

Electrokinetic effects -

The relative movement, with respect, to one another, of a solid and a liquid is accompanied by certain electrical phenomena.

Electrokinetics -

Science of the generation of an electric current by moving a non-conductor by an electric field.

Electrokinetic phenomena result from differential movement of two phases where the interface is an electrical double layer.

Electrokinetic phenomena -

① Electrophoresis - movement of electrically charged particles (solid, liquid or gaseous) in an electric field with liquid as second phase.

② Sedimentation potential - (reverse electrophoresis) - Generation of electrical potential by movement of solid or liquid particle in liquid caused by particles' sedimentation or coagulation.

③ Electro-osmosis - Movement of a liquid along a solid or liquid surface driven by an electric field.

In Galvanic cell -

Potential develops at any interface or junction, where there is a separation of charge.

Ex. potential can develop when metal electrode comes in contact with a solution containing its cation.

Electrical double layer -

Presence of charge on colloidal surface influences the distribution of surrounding ions in dispersion medium and distribution of charge.

Ions of opposite charge (counter ions) are attracted towards surface leading to formation of double layer.

Occurs between ions/molecules in solution and electrode surface.

There is strong attraction between both.

It uses to visualize the ionic environment in charged surface.

Where ? Why ???

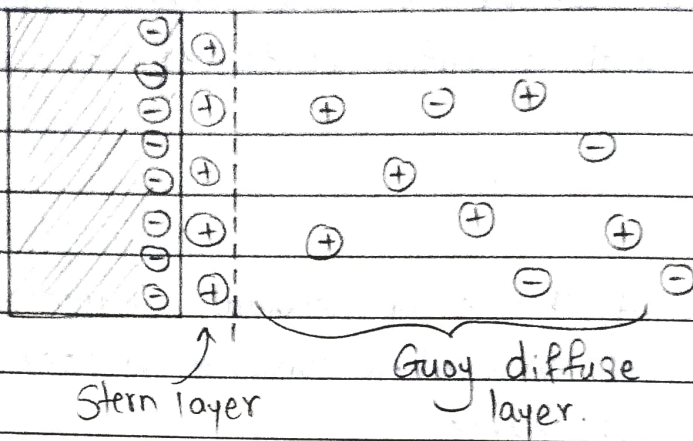
The ion distribute surrounding charged surface. Increases conc. of counter ions.

Liquid droplet, solid particles, gas bubble use as object.

- Preferential adsorption of ions.
- Dissociation of surface charged species.
- Isomorphous replacements.
- Charge crystal replacement.

Electrical double layer consists of -

1. Diffuse double layer
2. Stern layer (tightly bound layer)



1. Diffuse double layer -

Loosely associated layer

Also called bulk liquid layer.

There are excess of negative ion after uniform distribution

2. Stern layer -

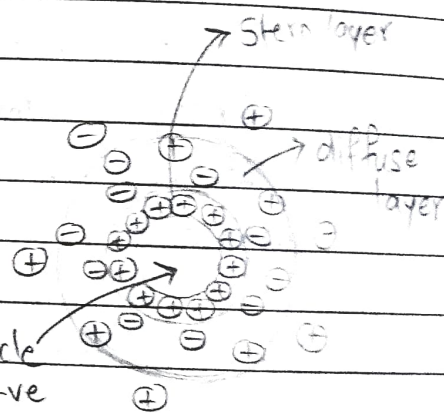
Inner region

Ions adsorbed due to chemical interaction.

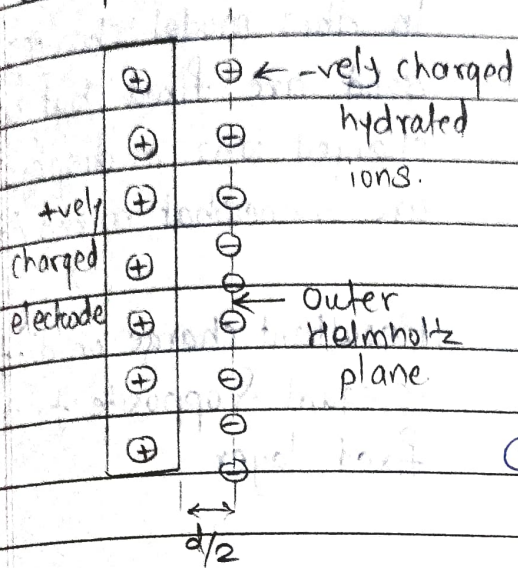
with -ve surface charge

Cations are adsorbed by negative surface.

Counter ions is positive charged cations.



