EWC 105
Environmental Chemistry

Lecture 4

Instructor

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Lecture Details

Topics	Sub-Topics	Reference
Non-aqueous phases in water	• Dissolved gases in water, Henry's Law to gas solubility • Solubility of solids in water • Solubility product • Colloidal suspensions in water • Ionic double layer theorem for colloidal particles	**Environmental Chemistry** – **Stanley E. Manahan** 8th ed. CRC Press.

Solubility of Gases in Water

Dissolved gases in water like

- **O_2** (essential for **fish)**
- **CO_2** (essential for **photosynthetic algae)**

- are crucial to the welfare of living species in water.

- The solubilities of gases in water are calculated by **Henry's Law.**

Solubility of Gases in Water

Henry's Law

- At constant temperature, the solubility of a gas is proportional to the partial pressure of the gas in contact with the liquid.

- For a gas – X, this law applies to the equilibria as follows:

$$X\,(g) \leftrightarrow X\,(aq)$$

Solubility of Gases in Water

Henry's Law

- Mathematically, Henry's Law is expressed as –

$$[X\,(aq)] = K\,P_x$$

where, **[X(aq)]** = aqueous concentration of gas

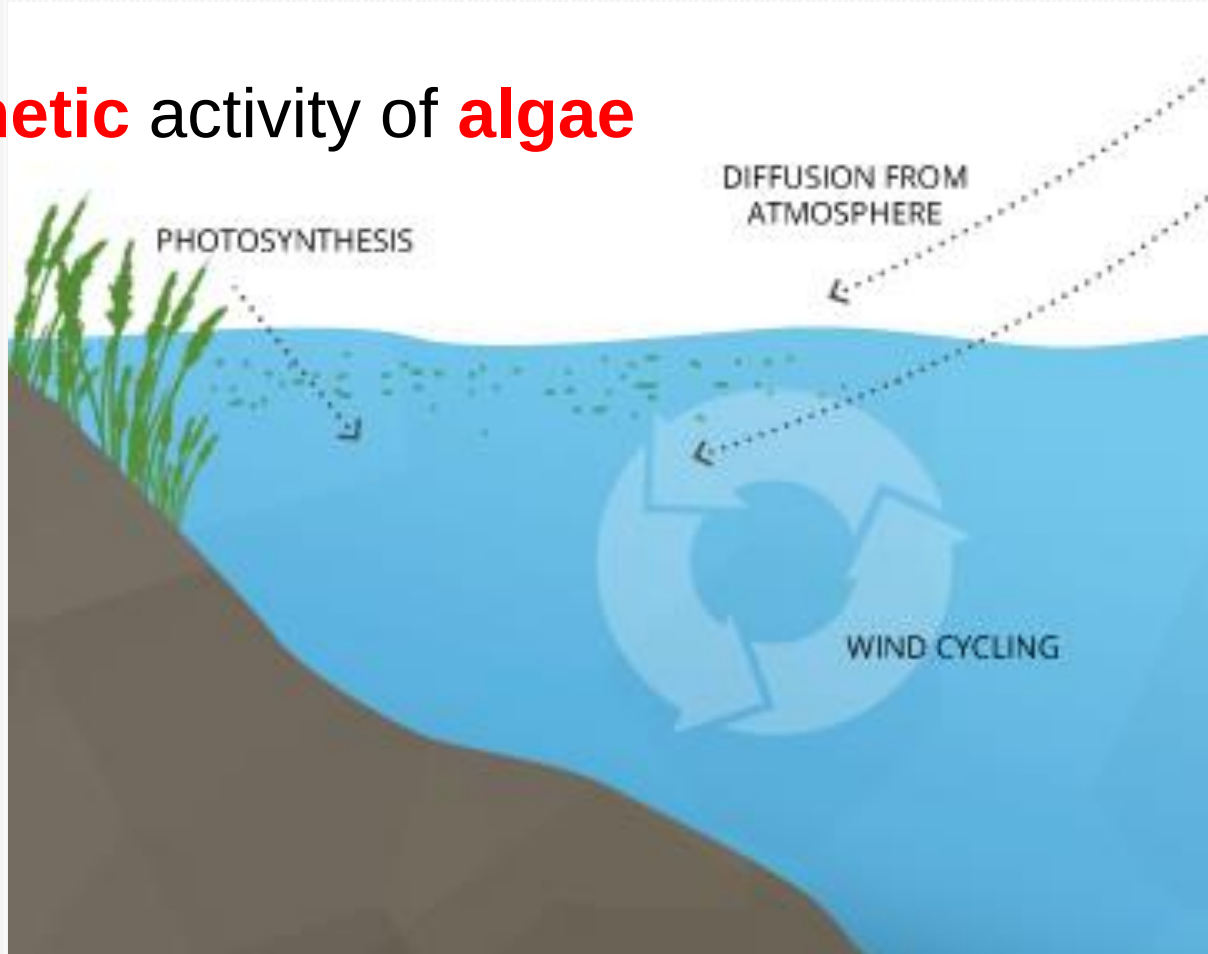
P_x = partial pressure of the gas

K = Henry's Law constant,
(applicable to a particular gas at a specified temperature)

Dissolved Oxygen in Water

Sources of aquatic O_2

- Mostly comes from **atmosphere** (20.95% by volume of dry air)
- From **photosynthetic** activity of **algae**

