



**Faculty of science**

# **Electrode/Solution Interface**

**2<sup>nd</sup> Year Students-General, Science**

**Course Code: 218 Chem.**

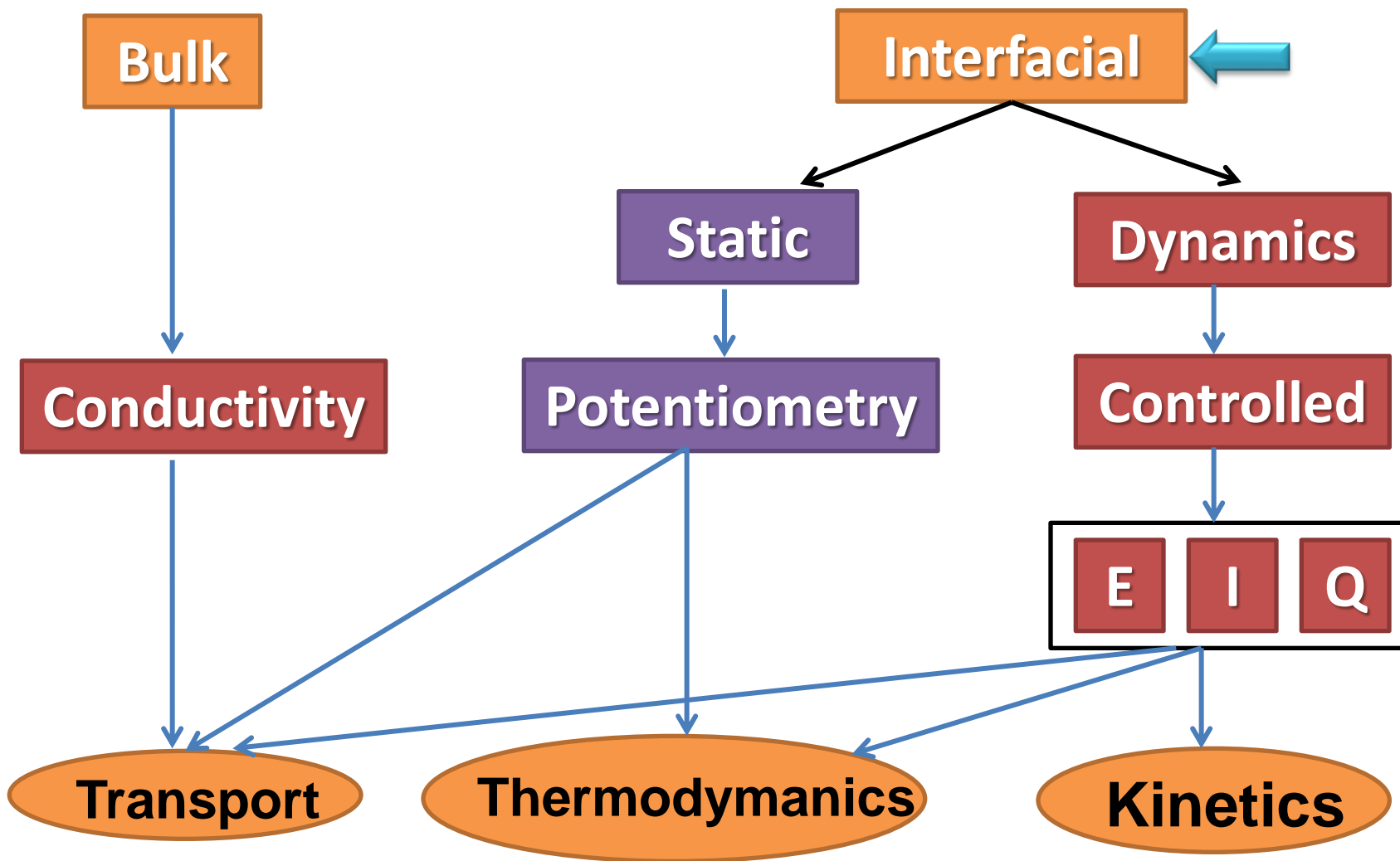
**Lecture # 5**

**Date: April 1, 2020**

# Course Contents

- **Electrochemical Thermodynamics**
- **Electrochemical cells**
- **Potential of Electrode & Cell**
- **Electrode/Solution Interface**
- **Electron Transfer and Energy Levels**

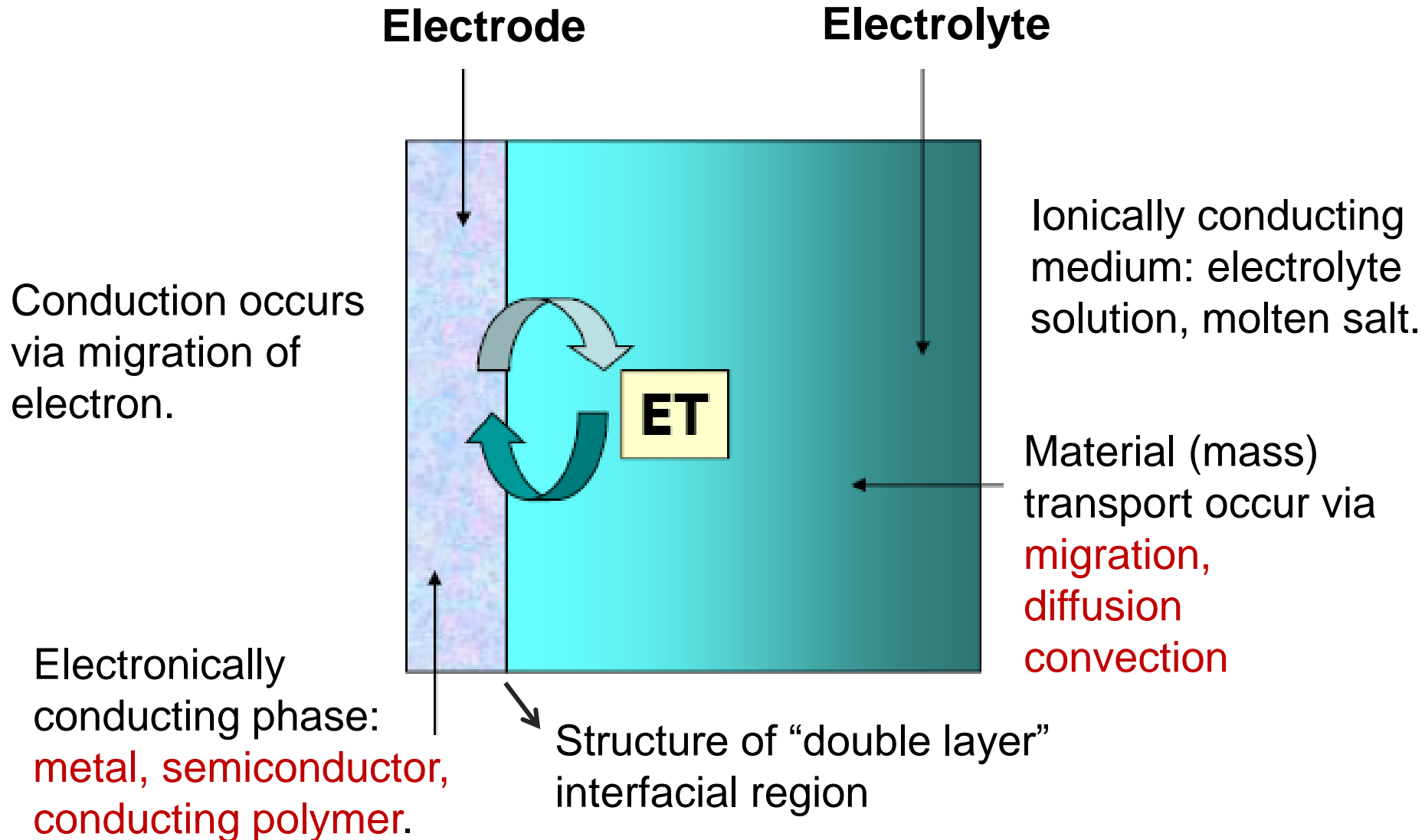
# Electrochemical Techniques



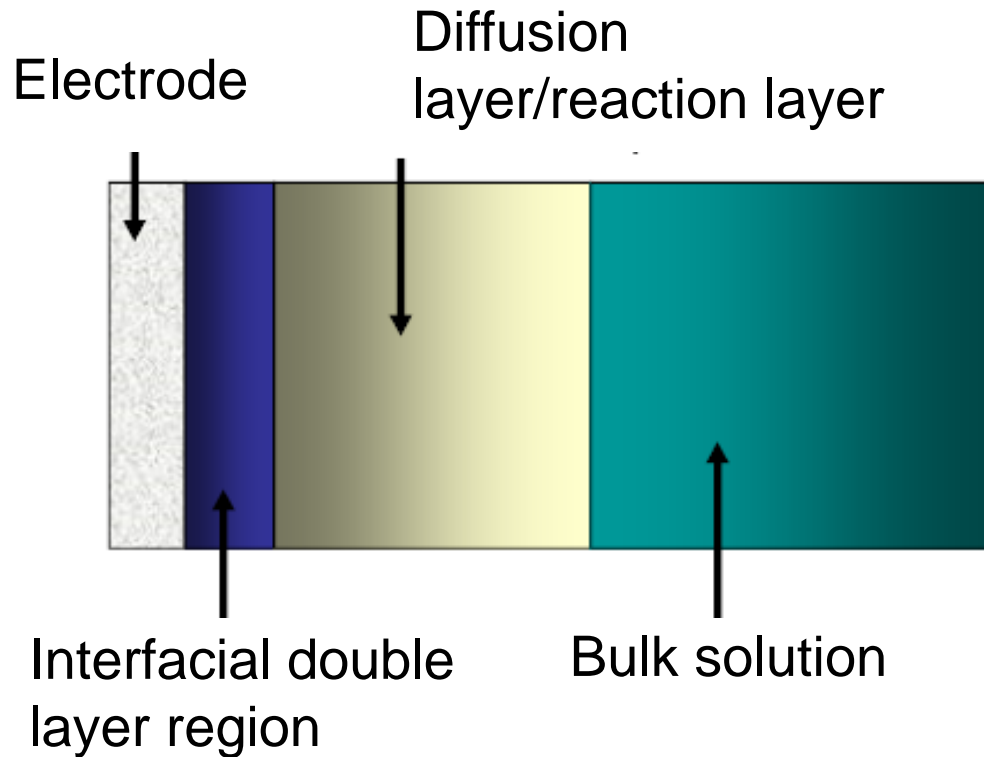
# Interfacial Electrochemistry

- The Double Layer at the Electrode/Solution Interface
- Electron Transfer & Energy Levels

