

**Modren Electrosurface**  
**Chemistry**

**كيمياء كهربائية السطح الحديثة**

**By**  
**Dr.Khulood Abid Saleh**

## *The Electrified Interphase*

An aqueous electrolyte solution consists of a variety of charged and uncharged species, e.g., cations, anions, H<sub>2</sub>O dipoles, organic molecules, trace impurities, etc., which under equilibrium conditions are randomly oriented so that within the solution there is no net preferential directed field.

- Under the interface of a potential difference, the charge will be transported through the solution by cations and anions that migrate to the cathode and anode, respectively; this migration of charge through an electrolyte is responsible of electrolytic conduction.
- At each electrode there will be a transfer of electrical charge and a consequent electrode reaction that results in a change in the concentration of the reacting species at the surface of the electrode.
- Under these circumstance the transport of species to and from the electrode is by diffusion and convection as well as migration; the term transport is used have to include diffusion, convection and migration.
- Transport of charge through a metal under the influence of a potential difference is due to the flow of free electrons, i.e., to electronic conduction. The simultaneous transport of electrons through a metal, transport of ions through a solution and the transfer of electrons at the metal/ solution interphases constitute on electrochemical reaction, in which the electrode at which positive current flows from the solution to the electrode is the cathode and the electrode at which positive current flows from it to the solution is the anode.
- At any interphase between two different phases there will be a redistribution of charge in each phase at the interphase with a

consequent less of its electroneutrality, at though the interphase as a whole remains electrically neutral.

- The separation of charge at metal / solution interphase results in a strong electric field in the space between the charged layers and a potential difference across the extremities, and although the potential differences are comparatively small ( $<1.0$ ), the small distance of separation of the charged layers results in a very high field strength, taking the distance of separation as  $0.1\text{nm}$  and the potential difference as  $0.1\text{V}$ , the field strength (potential difference / distance) will be approximately  $10^7\text{Vcm}^{-1}$  ( $10^9\text{Vcm}^{-1}$ ). This high field strength is responsible for the facility with which electrons can cross the interphase during the electrode reaction, and a very small change in the excess charge at the interphase during the electrode reaction, and a very small change in the excess charge at the interphase can have a very significant effect on the potential difference and the velocity of the electrode process.
- Thus it can be calculated that for a cathodic process involving one electrode an excess charge of only approximately  $0.1\text{C m}^{-2}$  ( $1\text{mol}$  of electrons =  $1\text{F} = 96500\text{C}$ ) so that  $0.1\text{C} = 10^{-6}$  mol of electrons) will change the potential difference by as much as  $-0.6\text{V}$ , and could increase the rate of the process by a factor of  $10^5$ .

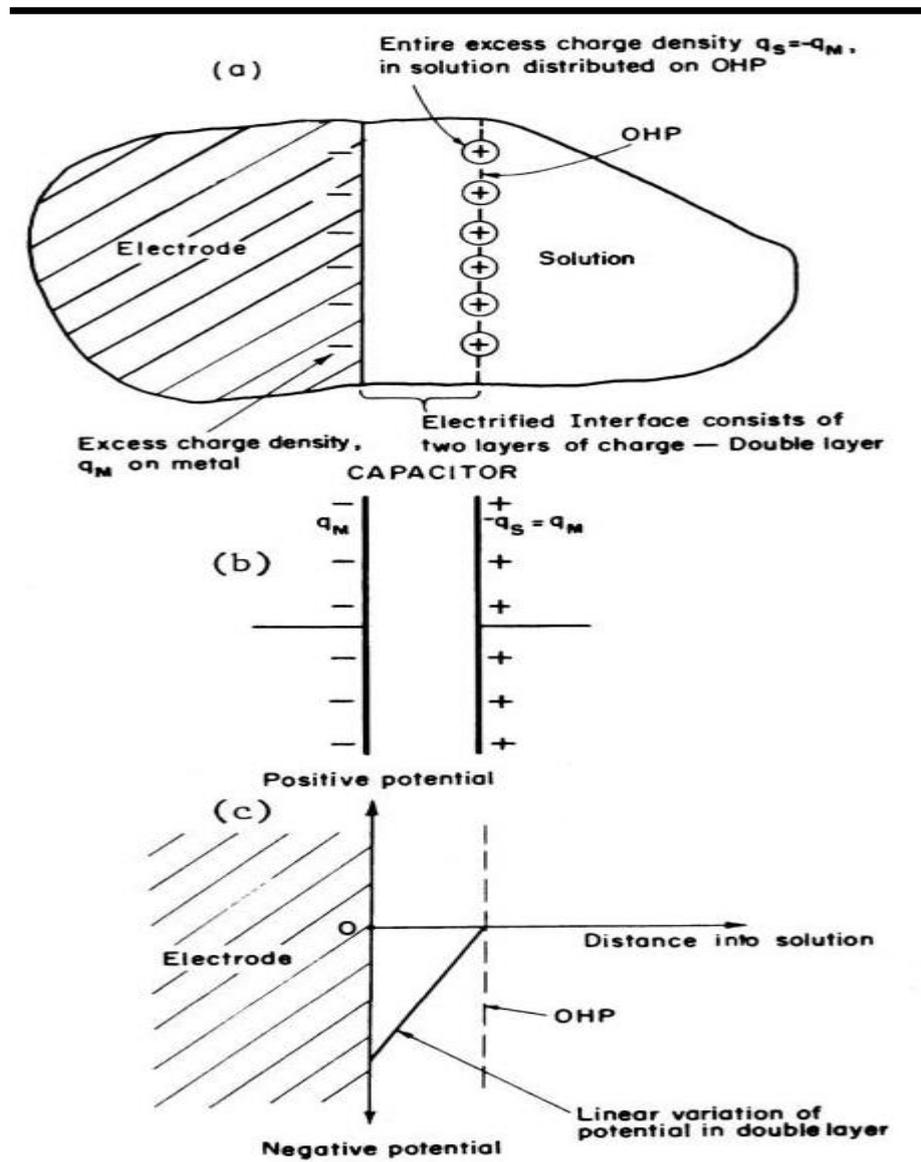
**Helmholz double layer (H.D.L)** consisting of a "plate" of excess negative charges on the surface of the metal and a counter balancing "plate" of excess positive charges (cations) in solution, the double layer as a whole being electrically neutral. The double layer can be regarded as equivalent to capacitor in which the "plate" are separated by a distance  $g$ .