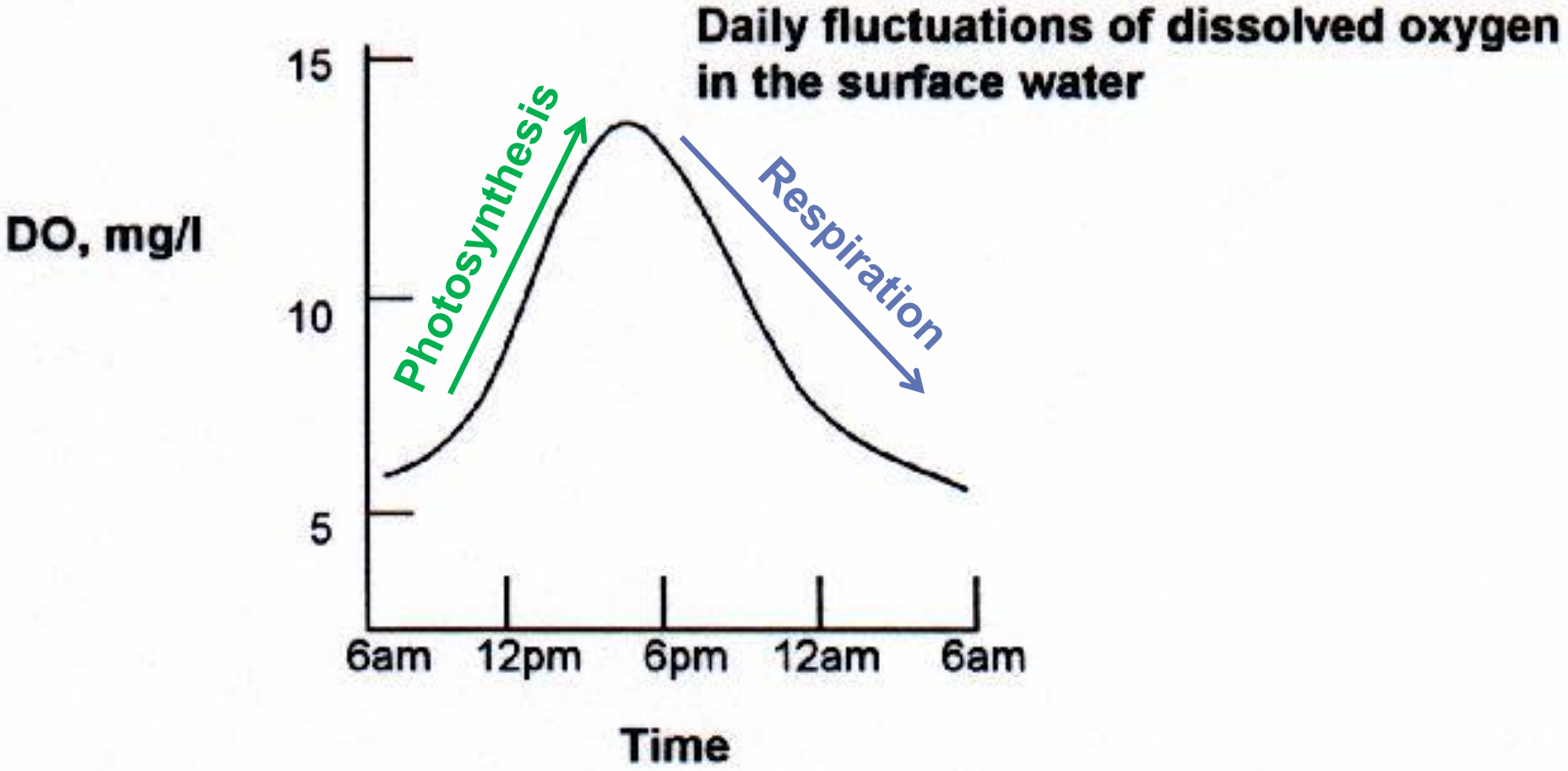


Dissolved Oxygen in Water

Sinks of aquatic O_2

- **Biodegradation** of organics, pollutants
- Metabolic activity of **algae** (during night)

Dissolved Oxygen in Water



Dissolved Oxygen in Water

Solubility of O_2 in water depends on

- Water **temperature**
- **Partial pressure** of **O_2** in **atmosphere**
- **Salt content** of water

Oxygen in Water

O_2 Solubility (maximum probable concentration)

