SURFACE CHEMISTRY: ADSORPTION AND COLLOIDS

I. ADSORPTION (05 LECTURES)

1. Physical and Chemical Adsorption

Adsorption is the phenomenon where a substance (adsorbate) accumulates on the surface of another substance (adsorbent). It is a surface phenomenon.

Distinction between Physical and Chemical Adsorption:

Feature	Physical Adsorption (Physisorption)	Chemical Adsorption (Chemisorption)
Nature of Force	Weak van der Waals forces	Strong chemical bonds (covalent or ionic)
Heat of Adsorption	Low (20-40 kJ/mol)	High (80-400 kJ/mol)
Reversibility	Reversible	Irreversible (usually)
Specificity	Non-specific	Highly specific
Effect of Temperature	Decreases with increasing temperature	Increases with increasing temperature (initially)
Layer Formation	Multilayer possible	Monolayer formed
Activation Energy	Low	High

2. Freundlich Adsorption Isotherm

An empirical relationship between the amount of adsorbate adsorbed per unit mass of adsorbent and the pressure of the adsorbate at a given temperature.

Equation: $\frac{x}{m} = kP^{1/n}$

Where:
- x = mass of adsorbate adsorbed
- m = mass of adsorbent

- P = pressure of adsorbate
- k and n are constants that depend on the nature of adsorbate and adsorbent, and temperature.

For better linear representation, the equation is often written in logarithmic form:

\log\left(\frac{x}{m} ight) = \log k + \frac{1}{n} \log P

A plot of $\log(x/m)$ versus $\log P$ yields a straight line with slope $1/n$ and intercept $\log k$.

Assumption: The amount adsorbed is a function of pressure only (at constant temperature).

Numerical Problem (Freundlich Isotherm):

Nitrogen gas is adsorbed on a solid surface at 293 K. The following data are obtained:

Pressure (10^{-1} Pa)	**Amount Adsorbed (cm^3 g^{-1})**
10.0	2.5
20.0	4.0
30.0	5.0
40.0	5.8
50.0	6.5

Assuming the Freundlich adsorption isotherm applies, calculate the constants k and n . Also, predict the amount adsorbed at 60.0 x 10^{-1} Pa.

3. Langmuir Adsorption Isotherm

An empirical model that assumes adsorption occurs on a homogeneous surface with a finite number of adsorption sites, and only monolayer formation is possible. It is based on kinetic considerations.

Equation: $\frac{P}{x/m} = \frac{1}{bV_m} + \frac{P}{V_m}$

Where:
- V_m = volume of adsorbate gas adsorbed at STP to form a monolayer on the adsorbent surface.
- b = a constant related to the adsorption energy and temperature.

A plot of $\frac{P}{x/m}$ versus P yields a straight line with slope $1/V_m$ and intercept $1/(bV_m)$.

Assumptions:
1. Adsorption sites are energetically homogeneous.
2. Adsorption is limited to monolayer formation.
3. Adsorbed molecules do not interact with each other.
4. Adsorption is reversible.

Numerical Problem (Langmuir Isotherm):

Adsorption of a gas on a solid surface at a particular temperature gives the following data:

Pressure (Pa)	Volume Adsorbed ($cm^3\ g^{-1}$)
200	10.0
400	15.0
600	18.0
800	20.0
1000	21.5

Using the Langmuir adsorption isotherm, determine the volume of gas adsorbed at STP required to form a monolayer (V_m) and the constant b .

4. Multilayer Adsorption and BET Isotherm

At higher pressures, physical adsorption can lead to multilayer formation because the forces are still significant even for adsorbed molecules. The Brunauer-Emmett-Teller (BET) theory describes multilayer adsorption.

BET Isotherm Equation:

\frac{p}{V(p_0 - p)} = \frac{1}{cV_m} + \frac{c-1}{cV_m} \left(\frac{p}{p_0} ight)

Where:
- p = equilibrium pressure of the adsorbate gas.
- p_0 = saturation vapor pressure of the adsorbate at the given temperature.
- V = volume of gas adsorbed at pressure p .
- V_m = volume of gas adsorbed at STP to form a monolayer.
- c = BET constant, related to the heat of adsorption of the first layer and the heat of liquefaction of the adsorbate.

A plot of $\frac{p}{V(p_0-p)}$ versus $\frac{p}{p_0}$ gives a straight line with slope $\frac{c-1}{cV_m}$ and intercept $\frac{1}{cV_m}$.

The BET isotherm is crucial for determining the surface area of solid materials by adsorbing inert gases like Nitrogen at low temperatures.

5. Gibbs Adsorption Isotherm and Surface Excess

The Gibbs adsorption isotherm relates the surface excess concentration (Γ) to the change in surface tension (γ) with concentration (C) of a solute.

Gibbs Adsorption Isotherm:

\Gamma = -\frac{1}{RT} \left(\frac{d\gamma}{d\ln C} ight)_T

Where:
- Γ = surface excess concentration (moles per unit area).
- R = gas constant.
- T = absolute temperature.
- γ = surface tension.
- C = concentration of the solute.

A negative value of $d\gamma/dC$ (which is typical for surface-active substances) implies a positive surface excess ($\Gamma > 0$), meaning the solute concentrates at the surface. Such substances are called surfactants.