### **The Electrical Double layer (E.D.L)**

- 1- Helmholtz model: in which the charges at the interface were regarded as the two plates constituting a parallel plate capacitor, e.g., a plate of metal with excess electrons (the inner Helmholtz plane I.H.P) and a plate of excess positively charged ions (the outer Helmholtz plane O.H.P) in the solution adjacent to the metal; the charges balance one another so that the e.d.l. is neutral as a whole. The distance of separation of charges is  $\sim 0.1\text{nm}$  (the diameter of

an ion). The excess charge on the metal  $q_m$ , and the solution plate  $q_s$  and the capacitance of the two parallel plates is  $C$ , then:

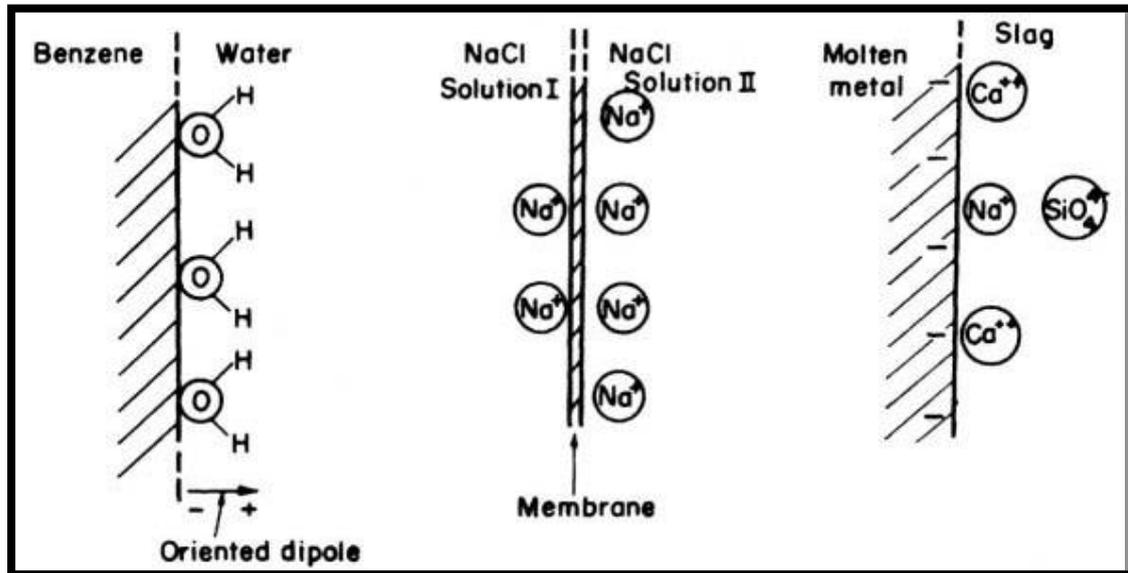
$C = q_m / \Delta\Phi$  where  $\Delta\Phi$  is potential difference since  $\Delta\Phi = q \cdot g / \epsilon_r \epsilon_0$  where  $\epsilon_r$  is the relative permittivity of material between the plates,  $\epsilon_0$  is the permittivity of a vacuum ( $8.85 \times 10^{-12} \text{ F m}^{-1}$ ) and  $g$  is the distance between the plates.



The potential difference at the interface between a metal and electrolyte solution is due to both the charges at the interface (electrostatic potential difference) and the surface dipole layers; the latter is referred to as the surface or adsorption potential difference. If the metal surface has an

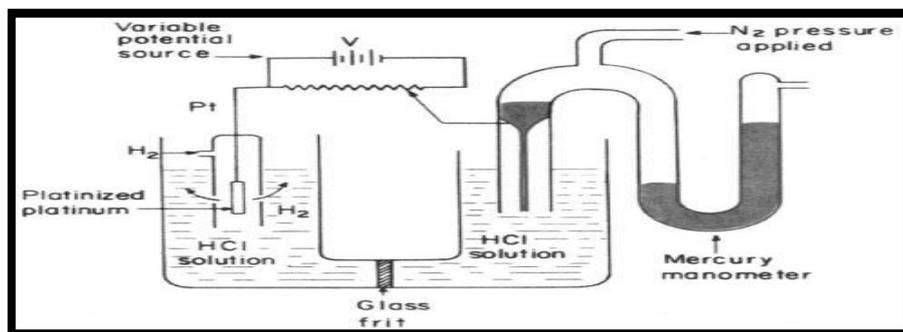
excess negative charge the cations are attracted to the surface and adsorbed whereas the anions are prevented from adsorbing.

The two binding electrons are closer to the oxygen atom than to the hydrogen atoms results in an electric field (electric dipole) and a potential difference exists across the molecule.



### Some examples of electrified interfaces.

**Lippmann Electrometer:** for studying the variation of the excess charge on mercury with variation in potential difference at the mercury solution interfaces.



### Electrocapillarity

Measurement of the surface tension of the mercury/solution interface is possible, and since this has been stated to be related to the surface excess,

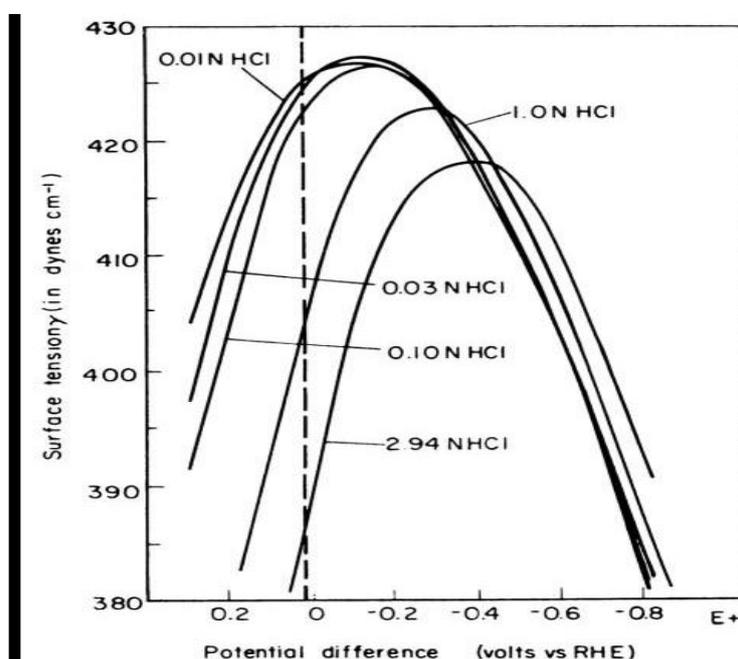
it becomes possible to measure this quantity for a given species in the interphase. In short, the system permits what are called *electrocapillary* measurements, i.e., the measurement of the surface tension of the metal (in contact with the solution) as a function of the electrical potential difference across the interface.

The potential of the mercury can be varied by means of a potentiometer and its potential measured by suitable reference electrode. A change in the potential of the mercury/ solution interface will result in a displacement of the mercury in the capillary, which can be determined with respect to a reference mark on the capillary by means of a travelling microscope.

The excess charge  $q_m$ , or charge density at constant temperature  $T$ , pressure  $P$  and concentration of electrolyte  $c$  is given by the Lippmann equation:

$$q_m = -(\partial q / \partial \Delta\Phi)_{T,P,C} = -(\partial \gamma / \partial E)_{T,P,C}$$

In which  $\gamma$  is the interfacial tension and  $\Delta\Phi$  is the potential difference between the mercury and the solution.



**Electrocapillary curves for HCl at various concentration** determined using a reversible hydrogen electrode (R.H.E) immersed in the same concentration of HCl as that used for the determination.

