



# **BASIC PRINCIPLES OF ELECTRODE PROCESSES**

**I**

# Potential creation on interface

## Heterogeneous system



solid conductive phase – interface – liquid conductive phase



1. Ag (Ag<sup>+</sup>)

2. Pt (Pt-Ir, graphite)



Ag<sup>+</sup> NO<sub>3</sub><sup>-</sup>

Fe<sup>2+</sup>, Fe<sup>3+</sup> (SO<sub>4</sub><sup>2-</sup>)

spontaneous ion crossing 1. or electron transfer 2.

⇒ spontaneous interface charging:

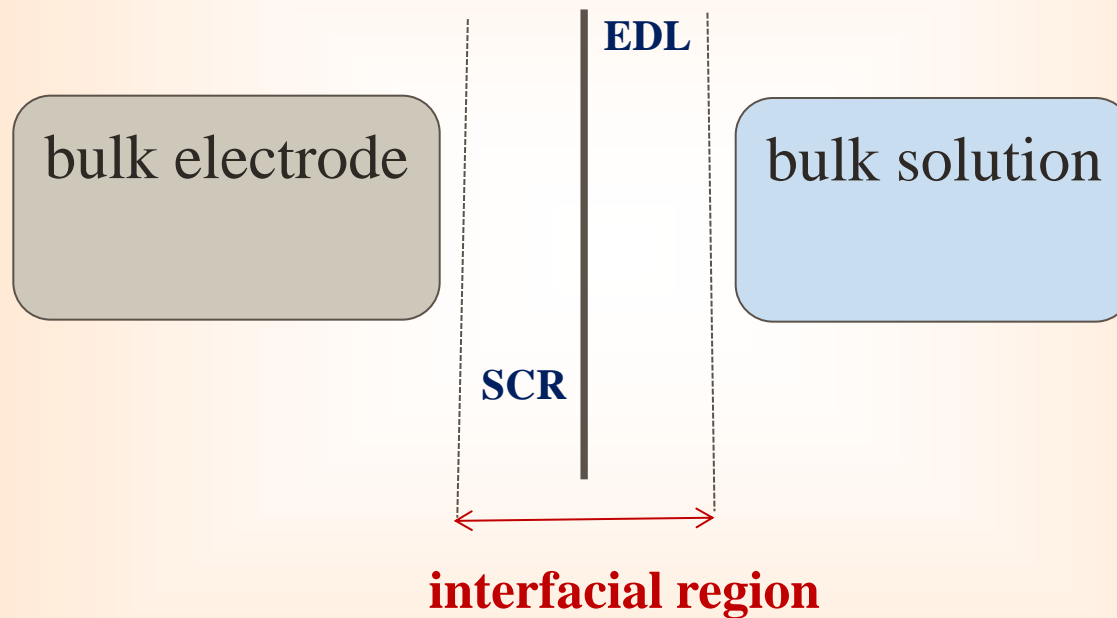


