Colloidal Dispersions:

I. Introduction & Basic Concepts

- **Definition:** A heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance (dispersion medium). Particle size is intermediate between true solutions and suspensions (approx. 1 nm to 1000 nm).
- **Key Distinction:** Not homogeneous (like true solutions) and not settling (like suspensions).
- **Phases:**
    - **Dispersed Phase:** The substance present in colloidal form.
    - **Dispersion Medium:** The medium in which the colloidal particles are dispersed.
- **Types (on basis of state of dispersed phase & medium):** (Refer to common table, e.g., solid in liquid = sol, liquid in gas = aerosol, solid in gas = aerosol, liquid in liquid = emulsion, gas in liquid = foam, etc.)
    - **Aerosols:** Solid/Liquid in Gas
    - **Sols:** Solid in Liquid
    - **Emulsions:** Liquid in Liquid
    - **Foams:** Gas in Liquid/Solid
    - **Gels:** Liquid in Solid

II. Classification of Colloids

- **A. Based on Physical State of Dispersed Phase and Dispersion Medium:** (See common table, e.g., milk is liquid in liquid emulsion, smoke is solid in gas aerosol, fog is liquid in gas aerosol, paint is solid in liquid sol, etc.) – **Be able to give examples!**
- **B. Based on Nature of Interaction between Dispersed Phase and Dispersion Medium:**
    - **1. Lyophilic Colloids (Solvent-Loving):**
        - **Nature:** Strong affinity between dispersed phase and medium.
        - **Examples:** Starch, gum, gelatin, proteins in water.
        - **Preparation:** Direct mixing (spontaneous).
        - **Stability:** Highly stable due to solvation layer and charge.
        - **Reversibility:** Reversible (if medium evaporated, can be reconstituted).
        - **Viscosity:** High viscosity.
        - **Surface Tension:** Lower than medium.
        - **Coagulation:** Difficult to coagulate; require high electrolyte concentration.
    - **2. Lyophobic Colloids (Solvent-Hating):**
        - **Nature:** Little or no affinity between dispersed phase and medium.
        - **Examples:** Metal sols (Au, Ag), metal hydroxides, sulfides in water.
        - **Preparation:** Special methods required (condensation or dispersion).
        - **Stability:** Less stable; stabilized primarily by charge repulsion.

    - **Reversibility:** Irreversible (once coagulated, cannot be easily reconstituted).
    - **Viscosity:** Similar to medium.
    - **Surface Tension:** Similar to medium.
    - **Coagulation:** Easily coagulated by small amounts of electrolytes.
  - **3. Association Colloids (Micelles):**
    - **Nature:** Formed by aggregation of molecules (e.g., soaps, detergents) above a certain concentration (Critical Micelle Concentration, CMC) and temperature (Krafft Temperature).
    - **Structure:** Hydrophilic head (polar) on surface, hydrophobic tail (non-polar) in core.
    - **Examples:** Soaps, synthetic detergents.
    - **Application:** Cleansing action (emulsification of grease).
- **C. Based on Type of Particles of the Dispersed Phase:**
  - **1. Multimolecular Colloids:**
    - **Nature:** Aggregates of many atoms/small molecules (e.g., sulfur sol, gold sol).
    - **Particle Size:** Individual particles are smaller than 1 nm, but aggregate is in colloidal range.
    - **Forces:** Held by van der Waals forces.
  - **2. Macromolecular Colloids:**
    - **Nature:** Large molecules (macromolecules) themselves are in colloidal range.
    - **Examples:** Polymers (nylon, polystyrene), starch, proteins, enzymes.
    - **Stability:** Resemble true solutions in many respects (stable).
  - **3. Associated Colloids (Micelles):** (Already covered above)

