

Chapter three

Interfacial Electrochemistry

3.1. Introduction

An **interface** is a surface forming a common boundary among two different phases of matter, such as an insoluble solid and a liquid, two immiscible liquids, a liquid and an insoluble gas or a liquid and vacuum. The importance of the interface depends on the type of system: the bigger the quotient area/volume, the more effect the surface phenomena will have. Therefore interfaces are very important in systems with big area to volume ratios, such as colloids.

Interfaces can be flat or curved. For example oil droplets in a salad dressing are spherical but the interface between water and air in a glass of water is mostly flat.

Interfaces may cause various optical phenomena, such as refraction. Optical lenses serve as an example of a practical application of the interface between glass and air.

Surfaces and interfaces define a boundary between a material and its surrounding environment and influence interactions with that environment. At the molecular level, the surface atoms have a different chemical environment, that is, fewer nearest neighbors, from that in the bulk. As a consequence, these surface atoms with changed atomic and electronic structures exhibit high chemical reactivity. This property makes surfaces and interfaces a favored medium for chemical and biological processes in nature and in technological applications.

Most of the events in electrochemistry take place at an interface and that is why the interfacial electrochemistry constitutes the major part of electrochemical science. Relevant interface here are:

- ✓ Metal - liquid interface
- ✓ Metal – solid electrolyte
- ✓ Semiconductor electrolyte interface and
- ✓ The interface between two immiscible electrolyte solutions

These interfaces are chargeable, that is when the external potential is applied charge separation of positive and negative charges on the two sides of the contact occurs. Such an interface can accumulate energy and be characterized by electric capacitance within the range of ideal polarizability beyond which faraday processes turn on.

Properties of the interface play a crucial role in electrochemical energy conversion, electrolysis, electro catalysis and electrochemical devices. On the other hand chargeable interface has been widely used to probe various surface properties. Indeed, due to Debye screening in electrolyte, the electric field at the electrochemical interface is localized in a narrow interfacial region.

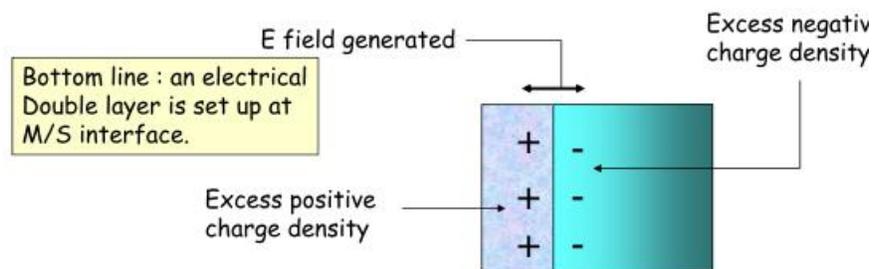
Generally, **Interfacial Electrochemistry** is the phenomena that take place at the electrified interface (metal| electrolyte, electronic| ionic conductor) to study:

- ✓ Potential differences across interface
- ✓ charge densities
- ✓ dipole moments
- ✓ electrical currents of interface
- ✓ conversion of energy
- ✓ conversion of chemical species and
- ✓ transformation of energy

3.2. Potential differences across interfaces

Distribution of potential near charged interface is crucial in electrode kinetics, since the potential drops plays a role of a variable driving force of reaction. The reactions take place at the interface and with participation of adsorbed reactants. However not only reactants but other species as well can adsorb at the interface.

The interface between two dissimilar interfaces is electrified. Almost all surfaces carry an excess electric charge. Hence when two dissimilar phases come into contact, charge separation occurs in the interfacial region which results in the generation of an interfacial potential difference or electric field.



Consider a metal electrode in contact with an aqueous solution containing salt (e.g KCl (aq)).

- ✓ The solution contains solvated charged ions and solvent dipoles.
- ✓ Forces experienced by ions and solvent molecules in bulk of solution are isotropic: spherical symmetry operates. Ions and water molecules (on a time average) experience forces which are position and direction independent.
- ✓ There is no net alignment of solvent dipoles, and positive and negative ions are equally distributed throughout any volume element of the solution.
- ✓ Electro neutrality operates in bulk solution region very far from electrode surface.
- ✓ In this region forces experienced by ions and solvent dipoles are no longer isotropic and homogeneous. The forces are anisotropic because of the presence of the electrode phase.
- ✓ New solvent structure, different from that of the bulk, develops because of the phase boundary.
- ✓ Electro-neutrality breaks down on the solution side of the interface.
- ✓ There will be a net orientation of solvent dipoles and a net excess charge in any volume element of the solution adjacent to the electrode surface.
- ✓ The solution side of the interface becomes electrified.
- ✓ Once the solution side of the interface becomes electrified (acquires a net or excess charge), an electric field will operate across the phase boundary.
- ✓ Since the metallic phase contains charged particles, the latter will respond to this E field.
- ✓ The free electrons will move away from or move towards the interface depending on the direction of the E field.
- ✓ Thus a net charge will be induced on the metal, which will be equal in magnitude and opposite in sign to that on the solution side of the phase boundary.