# Electrode/Electrolyte Interface



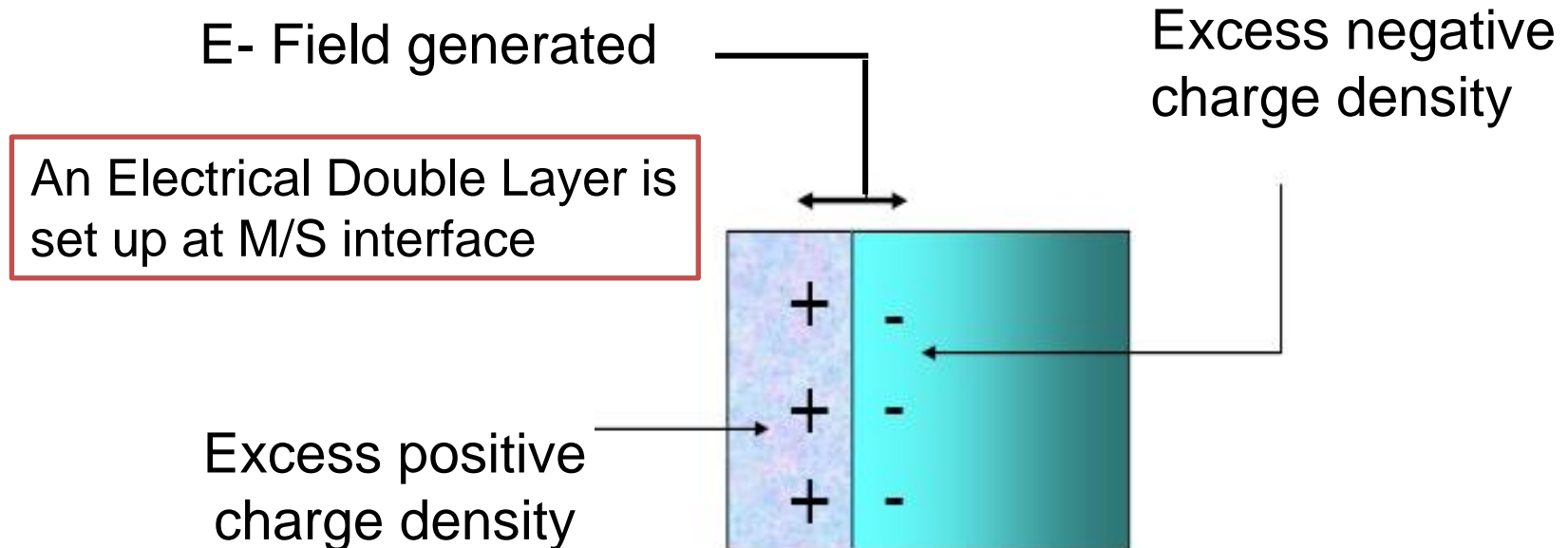
# Electrode/Solution Interface Regions



- The Electron Transfer reaction makes the composition of the solution near the electrode surface different from the nearby.
- There is a diffusion layer thicker than electrical double layer.

# Electrode /Solution Interface

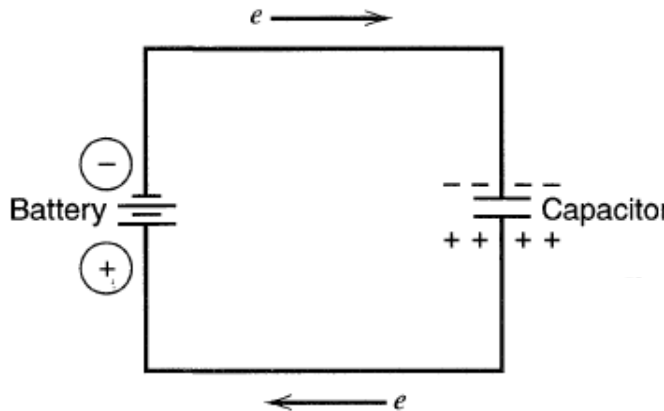
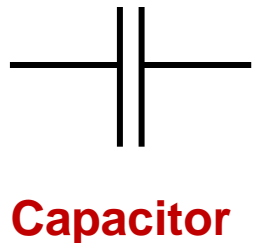
- The interface between two dissimilar interface is **Electrifies**.
- When two dissimilar phases come into contact, charge separation occur in the interfacial region which generate an **interfacial potential difference or electric field**.



# Capacitance and Charge of an Electrode

The electrode/solution interface under applied potential behaves as a capacitor.

A **capacitor** is an electrical circuit element composed of **two metal sheets separated by a dielectric material**.



A capacitor charging with battery

$$C = \frac{q}{E}$$

q = the charge stored on the capacitor (coulombs, C),

E = the potential across the capacitor (volts, V)

C = the capacitance (farads, F)

Upon applying potential across a capacitor, charge will accumulate on metal plates until q satisfies the equation.



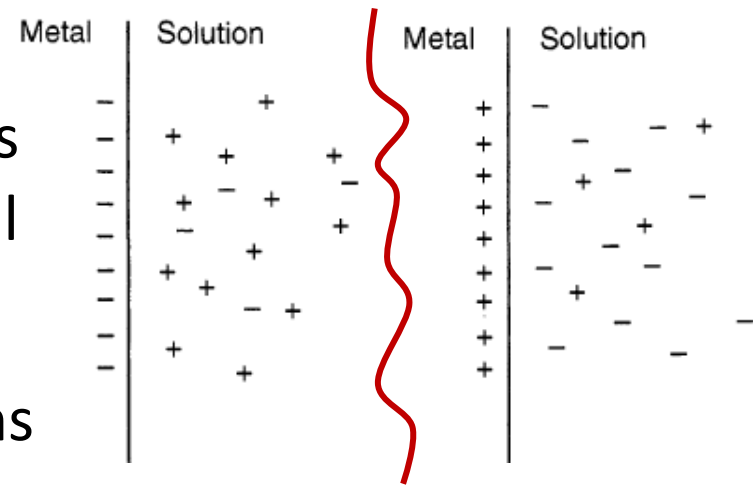
- During this charging process, charging current will flow.
- The charge on the capacitor consists of an excess of electrons on one plate and a deficiency of electrons on the other.

At a given potential, the **charge on the metal electrode**,  $q^M$  is neutralized by the **charge in the solution**,  $q^S$ .

$$q^M = -q^S$$

$q^M$  = an excess or deficiency of electrons at very thin layer (<0.1 Å) on the metal surface.

$q^S$  = an excess of either cations or anions in the vicinity of the electrode surface.



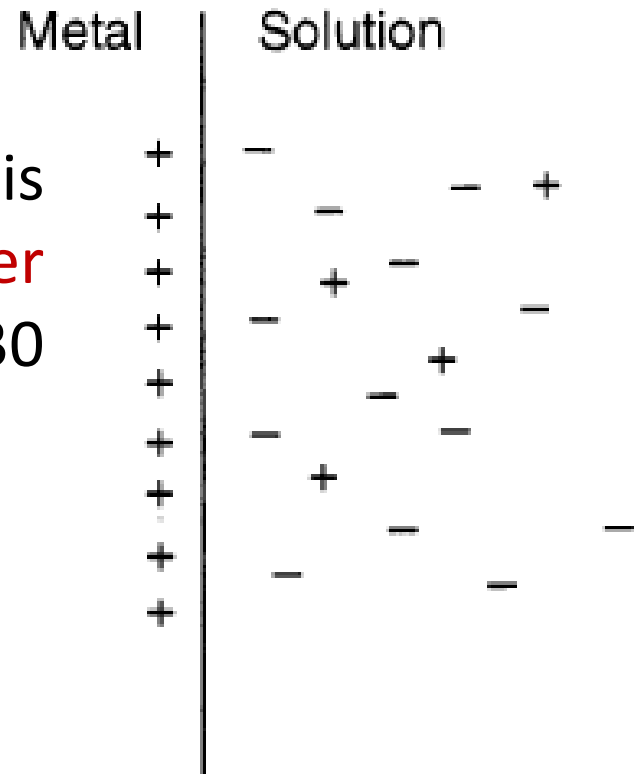
The metal/solution interface as capacitor with a charge on a metal  $q$  (negative or positive)

# Electrical Double Layer

Array of charged species and oriented dipoles existing at the metal/solution interface.

## At a given potential

The electrode/solution interface is characterized by a **double-layer capacitance**,  $C_d$ , in the range of 10 to 30  $\mu\text{F}/\text{cm}^2$ .

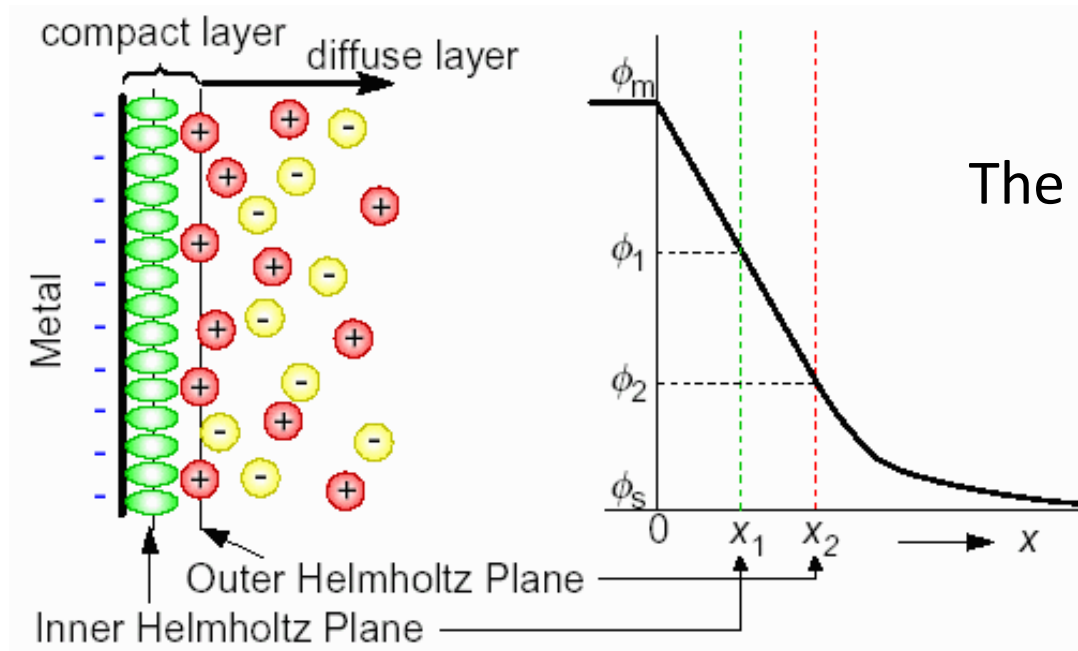


# Models of Electrode /Solution Interface

Theories explained structure of the Electrode/Electrolyte Interface

- Helmholz compact layer
- Gouy-chapman diffuse layer
- Stern (Elaborated Model)

# 1) Helmholtz Double Layer



The simplest approximation

- Assuming that the surface charge is neutralized by opposite sign counter ions placed at distance  $d$  away from the surface.
- The distance,  $d$ , is at the center of the counter ions, i.e. their radius.
- This model does not explain the **thermal motion of ions**, since it hypothesizes rigid layers of opposite charges.