# Electrode-solution interface

## Heterogeneous system



## Structure of the interfacial region



**EDL** – electrolyte double layer

**SCR** – space-charge region (thin)

**balance stabilization**  $\Rightarrow$  **electrochemical potential equality of ion  $i$  in both phases:**

$$\mu_i^* (l) = \mu_i^* (s)$$

$$\mu_i^* (l) = \boxed{\mu_i} + \boxed{zF \varphi}$$

**chemical work**                      **electrical work**

**Chemical potential:**  $\mu_i = \mu_i^0 + RT \ln a_i$

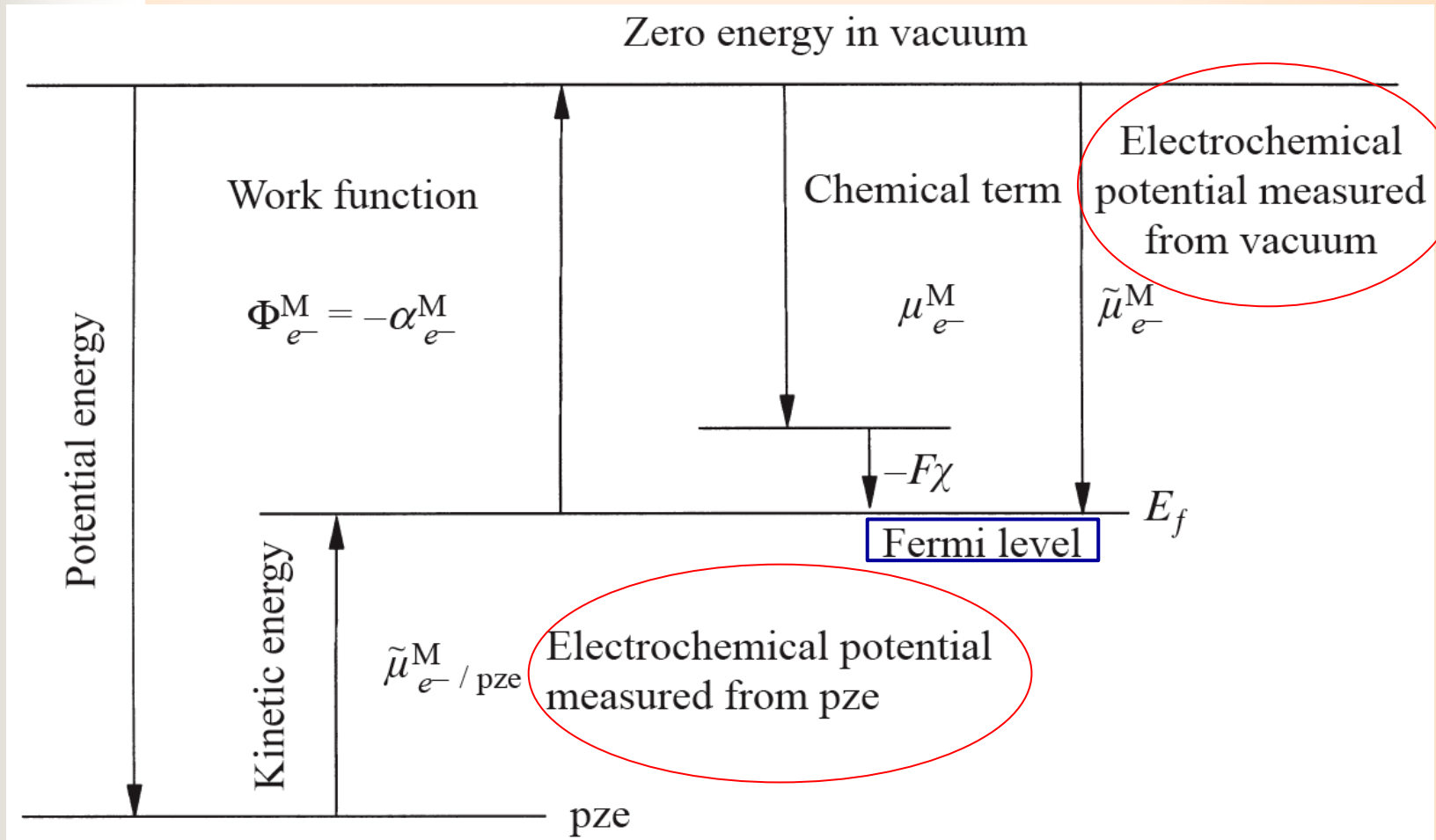
$$\Delta\mu_i^* = \Delta\mu_i + zF \Delta\varphi = 0 \quad \text{in balance}$$

