ELECTROCHEMISTRY

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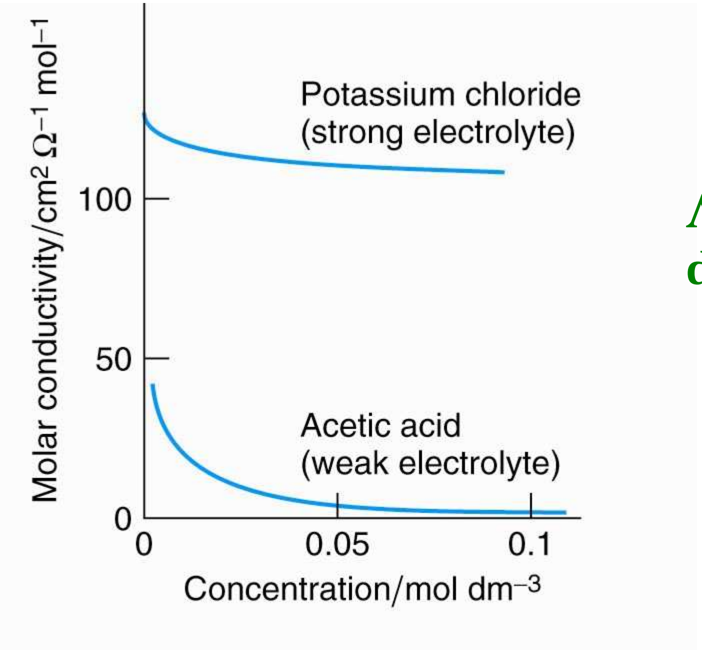
CONDUCTIVITY OF WEAK/STRONG ELECTROLYTES



Λ^o, the molar conductivity at infinite dilution, or zero concentration.

The importance of the molar conductivity is that it gives information about the conductivity of the ions produced in solution by 1 mol of a substance. In all cases the molar conductivity diminished as the concentration is raised, and two patterns of behavior can be distinguished.

strong electrolytes ~ the molar conductivity falls only slightly as the concentration is raised.

weak electrolytes ~ produce fewer ions and exhibit a much more pronounced fall of Λ with increasing concentration.

Debye-Huckel Theory

~The decrease in the molar conductivity of a strong electrolyte is attributed to the mutual interference of the ions, which becomes more pronounced as the concentration increases.

~The arrangement of ions in the solution is not completely random because of the strong attractive forces between ions of opposite signs.

~In the immediate neighborhood of any positive ion, there tend to be more negative than positive ions.

~The small amount of ordering that does exist is sufficient to exert an important effect on the conductivity of the solution.

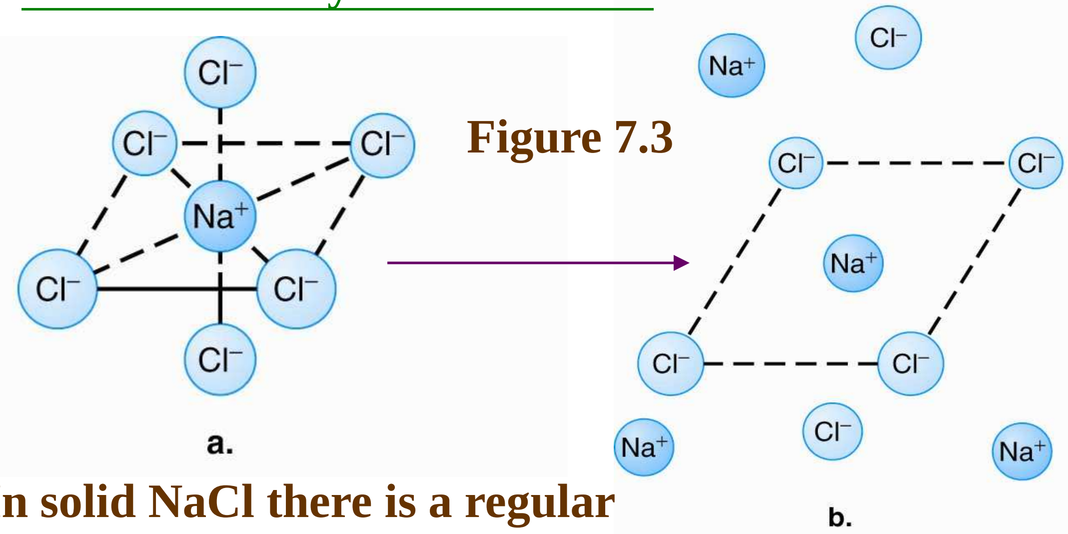


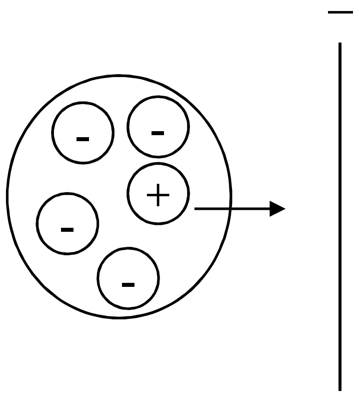
Figure 7.3

In solid NaCl there is a regular array of Na^+ and Cl^-.

When the NaCl is dissolved in water, this ordering is still preserved to a very slight extent. The ions are much farther apart than in the solid; the electrical attraction are therefore much smaller and the thermal motions cause irregularity.

Two effects are pronounced in the strong electrolytes:

1.relaxation or asymmetry effect



~Ions motion under potential applied is retarded by the interaction of opposite ions due to the asymmetry of ionic atmosphere.

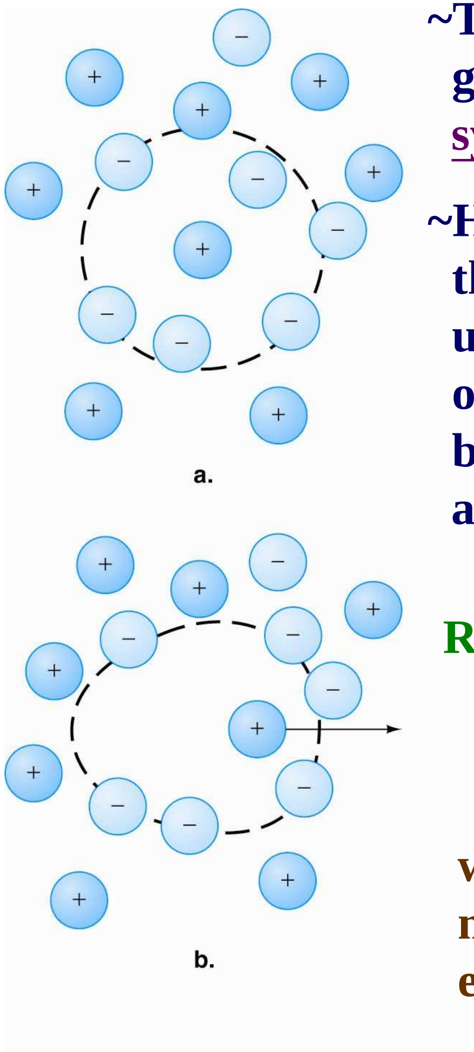
~If an electric potential is applied, a positive ion will move toward the negative electrode and must drag along with it an entourage of negative ions. The more concentrated the solution, the closer these negative ions are to the positive ion under consideration, and the greater is the drag. The ionic “atmosphere” around a moving ion is therefore not symmetrical; the charge density behind is greater than that in front, and this will result in a retardation in the motion of the ion.

