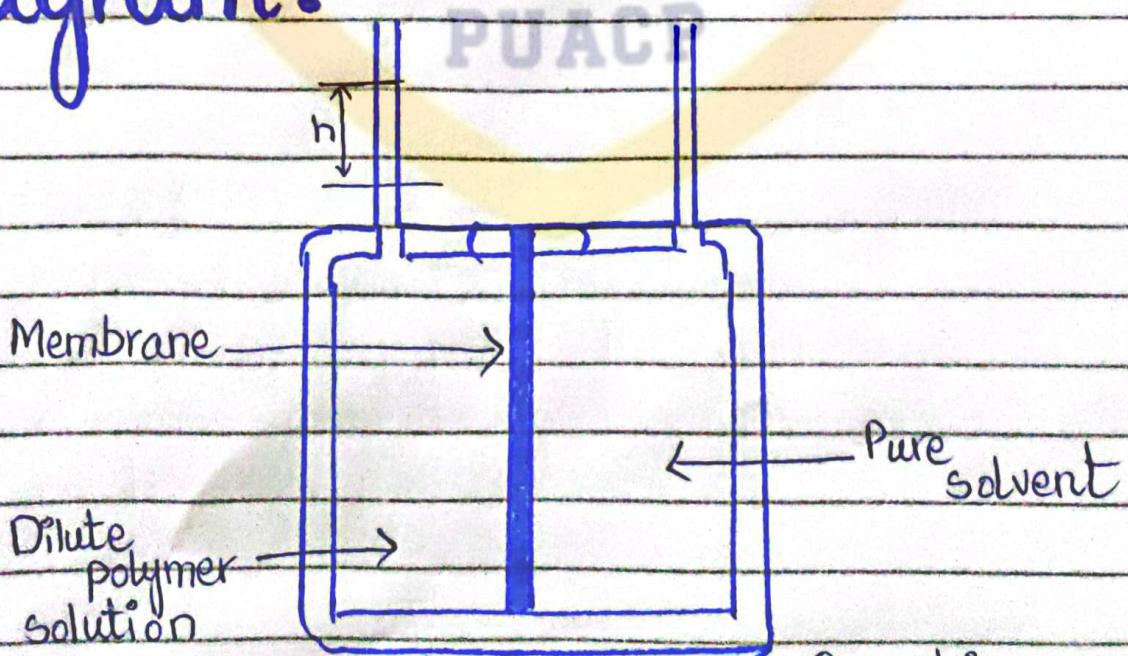
in the capillary ( $h$ ) is read off differentially to eliminate surface tension effect.

## Graph:-



plot  $\pi/c$  versus  $C$ :  
giving intercept =  $RT/M$

## Diagram:-



Fuo-Mead Osmometer for measuring Osmotic-pressure of polymer Solution.