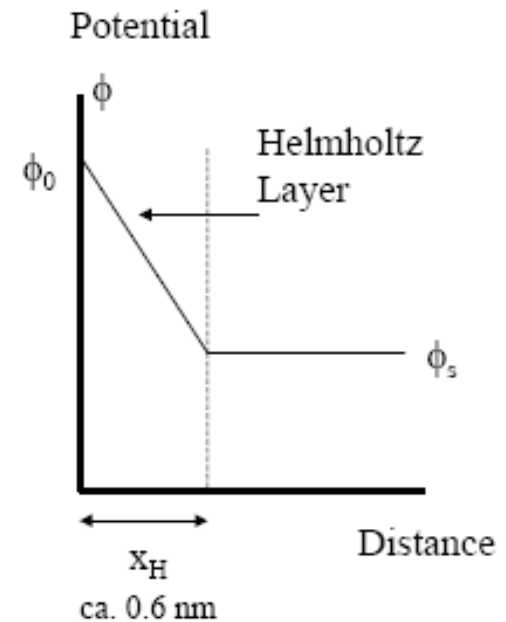
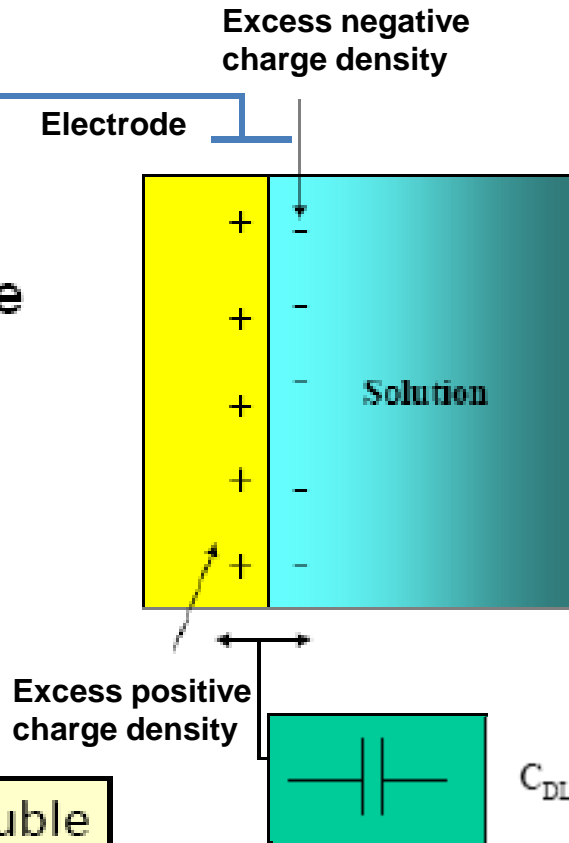
# Electrode/Solution Interface Region: Helmholtz compact layer model

Electric field present at interface

Double layer capacitance

$$C_{DL} = C_H = \frac{\epsilon_0 \epsilon_r}{x_H}$$

Structure of thin double layer region modeled as a parallel plate capacitor with a plate separation of molecular dimension



$$C_{DL} = 20 - 60 \mu F cm^{-2}$$

# Simple Models are not Always Good Ones

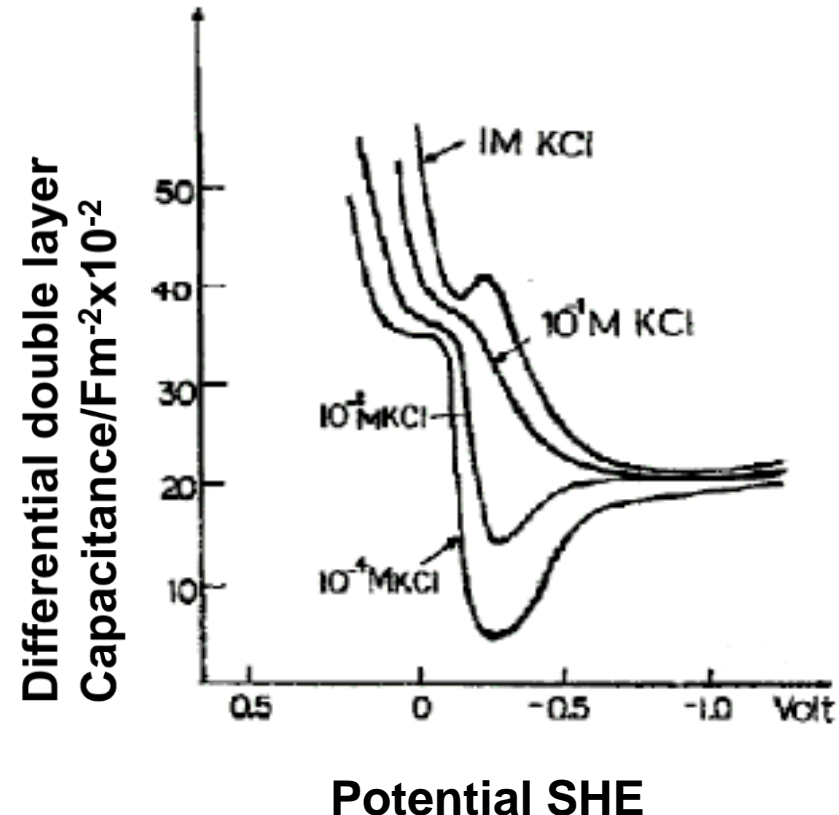
The simple Helmholtz model is not complete since it predicts that:

The double layer capacitance ( $C_{DL}$ ) is a constant and independent on the

- Ion Concentrations
- Electrode Potential

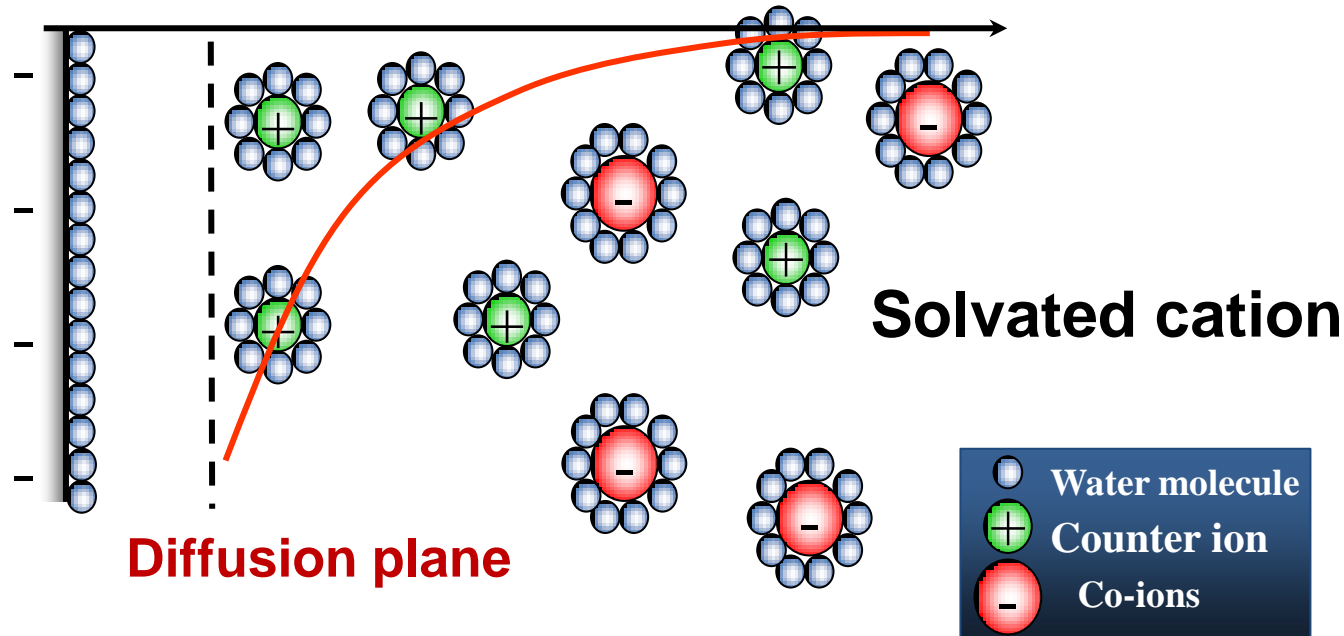
## However

Experiments indicated that the  $C_{DL}$  varies with both of these quantities.



More elaborate model is required!!

## 2) Gouy-Chapman Double Layer



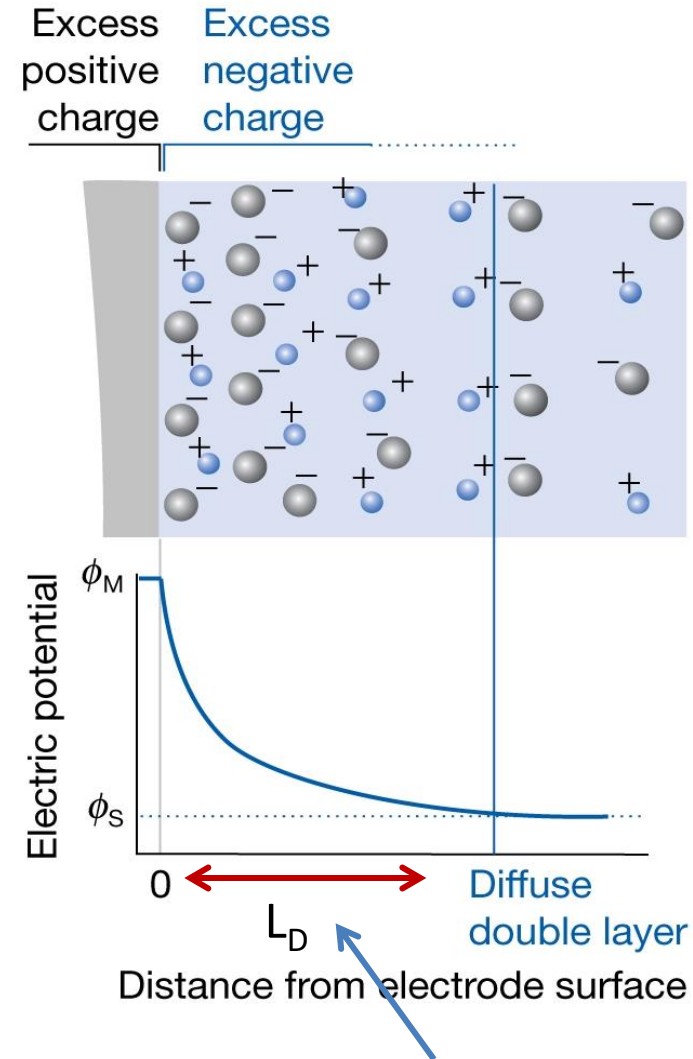
- Assumed Diffusion plane
- Distribution of ions from the surface
- Ions are point charges
- ions do not interact with each other
- Diffusion layer begins at some distance from the surface

# Gouy-Chapman Model of Diffuse Double Layer

Gouy and, independently, Chapman developed theories of diffuse double layer.

