

Characteristics and Relative Thickness of the Electrochemical Layers


UCI Department of Mechanical and Aerospace Engineering
Professor Marc Madou (MAE 212 - Electrochemistry)
Prepared by: Derosh George, John Stansberry, Bander Linjawi
February 7th, 2017

Table of Contents

- The various electrochemical & Transport layers
- The Electric Double Layer
 - The Debye Length approximation
- Hydrodynamic (Prandtl) Layer
- Diffuse (Nernst) Layer
- Schmidt Number: Physical Intuition
- Relation of Schmidt Number to Prandtl & Diffuse Layer

The Electrochemical Interface

The charged interface in electrochemistry can be subdivided into 5 layers

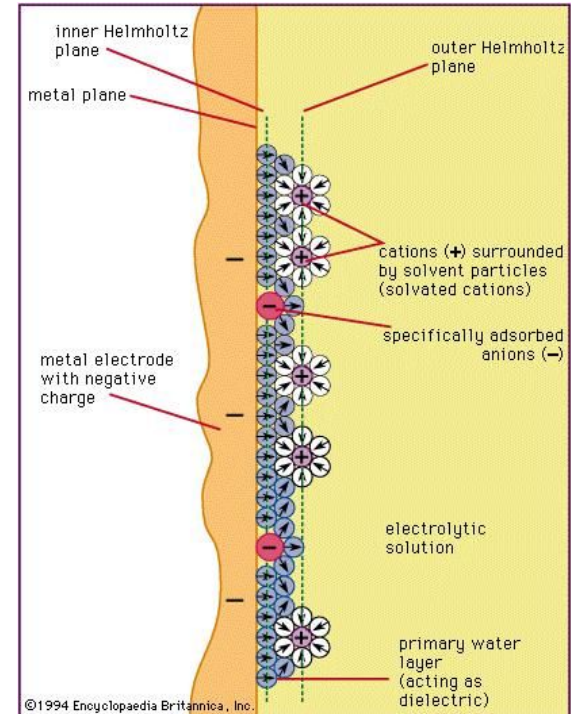
- 1) Electrode surface
 - 2) Inner Helmholtz Plane (IHP)
 - 3) Outer Helmholtz Plane (OHP)
 - 4) Diffusion Layer (or 'Nernst' Layer)
 - 5) Hydrodynamic Layer (or 'Prandtl' Layer)
- 
- A diagram consisting of a rectangular box with a horizontal line extending from its top-left corner to the left, and another horizontal line extending from its bottom-left corner to the left. These lines align with the text '1) Electrode surface' and '3) Outer Helmholtz Plane (OHP)' respectively. An arrow points from the right side of the box to the text 'Double Layer'.

$$J_j = \underbrace{-D_j \nabla C_j}_{\text{Diffusion}} + \underbrace{C_j \vec{V}}_{\text{Convection}} - \underbrace{\frac{Z_j F}{RT} D_j C_j \nabla \phi}_{\text{Migration}} \quad (1)$$

The Electric Double Layer

-Representative of the ionic environment in proximity to a charged surface

-Matter at the boundary of two phases have attributes that differentiate it from matter extended away from the boundary in each respective phase



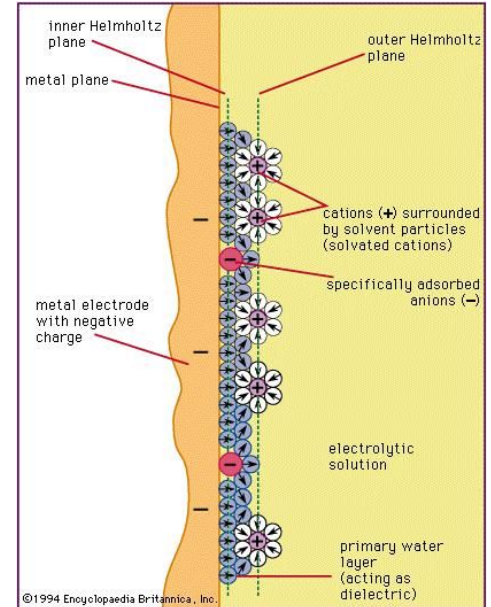
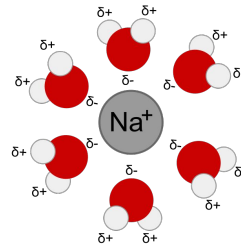
The Electric Double Layer

Helmholtz Model provides a simple approximation of the double layer behavior

-Inner Helmholtz Plane (IHP) is comprised of solvent molecules and specifically adsorbed ions in direct contact with the metal surface

-Outer Helmholtz Plane(OHP) is the plane of closest approach for solvated ions. Electric double layer extends from electrode surface to the center plane of these solvated ions.