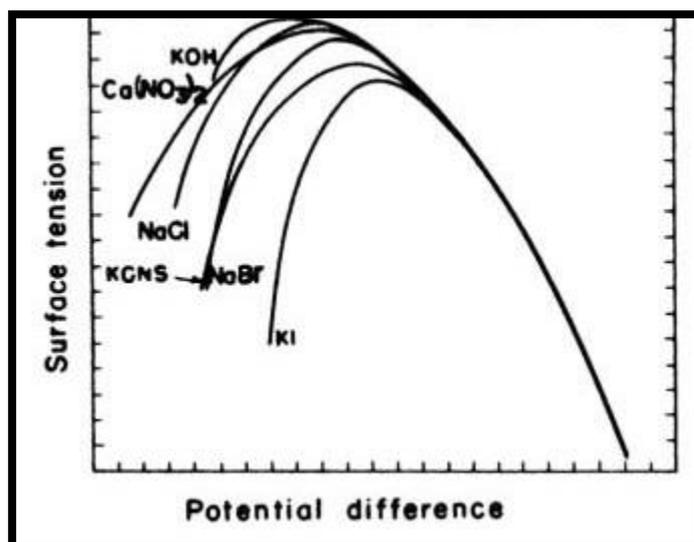
If the electric double layer is regarded as a simple parallel- plate condenser the electrocapillary curve should take the form of a perfect

parabola consisting of an ascending positive branch (excess positive charges on Hg and counterbalancing layer of negative charges in the solution). And a descending negative branch (excess negative charges on mercury and counter balancing layer of positive charges in solution).

Solution of different alkali nitrates at the same concentration give electrocapillary curves that coincide and that approximate to a perfect parabola, in spite of the fact that the cations that adsorb on the negative branch of the curve ( $\text{Na}^+$ ,  $\text{K}^+$ , etc.) are different.

**In the case of potassium halides**, although the negative branches of the curve (adsorption of  $\text{K}^+$ ) are similar, marked divergences are obtained on the positive branch of the curve (adsorption of halide), and it can be seen that the divergences from ideality are in the **order  $\text{I}^- > \text{Br}^- > \text{Cl}^-$** . In general, the departure of the curve from ideality occurs on the positive ascending branch at which anions are adsorbed at the mercury/solution interface.

Similar considerations apply to the curve for single electrolyte at different concentrations, and in the case of  $\text{HCl}$  whereas the ascending branches of the curve (adsorption of  $\text{Cl}^-$ ) show divergences that increase with increase in concentration coincide. Thus, it is the anion rather than cation (only large organic cations such as the tetra-alkyl ammonium ion have a significant effect that affects the shape of the electrocapillary curve.



### Potential at which an Electrode Has a Zero Charge

The potential difference across the system (or cell) at which the charge on the electrode is zero is the potential of zero charge and is given the symbol  $\phi_M$  or if this potential is measured on the hydrogen scale.

$$\phi_M = - \left( \frac{\partial \gamma}{\partial V} \right)_{\text{const.comp.}} = 0$$

With liquid metals, the most convenient method of determining the pzc is by making electrocapillary measurements. can be found and thus the value of  $\phi_M$ . The pzc, however, is such a fundamental characteristic of the interface that there is a considerable need to know its value for interfaces involving solid electrodes. Here, surface tensions cannot be determined with capillary electrodes, and one must resort to other methods of pzc determination. Some values of the pzc for solid metals are given in Table.

Metal	Solution	$E_{\text{pzc}}, V \text{ vs SHE}$
Aluminum	0.01 N KCl	-0.52
Antimony	0.10 HCl	-0.19
Bismuth	0.01 N KCl	-0.36
Cadmium	0.01 N KCl	-0.92
Cobalt	0.02 N Na <sub>2</sub> SO <sub>4</sub>	-0.32
Copper	0.02 N Na <sub>2</sub> SO <sub>4</sub>	+0.03
Gold	0.02 N Na <sub>2</sub> SO <sub>4</sub>	+0.23
Iron	0.001 N H <sub>2</sub> SO <sub>4</sub>	-0.37
Lead	0.01 N KCl	-0.69
Platinum	0.003 N HClO <sub>4</sub>	+0.41
Silver	0.02 N Na <sub>2</sub> SO <sub>4</sub>	-0.70

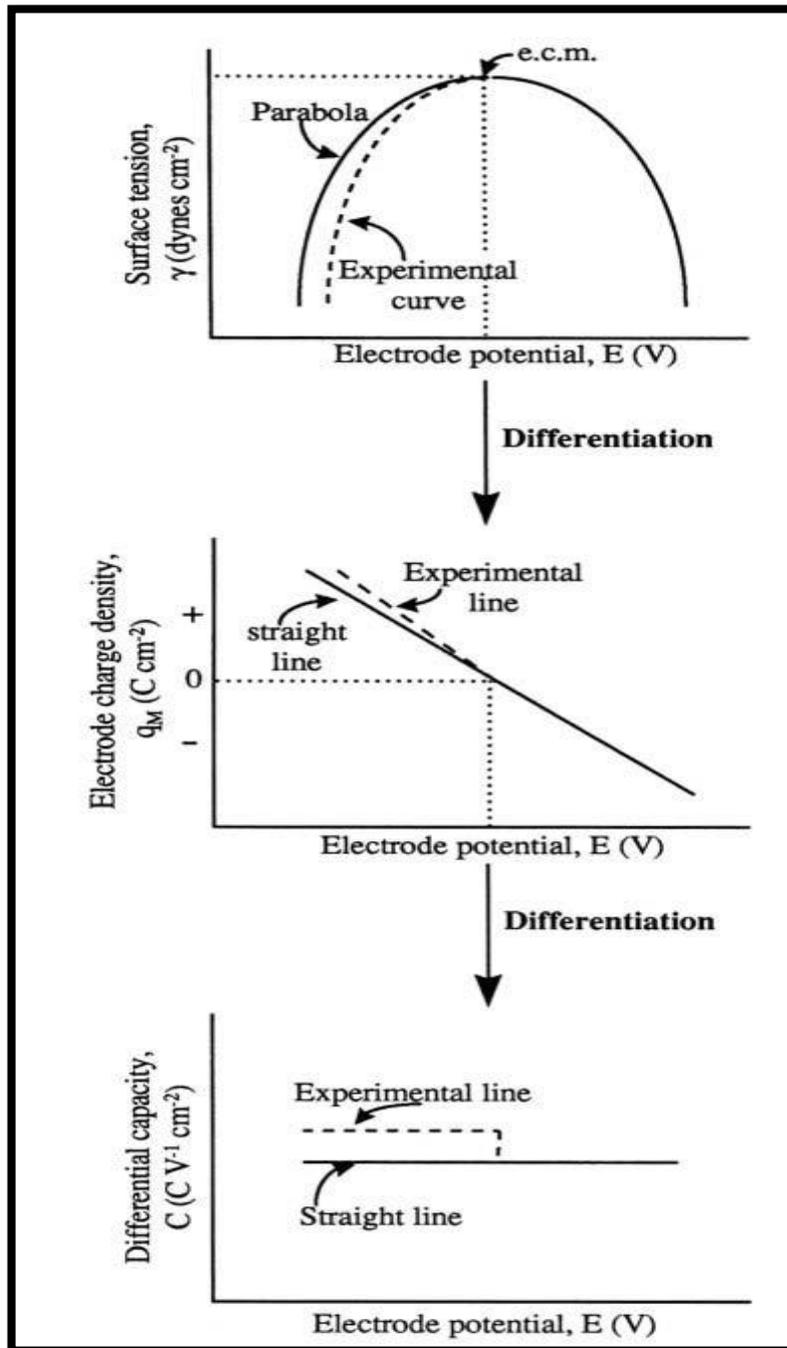
## Electrode Charge Varies with Applied Potential: Determination of the Electrical Capacitance of the Interface