It is assumed that the excess charge density on the solution side of the interface can be represented in terms of dimensional space charge region

The **thickness of the diffuse layer region** is depend on the potential applied to the electrode and on the concentration of ions in the electrolyte.



Ca. 1-10 nm

Diffuse layer thickness



### 3) Stern Model of the Interface Region

- Neither the Helmholtz compact layer model nor the Gouy Chapman diffuse layer is totally satisfactory
- In the GC model the solvated ions are modeled as point charges, while neglecting their ionic size.
- GC model assumes that there **is no physical limit** for the ions in their approach to the surface, which is not true.
- In reality the **solvated ion** can only approach the electrode at distance equal to its solvated radius **a**.
- **Stern model** combined the features of the Helmholtz and Gouy-Chapman approaches.

# The stern model is as follows:

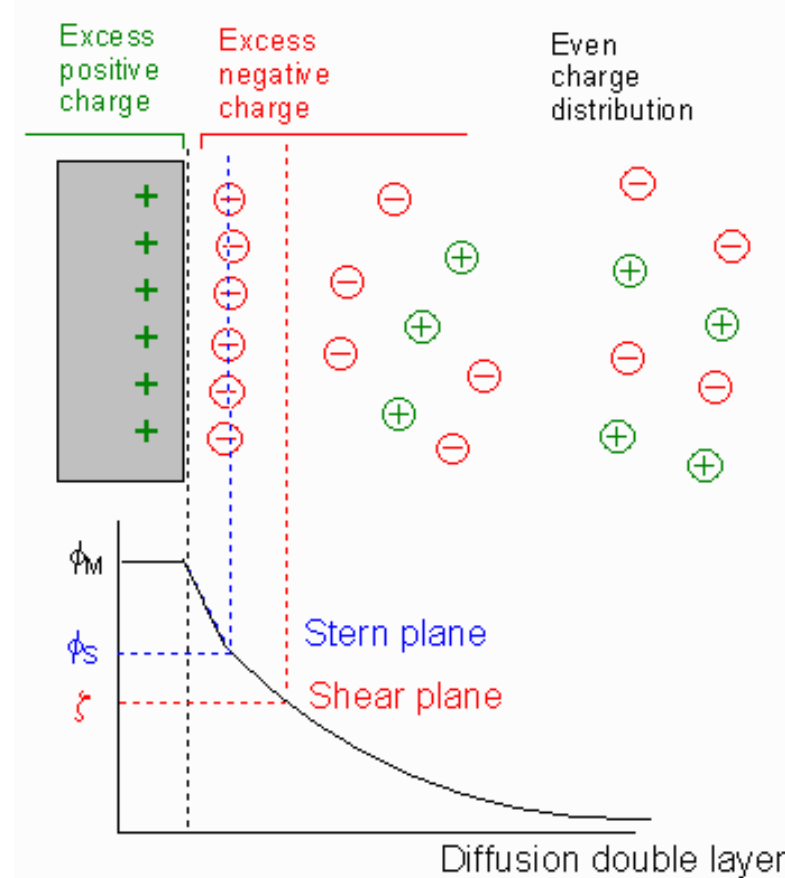
- Next to the electrode, we have a region of high electric field and low dielectric constant ( $\epsilon$  value  $\sim 0.6$ ) with a row of counter ions.

- Beyond that there is an ionic environment (**the diffuse layer**) where there is a balance between the electrostatic force and thermal motions.

- The electrical potential **varies linearly with distance (hydrates ion radius)** within the inner compact layer.

- The electrical potential **decreases exponentially with distance** within the diffuse layer.

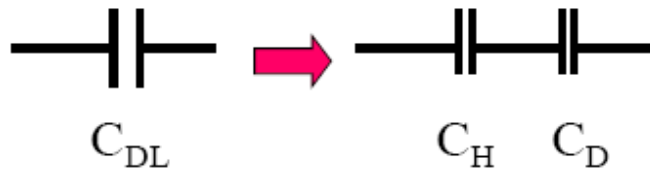
- The electrical potential **decaying to zero** in the bulk solution



# A reasonable model of the electrode/solution interface

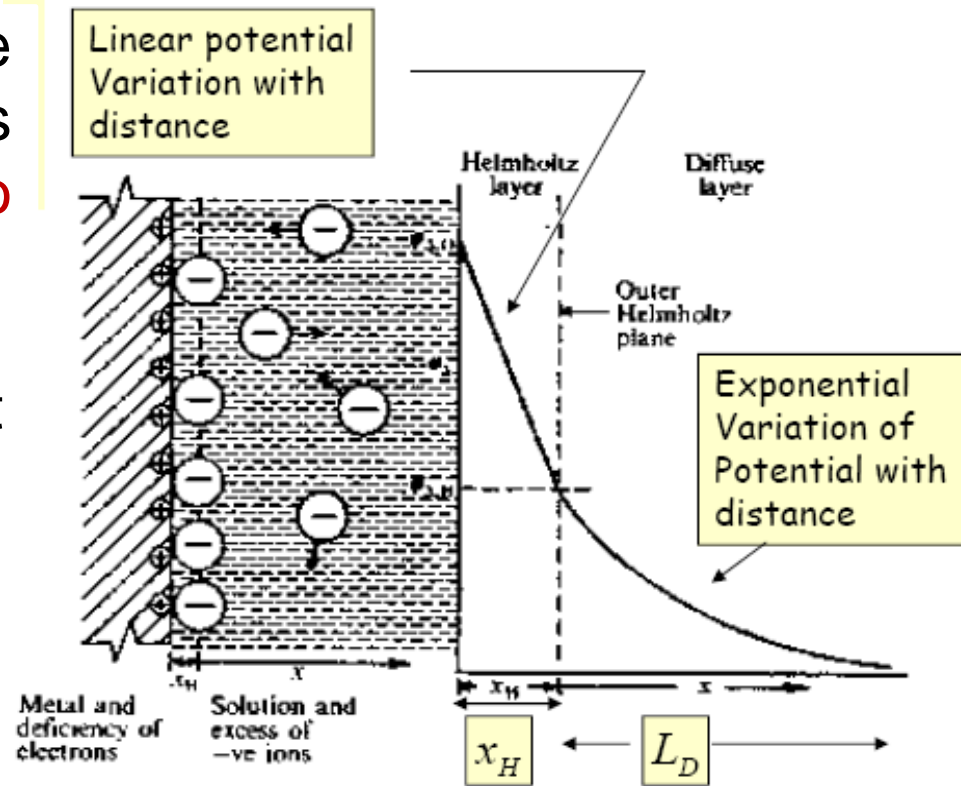
The electrode/solution interface is modeled as a series arrangement of the **two capacitors**.

This is a equivalent circuit representation of the interface.