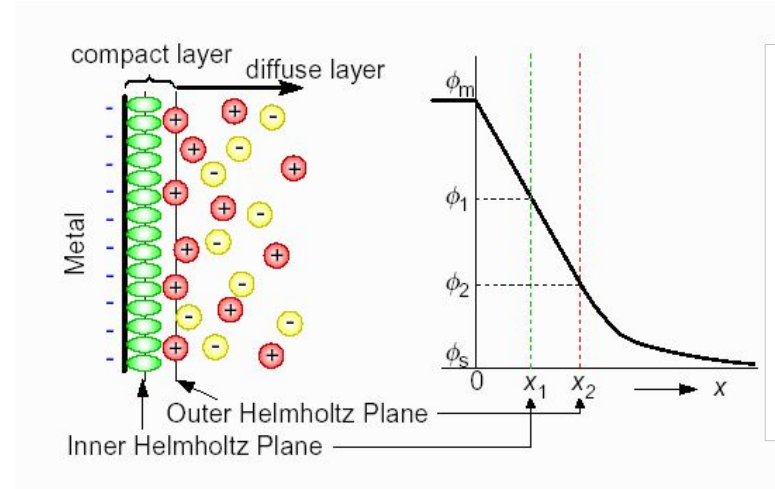
-Together these two planes facilitate the electron transfers to and from electrode surface that drive electrochemical redox reactions and contain a powerful electrical field.



The Electric Double Layer

In a metallic electrode the thickness is around 0.1 nm and is a function of the electron density due to the stationary nature of atoms in solids.

In the electrolyte the thickness varies more, in a range of .1 to 10 nm. Dependent on size of the solvated molecules and their concentration, which can be approximated by the Debye Length.



The Electric Double Layer

The Debye Length

In an electrolytic solution, the Debye Length (κ^{-1} [m]) is the measure of a charge carrier's net electrostatic effect in the solution in terms of the distance at which it persists. Thus, this metric gives a good approximation of the electric double layer thickness.

- Each unit of Debye Length represents a drop in electric potential on the order of $1/e$.
- Different theoretical methods approximate double layer thickness as $\sim 1-1.5x$ Debye Length

$$\kappa^{-1} = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{2c_0 z^2 e^2}}$$

Where,

ϵ_r : Dielectric constant (material property)

ϵ_0 : Permittivity of free space (physical constant)

k_B : Boltzmann constant (physical constant)

T : Absolute Temperature

c_0 : Bulk electrolyte concentration

e : Elementary Charge (physical constant)

z : Ionic charge

The Electric Double Layer

Apply Dimensional Analysis

$$\kappa^{-1} = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{2 c_0 z^2 e^2}}$$

$$= \sqrt{\frac{\frac{F}{m} \times \frac{J}{K} \times K}{\frac{mol}{L} \times ('charge')^2 \times \left(\frac{C}{('charge')}$$

$$= \sqrt{\frac{\frac{C^2}{N * m^2} \times \frac{J}{K} \times K}{\frac{mol}{L} \times \frac{1000L}{m^3} \times \frac{6.02E23}{mol} \times ('charge')^2 \times \left(\frac{C}{('charge')}$$