The next step is obvious. Differentiate the  $\gamma$  versus  $V$  electrocapillary curve at various values of cell potential, and plot these values of the slope (electrode charge) as a function of potential. If the electrocapillary curve were a perfect parabola, then the charge (strictly, excess charge density) on the electrode would vary linearly with the cell potential. An electrified interface can be considered a system capable of storing charge, considering that it is a region where charges are accumulated or depleted relative to the bulk of the electrolyte. However, the ability to store charge is the characteristic property of an electric capacitor. This is the *integral* capacitance, and it is generally used for electrical capacitors where the capacity is constant and independent of the potential. This constancy of

capacity may not be the case with electrified interfaces and in order to be prepared for this eventuality, it is best to define a *differential* capacity  $C$  thus:

$$C = \left( \frac{\partial q_M}{\partial V} \right)_{\text{const.comp.}} = - \left( \frac{\partial^2 \gamma}{\partial V^2} \right)_{\text{const.comp.}}$$

It shows that the slope of the curve of the electrode charge versus cell potential yields the value of the differential capacity of the double layer. In the case of an ideal parabolic versus  $V$  curve, which yields a linear  $q$  versus  $V$  curve, one obtains a constant capacitance.



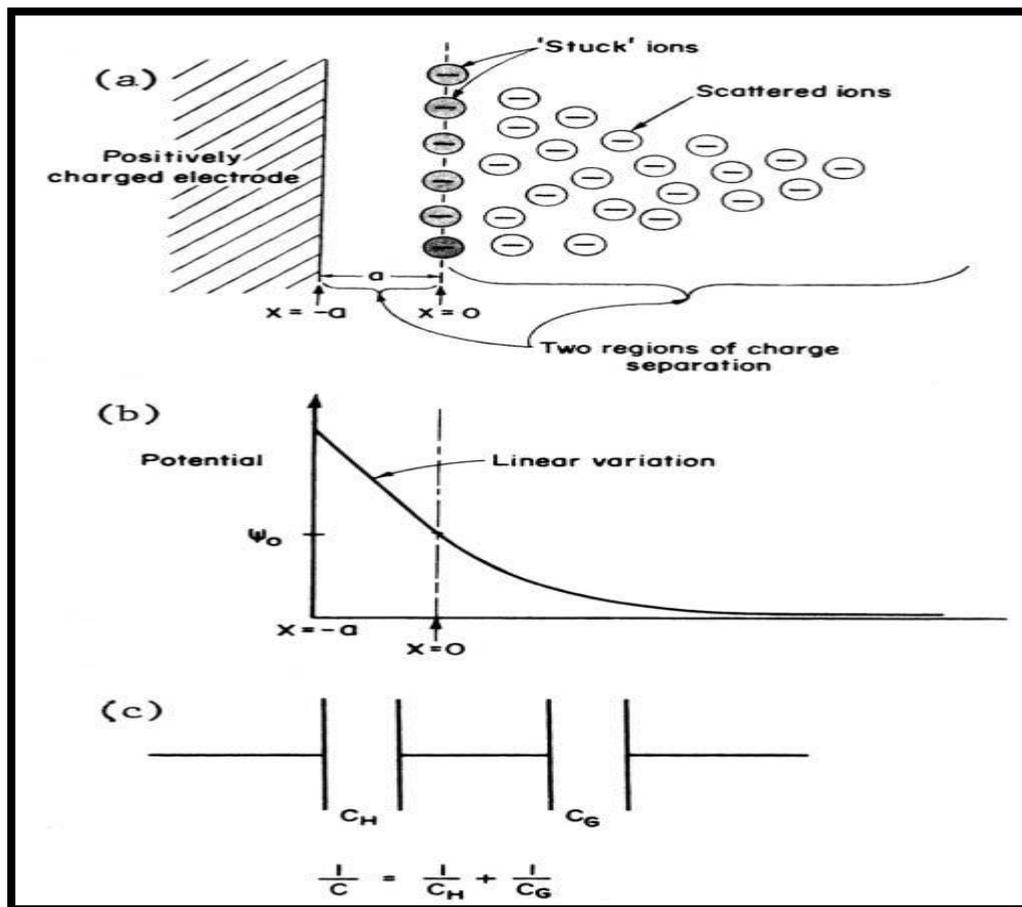
- Experimental (full time) and ideal parabolic electrocapillary curves.
- The corresponding electrode-charge density vs. potential.
- Capacity – potential curve.

## The Gouy–Chapman Model Provides a Potential Dependence of the Capacitance

After the initial jubilation that the diffuse-layer model has overcome the weakness of constant capacity with change of potential of the parallel-plate model, one has to face a few more somber facts about the details of

the model. The main fact is that the experimental capacity–potential curves are not the inverted parabolas that the Gouy–Chapman diffuse model (Only in very dilute solutions for 1:1 electrolytes) and at potentials near the pzc are there *portions* of the experimental curves that suggest that the interface is behaving in a Gouy–Chapman way. We could point to several reasons why the model fails to predict reality. For one, it neglects ion–ion interactions, which definitely become important at high concentrations. A second error, and perhaps the most important, is the assumption of pointcharge ions. Finally comes the value of the dielectric constant, which was taken as a constant in the region between the electrode and the bulk of the solution. However, even taking all these facts into account, this theory is not able to reproduce the capacitance–potential curves in the regions beyond the pzc proximity. The model seems, in fact, to be in sharp disagreement with the experimental behavior. The Gouy–Chapman theory might best be described as a brilliant failure. However, as will be seen, it represents an important contribution to a truer description of the double layer; it also finds use in the understanding of the stability of colloids and, hence, of the stability of living systems. The simplest version of the **Stern theory** consists in eliminating the point-charge approximation of the diffuse-layer theory. This is done in exactly the same way as in the theory of ion–ion interactions the ion centers are taken as not coming closer than a certain distance  $a$  from the electrode. The second modification of the Stern theory consists in dividing the solution charge into two contributions. Thus, according to the Stern picture, part of the charge on the solution is immobilized close to the electrode in the OHP (the Helmholtz–Perrin charge or and the remainder is diffusely spread out in the solution (the Gouy–Chapman charge or i.e.