2.electrophoretic effect

~Ions motion under potential applied is retarded by the attractive force between solvent molecules and ions due to the tendency of ionic atmosphere to drag the solvent molecules.

Mechanism of Conductivity

Relaxation or Asymmetry Effect



~The effect of the ionic atmosphere is to exert a drag on the movement of a given ion. If the ion is stationary, the atmosphere is arranged symmetrically about it and does not tend to move it in either direction.

~However, if a potential that tends to move the ion to the right is applied, the atmosphere will decay to some extent on the left of the ion and build up more on the right. Since it takes time for these relaxation processes to occur, there will be an excess of ionic atmosphere to the left of the ion (i.e., behind it) and a deficit to the right (in front of it). This asymmetry of the atmosphere will have the effect of dragging the central ion back.

Relaxation force f_r is

$$f_r = \frac{e^2 z_i \kappa}{24\pi \varepsilon_0 \varepsilon k_B T} wV'$$

where *V'* is the applied potential gradient and *w* is a number whose magnitude depends on the type of electrolyte; for a uni-univalent electrolyte, *w* is $2-\sqrt{2}=0.586$.

Electrophoretic Effect

~Ions are attracted to solvent molecules mainly by ion-dipole forces therefore, when they move, they drag solvent along with them.

~The ionic atmosphere, having a charge opposite to that of the central ion, moves in the opposite direction to it and therefore drags solvent in the opposite direction. This means that the central ion has to travel upstream, and it therefore travels more slowly than if there were no effect of this kind.

Electrophoretic force f_e is

$$f_e = \frac{e z_i \kappa}{6\pi\eta} K_c V'$$

where K_c is the coefficient of frictional resistance of the central ion with reference to the solvent and η is the viscosity of the medium. The viscosity enters into this expression because we are concerned with the motion of the ion past the solvent molecules, which depends on the viscosity of the solvent.

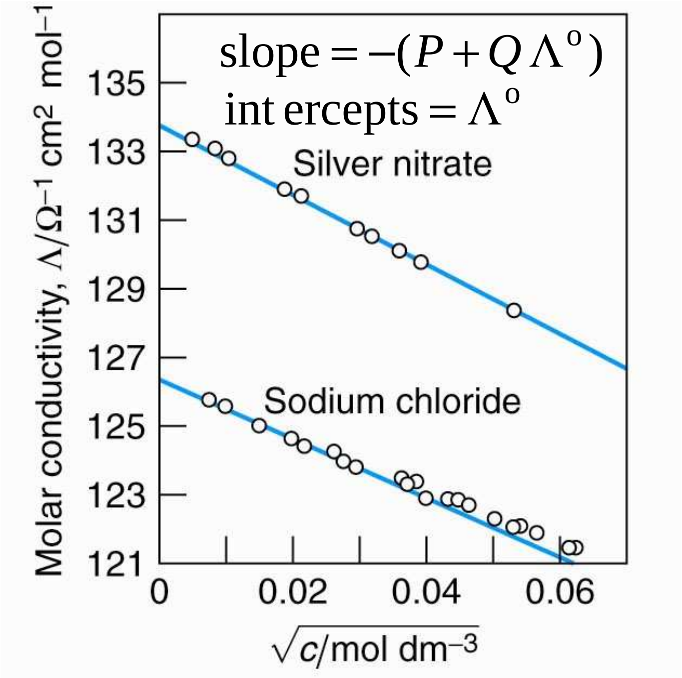
Debye-Huckel-Onsager Equation

$$\Lambda = \Lambda^{o} - (P + Q\Lambda^{o})\sqrt{c}$$ **Based on the assumption of complete dissociation**

where *P* and *Q* can be expressed in terms of various constants and properties of the system.

For the particular case of a symmetrical electrolyte [i.e., one for which the two ions have equal and opposite signs ($z_+ = z_- = z$)], *P* and *Q* are given by

$$P = \frac{zeF}{3\pi\eta}\left(\frac{2z^2e^2L}{\varepsilon_0\varepsilon k_BT}\right)^{1/2} \qquad Q = \frac{z^2e^2w}{24\pi\varepsilon_0\varepsilon k_BT}\left(\frac{2z^2e^2L}{\varepsilon_0\varepsilon k_BT}\right)^{1/2}$$



~For aqueous solution of uni-univalent electrolytes, the theoretical equation is found to be obeyed very satisfactorily up to a concentration of about 2×10^{-3} mol dm^{-3}; at higher concentrations, deviation are found.

~The corresponding equations for other types of electrolytes in water are also obeyed satisfactorily at very low concentrations, but deviations are found at lower concentration than with uni-univalent electrolytes.

Ion Asso ciation

$$\Lambda = \Lambda^{\mathrm{o}} - (P + Q\Lambda^{\mathrm{o}})\sqrt{c}$$

Bjerrum presented a theory that ions of opposite signs separated in solution by a distance *r form an associated ion pair held together by coulombic forces. The Bjerrum distance *r** is**

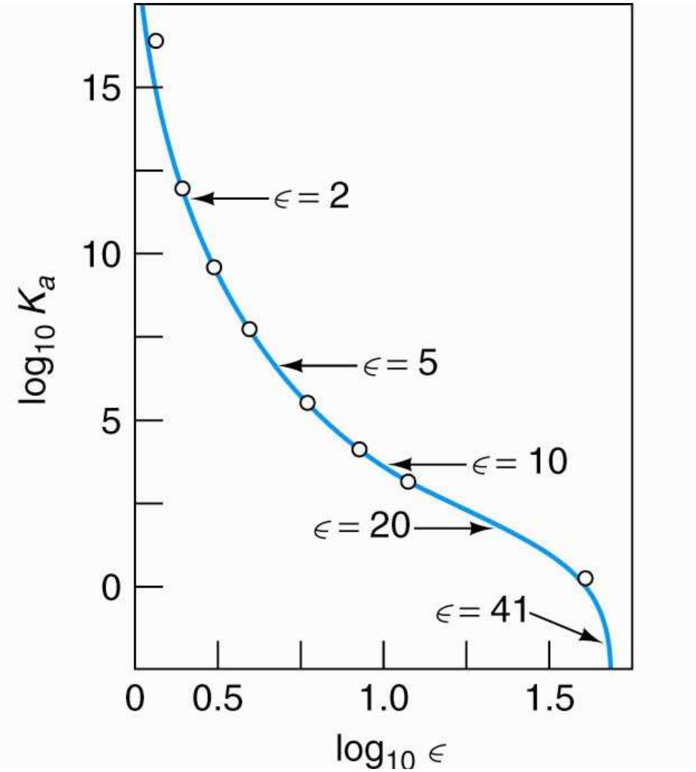
$$r^* = \frac{z_c z_i e^2}{8\pi\,\varepsilon_0\varepsilon\,k_{\mathrm{B}}T}$$