Series arrangement of capacitors

If  $C_H$  and  $C_D$  are different, the larger one may be neglected



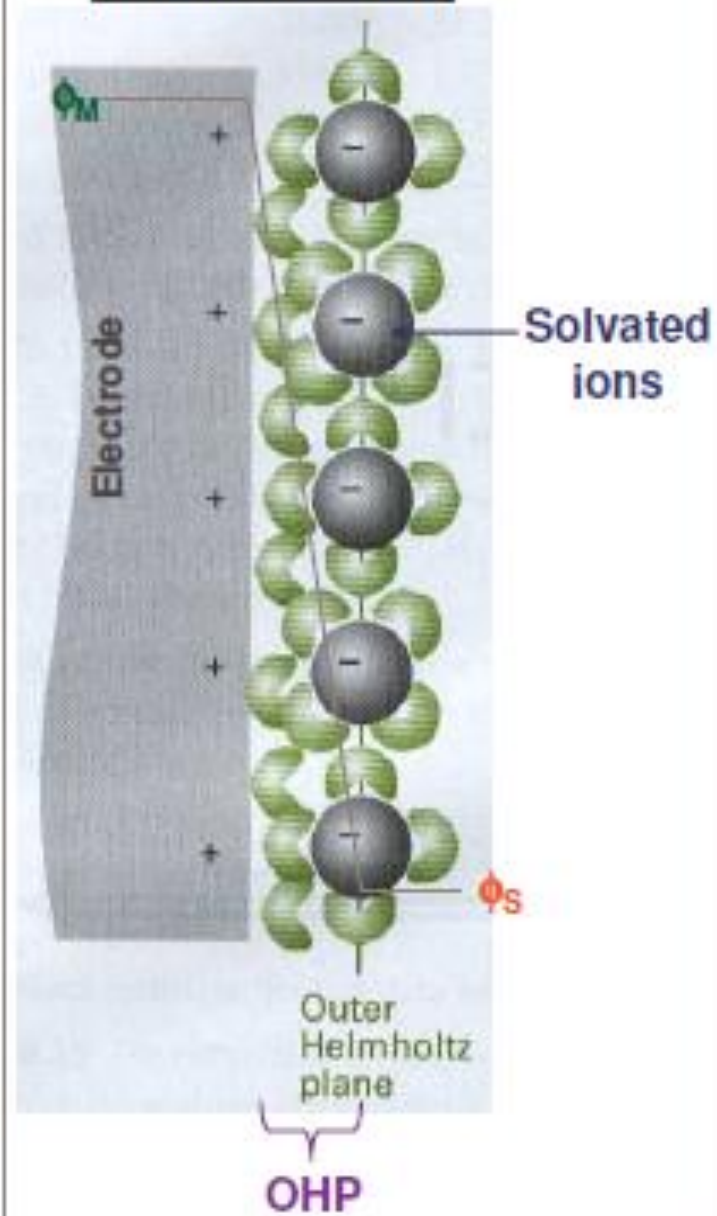
**Compact layer**

$$\frac{1}{C_{DL}} = \frac{1}{C_H} + \frac{1}{C_D}$$

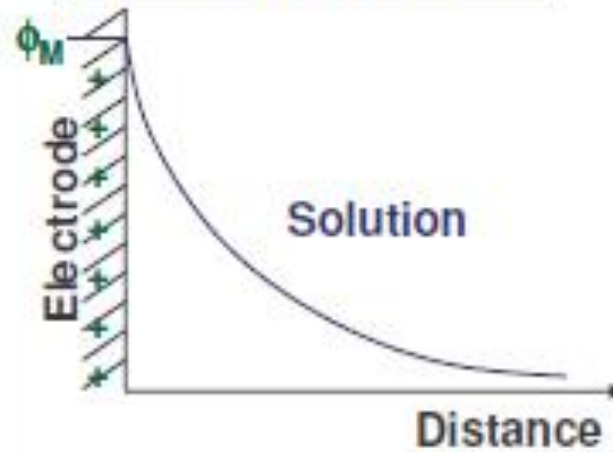
**Total Capacitance**

**Diffuse layer**

## Helmholtz Model

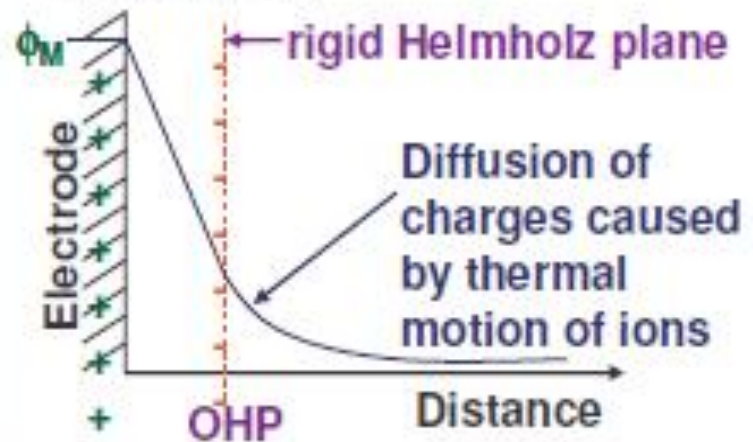


## Gouy-Chapman Model

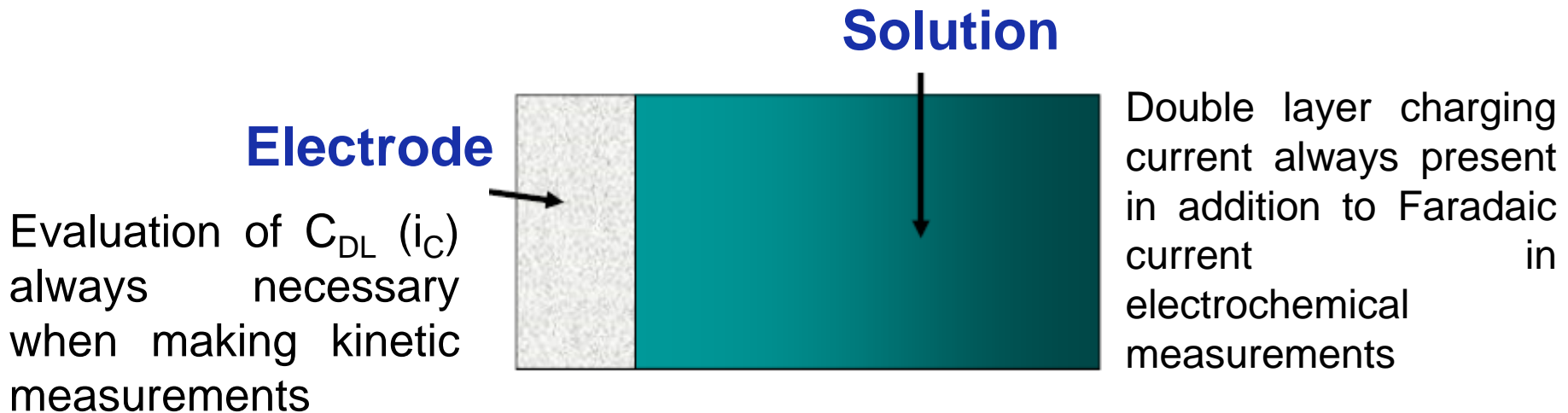
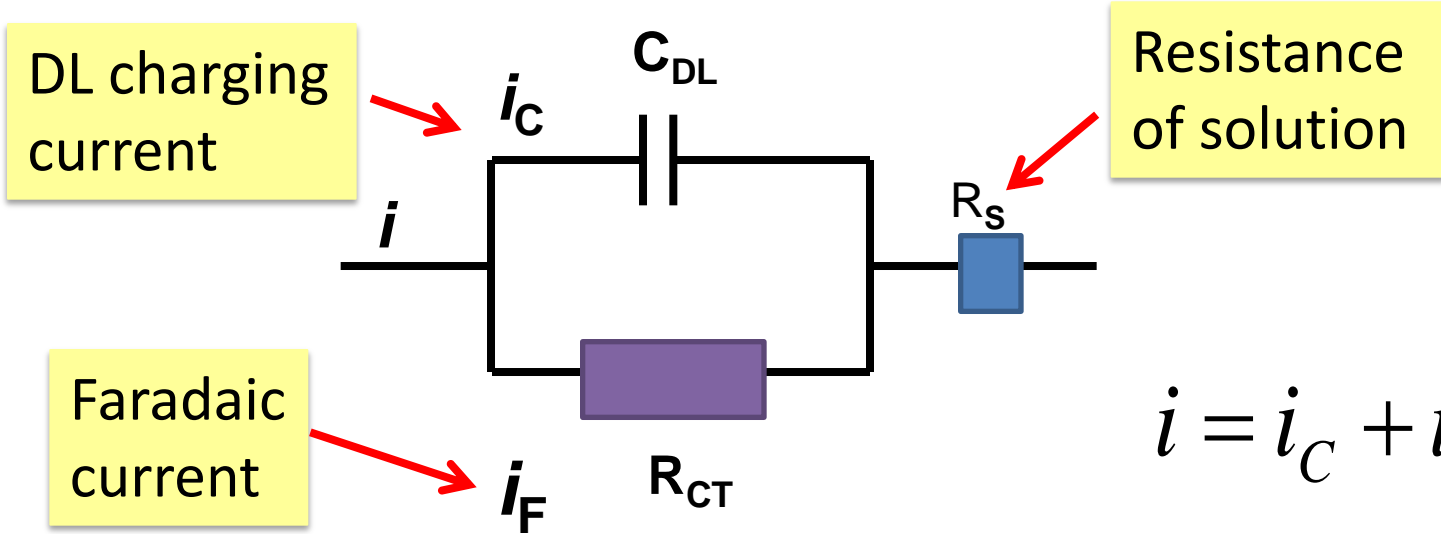


Double layer has no thickness and is diffused by thermal motion of ions

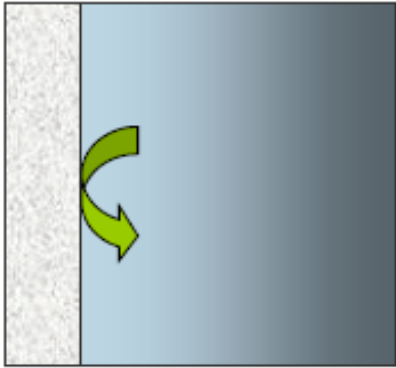
## Stern Model



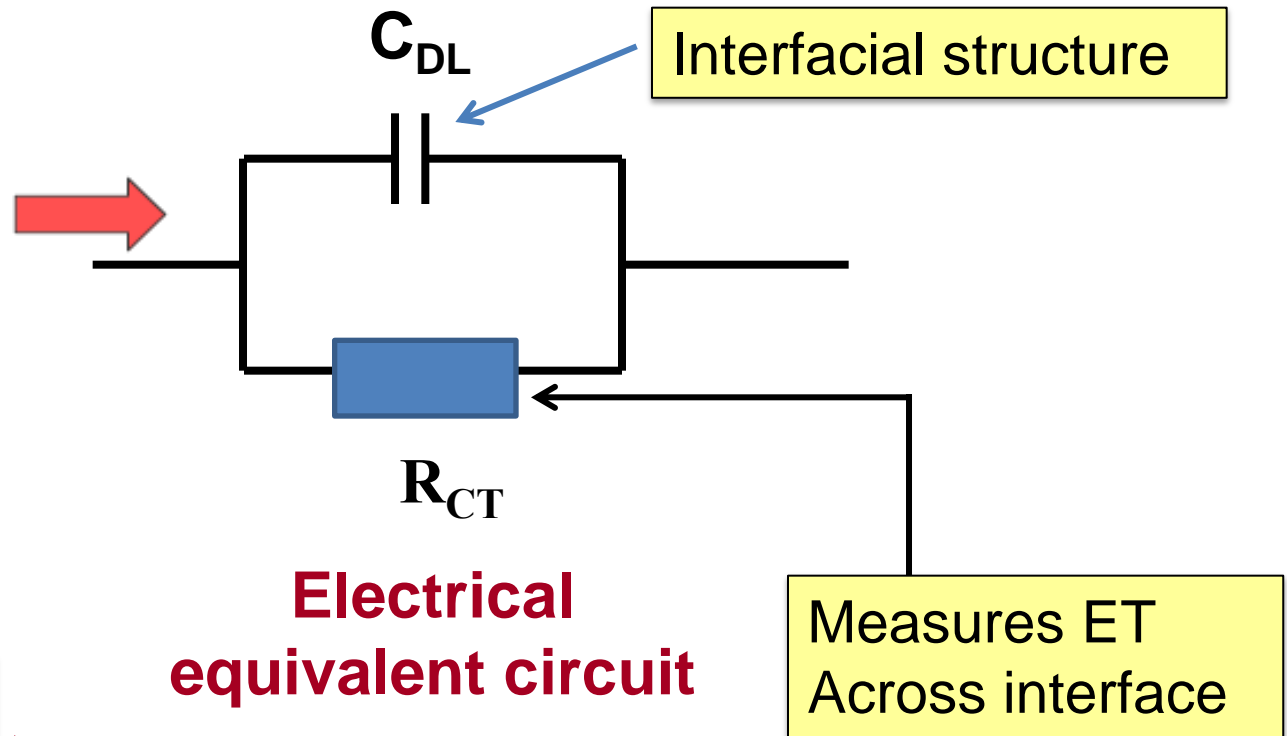
# Simple Equivalent Circuit Representation Of Electrode/Solution Interface



# Polarizable and non-Polarizable Interfaces



Electrode/solution interface



No leakage of charge across M/S interface

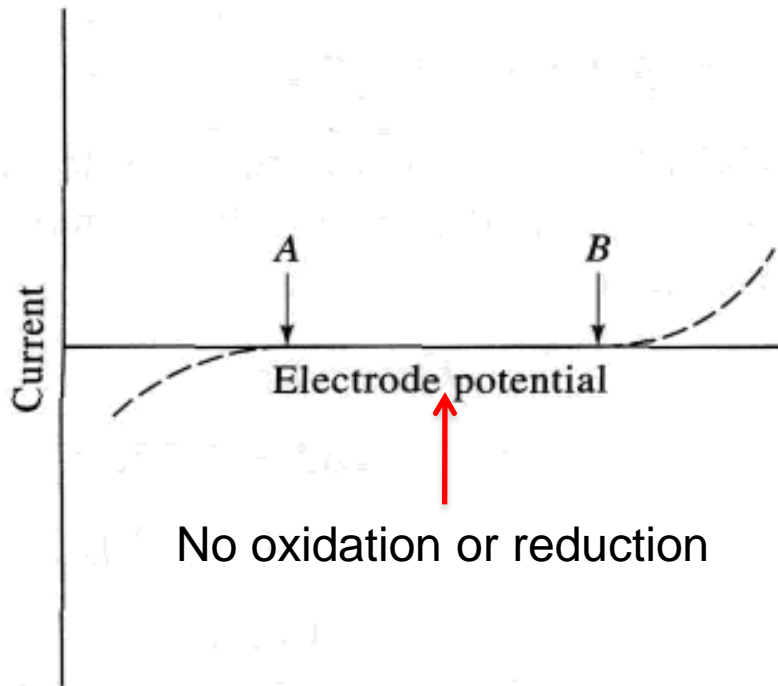
Ideally Polarizable Interface:  $R_{CT} \rightarrow \infty$