6. Heterogeneous Catalysis (Single Reactant)

In heterogeneous catalysis, the catalyst is in a different phase from the reactants. Adsorption plays a vital role. Reactants adsorb onto the catalyst surface, undergo reaction, and then the products desorb.

For a single reactant undergoing decomposition on a surface:

A(g) → Products

The rate of reaction is often dependent on the degree of surface coverage, which is governed by adsorption principles (e.g., Langmuir kinetics).

II. COLLOIDS (05 LECTURES)

1. Lyophobic and Lyophilic Sols

Colloidal systems consist of dispersed phase particles within a dispersion medium. Based on the interaction between the dispersed phase and the dispersion medium, they are classified as:

- **Lyophobic Sols** (Solvent-repelling): These are inherently unstable and require stabilizing agents. The dispersed particles have little or no affinity for the dispersion medium. Examples: Metal sols (gold, silver), sulfur sols.
- **Lyophilic Sols** (Solvent-attracting): These are relatively stable and do not easily precipitate. The dispersed particles have a strong affinity for the dispersion medium, forming solvated shells. Examples: Starch in water, gum in water, gelatin in water.

2. Origin of Charge and Stability of Lyophobic Colloids

Lyophobic colloids possess an electric charge on their surface. The origin of this charge can be:

- Preferential adsorption of ions from the dispersion medium.
- Dissociation of surface molecules into ions.
- Imparting of charges by the addition of an electrolyte.

Stability: The presence of like charges on colloidal particles prevents them from aggregating, leading to stability. This electrical repulsion overcomes the van der Waals attractive forces.

3. Coagulation and Schultz-Hardy Rule

Coagulation (or Flocculation): The process by which colloidal particles aggregate and settle down under the influence of an added electrolyte or by heating/cooling, or by mixing two oppositely charged sols.

Schultz-Hardy Rule: The coagulating power of an electrolyte is directly proportional to the magnitude of the charge on the flocculating ion (the ion of the electrolyte that carries the charge opposite to that of the colloid).

For a negatively charged sol, the coagulating power of cations follows the order:

$Al^{3+} > Ba^{2+} > K^{+}$

For a positively charged sol, the coagulating power of anions follows the order:

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

The minimum concentration of an electrolyte required to cause precipitation is called the flocculation or coagulation value.

Numerical Problem (Schultz-Hardy Rule):

Which of the following electrolytes is most effective in coagulating a negatively charged sol? Why?
a) NaCl
b) $CaCl_2$
c) $AlCl_3$

4. Zeta Potential and Stern Double Layer (Qualitative Idea)

Electrical Double Layer: When ions are adsorbed onto the surface of colloidal particles, they attract oppositely charged ions from the surrounding medium. This forms a diffuse layer of counter-ions around the particle. This system of a charged particle surface and the diffuse layer of oppositely charged ions is known as the electrical double layer.

Zeta Potential: The potential difference between the diffuse layer and the bulk of the dispersion medium is called the zeta potential. It is a measure of the electrostatic repulsion between colloidal particles. A higher zeta potential generally indicates greater stability.

5. Tyndall Effect

The scattering of light by colloidal particles is known as the Tyndall effect. When a beam of light passes through a colloidal solution, the path of the light beam becomes visible due to scattering. This is because the size of colloidal particles is comparable to the wavelength of visible light.

6. Electrokinetic Phenomena (Qualitative Idea Only)

These are phenomena that arise from the motion of charged particles or charged fluid relative to a stationary charged surface. Examples include electrophoresis (movement of colloidal particles under an electric field) and electroosmosis (movement of fluid relative to a stationary charged surface).

7. Stability of Colloids and Zeta Potential

The stability of lyophobic colloids is primarily due to the electrostatic repulsion arising from the positive or negative charge on their surfaces. The zeta potential quantifies this potential barrier. A sufficiently high zeta potential (usually > 25-30 mV) provides stability, while a lower zeta potential (approaching 0 mV) leads to instability and coagulation.

8. Micelles, Reverse Micelles; Micellization Equilibrium

Micelles: In aqueous solutions, surfactants (surface-active agents) can form aggregates called micelles above a certain concentration known as the Critical Micelle Concentration (CMC). In micelles, the hydrophobic tails of surfactant molecules turn inwards, away from water, forming a hydrophobic core, while the hydrophilic heads remain on the surface, interacting with water. These are common in detergent action and biological membranes.

Reverse Micelles: In non-polar organic solvents, reverse micelles can form. Here, the hydrophilic heads are in the core, shielded from the non-polar solvent, and the hydrophobic tails extend outwards into the solvent.

Micellization Equilibrium: The formation of micelles is an equilibrium process between individual surfactant molecules and the aggregated micellar form.

9. Thermodynamics of Micellization

Micellization is a spontaneous process that is driven by a decrease in Gibbs free energy (ΔG_{mic}).

$$\Delta G_{mic} = \Delta H_{mic} - T\Delta S_{mic}$$

Micellization is generally favored by:

- A negative or slightly positive enthalpy change (ΔH_{mic}), often due to van der Waals interactions in the micellar core.
- A significant positive entropy change (ΔS_{mic}), primarily due to the release of ordered water molecules from around the hydrophobic tails of the surfactant monomers when they aggregate into micelles.