For the case of a uni-univalent electrolyte (z_c=z_i=1) the value of *r at 25 °C, with ε=78.3, is equal to 3.5×10^{-10} m=0.358 nm. The expression for the electrostatic potential energy of interaction between two univalent ions separated by a distance *r* is**

$$E_{\text{electrostatic}} = \frac{e^2}{4\pi\,\varepsilon_0\varepsilon\,r} \rightarrow E^* = 2k_{\mathrm{B}}T$$

The electrostatic potential energy at this distance *r is thus four times the mean kinetic energy per degree of freedom. The energy at this distance is therefore sufficient for there to be significant ion association, which will be dynamic in character in that there will be a rapid exchange with the surrounding ions. At distance smaller than 0.358 nm the probability of ionic association increase rapidly. Therefore, to a good approximation one can say that if the ions are closer than 0.358 nm, they can be considered to be" undissociated" and to make no contribution to the conductivity.**

However, in aqueous solution univalent ions can rarely approach one another as closely as 0.358 nm, and ion association is therefore of little importance for such ions. In solvents having lower dielectric constants, however, there can be substantial ion-pair formation even for uni-univalent electrolytes.



K_a, the association constant for ion-pair formation with tetraisoamylammonium nitrate, against the dielectric constant of the solvent ranging from 2.2 to 78.6.

, the formation of ion pairs was negligible in solution of high dielectric constant, but very considerable in solutions of low dielectric constant. Dioxane has a dielectric constant of 2.2 at 25 °C, and the *r** value for a uni-univalent electrolyte is 12.7 nm; ion association is therefore expected to be important.

~Much more ion association is found with ions of higher valence. With salts having ions of different valences, such as Na_2SO_4, ion association will lead to the formation of species such as $Na^+SO_4^{2-}$. Again there will be reduction in conductivity, since these species will carry less current than the free ions.

~Bjerrum's theory has been extended to deal with such unsymmetrical electrolytes and also with the formation of triple ions.

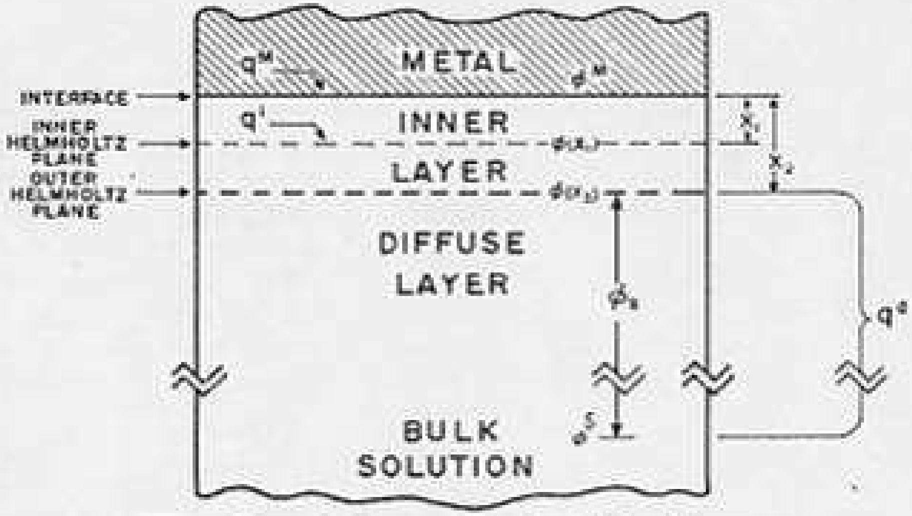
Conductivity at High Frequencies and Potentials

Suppose that the alternating potential is of sufficiently high frequency that the time of oscillation is small compared with the time it takes for the ionic atmosphere to relax. There will then not be time for the atmosphere to relax behind the ion and to form in front of it; the ion will be virtually stationary and its ionic atmosphere will remain symmetrical. Therefore, as the frequency of the potential increases, the relaxation and eletrophoretic effects will become less and less important, and there will be an increase in the molar conductivity.

~If the applied potential is 20000 Vcm^{-1}, an ion will move at a speed of about 1 ms^{-1} and will travel several times the thickness of the effective ionic atmosphere in the time of relaxation of the atmosphere. Consequently, the moving ion is essentially free from the effect of the ionic atmosphere which doe not have time to build up around it to any extent. Therefore, at sufficiently high voltages, the relaxation and eletrophoretic effects will diminish and eventually disappear and the molar conductivity will increase. This effect is known as the Wien effect.

~However, molar conductivities of weak electrolytes at high potentials are anomalously large, and it appears that very high potentials bring about a dissociation of the molecules into ions. This phenomenon is known as the dissociation field effect.

The electrical double layer



Schematic diagram of the electrical double layer.

Historical milestones

-The concept electrical double layer Quincke – 1862

-Concept of two parallel layers of opposite charges Helmholtz 1879 and Stern 1924

-Concept of diffuse layer Gouy 1910; Chapman 1913

- Modern model Grahame 1947

What is Electrochemistry?

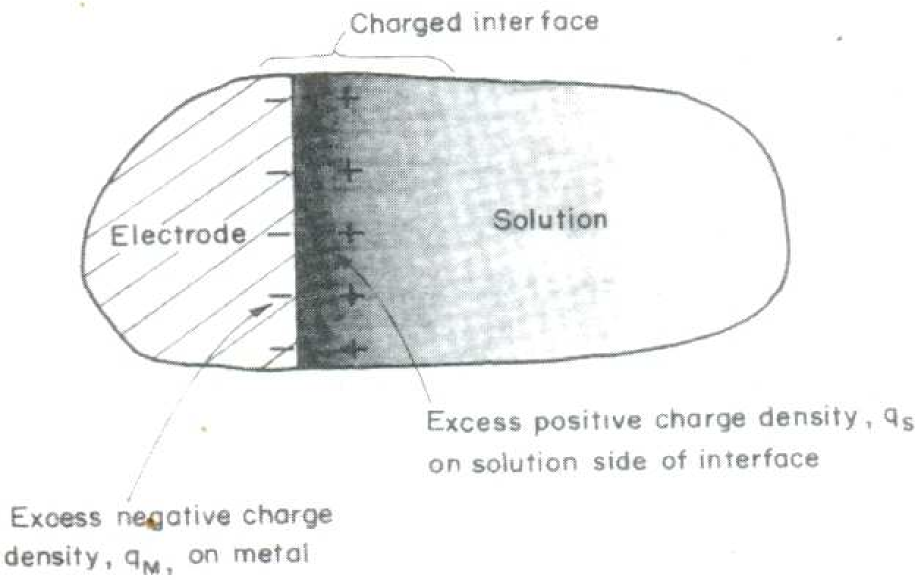
- all about the study of Electrified Interfaces and its consequences.