Concept of electrical double layer -



Theory of electrical double layer first proposed by Helmholtz in 1879 and later modified by Stern and others.

Helmholtz suggested -

① electrical double layer of \oplus & \ominus charges is formed at surface of two phases.

② The distance of separation of two layers is fixed since the layers are charges are assumed to be fixed (adsorbed layer of ions on solid surface is fixed and so also a layer of oppositely charged ions in the solution)

If D - dielectric constant of medium

l - distance of separation of 2 oppositely charged layers

σ - charge density (amt. of charge / sq. cm) of each layer

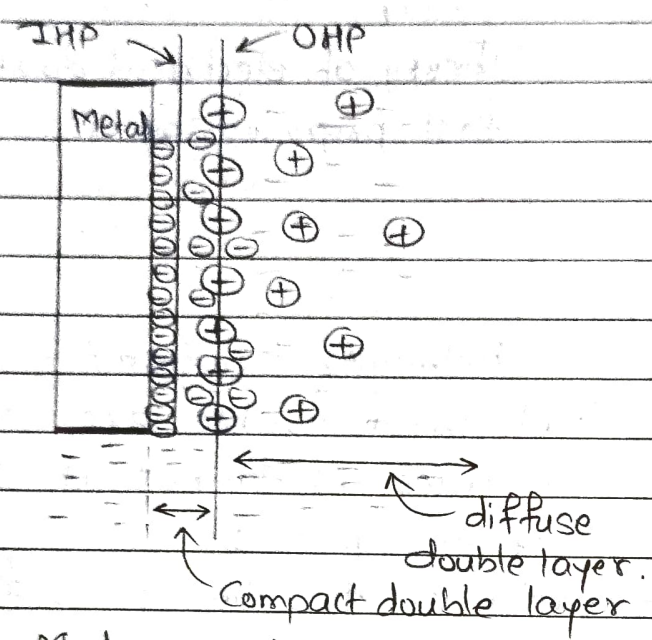
Potential difference between the two sides of the double layer is

$$P.D. = \frac{\sigma \cdot l}{D \cdot \epsilon^0}$$

Limitations / Drawbacks -

fixed nature of ions in the dispersion medium is not convincing since the thermal motion of liquid molecule tend to diffuse this layer.

Stern model of EDL -



Modern model.

In this model charges on solid are fixed but oppositely charged ions in dispersion med are somewhat mixed/diffused.

Resultant charge on diffuse layer is equal & opposite to that of fixed layer.

Potential difference bet fixed layer & diffused layer is zeta potential/electrokinetic potential (ζ).

- Stern theory eliminating the point-charge approximation of diffuse layer theory.
- G-C assumes that there is no physical limits for ions in their approach to surface, which is not true.
- First ions of G-C diffuse layer are not at surface, but some distance from the surface, the distance usually equal to radius of ions.
- Second is that the stern theory in dividing the solution charge into two contributions.

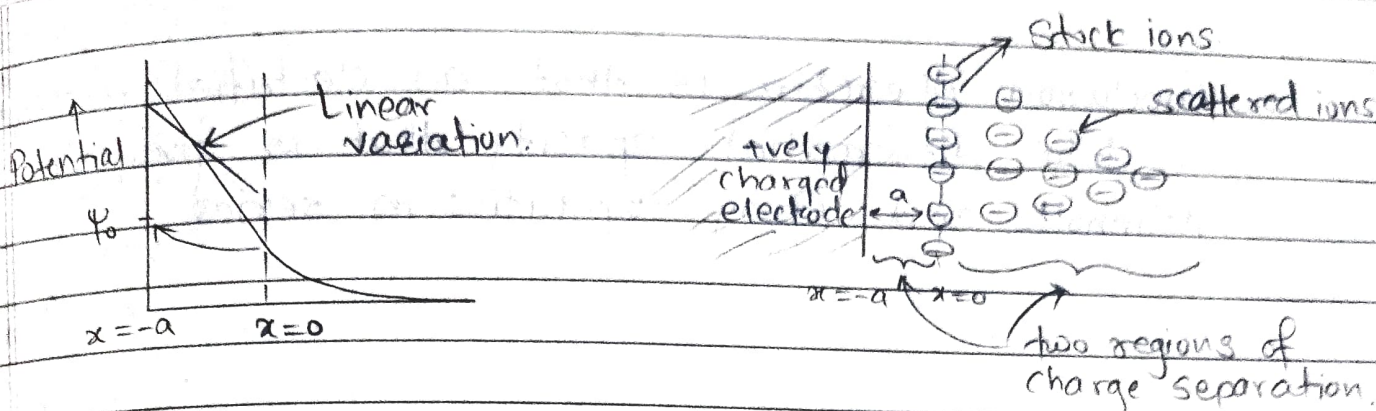
- Some of the ions are specifically adsorbed, close to the electrode in the OHP.