- **Maximum dissolved O_2** concentration at **equilibrium**

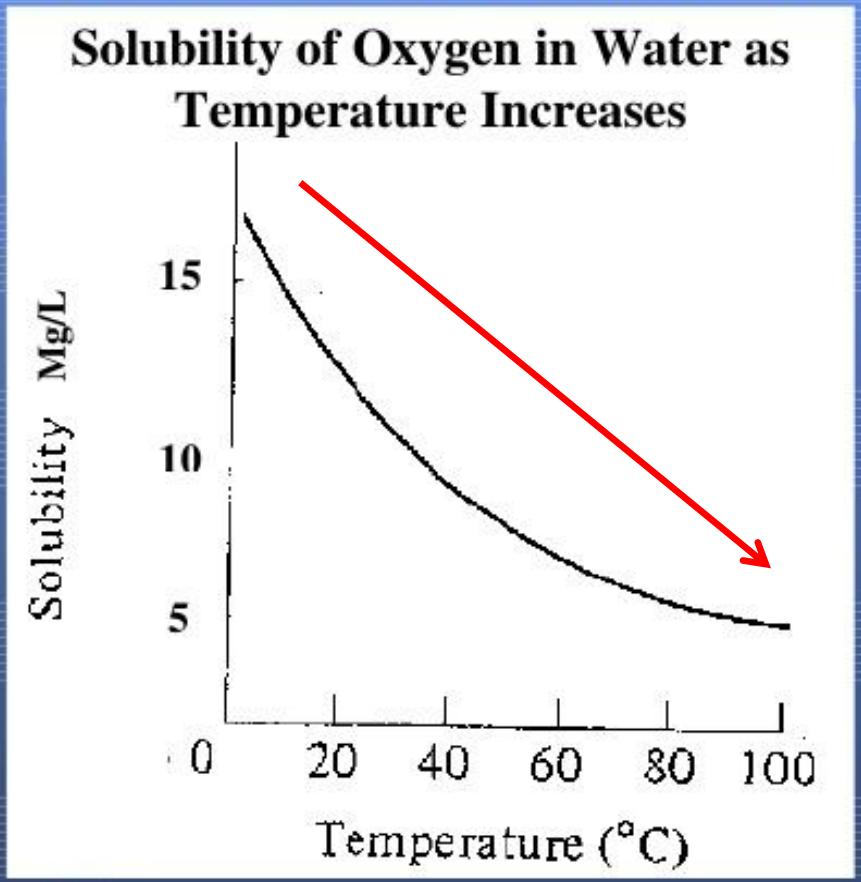
Dissolved O_2 concentration (actual concentration)

- Is limited by the **rate at which oxygen dissolves**
- **Not** the **equilibrium concentration**

Dissolved Oxygen in Water

OXYGEN: SOLUBILITY IN WATER

BACKGROUND INFORMATION



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Carbon Dioxide in Water

- The most important **weak acid** in water is **CO_2**.