What is an Electrified Interface?

It is the two dimentional geometrical boundary surface separating the two phases.

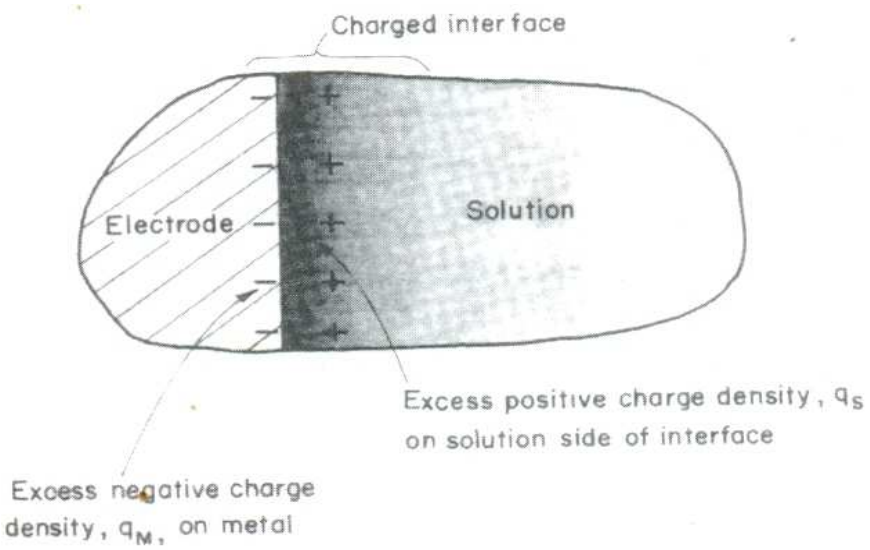
What is an Electrified Interphase?

It is the three dimensional region of contact between the two phases in contact at their boundary.



Electrified Interface

Electrified Interface

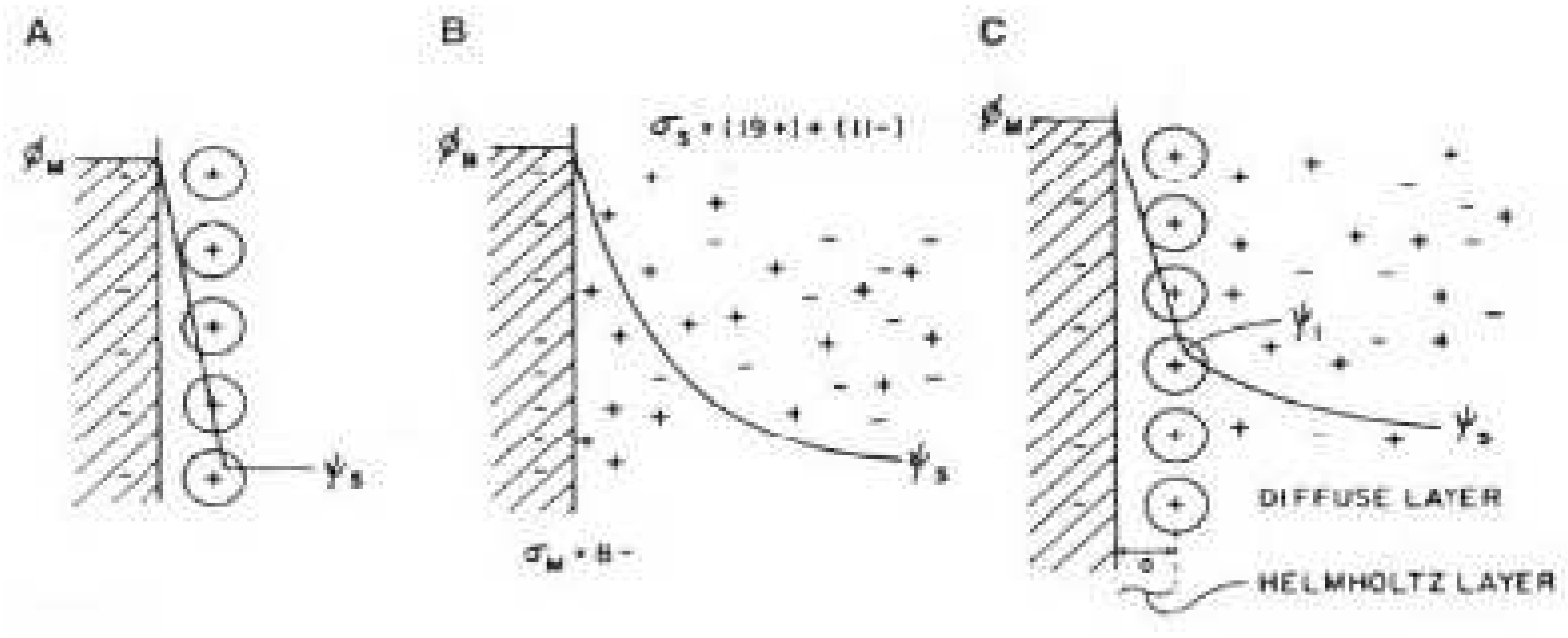


Whenever an uncharged metal or electron conductor contacts with an ionic solution manifests an excess surface electric charge on both sides of the interphase;

- Creates a gigavolt per meter (10^7 V/cm)field in the interface region, with the electroneutrality of the bulk metal.

The effect of this enormous field at the electrode interface is the essence of electrochemistry.