- ✓ Thus charge separation occurs across the M/S interface, and this gives rise to an interfacial potential difference.
- ✓ Typically the potential difference is 1.0 V. However the spatial dimensions of the interface region are very small, typically 1 nm thick. Thus the electric field strength present at the M/S interface will be typically 10^7 Vcm^{-1} which is very large.

Electrified interfaces represent a specific quasi two dimensional object in the vicinity of the geometrical boundary of two phases containing electronic or ionic charges and an electric field distribution generated by these charges. Practically at least one of these media in contact is conducting while the second one may be either a conductor of another kind.

The simplest example is given by the free metal surface. Owing to the Pauli principle the metal electrons at the highest occupation level possess a significant kinetic energy so that their density extends outside the ionic skeleton of the electrode. It results in the formation of a structure characteristics for numerous electrified interfaces; two oppositely charged spatial regions (with zero overall charge), this time a positively charged region inside the ion skeleton due to the depletion of electrons and a negatively charged region formed by the electronic tail. Because of this “Nano condenser”, the bulk metal has got a high positive potential of several volts with respect to the vacuum.

A more complicated example is provided by the contact of two electronic conductors, metals or semiconductors. At equilibrium the electrochemical potential of electrons must be equal in the bulk phases. The potential difference between them is determined by the bulk properties of the media in contact, i.e., by the difference between the chemical potential of electrons.

$$\Delta\phi^{m_1/m_2} = \frac{\mu_e^{m_1} - \mu_e^{m_2}}{e}$$

Where e is elementary charge

Generally, Electrode processes (reactions) take place at the surface of the electrode, and produce a slight unbalance in the electric charges of the electrode and the solution. The result is an interfacial potential difference which, as we saw above, can materially affect the rate and direction of the reaction. Much of the importance of electrochemistry lies in the ways that these

potential differences can be related to the thermodynamics and kinetics of electrode reactions. In particular, manipulation of the interfacial potential difference affords an important way of exerting external control on an electrode reaction.

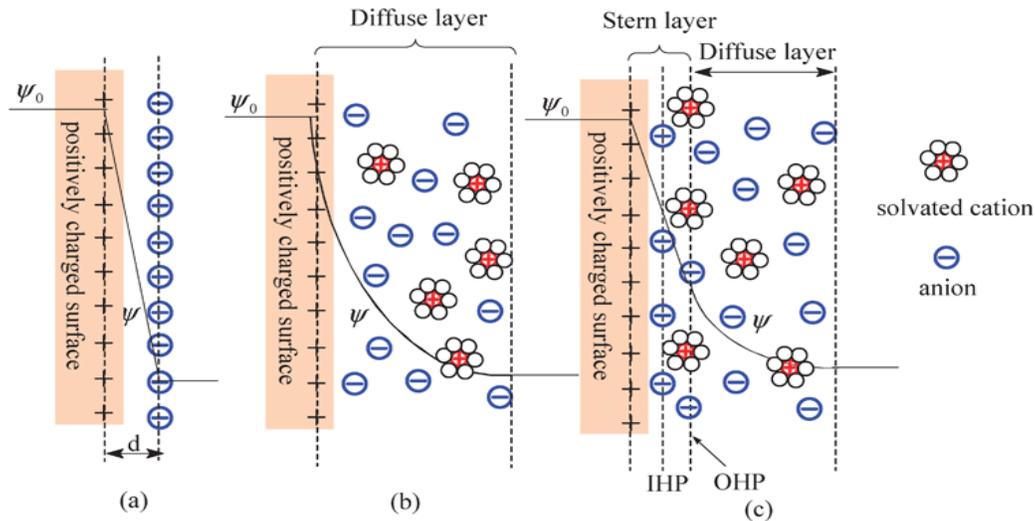
The interfacial potential differences which develop in electrode-solution systems are limited to only a few volts at most. This may not seem like very much, but it is important to understand that what is important is the distance over which this potential difference exists. Actually, interfacial potentials exist between any two phases in contact, even in the absence of chemical reactions. In many forms of matter, they are the result of adsorption or ordered alignment of molecules caused by non-uniform forces in the interfacial region. Thus colloidal particles in aqueous suspensions selectively adsorb a given kind of ion, positive for some colloids, and negative for others. The resulting net electric charge prevents the particles from coming together and coalescing, which they would otherwise tend to do under the influence of ordinary van der Waals attractions.