Sources of CO_2 in water

- **Dissolution** from **atmosphere**
- Microbial **decay** of organic matter
- **Metabolic activity** (respiration**)** of algae
- **Dissolved CO_2** is present in virtually **all natural waters and waste waters.**

CO_2 (water) ↔ CO_2 (atmosphere)

Carbon Dioxide in Water

Sinks of CO_2 in water

- **Photosynthesis** of algae

- **Synthesis of biomass** by algae

Importance of CO_2 in water

- CO_2 and its ionization products, bicarbonate ions (HCO_3^-) and carbonate ions (CO_3^{2-}) have an important influence upon the chemistry of water.

- Concentration of HCO_3^- and CO_3^{2-} increases the solubility of CO_2 in water.

Carbon Dioxide in Water

Importance of CO_2 in water

- High concentration of free CO_2 in water may adversely affect –

  ✓ respiration
  ✓ gas exchange of aquatic animal

Equilibrium of Chemical Reactions

- Where the combination of **reactants to form products** is just **balanced** by the **reverse reaction of products combining to form reactants**.

$$A + B \leftrightarrow C + D$$

- An increase in either A or B will shift the equilibrium further to right and vice versa.

Le Chatelier's Principle of Equilibrium

- A reaction, at equilibrium, will adjust itself in such a way as to relieve any force or stress that disturbs the equilibrium.

- A chemical reaction in equilibrium can be expressed as:

$$\frac{[C][D]}{[A][B]} = K$$

K = equilibrium constant, constant at a given temperature

Le Chatelier's Principle of Equilibrium

- For the general reaction :

$aA + bB + \ldots \leftrightarrow cC + dD + \ldots$

(where, a, b, c and d are the number of molecules of respective substances)

- The equilibrium relationship is :

$$\frac{[C]^c[D]^d \ldots\ldots}{[A]^a[B]^b \ldots\ldots} = K$$

… also called as **law of mass action / mass law equation**

Activity and Activity Coefficient

- As concentration of materials increase, their quantitative effect on equilibrium becomes progressively less than that calculated solely from the change in molar concentration.

- Thus effective concentration or activity decreases below the actual molar concentration.

- Hence activities rather than concentrations should be used in equilibrium expressions (mass law expressions)

Activity and Activity Coefficient

$$K = \frac{\{C\}^c \{D\}^d .....}{\{A\}^a \{B\}^b .....}$$

$$where, \{A\} = \gamma(A)$$

here, {A} = activity of A

(A) = molar concentration of A

γ = activity coefficient

- For very dilute solutions,

γ = 1

hence, {Activity} = (Concentration)

Activity and Activity Coefficient

- For dilute aqueous solution, $\{H_2O\} = [H_2O] = 1.0$
- For sea water containing lots of dissolved salts, $\gamma_{seawater} \approx 0.98$
- For pure solids or pure liquids in equilibrium with aqueous solution, , $\{i\} = [i] = 1.0$

Ion Product of Water

$$H_2O = H^+ + OH^-$$

$$\frac{(H^+)(OH^-)}{(H_2O) \approx 1} = K_w = \text{Ion product of water}$$

$$K_w = (H^+)\,(OH^-) = 10^{-14} \text{ at } 25^\circ\ C$$

$\log K_w = -4470.99/T + 6.0875 - 0.01706T$

where, T = absolute temperature

At 0° C, $K_w = 0.12 \times 10^{-14}$

At 50° C, $K_w = 0.12 \times 10^{-14}$

Ion Product of Water

$$pH = - \log (H^+)$$

$$pK = - \log (K)$$

Thus, at 25° C, $K_w = 10^{-14}$

$$pK_w = 14$$

Ionization of Acids and Bases

- **Acid**: yields H^+ ion upon addition of water
- **Base**: yields OH^- ion upon addition of water
- **Strong Acid/ Base**: Almost completely dissociates

  If HA is a strong acid, then

$$HA = H^+ + A^-$$

$$K_A = (H^+)\ (A^-) / (HA)$$

Here, (HA) is very small, because there is almost no undissociated HA. Hence, for strong acids, K_A values are very large.