$$q_S = q_H + q_G$$

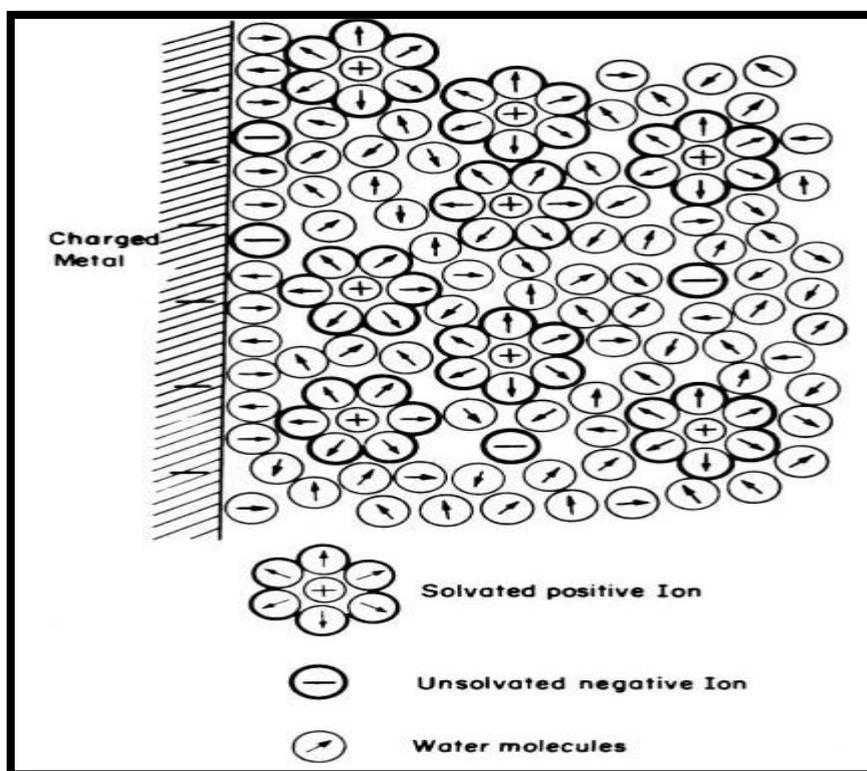


- a) A layer of ions stuck to the electrode and the remainder scattered in cloud fashion.
- b) The potential variation according to this model.
- c) The corresponding total differential capacity is given by helmholz and Gouy capacities.

## The Structure of Electrified Interfaces

Consider the picture of the metal/solution interface. It looks complicated, but actually the picture will be seen to consist of simple elements. The metal is made up of a lattice of positive ions and free electrons. When the metal is charged with an excess-charge density it means that there is either an excess (is negative), or a deficit (is positive) of free electrons at the surface of the metal. The metal surface can be compared to a stage occupied by this excess-charge density. The particles of the solution constitute the audience that responds to the scene on the stage. The first row is largely occupied by water dipoles. The excess charge on the metal produces a preferential orientation of the

water dipoles. This is the *hydration sheath* of the electrode. The net orientation of the dipoles varies with the charge on the metal, and the dipoles can even turn around and look away from the electrode.



### Electron Transfer under an Interfacial Electric Field

Electrode reactions are interfacial electron-transfer reactions, with the special circumstance that the electron transfer occurs between the solution and an electronic conductor, or vice versa. It was pointed out that the jump frequency of an ion is given by:

$$\nu = \frac{kT}{h} c_i e^{-\Delta G^\ddagger / RT}$$

Suppose the interfacial potential is divided (still in this thought experiment) into two parts. Each part will be less than the full which plays out across the whole double layer (or interphasial region between metal and solution). Suppose one takes a fraction of the potential difference, i.e.,  $\alpha$ , where  $\alpha$  regards this fraction of the interfacial potential difference as that which (when multiplied by the electric charge, on the ion) lowers the chemical energy barrier for the ion's movement right to left. Thus, because this electrostatic

energy is *helpful* (i.e., serves to attract the ion to move from right to left), one thinks of it as *lowering the energy barrier* for the transfer of the from the layer in the solution nearest to the electrode and onto the electrode.<sup>3</sup> Thus, one could define at this stage as

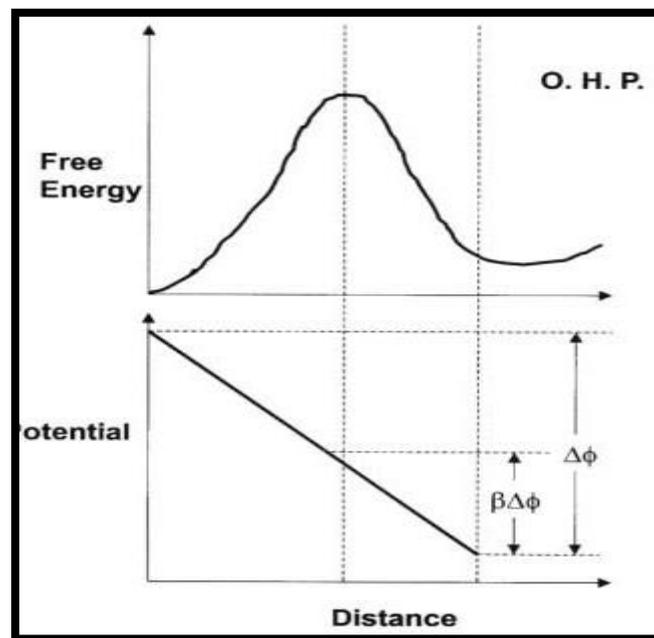
$$\beta = \frac{\text{Distance across around half the interfacial region}}{\text{Distance across the whole of the interfacial region}}$$

Correspondingly, is the amount (in energy terms) by which the energy barrier is raised for the converse metal solution reaction. Thus,

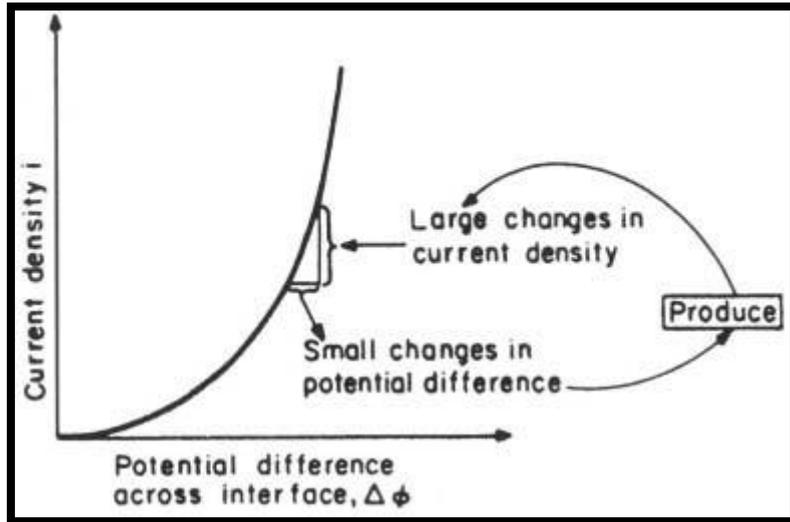
$$\Delta \vec{G}^{\circ \neq} = \Delta \vec{G}_{\text{chem}}^{\circ \neq} + \beta e_0 \Delta \phi$$

It follows as:

$$\vec{v}_e = \frac{kT}{h} e^{-\Delta \vec{G}_{\text{chem}}^{\circ \neq} / RT} e^{-\beta \Delta \phi e_0 / RT} = \vec{v}_{\text{chem}} e^{-\beta \Delta \phi e_0 / RT}$$



The electrical work of activating the ion



**Fig. 7.10.** The exponential nature of the current–potential dependence results in large changes in current for small changes in potential.