3.3. Electrical Double layer

When a metal M is immersed in a suitable electrolyte, initially its atoms oxidize at a relatively high rate and subsequently the oxidation (dissolution) process gradually ceases and eventually stops due to a negative charge build-up on the metal surface. Thus, the dynamic equilibrium is attained, provided that atoms are removed from their lattice sites to ionize as cations (M^+) into the electrolyte forming a negatively charged metal surface. The polar (H_2O) water molecules and the hydrogen cations (H^+) in electrolyte, they are attracted by the negatively charged metal surface to form an ionic structure (layer), which prevents other ions from the bulk solution to be part of it.

This structure is a complex ionic arrangement in an electric field and has a limited thickness. Eventually metal dissolution ceases if there is no external current flow, but it proceeds until the ionic structure is dense enough to protect and prevent the metal from reacting any further until equilibrium is reached. With respect to the metal-layer-bulk within which there must exist an electric potential decay. This ionic structure is known as electrical double layer (EDL). This layer is referred to as the Helmholtz layer which behaves like a charged capacitor.

The presence of charge gives rise to potential at the surface of a particle. This potential drops to zero at some distance away from the surface depending up on the concentration of the counter ions in the bulk phase. The region in which the influence of the charge is appreciable is known as Electrical Double Layer (EDL).



This model indicates that some negatively charged ions adsorbed on the metal electrode surface and polar water covers the rest of this surface, forming protective layer. The positively charged hydrogen is in contact with negatively charged metal surface. Thus one can conclude that:

- 1. The inner Helmholtz plane (IHP):** is an ionic layer that consists of adsorbed dipole H_2O molecules. The majority of the anions do not penetrate this layer. The inner potential on the boundary of this ionic plane is ϕ_1
- 2. The outer Helmholtz plane (OHP) :** consists of a plane of adsorbed ions due to electrostatic forces in contact with a diffuse ionic layer at the inner potential ϕ_2
- 3. The diffuse layer (DL) :** is a thick layer located in a region of diffusely ions in contact with the OHP and the bulk of solution at potential range $\phi_1 < \phi_{diffuse} < \phi_3$

The electric double layer consists of two regions: an inner region including adsorbed ions and a diffuse region in which ions are distributed according to the influence of electric forces and random thermal motion. The simplest quantitative treatment the diffuse part of DL is assumed (Gouy and Chapman model).

1. Surface is flat, infinite, uniformly charged.
2. The ions are point charges distributed according to the Boltzmann distribution.

The electric potential ψ_0 at a flat surface and ψ at distance x from the surface in the electrolyte solution. The potential decreases exponentially with distance from the charged surface:

$$\psi = \psi_0 \exp(-\kappa x) \quad \kappa \text{ Debye-Hückel parameter}$$

The interfacial potential within the electrolyte is defined as:

$$\phi(x) = -\frac{RT}{zF} \ln[K] \quad \text{Or} \quad \phi(x) = -\frac{RT}{zF} \ln\left[\frac{C(x)}{C_o}\right]$$

Where $K = \text{rate constant} = C(x)/C_o$

$C(x) = \text{concentration (activity) at } x > 0$

$C_o = \text{concentration at } x = 0$

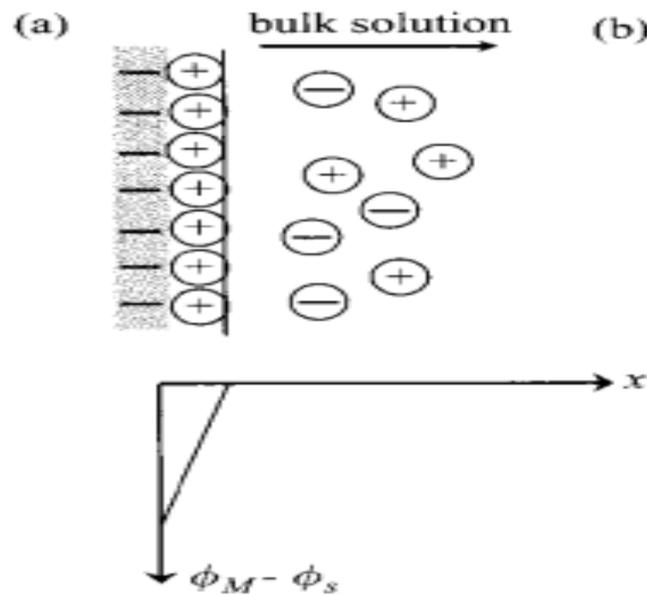
The metal surface has lattice of +ve and electron of -ve charge

The following models used to explain their behavior

- a) Helmholtz – Perrin model
- b) Gouy – Chapman diffuse charge model
- c) Stern Model

A) Helmholtz – Perrin Model: according to Helmholtz - Perrin model:-

- (i) Charge on the metal draws out by randomly distributed ions in solution which also make a counter layer of opposite charge
- (ii) The interface has two sheets of charge one on electrode and other in solution.
- (iii) A double layer formed which behave like all plate condenser
- (iv) Charge magnitude both sheets is equal but opposite in sign
- (v) The potential drop between the two layers of charge is linear.