$$\Delta\mu_i = |z| F \Delta\varphi$$

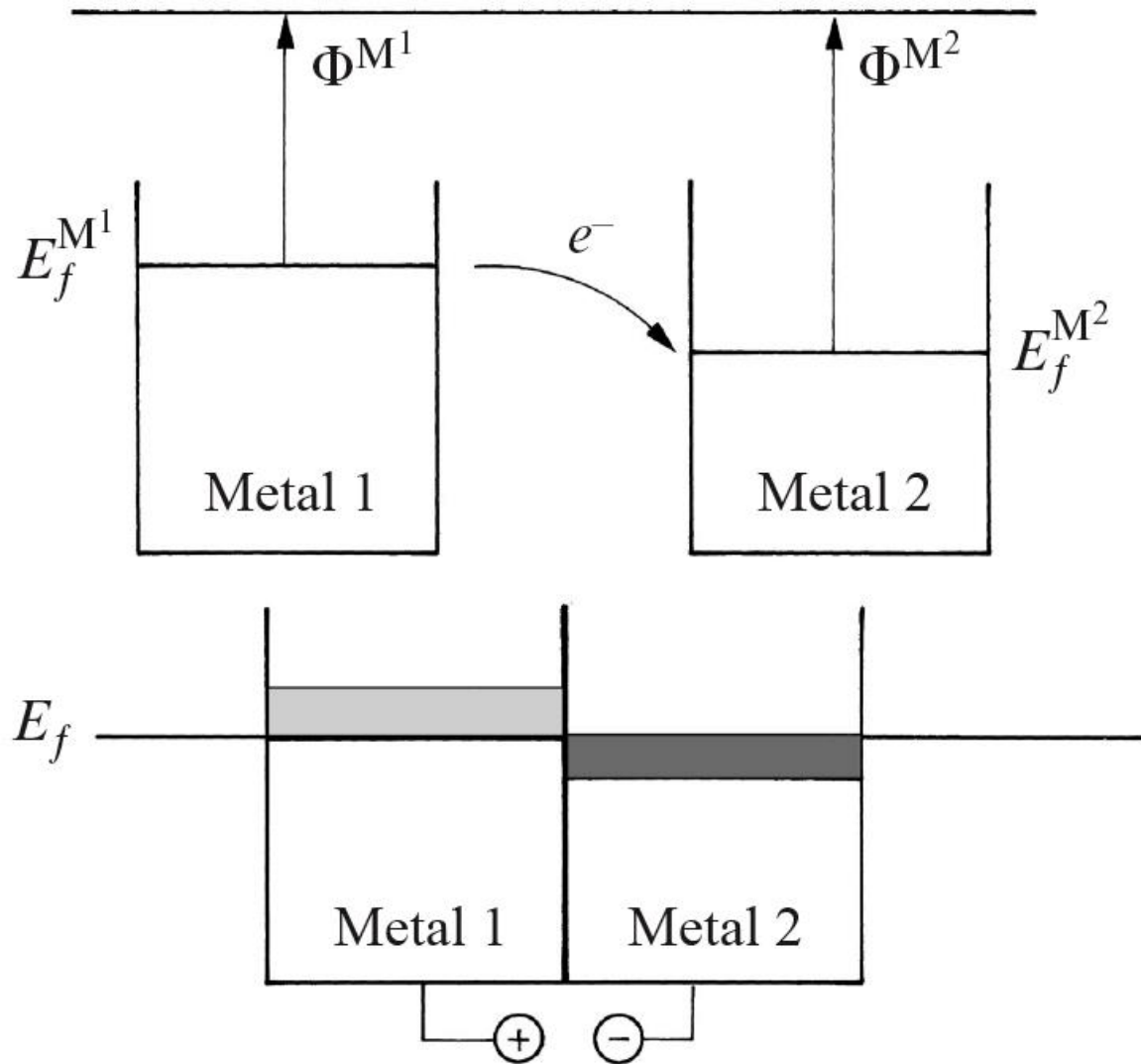
$\Delta\varphi =$  potential difference between solid phase and solution

$\Delta\varphi$  inner (Galvani) potential, **immeasurable!**

Each **chemical species** ( $\text{H}_2\text{O}$ ,  $\text{Na}^+$ ,  $e^-$ ....) has an electrochemical potential (a quantity with units of energy) at any given location



**Energy diagram for a non-charged metal**



**Contact between two metals having different work functions**

**Measurable**  $\Rightarrow$  cell potential **EMN**, made from 2

**hemi-cells:**

standard hydrogen electrode **SHE**  $E^\circ = 0 \text{ V}$

measured electrode  $E = b + \Delta\phi$   $b = \text{constant}$

$$EMN = E - 0 = E$$

**Nernst : 1.**  $E_{redox} = E_{redox}^0 + \frac{RT}{zF} \ln a_{ox}$

$$E_{Ag/Ag^+} = E_{Ag/Ag^+}^0 + \frac{RT}{F} \ln a_{Ag^+}$$

**2.**  $E_{redox} = E_{redox}^0 + \frac{RT}{zF} \ln \frac{a_{ox}}{a_{red}}$

$$E_{Fe^{2+}/Fe^{3+}} = E_{Fe^{2+}/Fe^{3+}}^0 + \frac{RT}{F} \ln \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}}$$

*That was a balance*



**From within entered potential on electrode:**

↳ **charge goes through an interface**

**impossible of charging  $\Rightarrow$**

**impolarizedable interface**

(impolarizedable electrode, Ag / Ag<sup>+</sup>)