- Remaining is diffusely spread out in the solution.

$$q_s = q_H + q_G$$

↑ Stern charge
↑ Helmholtz - Perrin charge
← Guoy - Chapman charge.

However, the charges are separated, potential drops result.



The Stern model implies, therefore, 2 potential drops

i.e. $\phi_m - \phi_{\text{bulk}} = (\phi_m - \phi_H) + (\phi_H - \phi_{\text{bulk}})$

ϕ_m - inner potential of metal

ϕ_H - inner potential of Helmholtz plane

ϕ_{bulk} - potential in bulk of the solution

On differentiating P.D. across interface w.r.t. charge on metal, q_m

$$\frac{\partial(\phi_m - \phi_{\text{bulk}})}{\partial q_m} = \frac{\partial(\phi_m - \phi_H)}{\partial q_m} + \frac{\partial(\phi_H - \phi_{\text{bulk}})}{\partial q_m}$$

In the denominator of last term, one can replace ∂q_m with ∂q_d 'cause total charge on electrode is equal to total diffuse charge.

$$\frac{\partial(\phi_m - \phi_{\text{bulk}})}{\partial q_m} = \frac{\partial(\phi_m - \phi_H)}{\partial q_m} + \frac{\partial(\phi_H - \phi_{\text{bulk}})}{\partial q_d}$$

Each term represents reciprocal of differential capacity, hence, eqⁿ can be rewritten as -

$$\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_d}$$

C - total capacity of interface, is the H-P capacity and G-C capacity.

Expression for total capacity displayed by two capacitors in series.

Conclusion therefore is that an electrified interface has a total differential capacity that is given by the Helmholtz and Gouy capacities in series.

Gouy - Chapman Model

- Concept of Helmholtz involving a sharp potential gradient, which was modified by Gouy - Chapman.
- G-C assumed that behaviour of ions in the vicinity of the electrode is affected by
 1. Electric force arising from charge on metal.
 2. Simple thermal agitation.
- Excess charge density on OHP is not equivalent to that on metal, but it is less.
- Some of the solvated ions leave their 2nd row seats and random walk in the solution.
- Excess charge density in solution decreases with distance from electrode.
- Net charge density is zero, because +ve and -ve ions are equal.

- so called diffuse double layer, by definition, the solution side of the double layer is not merely one molecule or so, in thickness extends to some distance in the liquid.

- K.E. of counter ions will, in part, affect the thickness of diffuse double layer.

- G.C. developed diffuse double layer in which the charge in conc. of counter ions near a charged surface, follows the Boltzmann distribution.

$$n = n_0 \cdot e^{-ze\psi/kT}$$

n_0 - bulk concentration

z - charge of the ion.

e - charge on a proton.

k - Boltzmann constant

ψ - potential difference.

Combining the Boltzmann distribution with Poisson eqⁿ, yields the electrical potential as a function of distance from the surface.

The thickness of double layer -

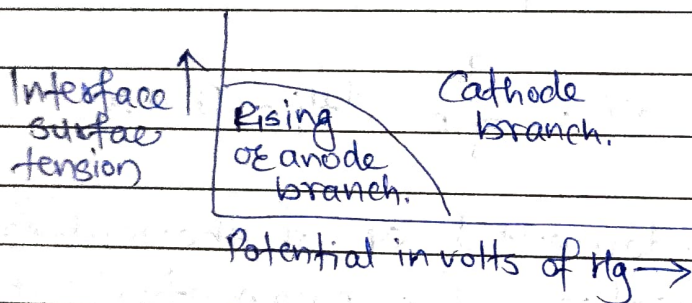
$$\lambda_{dl} = \left[\frac{\epsilon_r kT}{4\pi e^2 \cdot z n_0 z_i^2} \right]^{1/2}$$

At room temp. - $\lambda_{dl} = 3.3 \times 10^6 \left(\frac{\epsilon_r}{z_i^2} \right)$

Electrocapillary Phenomena and Electrocapillary curve -

Electrocapillary curve -

- Electrocapillary phenomena are related to changes in surface energy of dropping mercury electrode potential composition & conc. change.
- The term electro-capillary is used to describe the change in mercury (Hg) potential as the change in surface potential interfacial tension of the Hg determined by capillary rise method used to a function by capillary rise method.



(General form of capillary curve)