Now according to electrostatic theory of capacitor for the double layer, the potential difference across a condenser of unit area is give by:

$$v = \left(\frac{d}{E\epsilon_0}\right)\rho_m \quad \text{Or} \quad \partial v = \left(\frac{d}{E\epsilon_0}\right)\partial\rho_m$$

Where d = is the distance between the plates

E = the dielectric constant of the medium between the plates

ϵ_0 = the permittivity of free space (8.85×10^{-12} F/m)

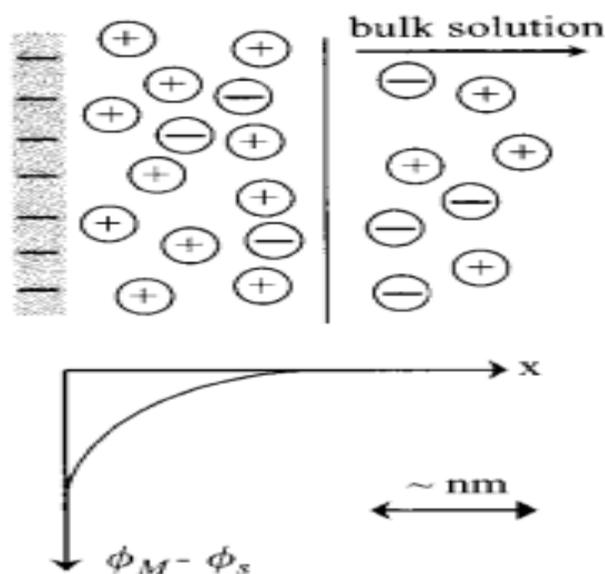
ρ_m = charge density

But the capacitance is $C = \frac{(\partial\rho_m)}{(\partial v)} = \frac{E\epsilon_0}{d}$ at constant composition

This model is satisfactory if E and d remain constant. The experimental results reveal that electrocapillary curves are asymmetric and not perfect parabolas, so the electrode interface does not behave like simple electrical double layer.

B. Gouy – Chapman Diffuse Model

- i) Contrary to Helmholtz – Perrin model ions liberate from sheath to electrode
- ii) Ions undergo thermal agitation with solution particles
- iii) Both electric forces of electrode along with thermal forces influence the behavior of ions in electrode vicinity.
- iv) The excess charge density on OHP is not equivalent to that on the metal but less
- v) Excess charge density in solution decreases with distance from the electrode like ionic atmosphere and become zero where thermal forces equalize the electrode force.
- vi) Ion – electrode interactions with electrode taken as source of electric field
- vii) This model has field in planar symmetry as electrode behave like an infinite plane.



This theory of diffuse double layer is analogous to that of long range ion –ion interaction, so the electric field or potential gradient at distance x from the electrode is given as:

$$\frac{d\phi}{dx} = -\left(\frac{8kTC_o}{E\epsilon_o}\right)^{1/2} \sinh \frac{ze\phi_x}{2kT}$$

Where C_o = concentration of species in the bulk of solution

ϕ_x = outer potential difference b/n point x from electrode and the bulk of solution

According to Gauss's law the charge is given by: $q = E\epsilon_o \frac{d\phi}{dx}$

To find the total diffused charge density Gaussian has been extended from $x = 0$ (near electrode)

to $x = \infty$ (in bulk solution) such that $\phi_x = 0$ and $\frac{d\phi_x}{dx} = 0$

After integration and rearranging equations, the differential capacitance

$$C = \left(\frac{\partial \rho_m}{\partial v} \right)_{cons.comp} = - \frac{\partial q_d}{\partial \phi_m} = \left[\frac{2E\epsilon_o z^2 e^2 C_o}{kT} \right] \times \left[\cosh \left(\frac{ze\phi_m}{2kT} \right) \right]$$

At 25 °C, $1/k = 30.4 \text{ A}^\circ$ ($1\text{A}^\circ = 10^{-10} \text{ m}$)

This function gives inverse parabola, so C at interface is not constant and is function of potential across interface, which is supported experimentally.

Weakness: the reason for the failure of this model is constancy of E (dielectric constant) between electrode and bulk of solution.