In another form. Thus,  $e$  is the electrical charge of a *single ion* and  $k$  is the gas constant *per molecule*. Converting now to gram-ions, or moles,  $k$  becomes  $R$  and becomes  $F$ , the faraday, the charge on an Avogadro's number of ions. Then:

$$\vec{v}_e = \frac{kT}{h} c_{Ag^+} e^{-\Delta\bar{G}^{\ddagger}/RT} e^{-\beta F \Delta\phi / RT}$$

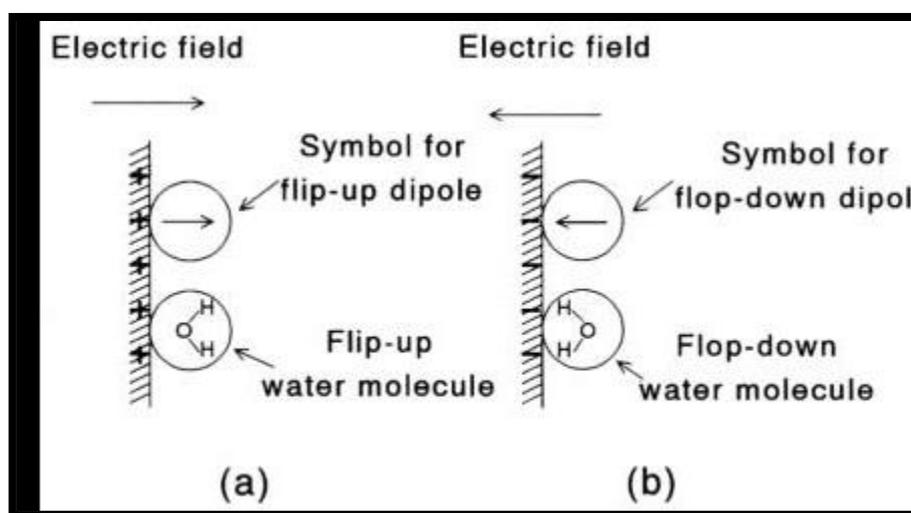
and this also represents the rate of the ion crossing the interface. When this is multiplied by the charge per mole of positive charges, it becomes the current density,  $i$ , in A/cm<sup>2</sup>

$$i = F \frac{kT}{h} c_{Ag^+} e^{-\Delta\bar{G}^{\ddagger}/RT} e^{-\beta \Delta\phi F / RT}$$

This last relation, that for the electric current *density* (so called because it is per unit area and time), represents the bridge relation between chemistry (where the rate of a surface reaction is expressed in moles ) and electrochemistry, where it is expressed in amperes.

## A Two-Way Traffic across the Interface: Equilibrium and the Exchange Current Density

The description given suggests that every interface should eventually stop letting charge leak through because the transfer of positive charge from solution to the electrode makes the latter more positive and hence hinders further transfers. According to this picture every interface should behave after a short time as an ideally polarizable interface. Thus, in the electronation reaction, the positive ion moves against the directed field, it moves with the field in the de-electronation.



- a) Flip-up orientation and b) flip-down orientation of molecule on an electrode

## Butler- Volmer Equation

Under equilibrium conditions, the individual electronation and de-electronation rates or current density  $i_0$ :

$$\vec{i} = F\vec{k}c_i e^{-\beta\Delta\phi F/RT}$$

The reverse of this, the electrons being donated back to this metal, would be given by:

$$\vec{i} = F\vec{k}c_{M^+} e^{(1-\beta)F\Delta\phi/RT}$$

The special case of equilibrium:

$$\overleftarrow{i} = \overrightarrow{i}$$

$$i_{\text{cath}} = i_{\text{an}} = 0$$

For a net cathodic current density:

$$i_{\text{cath}} = F\overrightarrow{k}c_i e^{-\beta\Delta\phi F/RT} - F\overleftarrow{k}c_A e^{(1-\beta)\Delta\phi F/RT}$$

Where  $i$  is the concentration of an ionic species  $i$  and  $A$  is atoms.

$$\text{when } i_{\text{cath}} = 0$$

$$\text{hence } F\overrightarrow{k}c_i e^{-\beta\Delta\phi_e F/RT} = i_0 = F\overleftarrow{k}c_A e^{(1-\beta)\Delta\phi_e F/RT}$$

Where  $i_0$  is called the *exchange current density*

$$\Delta\phi = \eta + \Delta\phi_e$$

$$i_{\text{cath}} = i_0(e^{-\beta\eta F/RT} - e^{(1-\beta)\eta F/RT})$$

This is the famous Butler–Volmer (B-V) equation, the central equation of phenomenological electrode kinetics, valid under conditions where there is a plentiful supply of reactant (e.g., the ions) by easy diffusion to and from electrodes in the solution, so that the rate of the reaction is indeed controlled by the electric charge transfer at the interface, and not by transport of ions to the electrode or away from it. The B-V equation has been derived here for the case of a negative whereupon the current passing will be cathodic, i.e., electrons will flow from the electrode to the solution. There can be an exactly similar anodic deduction and the result will be:

$$i_{\text{an}} = i_0(e^{(1-\beta)\eta F/RT} - e^{-\beta\eta F/RT})$$

Here the first (anodic) term dominates, is positive, and the current will be by means of transfer of electrons from the solution to the electrode.

**Low overpotential case:** the overpotential ( $\eta$ ) is numerically less than  $RT/\beta F$  around 50 mV at room temperature in most cases), expansion of the B-V equation under this condition given by:

$$i = i_0 \frac{\eta F}{RT}$$

i.e., the current density (the rate of electron transfer across the electrode/solution interface) is linear with the overpotential, The sign of the current density will be determined by that of negative for a cathodic (electronation) current and positive for an anodic (or deelectronation) one.

**High overpotential case:** the overpotential ( $\eta$ ) is numerically is greater than  $RT/\beta F$ , then for cathodic current densities ( $\eta$  is negative),

$$\left| e^{-\beta\eta F/RT} > e^{(1-\beta)\eta F/RT} \right.$$

Therefore, if  $\eta$  is negative:

$$i_{\text{cath}} = i_0 e^{-\beta\eta F/RT}$$

Thus, as becomes increasingly negative, the current rises exponentially, It is trivial to show that form:

$$\eta = \frac{RT}{\beta F} \ln i_0 - \frac{RT}{\beta F} \ln i$$

That for a given reaction and constant temperature:

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

Where  $a$  and  $b$  are constants,  $2.303RT/\beta F$  (Tafel equation), at  $T=298\text{K}$

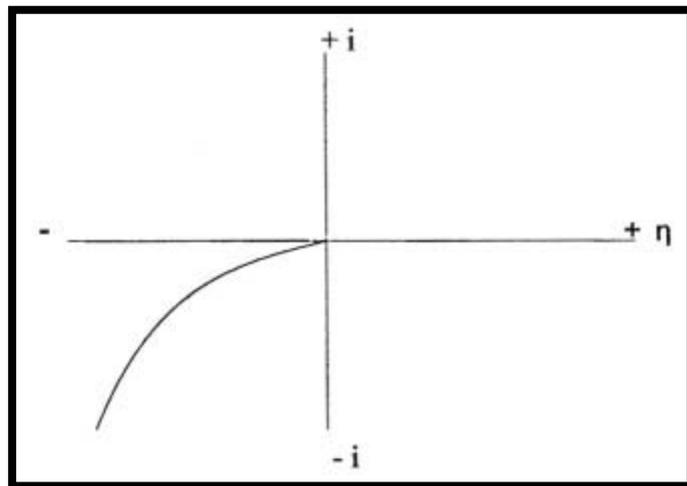
$$2.303 \frac{RT}{F} = 2.303 (8.315)(298)/9.65 \cdot 10^4 = 0.058.$$