Ionization of Acids and Bases

Examples of strong acids

Perchloric Acid : $HClO_4 = H^+ + ClO_4^-$; $K_A = 10^7$

Hydrochloric Acid : $HCl = H^+ + Cl^-$; $K_A = 10^3$

Sulfuric Acid : $H_2SO_4 = H^+ + HSO_4^-$; $K_A = 10^3$

Nitric Acid : $HNO_3 = H^+ + NO_3^-$; $K_A = 10^1$

Bisulfate : $HSO_4^- = H^+ + SO_4^{2-}$; $K_A = 10^{-1.9}$

Thus, if we have

10^{-3} M HCl solution, $(H^+) \approx 10^{-3}$ M

10^{-3} M H_2SO_4 solution, $(H^+) \approx 2 \times 10^{-3}$ M

10^{-3} M NaOH solution, $(OH^-) \approx 10^{-3}$ M

Ionization of Acids and Bases

- **Weak Acid/ Base**: poorly ionized

acetic acid, $CH_3COOH = CH_3COO^- + H^+$

$$K_A = (CH_3COO^-)\,(H^+) / (CH_3COOH) = 10^{-4.7}$$

Ionization of Acids and Bases

Examples of weak acids

Carbonic Acid : $H_2CO_3 = HCO_3^- + H^+$; $K_A = 10^{-6.3}$

Hypochlorous Acid : $HOCl = H^+ + OCl^-$; $K_A = 10^{-7.6}$

Hydrogen cyanide : $HCN = H^+ + CN^-$; $K_A = 10^{-9.2}$

Boric Acid : $H_3BO_3 = H^+ + HBO_3^-$; $K_A = 10^{-9.3}$

Bicarbonate : $HCO_3^- = H^+ + CO_3^{2-}$; $K_A = 10^{-10.3}$

Solubility of Solids in Water

- All solids are soluble in water to some extent.

For example:

$$CaCO_3\ (s) = Ca^{2+} + CO_3^{2-}$$

At equilibrium, **$K = (Ca^{2+})\ (CO_3^{2-}) / (CaCO_3)\ (s)$**

[According to Le Chatelier's Principle of Equilibrium]

We know, activities of pure phase solids = 1

Hence, **$K_{sp} = (Ca^{2+})\ (CO_3^{2-})$**

Solubility Product

Similarly:

$$AgCl\ (s) = Ag^+ + Cl^-$$

At equilibrium, $K = (Ag^+)\ (Cl^-) / AgCl\ (s)$

$$\mathbf{K_{sp} = (Ag^+)\ (Cl^-)}$$

$$Ca_3(PO_4)_2\ (s) = 3\ Ca^{2+} + 2\ PO_4^{3-}$$

$$\mathbf{K_{sp} = (Ca^{2+})^3\ (CO_3^{3-})^2}$$

Thus if **a** mole of $Ca_3(PO_4)_2$ (s) dissolves, then **3a** moles of Ca^{2+} and **2a** mole of PO_4^{3-} come into solution.

Solubility Product

If for a solid, solubility product expression is given by : $(A^+)^a\ (B^-)^b = K_{sp}$, then

- $(A^+)^a\ (B^-)^b < K_{sp}$, the solution is undersaturated, more solid would eventually dissolve
- $(A^+)^a\ (B^-)^b > K_{sp}$, the solution is supersaturated, solid would tend to precipitate
- $(A^+)^a\ (B^-)^b = K_{sp}$, the solution is saturated

Colloids in Water

Example of Colloids in Water:

- Minerals
- Organic pollutants
- Proteinaceous material
- Algae
- Bacteria

Colloids in Water

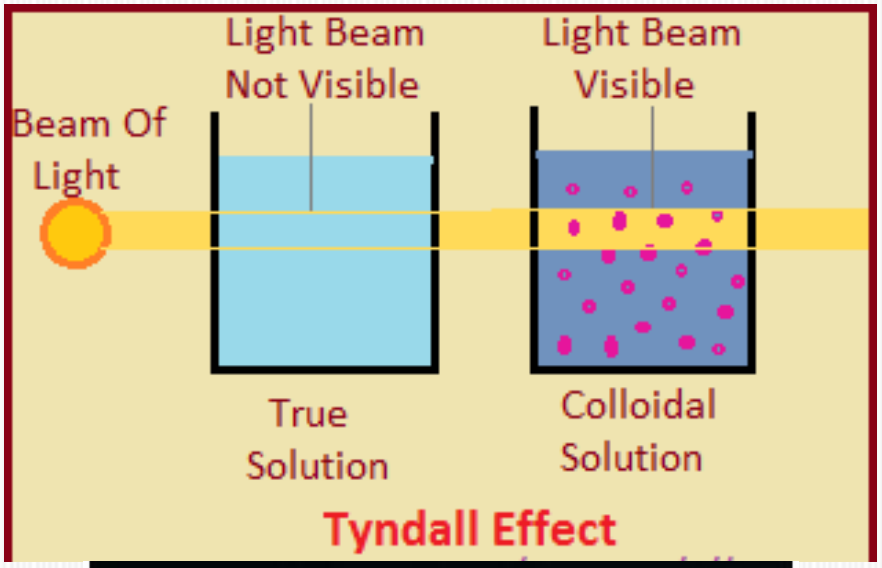
Characteristics of Colloids:

- Have characteristics of both species in solution and larger particles in suspension.
- Ranges in diameter from about 0.001 to 1 µm.
- Scatters white light as a light blue hue observed at right angles to the incident light through the colloidal suspension. It is known as **Tyndall Effect**.
- Do not separate into layers.
- Will not be trapped by a filter.

Tyndall Effect on Colloidal Particles

- Colloids and suspensions scatter light, making a beam visible, due to their large particle size.

- Solutions do not scatter light, because of their small particle size.





Colloids in Water

- Colloidal system in which the solid forms the dispersed phase and the liquid dispersion medium, has a fluid like consistency and is called as **colloidal solution or sol**.

- The particles of the dispersed phase in colloidal solution are called as **colloidal particles or sol particles or micelles**.

Colloids in Water

Importance of Colloids

- Colloidal particles in water cause turbidity and color in water.

- Colloidal particles that cause color and turbidity are difficult to separate from water because –

  ✓ the particles will not settle by gravity

  ✓ are so small that they pass through the pores of most common filtration media.

Colloids in Water

Importance of Colloids

- An important influence of colloids in aquatic chemistry is their ability to transport various kinds of organic and inorganic contaminants.

- Colloid-facilitated transport, in which contaminants bind to the surface of colloidal particles, can be an important means of moving substances that would otherwise be sorbed to sediments or aquifer rocks.

- Colloid-facilitated transport enhances the pollutants to be dissolved in water and thus aggravating the pollution scenario.

Types of Colloids in Water

- The colloidal particles are not visible under microscope but can be observed under an ultramicroscope.

Types of Colloidal solutions:

a) Lyophilic (solvent loving) called **emulsions**,

- there is an affinity between the particles of the two phases
- When water is the dispersion medium it is called hydrophilic colloid.
- Hydrophilic colloids are generally consist of macromolecules such as proteins and synthetic polymers.

Types of Colloids in Water

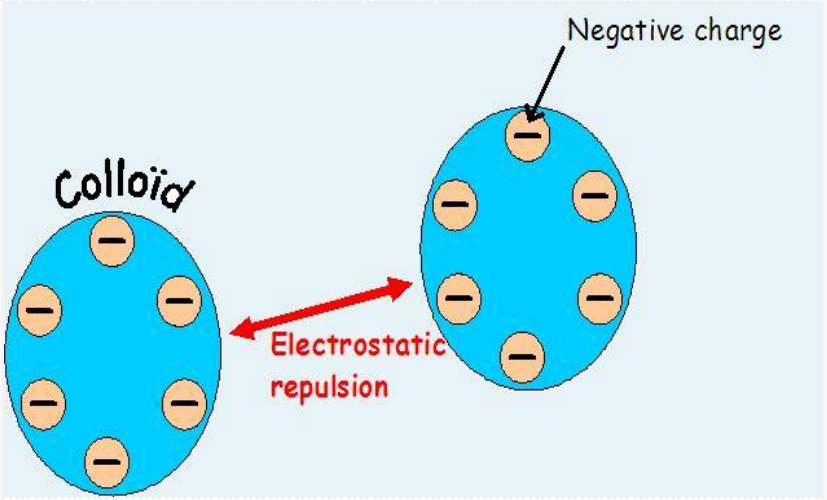
- Hydrophilic colloids are characterized by strong interaction with water, resulting in spontaneous formation of colloids when they are placed in water.

b) Lyophobic (solvent hating) called **suspensions**, When water is the dispersion medium it is called **hydrophobic**.