C) Stern Model

- i) This is the combination of Helmholtz – Perrin and Gouy – Chapman model.
- ii) Point charge approximation is ruled out and divides solution in to two parts.
- iii) $q_s = q_H + q_G$ where q_s = the solution charge

q_H = Helmholtz – Perrin charge

q_G = Gouy – Chapman charge

- iv) Potential drop occur due to separation of charge
- v) It include two potential drop i.e.,

$\phi_m - \phi_{bulk} = (\phi_m - \phi_H) + (\phi_H - \phi_{bulk})$ Here ϕ_m is inner potential at metal, ϕ_H is Helmholtz potential and ϕ_{bulk} is potential of bulk solution.

vi) Potential drop curve with distance satisfy the behavior of both models

a) Linear variation from $x = 0$ to position of OHP ($x = 0$) region

b) Exponential variation from OHP ($x = 0$) to bulk region ($x = \infty$)

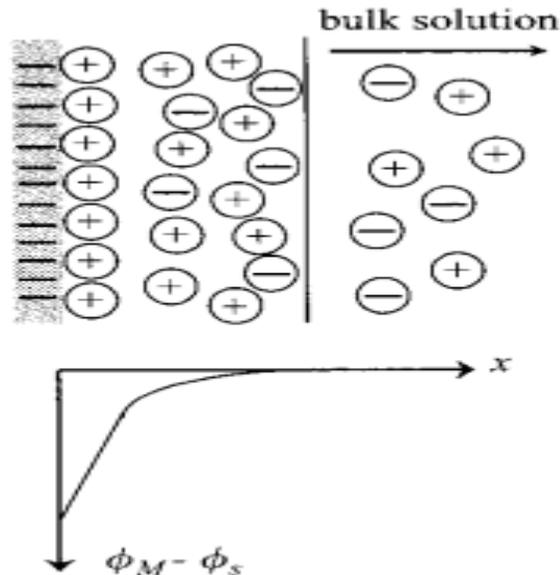
The separation of charges and potential regions produce a separation of differential capacities.

On differentiating potential difference across interface wrt charge on the metal we have:

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

$$\text{But } C = \frac{\partial \rho_m}{\partial \phi_m}$$

Therefore $\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_G}$ where C = total charge capacity, C_H = Helmholtz – Perrin capacity and C_G = Gouy – Chapman capacity



Special Case:

a) When a concentration of ions is very large C_G increase with C_o increase and C_H remain constant.

$$\frac{1}{C_G} \lll \frac{1}{C_H} \text{ for all practical purposes } C \approx C_H$$

This suggests that most of the solution charge confined in region close to Helmholtz - Perrin plane and very small scatter diffusely in solution.

b. In dilute solution or when concentration of ions in solution is very low:

$$\text{Then } \frac{1}{C_G} \ggg \frac{1}{C_H} \text{ Thus } C \approx C_G$$

It implies that the solution charge scattered under the combined effect of electrical and thermal forces and electrolyte – electrode interface.

Weakness: This model fails when ion like Cl^- , Br^- , I^- adsorbs on the electrode.

3.4. Thermodynamics of Electrified Interfaces

There are two thermodynamic approaches for treating interfaces. The oldest was put forward by Willard Gibbs, and the more recent by Edward Guggenheim. The fact that it is not possible to determine a physical boundary of separation between two phases is a dilemma for treating an interface: there is always a region of space where the two phases mix. We shall adopt here Guggenheim's approach, based on the definition of an interphase. An interphase is defined as a phase that contains all the discontinuities. Its boundaries are arbitrary as long as the phases separated by the interphase are homogeneous.

Consider two phases α and β separated by an interphase σ (see Figure x). Even though the boundaries $\alpha|\sigma$ and $\sigma|\beta$ are arbitrary, the total volume V remains the sum of the volumes of the three phases.

$$V = V^\alpha + V^\sigma + V^\beta$$

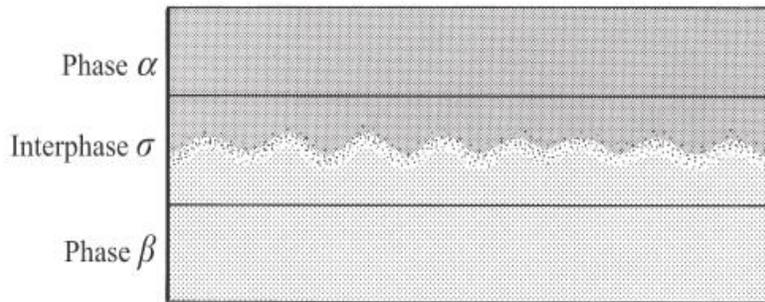


Fig. x: Schematic diagram of an interphase σ between two phases α and β .

In the same way, for all the extensive variables X of the system (n_i , U , S , etc.), we will have:

$$X = X^\alpha + X^\sigma + X^\beta$$

At equilibrium, all the intensive variables (T , p , μ_i , etc.) must be equal in the three phases.