Of course, for an anodic reaction, a corresponding argument with sufficiently positive gives:

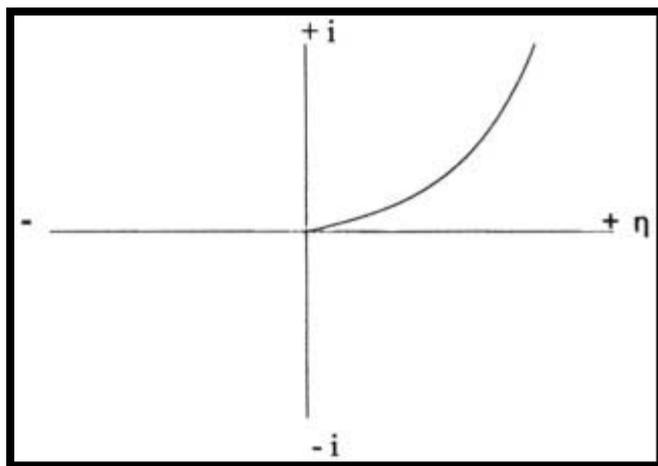
$$i = i_0 e^{(1-\beta)\eta F/RT}$$

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

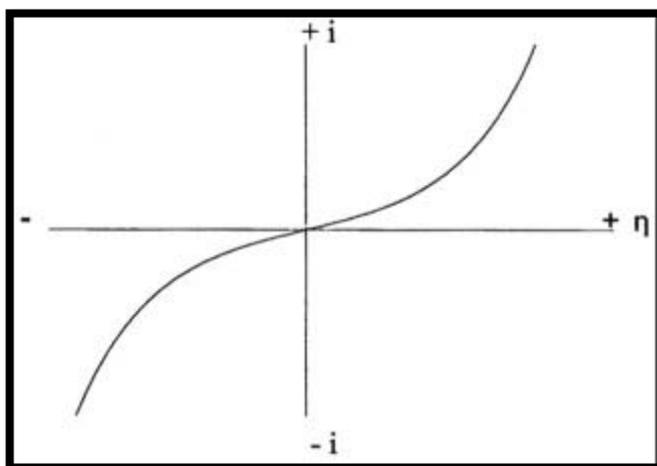
if  $\beta=1/2$ ,  $b= (2.303) 2(RT/F) = 0.116$  , In fact, experiments show that for simple electron- and ion-transfer reactions, one often finds that i.e., they agree with the simplest supposition, which corresponds to the picture one gets if the energy barrier at the surface is symmetrical. There are two kinds of charge-transfer reactions at electrodes. An *electron* transfer reaction is the first kind and is exemplified by the reduction of to at the interface. The ions in the layer hardly move while the electron comes from the electrode or leaves the ions in the layer of solution adjacent to the electrode and goes to the electrode. The charge transfer is dominated by means of electrons transferring from electrode to ions and vice versa. An *ion*-transfer reaction, on the other hand, is one in which, for example, in the cathodic deposition of ions, the ion begins in the solution layer nearest the electrode but toward the electrode. At some point on the way, electron transfer occurs. The point is, the ion has also transferred. Correspondingly, for anodic ion-transfer reactions, a surface atom leaves the electrode, becoming in this act an ion and leaving an electron behind in the metal.



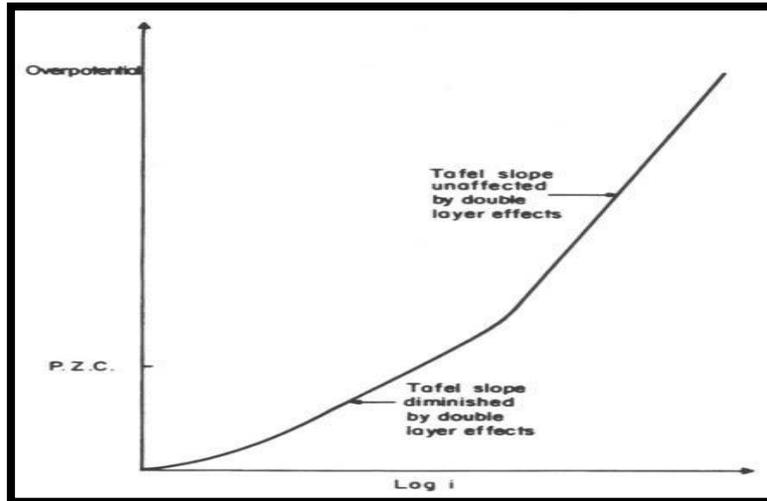
Dependence of current density on negative overpotential.



Dependence of current density on positive overpotential



Dependence of current density on overpotential



A typical Tafel line for one-electron transfer electrode reaction.

## Polarizable and Non-polarizable Interfaces

**Non-polarizable interface** is one at which the potential difference does not change easily with the passage of current. It does not polarize.

Since  $\eta = RT/F \ln i/i_0$  or  $\eta/i = RT/Fi_0 = R_p =$  polarization resistance

**It is better to write:**

$$(d\eta/di)_{CA,CD,T} = RT/Fi_0 = R_p$$

### Non-polarizable interface

- 1-  $i_0$  tends to very high values, i.e., towards infinity. As  $i$  to  $i_0$ ,  $R_p = (d\eta/di)_{CA,CD,T}$
- 2- The slope of  $\eta$  vs.  $I$  curve is zero, i.e, despite the passage of a current density across the interface; the overpotential tends to be zero.
- 3- The interface remains virtually at its equilibrium potential difference.
- 4- The higher the value of  $i_0$  is, the less does the potential difference across an interface depart from the equilibrium value on the passage of a current.
- 5- The (hypothetical) ideally non-polarizable interface therefore is always at the equilibrium potential.
- 6- An exchange-current density of infinity is of course an idealized case. All values of  $i_0$  must be finite, which means that all interface

show some degree of polarizability. It is shown in the table below that layer the values  $i_0$  are, the greater is the current density  $i$  required to produce a given change of potential from equilibrium value  $\Delta\Phi$  characteristic of the given reaction.

$i_0$ A/cm <sup>2</sup>	0.001	0.01	0.100	0.300
$10^{-6}$	$4 \times 10^{-8}$	$3.9 \times 10^{-7}$	$6.9 \times 10^{-6}$	$4.9 \times 10^{-4}$
$10^{-3}$	$4 \times 10^{-5}$	$3.9 \times 10^{-4}$	$6.9 \times 10^{-4}$	$4.9 \times 10^{-2}$
1	$4 \times 10^{-2}$	0.39	6.9	49.4

### Polarizable Interface

- 1-  $i_0$  tends to very low values; i.e, toward zero as  $i_0 = \text{zero}$ ,  $R_p = \text{infinity}$ .
- 2- Here,  $d\eta/di$ , the polarizability, and the reaction resistance  $R_p$  becomes infinite.
- 3- The potential departs from the equilibrium values even with a very small current density across the interface; its potential is easily chargeable; it can be varied at will by an external power source without passing significant current.