- Hydrophobic colloids interact to a lesser extent to water and are stable because of their positive or negative electrical charge.

Electrostatic Properties of Colloidal Particles

- The colloidal particles constituting the dispersal phase carry an electric charge probably due to the preferential adsorption of ions present in the dispersion medium.



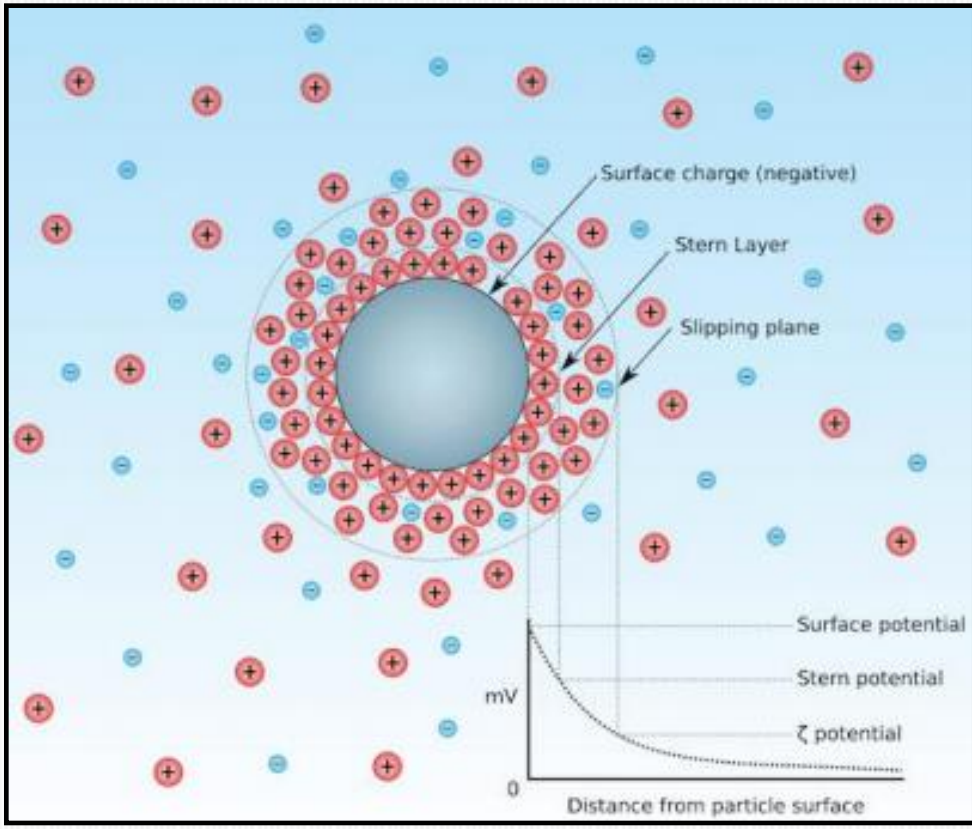
- All these colloidal particles in a particular colloidal system carry electric charge of the same sign.

- Thus all colloidal particles are charged with either positive or negative charge.

Electrostatic Properties of Colloidal Particles

- As a result, they repel each other and remain dispersed in the dispersion medium and Gravitational settling does not occur

- If the colloidal solution is placed under an electric field, all these particles move towards the oppositely charged pole.



Electrical Double Layer of Colloidal Particles

- Development of a net charge at the colloidal particle surface affects the distribution of ions in the surrounding interfacial region.
- As a result, concentration of counter ions increase at the surface.
- Thus, an electrical double layer exists around each particle.