Consequently, we can write the variations in internal energy of each phase as:

$$dU^\alpha = TdS^\alpha - PdV^\alpha + \sum_i \mu_i dn_i^\alpha$$

$$dU^\sigma = TdS^\sigma - PdV^\sigma + \gamma dA + \sum_i \mu_i dn_i^\sigma$$

$$dU^\beta = TdS^\beta - PdV^\beta + \sum_i \mu_i dn_i^\beta$$

The internal energy being a homogeneous first order state function, we can apply Euler's theorem of integration with constant intensive variables and write:

$$U = \sum_j \left(\frac{\partial U}{\partial X_j} \right)_{k \neq j} X_j$$

Which in this instance reads:

$$U^\alpha = TS^\alpha - PV^\alpha + \sum_i \mu_i n_i^\alpha$$

$$U^\sigma = TS^\sigma - PV^\sigma + \gamma A + \sum_i \mu_i n_i^\sigma$$

$$U^\beta = TS^\beta - PV^\beta + \sum_i \mu_i n_i^\beta$$

By differentiating these equations and subtracting respectively

$$S^\alpha dT - V^\alpha dP + \sum_i n_i^\alpha d\mu_i = 0$$

$$S^\sigma dT - V^\sigma dP + Ad\gamma + \sum_i n_i^\sigma d\mu_i = 0$$

$$S^\beta dT - V^\beta dP + \sum_i n_i^\beta d\mu_i = 0$$

The equations defined for the phases α and β are the Gibbs - Duhem equations for these phases, which show that we cannot independently vary the temperature, the pressure and the composition of a phase. The Gibbs - Duhem equation for the interphase is called the Gibbs adsorption equation.

$$-Ad\gamma = S^\sigma dT - V^\sigma dP + \sum_i n_i^\sigma d\mu_i$$

This equation provides a thermodynamic definition of:

$$\gamma = \left(\frac{\partial U^\sigma}{\partial A} \right)_{S, V, n_i}$$

But this is not a practical definition since U^σ depends on the arbitrary boundaries.

There are various types of electrified interfaces between conducting phases that can be metallic, semi-conductors, ionic crystals (e.g. AgI), molten salts, electrolyte solutions etc.

It is convenient to distinguish between polarisable and unpolarisable interfaces. A polarisable interface is one where we can apply a Galvani potential difference without causing noticeable changes in the chemical composition of the phases in contact, in other words without the passage of any noticeable faradaic current. So a polarisable interface is, from a thermodynamic point of view, always in equilibrium, and the Galvani potential difference is therefore an adjustable parameter of the system in addition to the classical adjustable parameters that are the concentrations of the different species, the temperature or the pressure.

3.5. Electrochemical Kinetics

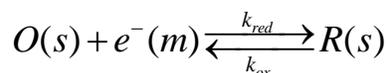
As we have noted in the first section it is possible to transfer electrons between an electrode and a chemical species in solution. This process is called electrolysis and results in a reactant undergoing an oxidation or reduction reaction. Unlike equilibrium measurements recorded using a two electrode, two compartment cell and electrolysis results in the flow of current around an electrical circuit.

The current can be controlled by a numbers of factors: the two most common are:

- ✓ The rate of electron transfer between the metal and species in solution
- ✓ The transport of material to and from the electrode interface.

Kinetics of Electron transfer

The current flowing in either the reductive or oxidative steps can be predicted using the following expressions model for the influence of electrode on the rate of electron transfer. For simplicity we will consider a single electron transfer reaction between two species (O) and (R).



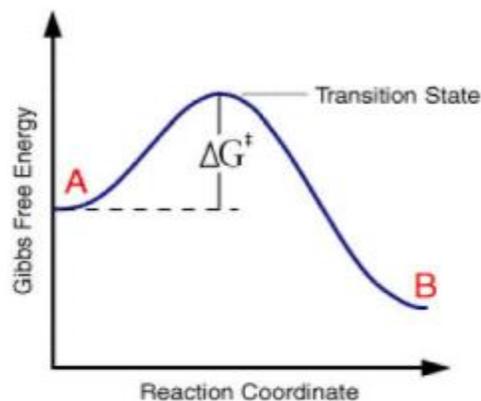
The current flowing in either the reductive or oxidative steps can be predicted using the following expressions

$$i_c = -FAk_{red}[O]_o$$

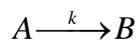
$$i_a = FAk_{ox}[R]_o$$

For the reduction reaction the current (i_c) is related to the electrode area (A), the surface concentration of the reactant $[O]_o$, the rate constant for the electron transfer (k_{Red} or k_{Ox}) and Faraday's constant (F). A similar expression is valid for the oxidation, row the current is labeled (i_a), with the surface concentration that of the species R. Similarly the rate constant for electron transfer corresponds to that of the oxidation process. Note that by definition the reductive current is negative and the oxidative positive, the difference in sign simply tells us that current flow in

opposite directions across the interface depending upon whether we are studying an oxidation or reduction. To establish how the rate constants k_{Ox} and k_{Red} are influenced by the applied voltage we will use transition state theory from chemical kinetics. You will recall that in this theory the reaction is considered to proceed via an energy barrier. The summit of this barrier is referred to as the transition state.