Take,

$$\epsilon_r = 8.854E - 12 \frac{F}{m}$$

$$\epsilon_0 = 80.1 \text{ (Dielectric is water @ } 20^\circ \text{ C)}$$

$$k_B = 1.381E - 23 \frac{J}{K}$$

$$T = 20^\circ \text{ C} = 293 \text{ K}$$

$$c_0 = 10E - 3 \text{ M}$$

$$z = 1 \text{ (Monovalent)}$$

$$e = 1.602E - 19 \frac{C}{('charge')}$$

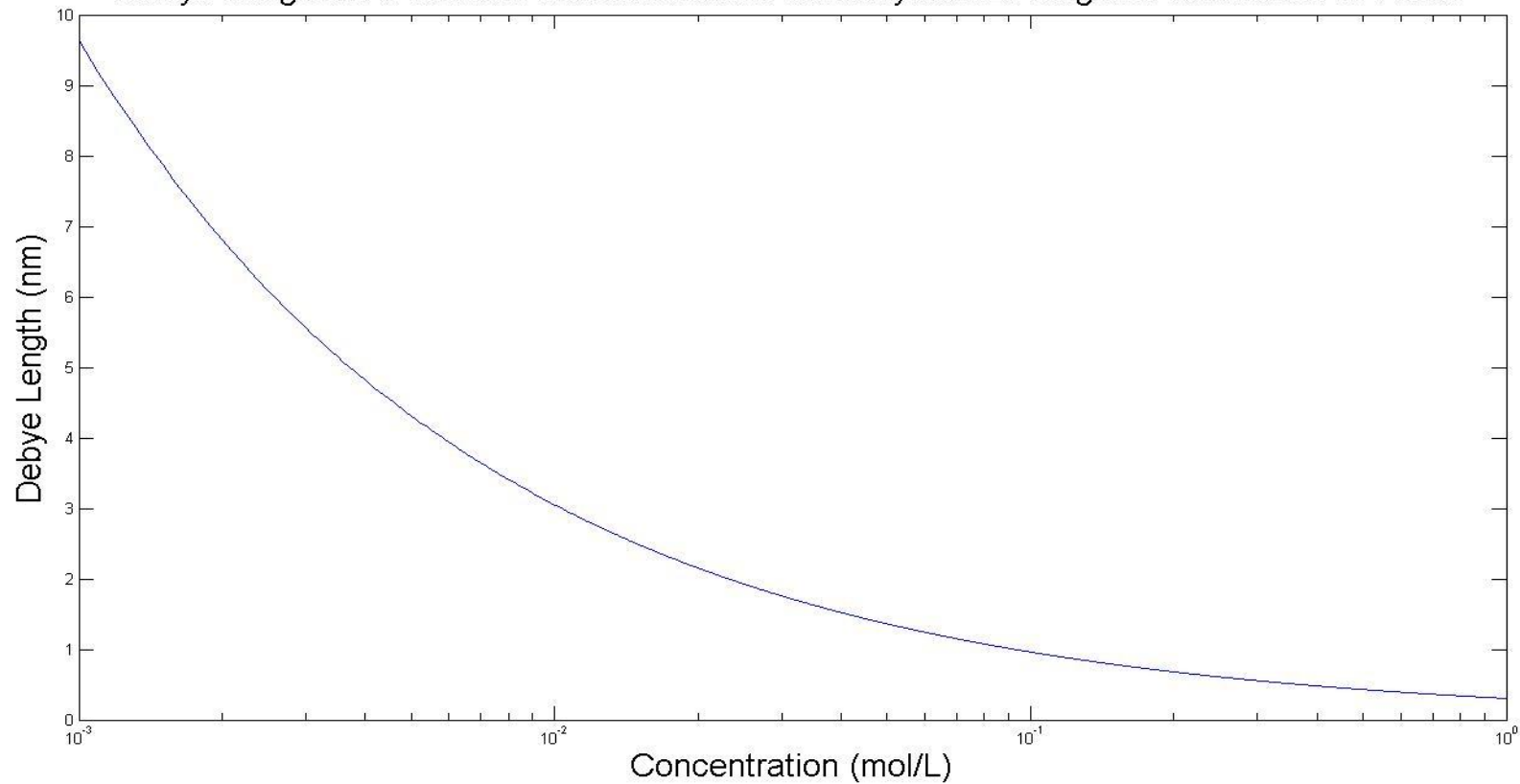
$$\dots = \sqrt{m^2} = m$$

Result agrees!

$$\kappa^{-1} = 9.637E - 9 \text{ m}$$

$$\underline{\underline{\kappa^{-1} = 9.637 \text{ nm}}}$$

Debye Length as a function of a Monovalent electrolyte at 20 Degrees C solvated in Water



Prandtl layer thickness

Continuity equation : $\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0$

Momentum equation: $\rho \left(u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} \right) = \mu \frac{\partial^2 u}{\partial y^2}$

Scaling analysis- $u \sim U_\infty$ $y \sim \delta$

Continuity equation: $\frac{U_\infty}{x} + \frac{v}{\delta} \approx 0$ $v \sim \frac{U_\infty \delta}{x}$