Models of the Double Layer Structure of Electrified Interface



a) Helmholtz model b) Gouy-Chapman model of the diffuse layer c) Stern's model, combining (a) and (b)

The electrical double layer

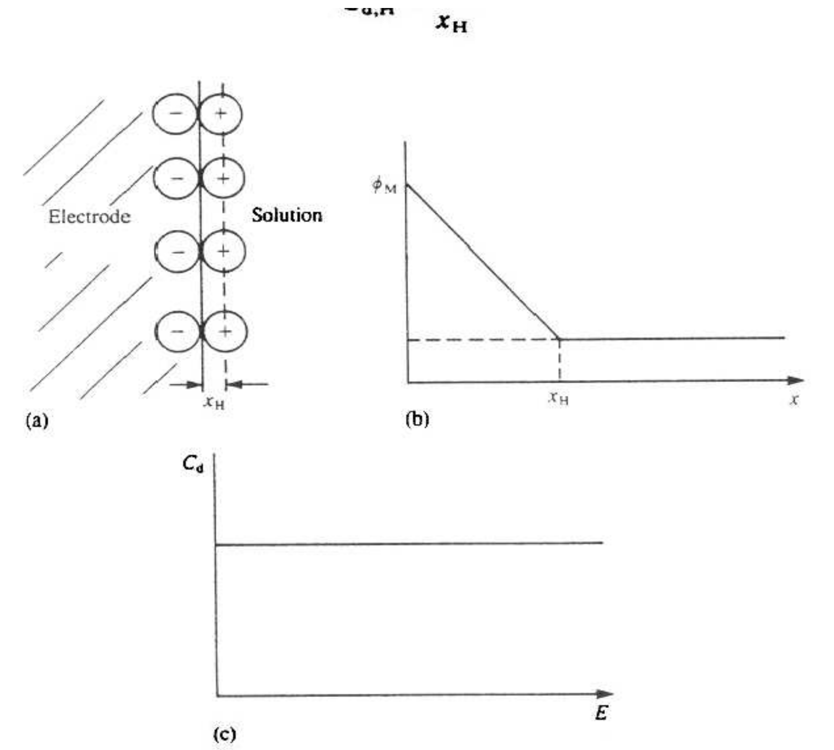
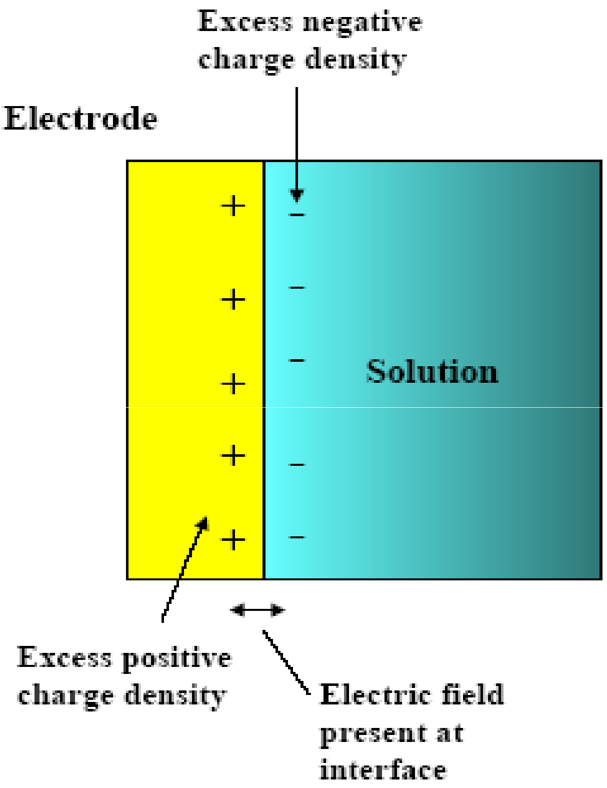


Fig. 3.5 The Helmholtz model of the double layer. (a) Rigid arrangement of ions; (b) Variation of the electrostatic potential, ϕ, with distance x, from the electrode; (c) Variation of C_d with applied potential.



Excess negative charge density

Electrode

Solution

Excess positive charge density

Electric field present at interface

$$C_{DL} = C_H = \frac{\varepsilon_0 \varepsilon_r}{x_H}$$

Gouy-Chapmann model

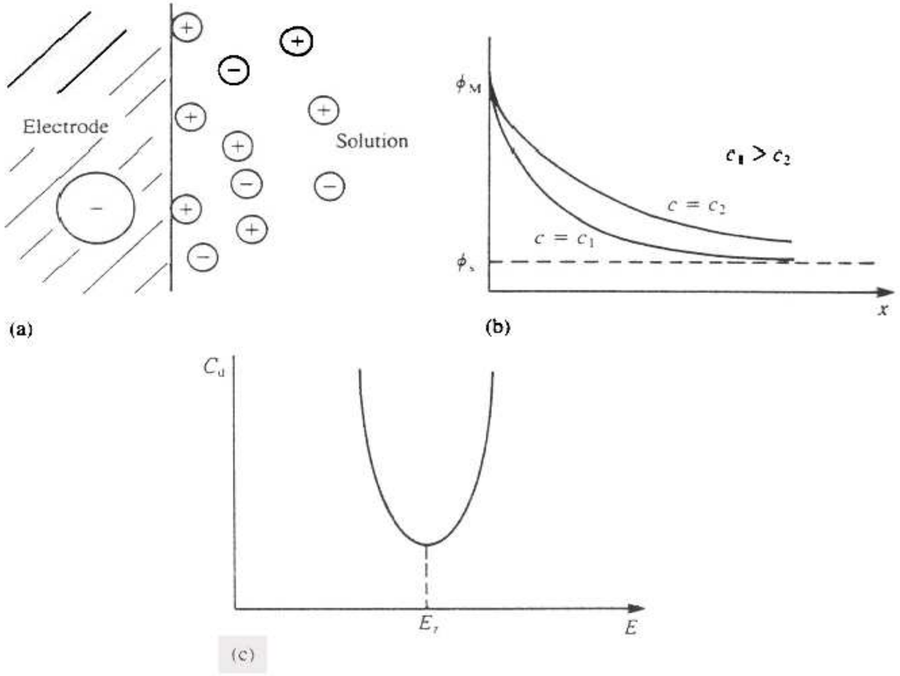


Fig. 3.6 The Gouy–Chapman model of the double layer. (a) Arrangement of the ions in a diffuse way; (b) Variation of the electrostatic potential, ϕ, with distance, x, from the electrode, showing effect of ion concentration, c. (c) Variation of C_d with potential, showing the minimum at the point of zero charge E_z.