Charge transfer occurs across M/S interface

Ideally non-Polarizable Interface:  $R_{CT} \rightarrow 0$

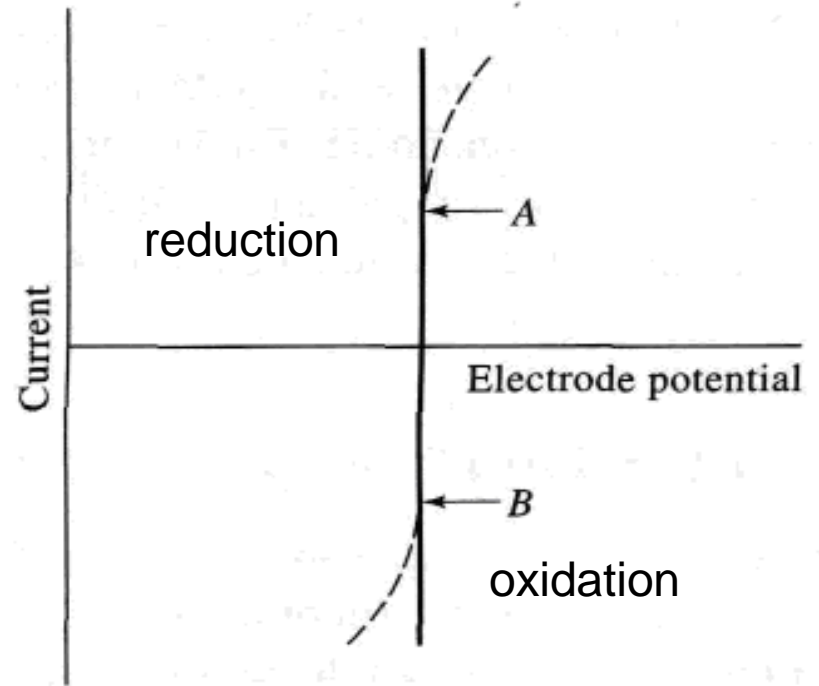
# Polarization - Theoretical

## Ideal Polarized Electrode



(a)

## Ideal Non-Polarized Electrode



(b)

**Figure 22-6** Current-voltage curves for an ideal (a) polarized and (b) nonpolarized electrode. Dashed lines show departure from ideal behavior by real electrodes.



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# **Electron Transfer and Energy Levels**

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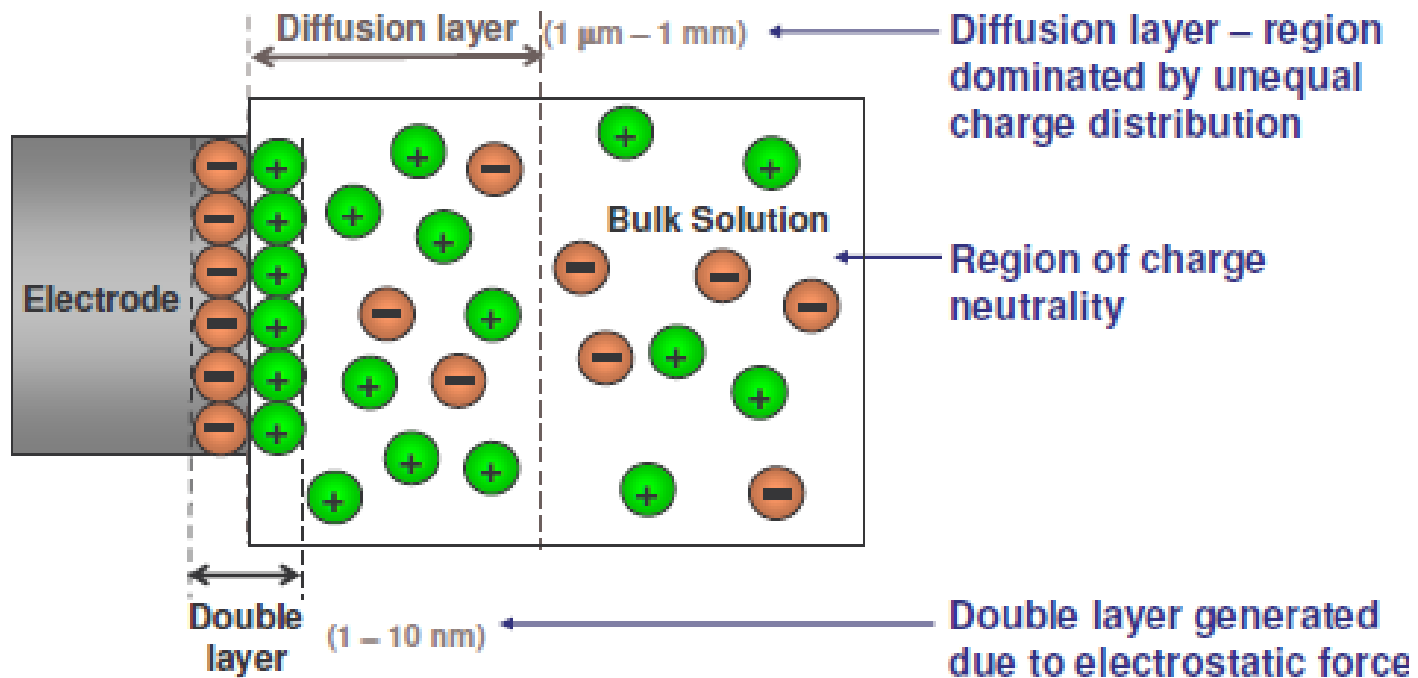
**Lecture #6**

**Date: April 8, 2020**



# What happens at the Electrode Interface when a voltage is applied?

The electrode is charged and attracts oppositely charged ions to the surface- formation of double layer.



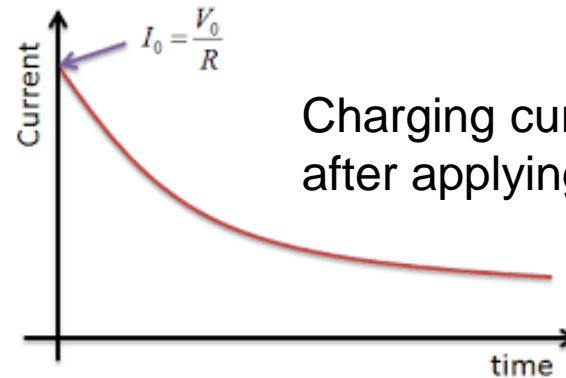
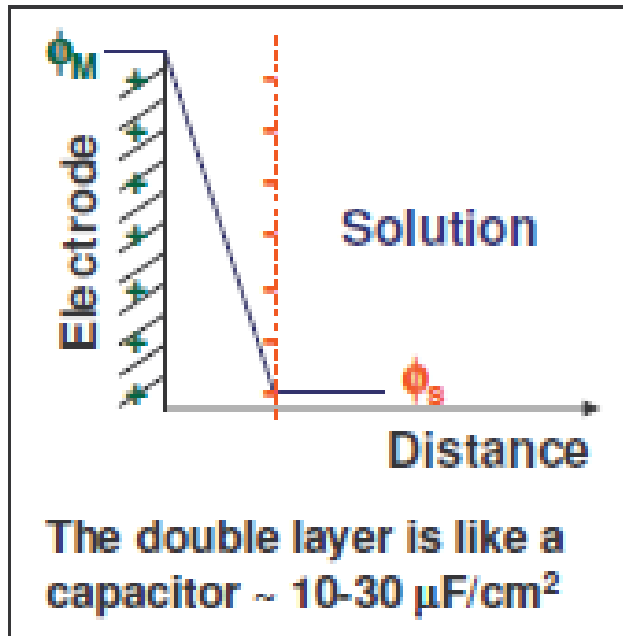
Only when sufficient energy is supplied, electrons will move from electrode to chemical species in solution, and vice versa.

# Non-Faradaic process

Under some conditions an electrode/solution interface shows a range of currents where no charge transfer reaction occurs

E.g. capacitive or charging current

**Capacitive current** – current generated by the alignment of surface charges in an attempt to offset the applied potential and reach thermodynamic equilibrium.

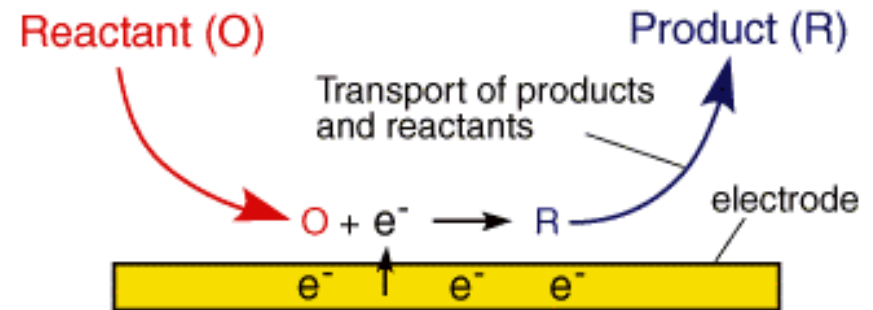
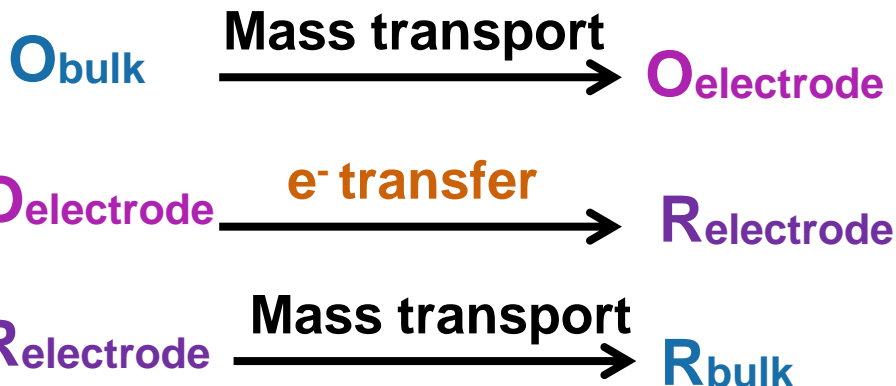


Charging current decay rapidly after applying a potential

The double layer depends on:  
The applied potential, the electrode surface,  
the solution composition and the solvent.