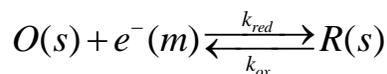
The rate of reaction for a chemical process



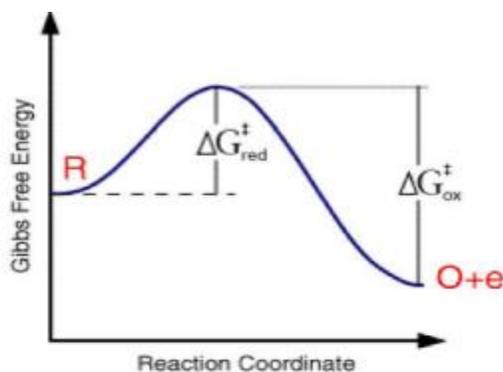
is predicted by an equation of the form

$$k = Z \exp\left(\frac{-\Delta G}{RT}\right)$$

Where the term in the exponential is the free energy change in taking the reactant from its initial value to the transition state divided by the temperature and gas constant. This free energy plot is also qualitatively valid for electrode reactions



Where the free energy plot below corresponds to the thermodynamic response at a single fixed voltage.



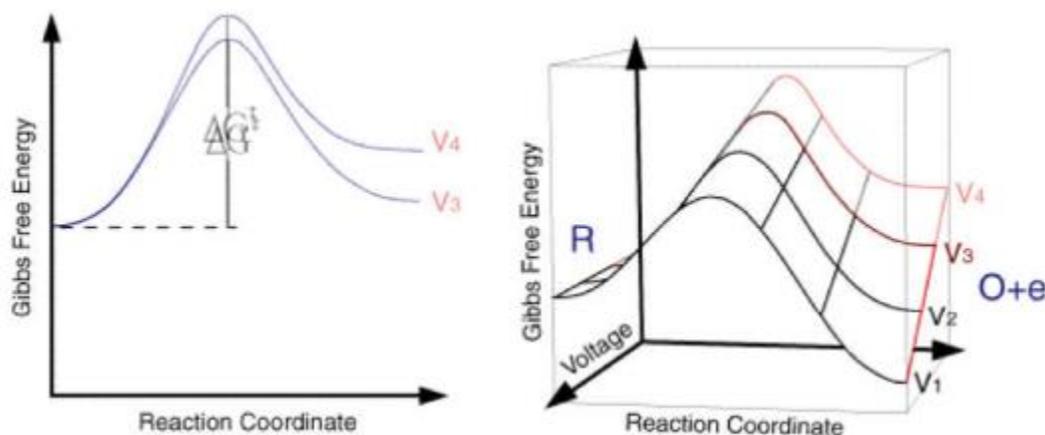
Using this picture the activation free energy for the reduction and oxidation reactions are:

$$\Delta G_{red}^{\ddagger} = G^{\ddagger} - G^O \quad \text{and} \quad \Delta G_{ox}^{\ddagger} = G^{\ddagger} - G^R$$

and so the corresponding reaction rates are given by:

$$k_{red} = Z \exp\left(\frac{-\Delta G_{red}^{\ddagger}}{RT}\right) \quad \text{and} \quad k_{ox} = Z \exp\left(\frac{-\Delta G_{ox}^{\ddagger}}{RT}\right)$$

So for a single applied voltage the free energy profiles appear qualitatively to be the same as corresponding chemical processes. However if we now plot a series of these free energy profiles as a function of voltage it is apparent that the plots alter as a function of the voltage. It is important to note that the left hand side of the figure corresponding to the free energy of R is invariant with voltage, whereas the right hand side (O + e) shows a strong dependence.



At voltage V_1 the formation of the species O is thermodynamically favoured. However as we move through the voltages to V_4 the formation of R becomes the thermodynamically favoured product. This can be explained in terms of the Fermi level diagrams noted earlier; as the voltage is altered the Fermi level is raised (or lowered) changing the energy state of the electrons. However it is not just the thermodynamic aspects of the reaction that can be influenced by this voltage change as the overall barrier height (ie activation energy) can also be seen to alter as a function of the applied voltage. We might therefore predict that the rate constants for the forward and reverse reactions will be altered by the applied voltage. In order to formulate a model we will assume that the effect of voltage on the free energy change will follow a linear relationship (this is undoubtedly an over simplification). Using this linear relationship the activation free energies for reduction and oxidation will vary as a function of the applied voltage (V) as follows:

$$\Delta G_{red}^{\ddagger} = \Delta G_{red\,no\,voltage}^{\ddagger} + \alpha FV \quad \text{and} \quad \Delta G_{ox}^{\ddagger} = \Delta G_{ox\,no\,voltage}^{\ddagger} + (1 - \alpha)FV$$