Stern and Grahame Models

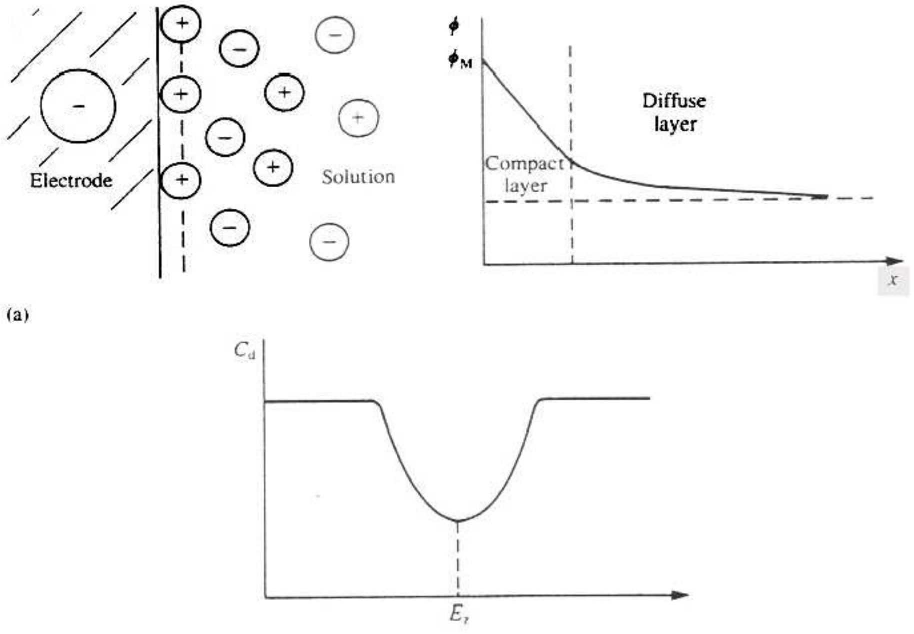


Fig. 3.7 The Stern model of the double layer. (a) Arrangement of the ions in a compact and a diffuse layer; (b) Variation of the electrostatic potential, ϕ, with distance, x, from the electrode; (c) Variation of C_d with potential.

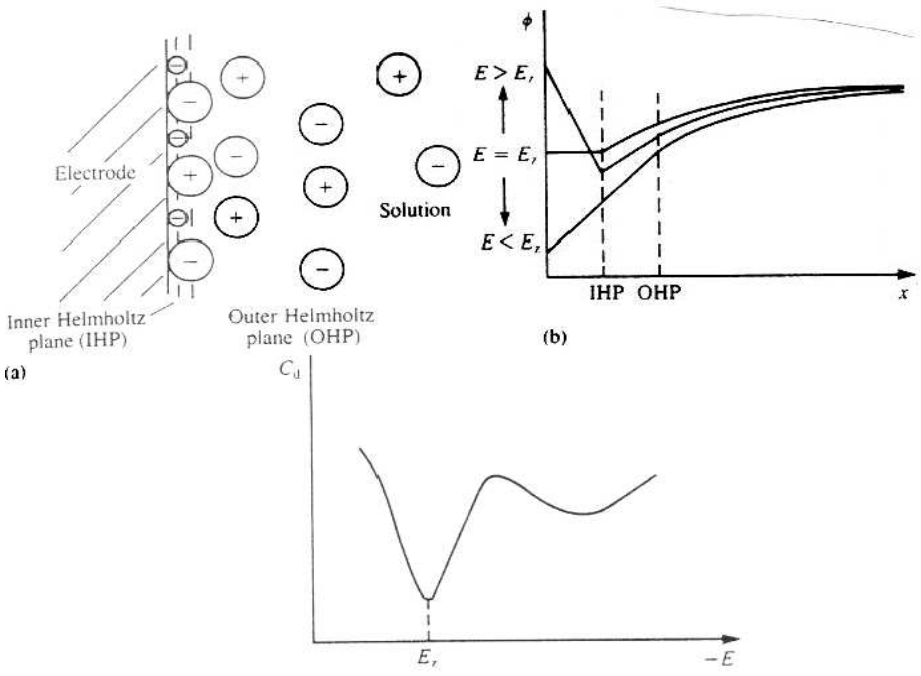


Fig. 3.8 The Grahame model of the double layer, for the mercury electrode. (a) Arrangement of ions; (b) Variation of the electrostatic potential, ϕ, with distance, x, from the electrode, according to the applied potential; (c) Variation of C_d with potential.

Presently accepted model of the electrical double layer

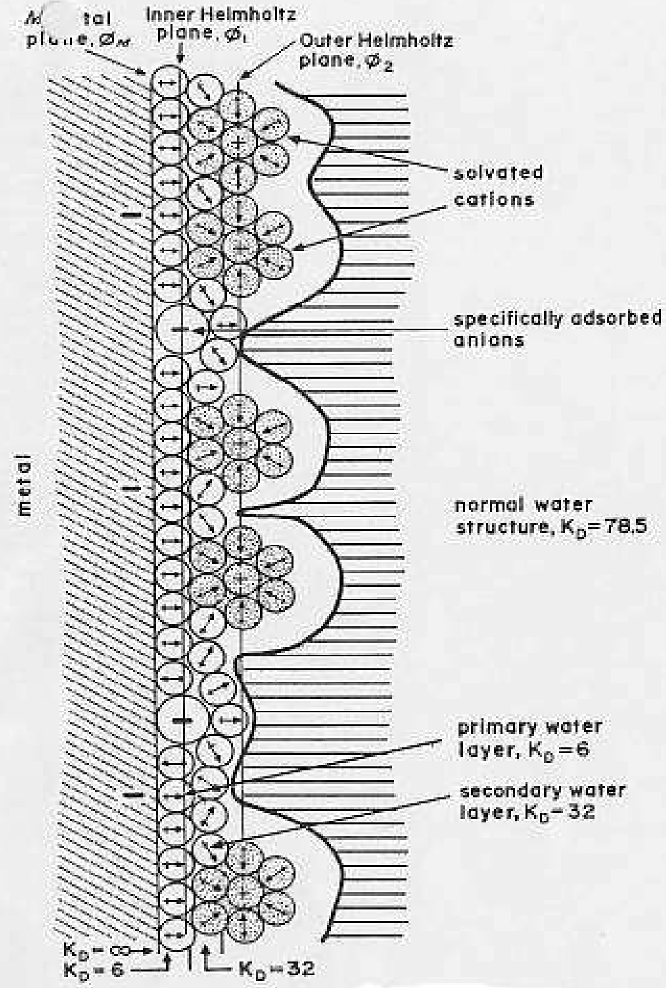
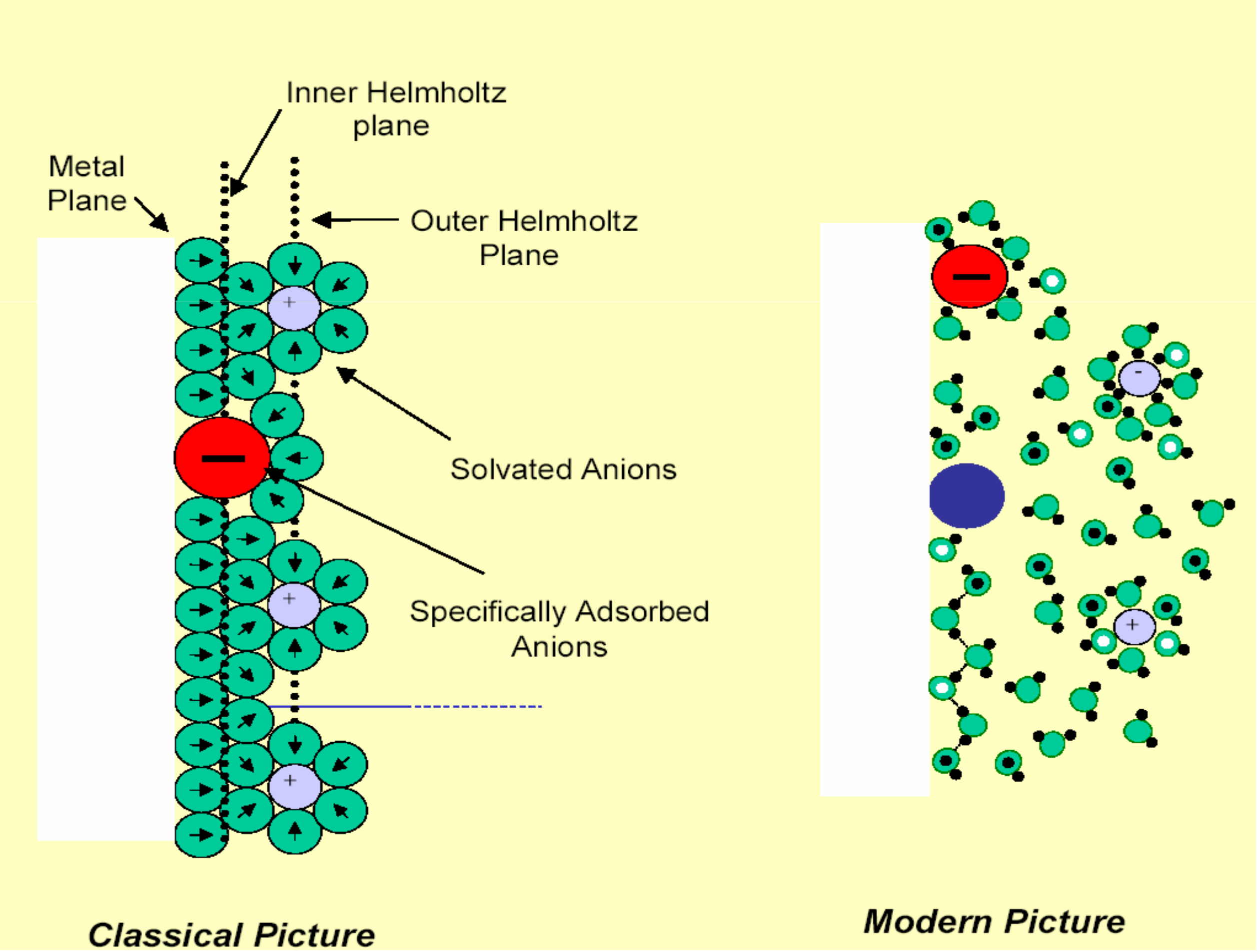