# How an Electrochemical Reaction Occurs?

1. Mass transport from the bulk electrolyte to the nearby region of electrode (electrical double layer, electrode/solution interface).
2. Electron transfer (oxidation or reduction) to the species under investigation.
3. Mass transport of the product from the electrode/solution interface to the bulk solution.
4. The rate of **ET** reaction is dependent of the **Mass Transport** and the **ET** that depends on the **rate-determining step** (the slowest step).



# Modes of Mass Transport

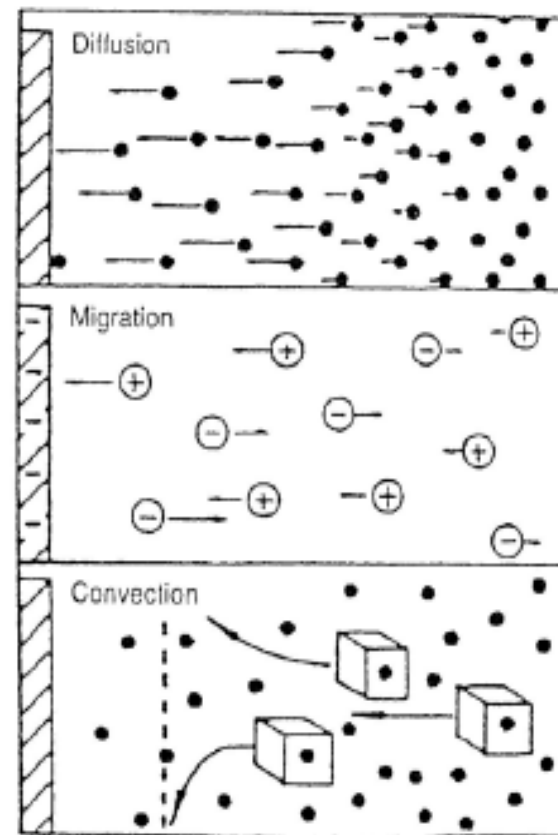
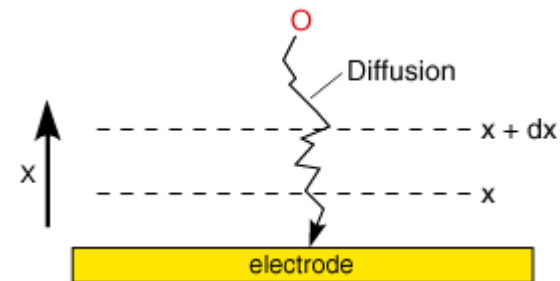
**1. Diffusion**—transport due to concentration gradient (most common)

**2. Migration**—Transport or movement due to Electric Potential gradient

To diminish it, high concentration of supporting electrolyte is usually used.

**3. Convection**—Transport due to stirring, rotation, thermal gradients.

Use static conditions (no stirring)

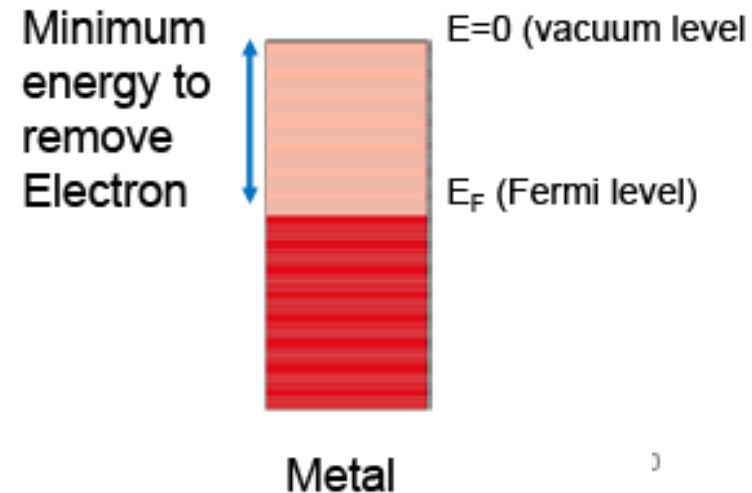


# Electron Transfer and Energy Levels

Why could we derive a non-spontaneous redox process by applying a voltage?

When a voltage is applied to an electrode → we supply an electrical energy.

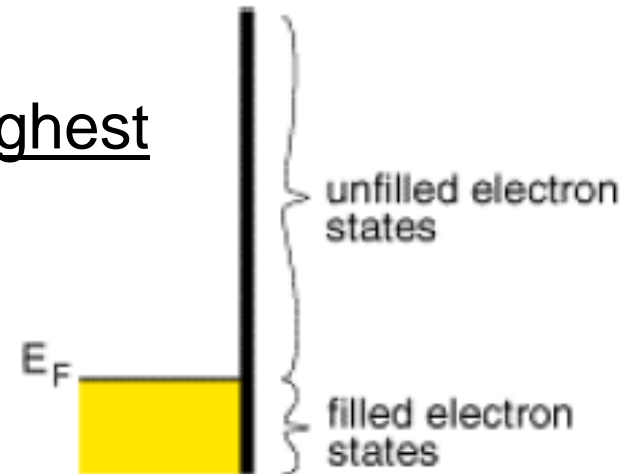
Since electrons possess charge, an applied voltage can alter the energy of the electrons with a metal electrode.



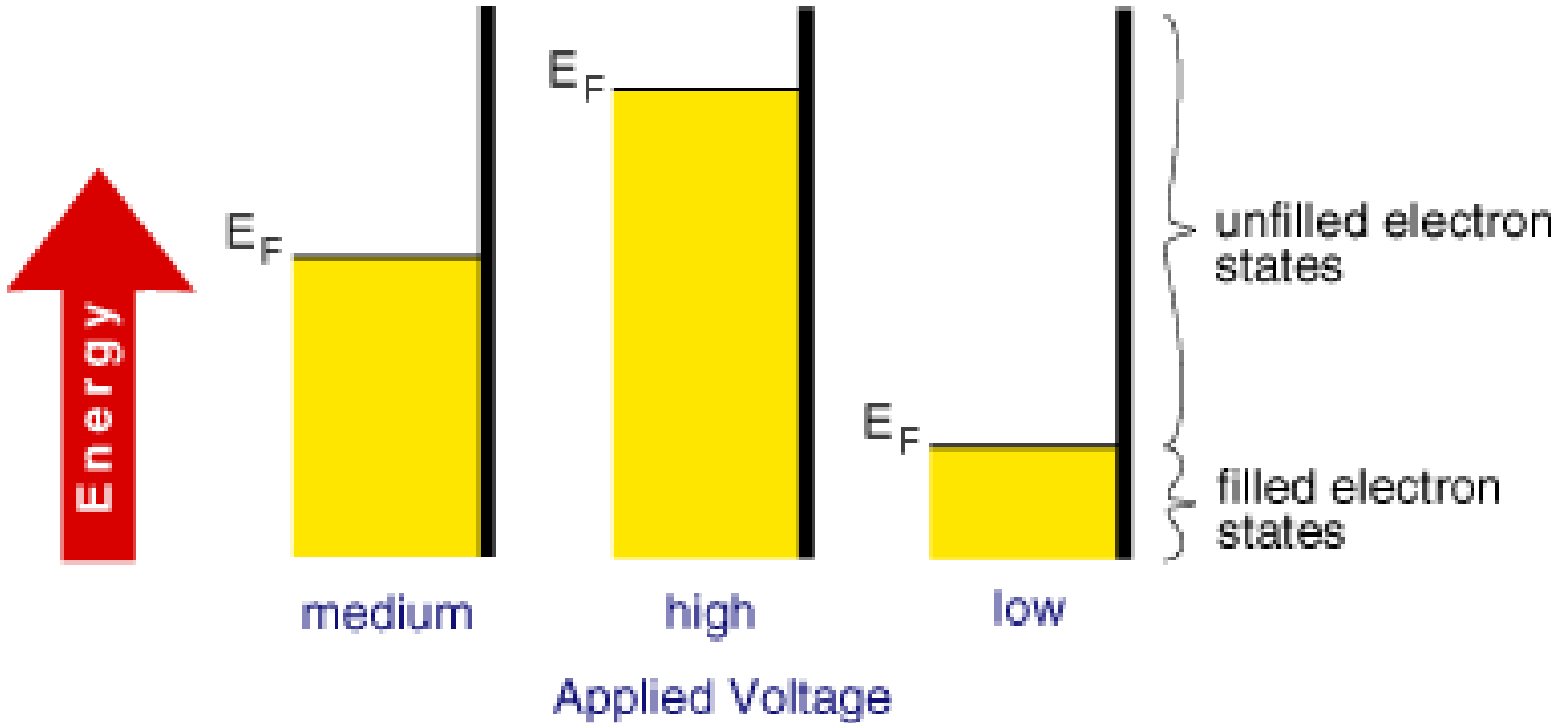
# Fermi Level ( $E_F$ ) and Electron Transfer

The behavior of electrons in a metal can be understood by considering the Fermi ( $E_F$ ).

- A metal does not possess individual well defined electron energy levels as in a single atom of the same material.
- Instead, a continuum of levels are created with the available electrons filling the states from the lowest energy upwards.
- The Fermi-level is corresponding to the highest energy the electrons can possess.
- The Fermi-level is not fixed, **but could be altered by supplying the electrical energy.**



**Electrochemists are able to alter the energy of the Fermi-level by applying a voltage to an electrode**



**Fermi-level in a metal at three applied voltages**

<https://www.ceb.cam.ac.uk/research/groups/rg-eme/teaching-notes/introduction-403>

# Reduction of species in solution

Fermi-level within a metal together with the orbital energies (HOMO and LUMO) of a molecule (O) in solution.