↳ **charge doesn't go through an interface**

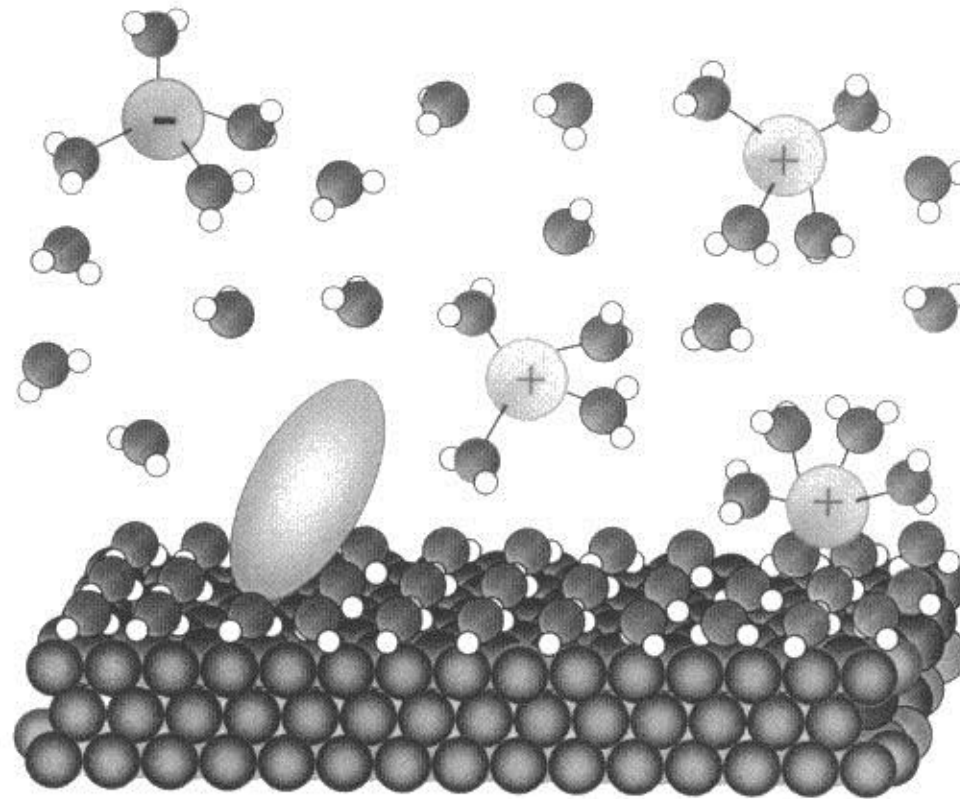
**possible of charging  $\Rightarrow$**

**polarizedable interface**

(polarizedable electrode, Pt, graphite, Hg, without Hg<sup>z+</sup> in solution)



# ELECTRODE DOUBLE LAYER



●●● electrode surface

●○ water molecule

⊕ cation

⊖ anion

○ adsorbed neutral species

# ELECTRODE DOUBLE LAYER

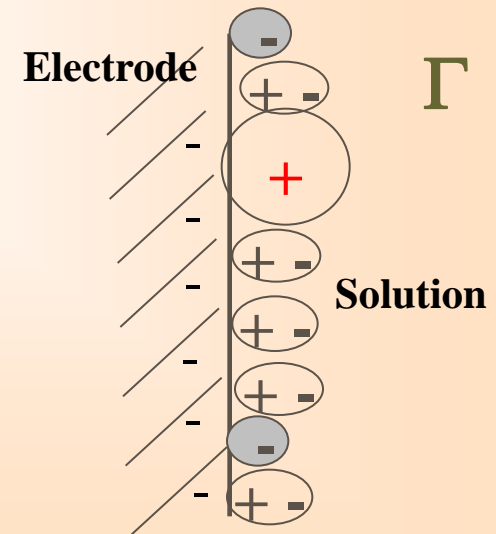
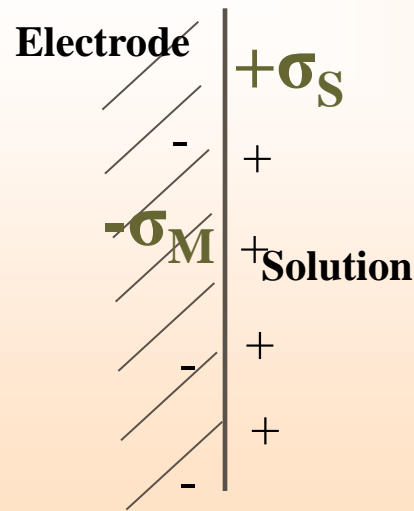
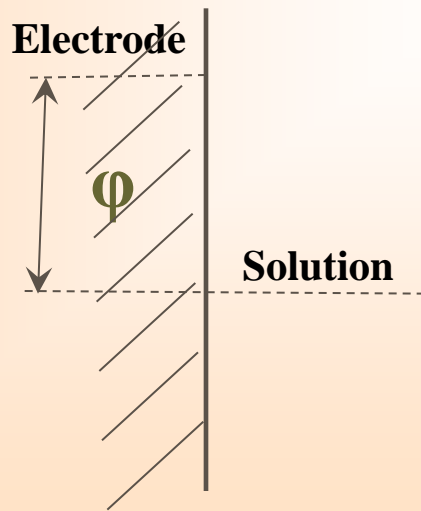
electrostatic potential  $\Phi$