Fig. 2. Model of the electrical double layer [redacted] of the Royal

Current Model

BDM (Bockris, Devanathan, Muller)



Examples of Electrified Interfaces

- ➢ Why do Colloidal particles move under electric fields?

The electrified interface between the Colloidal particle and the medium causes a potential difference in the interface, which interacts with the externally applied electric field ➔ lies the basis for coating of metals.

- ➢ Is the friction between two solids in presence of liquid film an Electrified interface?

Yes ➔ the efficiency of a wetted rock drill depends on the double layer structure at the metal/drill/aqueous solution interface.

- ➢ The mechanism by which a nerves carry messages from brain to muscles is based on the potential difference across the membrane that separates a nerve cell from the environment.

Description of Electrochemical Techniques

- The technique is named according to the parameters measured
- E.g.
- Voltammetry – measure current and voltage
- Potentiometry – measure voltage
- Chrono-potentiometry – measure voltage with time (under an applied current)
- Chrono-amperometry – measure current with time (under an applied voltage)

Electro-Kinetics

- Movement of Ions
- Butler Volmer Equation
- Rotating Disc Electrode
- Rotating Cylinder Electrode
- Voltammetry
- Cyclic Voltammetry
- Chrono-potentiometry
- Chrono-amperometry

Butler-Volmer Equation

- The **Butler-Volmer equation** is one of the most fundamental relationships in electrochemistry. It describes how the electrical current on an electrode depends on the electrode potential, considering that both a cathodic and an anodic reaction occur on the same electrode:

Butler-Volmer Equation

$$I = A \cdot i_0 \cdot \left\{ \exp\left[\frac{(1-\alpha) \cdot n \cdot F}{R \cdot T} \cdot (E - E_{eq}) \right] - \exp\left[-\frac{\alpha \cdot n \cdot F}{R \cdot T} \cdot (E - E_{eq}) \right] \right\}$$

- where:
- I = electrode current, Amps
- I_o= exchange current density, Amp/m^2
- E = electrode potential, V
- E_{eq}= equilibrium potential, V
- A = electrode active surface area, m^2
- T = absolute temperature, K
- n = number of electrons involved in the electrode reaction
- F = Faraday constant
- R = universal gas constant
- α = so-called symmetry factor or charge transfer coefficient dimensionless

The equation is named after chemists John Alfred Valentine Butler and Max Volmer

Butler-Volmer Equation

- The equation describes two regions:
- At high overpotential the Butler-Volmer equation simplifies to the Tafel equation
- $E - E_{eq} = a - b\log(i_c)$ for a cathodic reaction
- $E - E_{eq} = a + b\log(i_a)$ for an anodic reaction
- Where:
- a and b are constants (for a given reaction and temperature) and are called the Tafel equation constants
- At low overpotential the Stern Geary equation applies

Butler Volmer Equation

- While the Butler-Volmer equation is valid over the full potential range, simpler approximate solutions can be obtained over more restricted ranges of potential. As overpotentials, either positive or negative, become larger than about 0.05 V, the second or the first term of equation becomes negligible, respectively. Hence, simple exponential relationships between current (i.e., rate) and overpotential are obtained, or the overpotential can be considered as logarithmically dependent on the current density. This theoretical result is in agreement with the experimental findings of the German physical chemist Julius Tafel (1905), and the usual plots of overpotential versus log current density are known as Tafel lines.
- The slope of a Tafel plot reveals the value of the transfer coefficient; for the given direction of the electrode reaction.