III. Preparation of Colloidal Sols

- **A. Condensation Methods (Aggregating Smaller Particles):**
  - **1. Chemical Methods:** Double decomposition, oxidation, reduction, hydrolysis.
    - *Examples:*
      - As_2S_3 sol: $2H_2S + As_2O_3 \rightarrow As_2S_3$ (sol) + $3H_2O$ (double decomposition)
      - Sulfur sol: $2H_2S + SO_2 \rightarrow 3S$ (sol) + $2H_2O$ (oxidation)
      - Gold sol: $2AuCl_3 + 3HCOOH \rightarrow 2Au$ (sol) + $3CO_2 + 6HCl$ (reduction)
      - Ferric hydroxide sol: $FeCl_3 + 3H_2O \rightarrow Fe(OH)_3$ (sol) + $3HCl$ (hydrolysis)
  - **2. Exchange of Solvent:** Substance insoluble in one solvent but soluble in another (e.g., sulfur in alcohol + water).
  - **3. Excessive Cooling:** Ice particles in ether/chloroform.
- **B. Dispersion Methods (Breaking Down Larger Particles):**
  - **1. Mechanical Dispersion:** Colloid mill (e.g., paints, inks, ointments). Grinding larger particles in a mill to colloidal size.
  - **2. Electrical Disintegration (Bredig's Arc Method):** For preparing metal sols (Au, Ag, Pt). Electric arc struck between electrodes of metal immersed in dispersion medium. Intense heat vaporizes metal, which condenses to form colloidal particles.
  - **3. Peptization:** Process of converting a precipitate into a colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte (peptizing

agent). Adsorption of ions from peptizing agent onto precipitate surface leads to repulsion and disintegration.

    - *Example:* Freshly prepared $Fe(OH)_3$ precipitate + small amount of $FeCl_3$ → $Fe(OH)_3$ sol.

IV. Purification of Colloidal Sols

- **Purpose:** To remove excess electrolytes and other soluble impurities that destabilize colloids.
- **A. Dialysis:**
  - **Principle:** Diffusion of ions and small molecules through a semi-permeable membrane, while colloidal particles (too large) are retained.
  - **Setup:** Dialyzing bag (parchment paper, cellophane) containing sol, suspended in continuously flowing pure water.
  - **Limitations:** Slow process.
- **B. Electrodialysis:**
  - **Principle:** Faster dialysis using electric field. Ions move faster towards oppositely charged electrodes.
  - **Setup:** Electrodes placed across the membrane.
- **C. Ultrafiltration:**
  - **Principle:** Forcing sol through special filters (ultrafilters) with pores smaller than colloidal particles, but large enough for solvent and small impurities.
  - **Preparation of Ultrafilters:** Collodion solution (nitrocellulose in alcohol/ether) hardened by formaldehyde.
  - **Application:** More effective for separating colloids from impurities.

V. Properties of Colloidal Dispersions

- **A. Colligative Properties:**
  - Colloidal particles are aggregates, so number of particles is small.
  - Osmotic pressure, freezing point depression, boiling point elevation, relative lowering of vapor pressure are *small* compared to true solutions of same concentration.
- **B. Tyndall Effect:**
  - **Phenomenon:** Scattering of light by colloidal particles when a beam of light is passed through the sol, making the path visible.
  - **Conditions:**
    1. Diameter of dispersed particles not much smaller than wavelength of light used.
    2. Refractive indices of dispersed phase and dispersion medium must differ appreciably.
  - **Applications:**
    - Distinguishes true solutions (no Tyndall effect) from colloids.
    - Used in ultramicroscope to observe colloidal particles indirectly.
- **C. Color:**
  - Dependent on wavelength of light scattered (which depends on particle size, nature,

  and observer's position).
  - *Example:* Gold sol can be red, purple, blue, gold depending on particle size.
- **D. Brownian Movement:**
  - **Phenomenon:** Continuous, random, zigzag motion of colloidal particles.
  - **Cause:** Unbalanced bombardment by molecules of the dispersion medium.
  - **Importance:** Provides evidence for kinetic theory of matter; prevents particles from settling (stability).
- **E. Electrical Properties:**
  - **1. Charge on Colloidal Particles:**
    - All colloidal particles in a given sol carry the same type of charge (either positive or negative). This is the *main reason for their stability* (repulsion prevents aggregation).
    - **Origin of Charge:**
      - **Preferential Adsorption of Ions:** Most common. Particles adsorb ions from the medium that are common to their own lattice or those that are preferentially adsorbed.
        - *Example:* $Fe(OH)_3$ sol (prepared from $FeCl_3$): $Fe(OH)_3 + Fe^{3+} \longrightarrow Fe(OH)_3/Fe^{3+}$ (positive sol). Or As_2S_3 sol: $As_2S_3 + S^{2-} \longrightarrow As_2S_3/S^{2-}$ (negative sol).
      - **Adsorption of Dipolar Molecules:** (e.g., soaps, proteins).
      - **Dissociation of Surface Molecules:** (e.g., proteins).
    - **Common Positive Sols:** Hydrated metal oxides ($Fe(OH)_3$, $Al(OH)_3$), basic dyes (methylene blue), hemoglobin.
    - **Common Negative Sols:** Metal sols (Au, Ag, Pt), metal sulfides (As_2S_3, CdS), acid dyes (Congo red), starch, gum.
  - **2. Electrophoresis (Cataphoresis):**
    - **Phenomenon:** Movement of charged colloidal particles under an applied electric field towards the oppositely charged electrode.
    - **Applications:** Determining charge on sol particles, separating charged particles.
  - **3. Electro-osmosis:**
    - **Phenomenon:** Movement of dispersion medium (solvent) relative to the stationary dispersed phase under an applied electric field. Occurs when colloidal particles are prevented from moving.
  - **4. Zeta Potential (Electrokinetic Potential):**
    - **Concept:** The potential difference between the fixed layer and the diffuse layer of opposite charge in the electrical double layer around a colloidal particle.
    - **Significance:** Higher zeta potential means greater repulsion between particles, leading to greater stability of the sol.
- **F. Coagulation/Flocculation/Precipitation:**
  - **Definition:** The process of aggregation of colloidal particles to form larger particles which settle down.
  - **Methods of Coagulation:**
    - **1. By Electrophoresis:** Particles move to electrode, lose charge, coagulate.