The Fermi-level has a lower energy than the LUMO of (O)

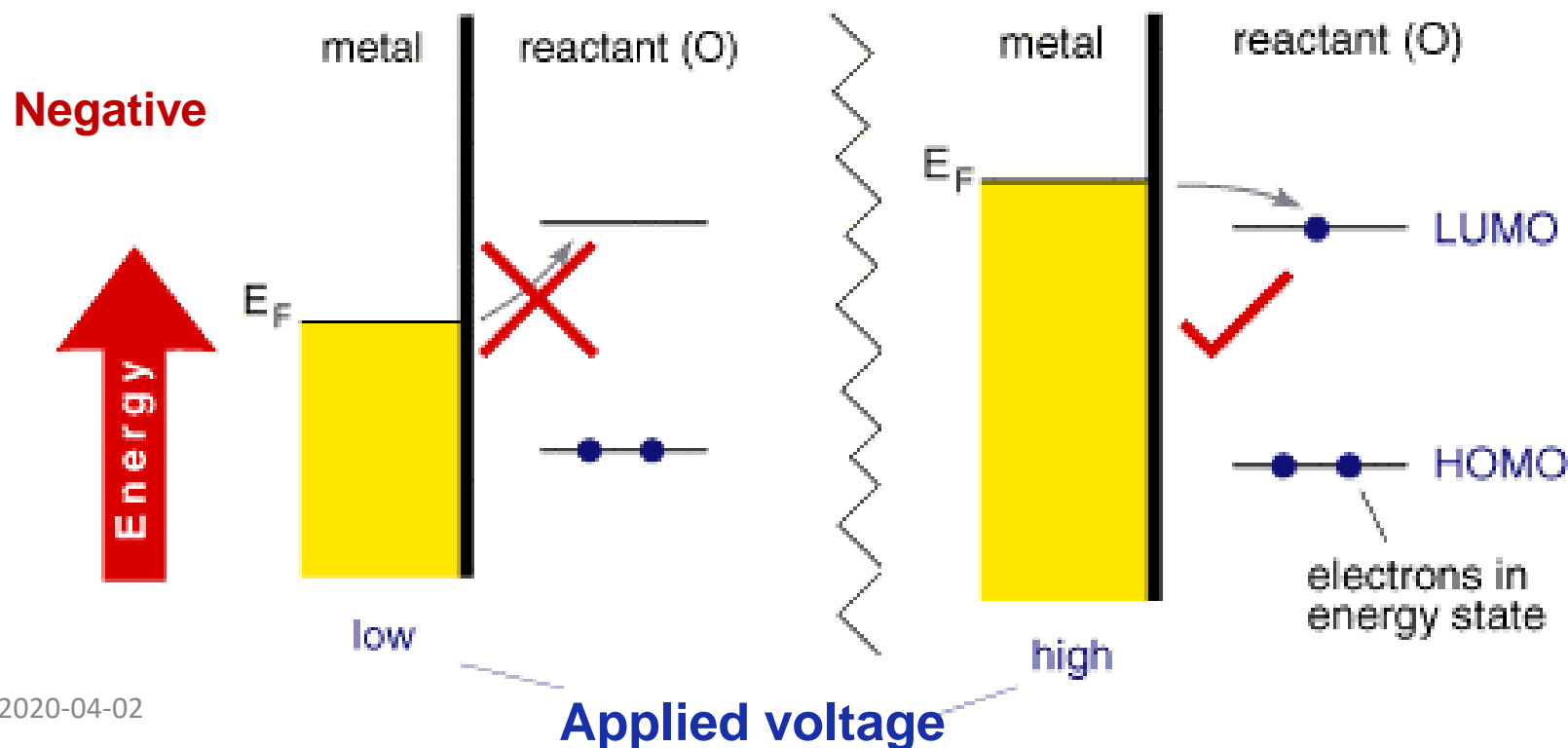
**Thermodynamics unfavorable**

For an electron to transfer from the electrode to the molecule.

The Fermi-level has a higher energy than the LUMO of (O)

**Thermodynamics favorable**

For an electron to transfer to occur, i.e. the reduction of O

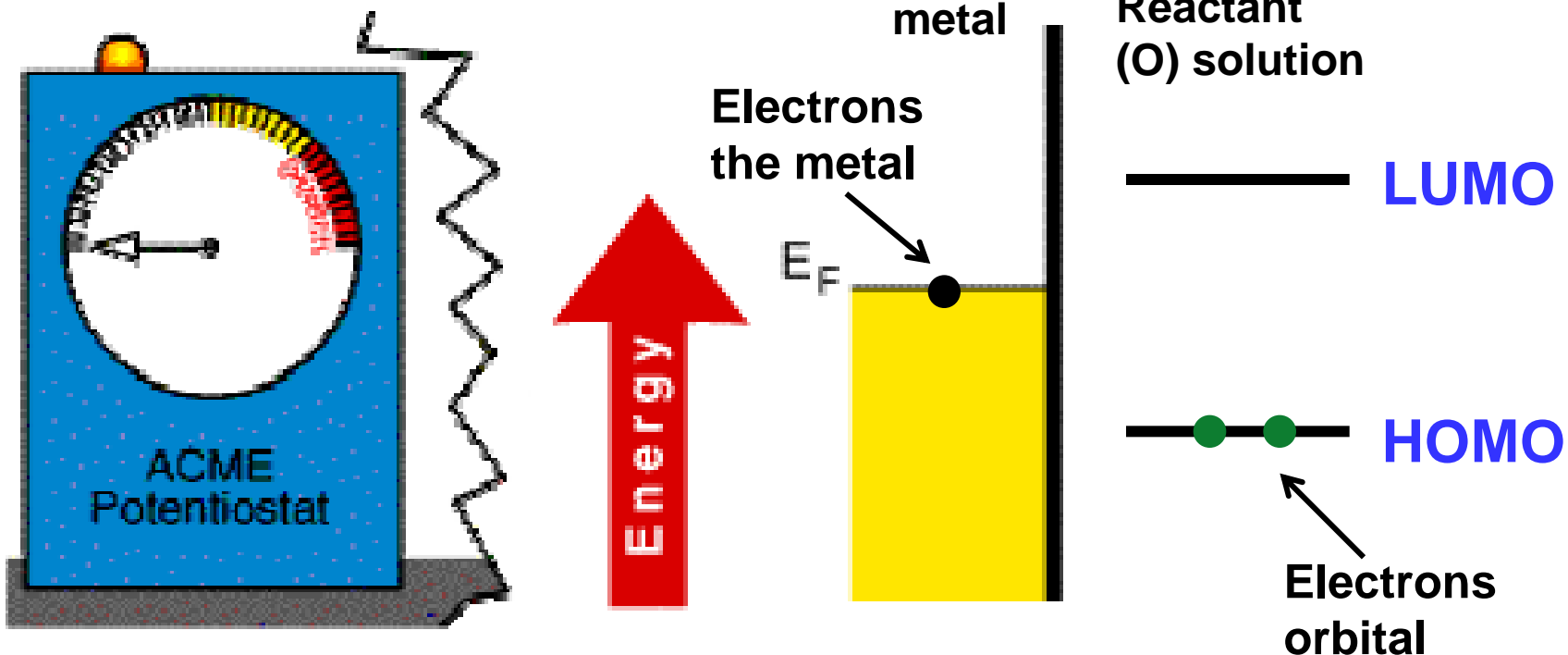




# Overall story

# Faradaic process= Electron transfer

The Fermi level in the metal is too low for electron transfer



The process is significant depends upon the rate of the electron transfer (reaction- kinetics)

What happens when a solution species is oxidized?

# Oxidation of species at the electrode surface

Fermi-level within a metal together with the orbital energies (HOMO and LUMO) of a molecule (R) in solution.

The Fermi-level has a higher energy than the LUMO of (R)

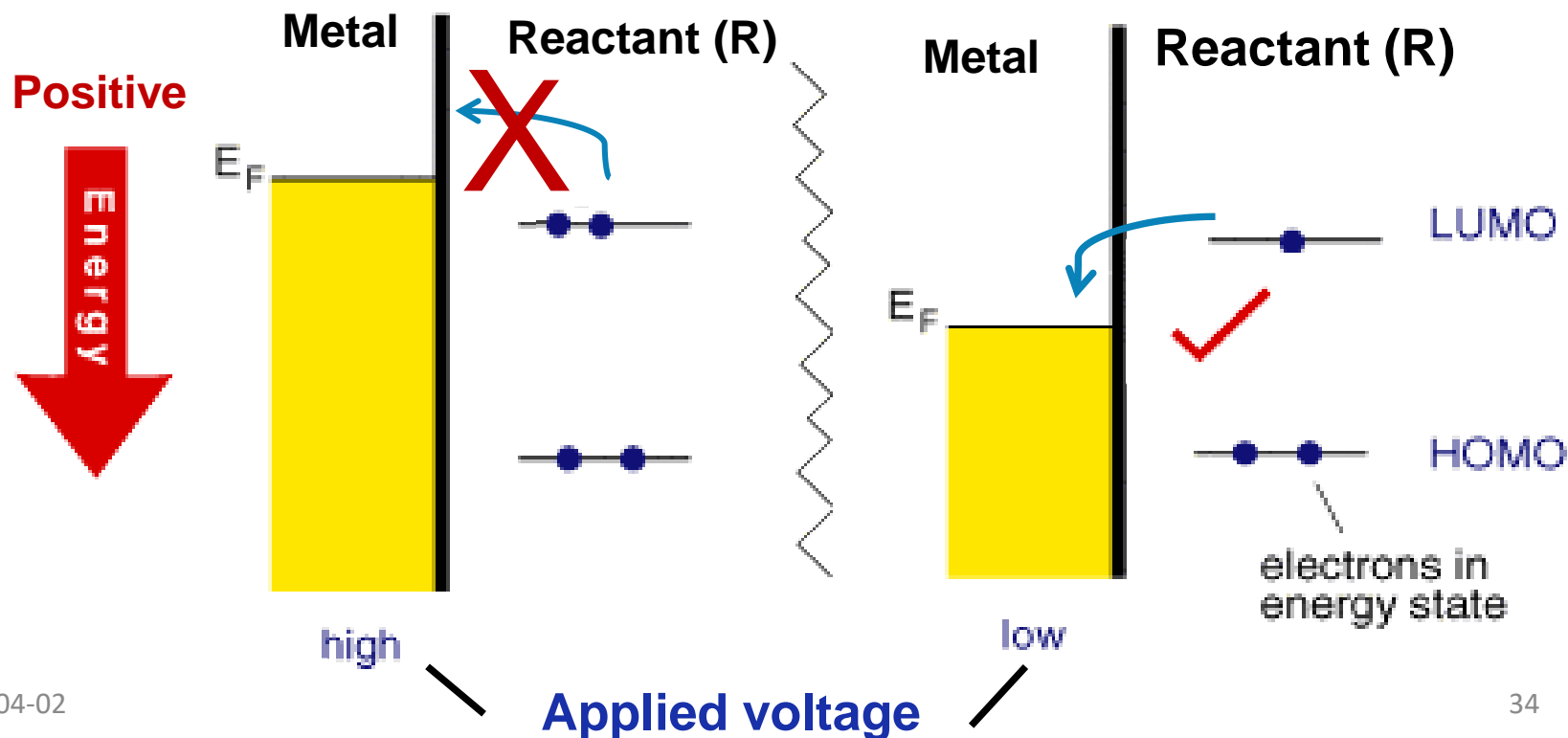
## Thermodynamics unfavorable

For an electron to transfer from the molecule to the electrode.

The Fermi-level has a lower energy than the LUMO of (R)

## Thermodynamics favorable

For an electron to transfer to occur, i.e. the oxidation of R.



# References

1. Allen J. Bard and Larry R. Faulkner, “**Electrochemical Methods: Fundamentals and Applications**”, 2nd Edition, New York: Wiley, 2001.
2. Joseph Wang “**Analytical Electrochemistry**”, 3rd Edition, New York, 2000, pp 209.