Butler-Volmer Equation

$$i_{a`} = i_0 \exp\left[\frac{(1-\alpha)nF\eta_a}{RT} \right]$$

at high anodic overpotential

$$i_{c`} = i_0 \exp\left[-\frac{\alpha nF\eta_c}{RT} \right]$$

at high cathodic overpotential

i_a and i_c are the exhange current densities for the anodic and cathodic reactions

These equations can be rearranged to give the Tafel equation which was obtained experimentally

Butler Volmer Equation - Tafel Equation

$$\eta_c = \frac{RT}{\alpha_c nF}\ln i_0 - \frac{RT}{\alpha_c nF}\ln i_c$$

$$\eta_c = \frac{0.059}{\alpha_c n}\log i_0 - \frac{0.059}{\alpha_c n}\log i_c \text{ at } 25^0\text{C for the cathodic process}$$

$$\eta_a = \frac{0.059}{\alpha_a n}\log i_0 - \frac{0.059}{\alpha_a n}\log i_a \text{ at } 25^0\text{C for the anodic process}$$

The equation is the well known Tafel equation

$$\eta = a + b\log i$$

and

$$a = \frac{0.059}{\alpha n}\ln i_o$$

$$b = \frac{0.059}{\alpha n}$$

Tafel Equation

- The Tafel slope is an intensive parameter and does not depend on the electrode surface area.
- i_0 is and extensive parameter and is influenced by the electrode surface area and the kinetics or speed of the reaction.
- Notice that the Tafel slope is restricted to the number of electrons, *n*, involved in the charge transfer controlled reaction and the so called symmetry factor, α.
- n is often = 1 and although the symmetry factor can vary between 0 and 1 it is normally close to 0.5.
- This means that the Tafel slope should be close to 120 mV if n = 1 and 60 mV if n = 2.

Tafel Equation

- We can write:

$$\eta = \frac{RT}{\alpha nF} \ln\left(i/i_0\right) \text{ or } \eta = b \ln\left(i/i_0\right)$$

where

$$b = \frac{2.303\,RT}{\alpha nF} = \text{the Tafel slope}$$

$$\ln i = 2.303 \log i$$

Tafel Equation

- The Tafel equation can be also written as:

$$i = nFk \exp\left(\pm \alpha F \frac{\Delta V}{RT}\right)$$

- where
- the plus sign under the exponent refers to an anodic reaction, and a minus sign to a cathodic reaction, n is the number of electrons involved in the electrode reaction k is the rate constant for the electrode reaction, R is the universal gas constant, F is the Faraday constant. *k* is Boltzmann's constant, *T* is the absolute temperature, *e* is the electron charge, and α is the so called "charge transfer coefficient", the value of which must be between 0 and 1.

Tafel Equation

- The following equation was obtained experimentally

$$\eta = a + b \log i$$

- Where:
- η = the over-potential
- i = the current density
- a and b = Tafel constants

Tafel Equation

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- a and b = Tafel constants

Stern Geary Equation

- Applicable in the linear region of the Butler Volmer Equation at low over-potentials

$$i_{corr} = \frac{B}{R_p}$$

Where

$$B = \text{the Tafel constant}$$

$$= \frac{\beta_{\mathrm{a}} \times \beta_c}{2.3\left(\beta_{\mathrm{a}} + \beta_c\right)}$$

$$R_p = \text{the measured polarisation resistance}$$

$$= \Delta E / \Delta i$$

Tafel Equation

- **Overview of the terms**
- The exchange current is the current at equilibrium, i.e. the rate at which oxidized and reduced species transfer electrons with the electrode. In other words, the exchange current density is the rate of reaction at the reversible potential (when the overpotential is zero by definition). At the reversible potential, the reaction is in equilibrium meaning that the forward and reverse reactions progress at the same rates. This rate is the exchange current density.

Tafel Equation

- The Tafel slope is measured experimentally; however, it can be shown theoretically when the dominant reaction mechanism involves the transfer of a single electron that

$$b = \frac{2.303\,RT}{\alpha F}$$

- *T* is the absolute temperature,
- *R* is the gas constant
- α is the so called "charge transfer coefficient", the value of which must be between 0 and 1.

Levich Equation

- The **Levich Equation** models the diffusion and solution flow conditions around a rotating disc electrode (RDE). It is named after Veniamin Grigorievich Levich who first developed an RDE as a tool for electrochemical research. It can be used to predict the current observed at an RDE, in particular, the Levich equation gives the height of the sigmoidal wave observed in rotating disk voltammetry. The sigmoidal wave height is often called the Levich current.
- In work at a RDE the electrode is usually rotated quite fast (1000 rpm) in order to establish a well defined diffusion layer.
- The scan rate is relatively slow – typically 2-5 mV s^{-1}

Levich Equation

- The Levich Equation is written as:

$$i_L = (0.620) n F A D^{\frac{2}{3}} w^{\frac{1}{2}} v^{\frac{-1}{6}} C$$

- where
- i_L is the Levich current
- n is the number of electrons transferred in the half reaction
- F is the Faraday constant
- A is the electrode area
- D is the diffusion coefficient (see Fick's law of diffusion)
- w is the angular rotation rate of the electrode
- v is the kinematic viscosity
- C is the analyte concentration
- While the Levich equation suffices for many purposes, improved forms based on derivations utilising more terms in the velocity expression are available.[1][2]

Levich Equation

- It is important to note that the layer of solution immediately adjacent to the surface of the electrode behaves as if it were stuck to the electrode. While the bulk of the solution is being stirred vigorously by the rotating electrode, this thin layer of solution manages to cling to the surface of the electrode and appears (from the perspective of the rotating electrode) to be motionless.
- This layer is called the stagnant layer in order to distinguish it from the remaining bulk of the solution. The act of rotation drags material to the electrode surface where it can react. Providing the rotation speed is kept within the limits that laminar flow is maintained then the mass transport equation is given by the Levich equation.

Levich Equation RDE

- The Levich equation takes into account both the rate of diffusion across the stagnant layer and the complex solution flow pattern. In particular, the Levich equation gives the height of the sigmoidal wave observed in rotated disk voltammetry. The sigmoid wave height is often called the Levich current, $\mathbf{i_L}$, and it is directly proportional to the analyte concentration, **C**. The Levich equation is written as:
  - $\mathbf{i_L = (0.620)\ n\ F\ A\ D^{2/3}\ w^{1/2}\ v^{-1/6}\ C}$
- where **w** is the angular rotation rate of the electrode (radians/sec) and **v** is the kinematic viscosity of the solution (cm^2/sec). The kinematic viscosity is the ratio of the solution's viscosity to its density.

Levich Equation - RDE

- The linear relationship between Levich current and the square root of the rotation rate is obvious from the Levich plot. A linear least squares fit of the data produces an equation for the best straight line passing through the data. The specific experiment shown, the electrode area, A, was 0.1963 cm^2, the analyte concentration, C, was $2.55x10^{-6}$ mol/cm^3, and the solution had a kinematic viscosity, v, equal to 0.00916 cm^2/sec. After careful substitution and unit analysis, you can solve for the diffusion coefficient, D, and obtain a value equal to $4.75x10^{-6}$ cm^2/s. This result is a little low, probably due to the poor shape of the sigmoidal signal observed in this particular experiment.
- The kinematic viscosity is the ratio of the absolute viscosity of a solution to its density. Absolute viscosity is measured in poises (1 poise = gram cm^{-1} sec^{-1}). Kinematic viscosity is measured in stokes (1 stoke = cm^2 sec^{-1}). Extensive tables of solution viscosity and more information about viscosity units can be found in the *CRC Handbook of Chemistry and Physics*.

Thank You