The parameter α is called the transfer coefficient and typically is found to have a value of 0.5. Physically it provides an insight into the way the transition state is influenced by the voltage. A value of one half means that the transition state behaves mid way between the reactants and products response to applied voltage. The free energy on the right hand side of both of the above equations can be considered as the chemical component of the activation free energy change, i.e., it is only dependent upon the chemical species and not the applied voltage. We can now substitute the activation free energy terms above into the expressions for the oxidation and reduction rate constant, which gives:

$$k_{red} = Z \exp\left\{\left(\frac{-\Delta G_{red\,no\,voltage}^{\ddagger}}{RT}\right)\left(\frac{-\alpha FV}{RT}\right)\right\}$$

$$k_{ox} = Z \exp\left\{\left(\frac{-\Delta G_{ox\,no\,voltage}^{\ddagger}}{RT}\right)\left(\frac{(1 - \alpha)FV}{RT}\right)\right\}$$

These results show us that rate constants for the electron transfer steps are proportional to the exponential of the applied voltage. So the rate of electrolysis can be changed simply by varying the applied voltage. This result provides the fundamental basis of the experimental technique called voltammetry which we will look at more closely later.

In conclusion we have seen that the rate of electron transfer can be influenced by the applied voltage and it is found experimentally that this behaviour can be quantified well using the simple model presented above. However the kinetics of the electron transfer is not the only process which can control the electrolysis reaction. In many circumstances it is the rate of transport to the electrode which controls the overall reaction.

The effect of mass transfer

The effect of mass transfer on the kinetics of the electrode is studied as follows:

Let us consider a reduction reaction as



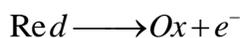
As an electron transferred from one electrode to another, the electrical work done is $e\Delta\phi$ where e is electronic charge and $\Delta\phi$ is potential difference between electrodes.

Gibbs free energy of activation is changed from ΔG^\ddagger to $\Delta G^\ddagger + F\Delta\phi$ if the transition state corresponds to Ox being very close to the electrode.

If $\Delta\phi > 0$, more work will be done to bring Ox to its transition state which results an increase in Gibbs free energy of activation. Contrary to it, if transition state corresponds to Ox being far from electrode i.e., close to OHP of double layer, then ΔG^\ddagger is independent of $\Delta\phi$. But actually, situation is somewhere in midway of the two. Hence GFE of activation for reduction as

$$\Delta G^\ddagger + \alpha F\Delta\phi$$

Now let us consider an oxidation reaction



Here Red give up electron and result that extra work needed to reach the transition state is zero, if this state lies close to the electrode.

If it lies away from the electrode is close to OHP of double layer, the work need is $-F\Delta\phi$ so that ΔG^\ddagger changes to $\Delta G^\ddagger - (1-\alpha)F\Delta\phi$

$$i = \{Fk_a[\text{red}]\exp(-\Delta G^\ddagger/RT)\}e^{(\frac{(1-\alpha)F\Delta\phi}{RT})} - \{Fk_c[\text{Ox}]\exp(-\Delta G^\ddagger/RT)\}e^{\frac{-\alpha F\Delta\phi}{RT}}$$

$$i = i_a - i_c$$

At equilibrium $\Delta\phi = \Delta\phi_{eqm}$ and net current is zero and equilibrium current densities are equal. If potential difference differs from its equilibrium value by over potential value η such that $\Delta\phi - \Delta\phi_{eqm}$

The two current densities are:

$$i_a = i_{a,eqm} e^{\frac{(1-\alpha)\eta F}{RT}} \quad \text{and} \quad i_c = i_{c,eqm} e^{\frac{-\alpha\eta F}{RT}}$$

Since both $i_{a,eqm} = i_{c,eqm}$ are equal current densities, then

$$i = i_o \left[e^{\frac{(1-\alpha)\eta F}{RT}} - e^{\frac{-\alpha\eta F}{RT}} \right] \quad \text{This is called **Butler – Volmer** Equation}$$

Special case of Butler – Volmer Equation

i) When η is very small and positive such that $\eta F/RT \ll 1$

$$i = i_o \eta F/RT \quad (\text{Here the current density directly proportional to over potential})$$

$$\eta = \frac{RT}{F} \left(\frac{i}{i_o} \right) \quad (\text{if } \eta \text{ is +ve the current is anodic and if } \eta \text{ is -ve, current is cathodic})$$

ii) When η is very large and +ve

$$i = i_o e^{\frac{(1-\alpha)\eta F}{RT}} \quad \text{Or} \quad \ln i = \ln i_o + \frac{(1-\alpha)\eta F}{RT} \dots\dots\dots (x)$$

If η is very large but -ve

$$i = -i_o e^{\frac{-\alpha\eta F}{RT}} \quad \text{Or} \quad \ln(-i) = \ln i_o - \frac{\alpha\eta F}{RT} \dots\dots\dots (y)$$

Equation (x) and (y) are called **Tafel** equations

Example

At 25 °C the exchange current density of Pt|H₂|H⁺ (aq) electrode is 0.79 mAcm⁻². Calculate the current flowing through a standard electrode of area 5.00 cm² at over potential 5.00mV.