        - **2. By Mixing Two Oppositely Charged Sols:** Mutual coagulation (e.g., positive $Fe(OH)_3$ sol + negative As_2S_3 sol).
        - **3. By Boiling:** Increases collisions, removes adsorbed layer, reduces charge.
        - **4. By Persistent Dialysis:** Removes stabilizing electrolyte, leading to coagulation.
        - **5. By Adding Electrolytes:** *Most important method.*
            - **Hardy-Schulze Rule:**
                - The coagulating power of an electrolyte is directly proportional to the valency of the active ion (the ion carrying charge opposite to that on the colloidal particles).
                - *Example:* For a negative sol (e.g., As_2S_3), the coagulating power of cations follows: $Al^{3+} > Ba^{2+} > Na^+$.
                - For a positive sol (e.g., $Fe(OH)_3$), the coagulating power of anions follows: $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$.
            - **Flocculation Value:** Minimum concentration of an electrolyte required to cause coagulation of a sol in 2 hours. Lower flocculation value means higher coagulating power.
- **G. Protection of Colloids:**
    - **Concept:** Lyophilic colloids can protect lyophobic colloids from coagulation.
    - **Mechanism:** Lyophilic colloid forms a protective layer around lyophobic particles, preventing them from coming together and also contributing to stability through solvation.
    - **Gold Number:** Minimum weight of a protective colloid (in milligrams) which prevents the coagulation of 10 mL of a standard gold sol when 1 mL of 10% NaCl solution is added to it. Lower gold number indicates higher protective power. (Gelatin has a low gold number, high protective power).
    - **Conductivity Test:** O/W shows higher conductivity than W/O (due to continuous water phase).
- **Demulsification:** Breaking an emulsion into its constituent liquids.
    - **Methods:** Boiling, freezing, centrifugation, adding electrolytes, adding demulsifiers.

VII. Applications of Colloids

- **Medicine:** Colloidal medicines are more effective due to large surface area and easy absorption (e.g., Argyrol - silver sol as eye lotion, milk of magnesia, colloidal gold/calcium/iron).
- **Industry:**
    - **Purification of Water:** Alum (Al_2O_3) used to coagulate suspended impurities.
    - **Smoke Precipitation (Cottrell Precipitator):** Electrostatic precipitation of carbon particles from smoke in chimneys.
    - **Tanning:** Animal hides (positively charged protein) treated with negatively charged tannin to form leather.
    - **Rubber Industry:** Latex (negatively charged rubber particles) is coagulated with acid to form rubber.

  - **Photography:** Gelatin (protective colloid) with AgBr in photographic plates.
  - **Dyeing:** Colloidal dyes adsorbed by fabrics.
  - **Cleansing Action of Soaps/Detergents:** Micelle formation.
  - **Sewage Disposal:** Electrical precipitation of sewage particles.
  - **Formation of Deltas:** River water (colloidal clay) coagulates upon meeting sea water (electrolytes).
- **Everyday Life:** Milk, butter, cheese, ink, paints, blood (albuminous substance is a protective colloid), fog, clouds.