### The idealized cases

- a- The value  $i_0 = 0$  is the idealized extreme of a polarizable interface.
- b- The value  $i_0 = \text{infinity}$  is the idealized extreme of non-polarizable interface.

### The origin of concentration overpotential

Experiment shows that when the transport of reactants cannot keep pace with the charge-transfer reaction, the potential observed at the current density  $i$  is not equal to the zero-current, or equilibrium potential difference. If an electronation reaction is considered.



The potential sinks to more negative values than that corresponding to equilibrium although the exchange-current density has been assumed to

be very high (negligible departure from caused by electron transfer). A simple explanation for this phenomenon can be given. Since the charge transfer is assumed to be virtually at equilibrium, one can again use the Nernst equation to express the potential difference across the interface. Thus, when the current is zero,

$$\Delta\phi_e = \Delta\phi_{i=0} = \Delta\phi^0 + \frac{RT}{nF} \ln c^0$$

Because it is known that, owing to diffusional holdup, the interfacial concentration is less than the bulk value. One has to write:

$$\Delta\phi = \Delta\phi^0 + \frac{RT}{nF} \ln c_{x=0}$$

This concentration-produced<sup>76</sup> potential difference is often known as concentration overpotential to distinguish it from the usual overpotential

$$\eta_c = \Delta\phi - \Delta\phi_e = \frac{RT}{nF} \ln \frac{c_{x=0}}{c^0}$$

It is now necessary to take a more unified view by considering situations in which the rate of the electrodic process at the interface is subject both to activation and to transport limitations. One refers to a *combined activation-transport control* of the electrodic reaction. Under such conditions, there will be, in addition to the overpotential produced by the concentration change (from to at the interface, an activation overpotential because the charge-transfer reaction is not at equilibrium. The total overpotential is the difference between the interfacial-potential difference corresponding to a current density  $i$ , and the equilibrium-potential differ

$$\eta = \Delta\phi - \Delta\phi_e$$

$$\eta = \Delta\phi - \Delta\phi_e = \eta_a + \eta_c$$

## The Diffusion Layer

There is a variation of concentration with distance from the interface toward the bulk of the solution. However, as far as the charge-transfer reaction is concerned, is the gradient of concentration *at the interface* because it is this gradient that drives the diffusion flux. Even when there is convection with a laminar flow of electrolyte and the flux  $J$  is governed by the concentration gradient in the layer. Thus, using Fick's law of diffusion

$$\frac{i}{nF} = J_D = -D \left( \frac{dc}{dx} \right)_{x=0}$$

The linear part of the concentration vs. distance curve until it intersects the bulk value of the concentration at some distance from the interface. Then the gradient of the concentration at  $x = 0$ ,

$$\frac{i}{nF} = J_D = -D \frac{c^0 - c_{x=0}}{\delta}$$

In this approximation, therefore, one can consider that the diffusion occurs across a region parallel to the interface, i.e., across a ***Nernst diffusion layer of effective thickness***.

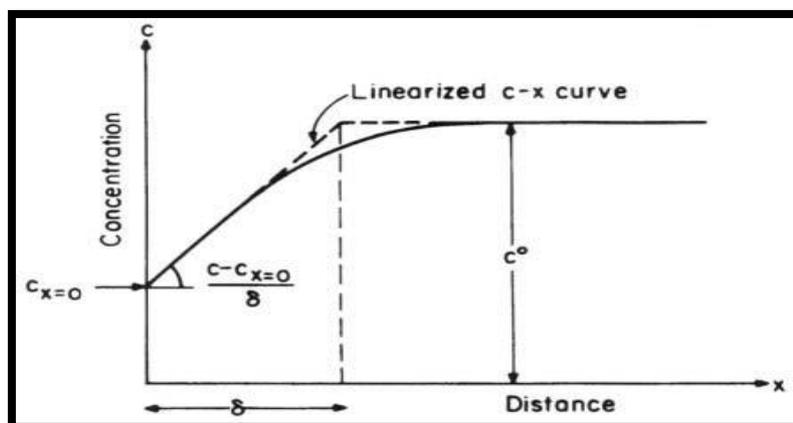
The time variation of *before* the onset of natural convection depends on how the diffusion process is provoked. If a constant current density is switched on at  $t = 0$ , then the time variation of the effective diffusion-layer thickness can be obtained from Eqs.

$$c^0 - c_{x=0} = -\frac{i_g}{nF} \frac{\delta}{D} = -\frac{2i_g}{nF} \sqrt{\frac{t}{\pi D}}$$

$$\delta = \frac{2}{\sqrt{\pi}} \sqrt{Dt}$$

The diffusion-layer concept is an artifice for handling the flux arising from would be, if treated in a proper hydrodynamic way, a complicated space variation of concentration at the interface. There is always some gradient of concentration at the interface; there is an initial region in

which the concentration changes linearly with distance, but there is, in the real case, no sharply defined layer of definite thickness.



## The Steady-State Current–Potential Relation under Conditions of Transport Control

The concept of limiting current density permits a simple derivation of a relation between the steady-state concentration overpotential and the current density  $i$  if the reaction is such that other forms of overpotential are negligible. One starts from the expression for the concentration overpotential :

$$\eta_c = \frac{RT}{nF} \ln \frac{c_{x=0}}{c^0}$$

The electronation current density is given by:

$$i = -DnF \frac{c^0 - c_{x=0}}{\delta}$$

$$c^0 - c_{x=0} = \frac{-\delta}{DnF} i$$

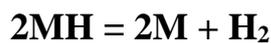
$$\frac{\delta}{DnFc^0} = -\frac{1}{i_L}$$

Hence:

$$\frac{c_{x=0}}{c^0} = 1 - \frac{i}{i_L}$$

### **Transfer coefficient, symmetry factor and stoichiometric number**

In a multistep reaction the number of times the r.d.s must occur for each act of the overall reaction is referred to as the stoichiometric number

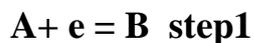


And since the discharge step must occur twice for each act of the overall reaction then  $V=2$ . On the other hand for rate determining step discharge followed by E.D



The rate determining step is required to take place only once and  $V=1$ .

Generalizing for a multistep reaction of the type  $A + Ze = 2$  in which all steps involve the transfer of one electron and the rate determining step involves  $\Omega$  electrons:



path	steps	R. D. S	$\gamma$ (cath).	$\gamma$ (anode)	$\Omega$	V	Cathodic transfer coefficient
chemical	$H^{++}M+e=MH$	1	0	0	1	2	$\beta$
combination	$2MH = H_2+2M$	2	2	0	0	1	2
Electrode	$H^{++}M+e=MH$	1	0	1	1	1	$\beta$
desorption	$H^+ + MH + e = M + H_2$	2	1	0	1	1	$1+\beta$