Momentum: $U_\infty \frac{U_\infty}{x} + \left(\frac{U_\infty \delta}{x} \right) \times \frac{U_\infty}{\delta} \approx \frac{\mu U_\infty}{\rho \delta^2}$ $\Rightarrow \delta^2 \sim \frac{\mu x}{U_\infty \rho} \sim \frac{\nu x}{U_\infty}$ $\Rightarrow \delta \sim \sqrt{\frac{\nu x}{U_\infty}}$

More precisely:

$$\delta \approx 5 \sqrt{\frac{\nu x}{U_\infty}}$$

Diffusion layer thickness

Convection-Diffusion equation: $\frac{\partial c}{\partial t} = \nabla \cdot (D \nabla c) - \nabla \cdot (\vec{v}c) + R$ (Steady & No source)

Resulting 2D Equation: $v_x \frac{\partial C_i}{\partial x} + v_y \frac{\partial C_i}{\partial y} = D_{ij} \left(\frac{\partial^2 C_i}{\partial x^2} + \frac{\partial^2 C_i}{\partial y^2} \right)$

Two length scales in the y direction

- Momentum boundary layer thickness δ_M
- Concentration boundary layer thickness δ_C

The Schmidt number controls the relative importance of momentum and diffusive transport.

Diffusion layer thickness

In general for aqueous solution: $Sc \sim 1000 \rightarrow \delta_c \ll \delta_m$

\rightarrow Linear velocity profile $v_x = U_o \frac{y}{\delta_M} \sim U_o \frac{\delta_c}{\delta_M}$

Conservation of mass and linear profile for $v_x \rightarrow v_y = \int \frac{\partial v_x}{\partial x} dy \sim U_o \frac{y^2}{\delta_M x} \sim U_o \frac{\delta_c^2}{\delta_M L}$

For solute transport, the dimensionless equation is: $\frac{U_o}{L} \frac{\delta_c}{\delta_M} \left(v_x^* \frac{\partial C^*}{\partial x^*} + v_y^* \frac{\partial C^*}{\partial y^*} \right) = \frac{D_{ij}}{\delta_c^2} \left(\frac{\delta_c^2}{L^2} \frac{\partial^2 C^*}{\partial x^{*2}} + \frac{\partial^2 C^*}{\partial y^{*2}} \right)$

Since $\delta_c \ll L$, the underlined terms can be neglected $\rightarrow \frac{U_o}{D_{ij} L} \frac{\delta_c^3}{\delta_M} \left(v_x^* \frac{\partial C^*}{\partial x^*} + v_y^* \frac{\partial C^*}{\partial y^*} \right) \sim \frac{\partial^2 C^*}{\partial y^{*2}}$

Diffusion layer thickness

Since diffusive and convective transport are equally important, the non-dimensionalization indicates that

$$\frac{U_o}{D_{ij}L} \frac{\delta_c^3}{\delta_m} \sim 1$$

$$\delta_c \approx L^{2/3} \delta_m^{1/3} Pe^{-1/3} = L^{2/3} (L Re^{-1/2})^{1/3} (Re Sc)^{-1/3} = L Sc^{-1/3} Re^{-1/2}$$

$$\delta_c \approx L Sc^{-1/3} Re^{-1/2} = \delta_m Sc^{-1/3}$$

Diffusion Layer Dependence on Diffusivity: 0.1-0.001 mm

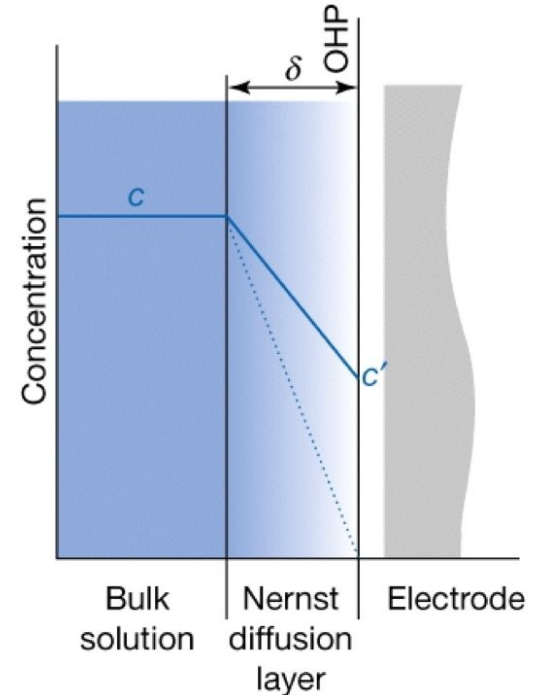
Nernst Layer is described by Fick's First Law:

$$J = -D \frac{\partial C}{\partial x}$$
$$\left(\frac{\partial C}{\partial x} \right)_{x=0} = \frac{C_0 - C_c}{\delta_c}$$

Where $C(x) = C_0$.

For a Flat Plate:

$$\delta_N \approx D^{1/3} \nu^{1/6} (x/U)^{1/2}$$



Hydrodynamic Layer Dependence on Viscosity: 3-0.03 mm

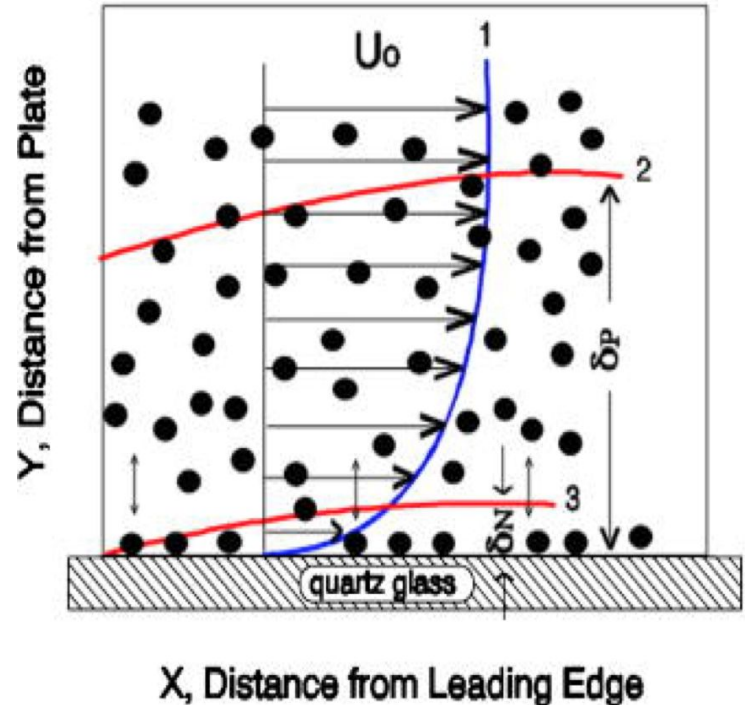
Hydrodynamic Layer Depends on Velocity $U(y)$:

$$\tau = -\nu \frac{\partial \rho v}{\partial x}$$

Where $U(y) = 0.99U_0$.

For a Flat Plate, based on Blasius Velocity Profile:

$$\delta_p \approx 5(\nu x/U)^{1/2}$$



Schmidt Number: Physical Intuition

$$Sc = \frac{\nu}{D_{AB}} = \frac{\text{Ability of a fluid to transport momentum by molecular means}}{\text{Ability of that fluid to transport species by molecular means}}$$

From a molecular view, liquids are tightly packed, yet freely moving molecules. Where solids are made of repeated, densely packed crystal structures, and gases are made of highly dispersed molecules, liquids sit in the middle, and they are the least understood state of matter.

Since the mean free path of liquid molecule taken to collide with another is much shorter than that in gasses (much higher in density), rate of momentum transfer is much higher. However, the case is opposite for diffusivity, where is it much easier for a mole of particles to move through a gas than through a liquid, precisely for the same reason.

In aqueous electrolytes, we expect high momentum transport and lower mass transport (especially in laminar region), thus giving us a high Schmidt number (~ 1000). Since transport of ions is what we're concerned about, use of aqueous solution serves to dissociate ions (hydrogen bonding) for easy removal of migration effect by adding salt.

Relative Thickness

Electrode Surface: $\sim < 0.1\text{nm}$

IHP/OHP: $\sim 0.1 - 10\text{ nm}$

Diffusion Layer: $.001 - .1\text{mm}$

Hydrodynamic Layer: $0.03\text{-}3\text{mm}$

Thank you

Questions?