charge density  $\sigma$

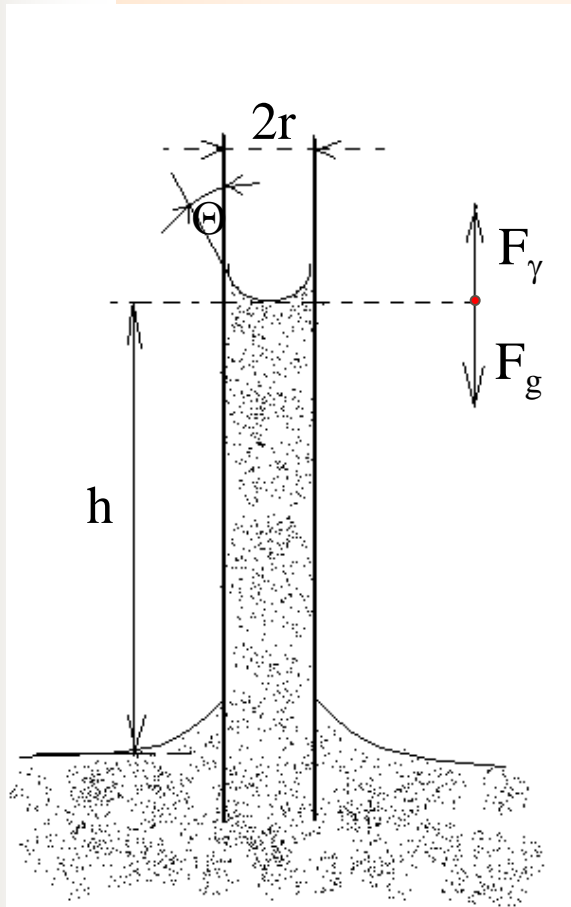
surface tension  $\gamma$

capacity  $C$

adsorption  $\Gamma$



surface tension  $\gamma$



**a) capillary elevation**

$$F_\gamma = F_g$$

$$2\pi r \gamma \cos\Theta = \pi r^2 h \rho g$$

$$\gamma = \frac{r h \rho g}{2 \cos\Theta}$$

**b) stalagmometr (also DME)**

$$m g = 2\pi r \gamma$$

$$\gamma = \frac{m g}{2\pi r}$$

$$\gamma : \gamma_0 = m : m_0$$

## charge density $\sigma$

$$\frac{\partial \gamma}{\partial E_{\Delta}} = -\sigma_M$$

Lippman equation

## capacity $C$

**differential capacity  $C_d$**

$$\frac{\partial \sigma_M}{\partial E_{\Delta}} = C_d$$

**integral capacity  $C_i$**

$$\frac{\sigma_M}{E - E_{\Delta}} = \frac{\int_{E_z}^E C_d dE}{\int_{E_z}^E dE} = C_i$$

## adsorption $\Gamma$

**Langmuir isotherm**

$$\frac{\Theta}{1 - \Theta} = \beta_i a_i$$

$\Theta$  fraction of coverage

$\Gamma, \Gamma_{\infty}$  surface or maximum surface excess

$\beta_i$  adsorption coefficient

$a_i$  activity of species  $i$  in bulk solution

$$\Theta = \frac{\Gamma}{\Gamma_{\infty}}$$

## Temkin isotherm

$$\Gamma_i = \frac{RT}{2g} \ln(\beta_i a_i)$$

$g$  .... parameter treating the interaction energy between the adsorbed species

## Frumkin isotherm

$$\beta_i a_i = \frac{\Gamma_i}{\Gamma_\infty - \Gamma_i} \exp \frac{2g\Gamma_i}{RT}$$

## Esin-Markov effect

The degree of specific adsorption should vary with electrolyte concentration, just as there should be a change in the point of zero charge

$$\beta_{E-M} = \frac{1}{RT} \left( \frac{\partial(\Delta E_z)}{\partial \ln a} \right)_{\sigma_M}$$



# **ELECTRODE DOUBLE LAYER STRUCTURE ON INTERFACE ELECTRODE - ELECTROLYTE**

## **Electrostatic Models**

**Helmholtz Model (1879)**

**Gouy-Chapman Model (1910-1913)**

**Stern Model (1924)**

**Grahame Model (1947)**

**Bockris, Devanathan, Müller Model (1963)**

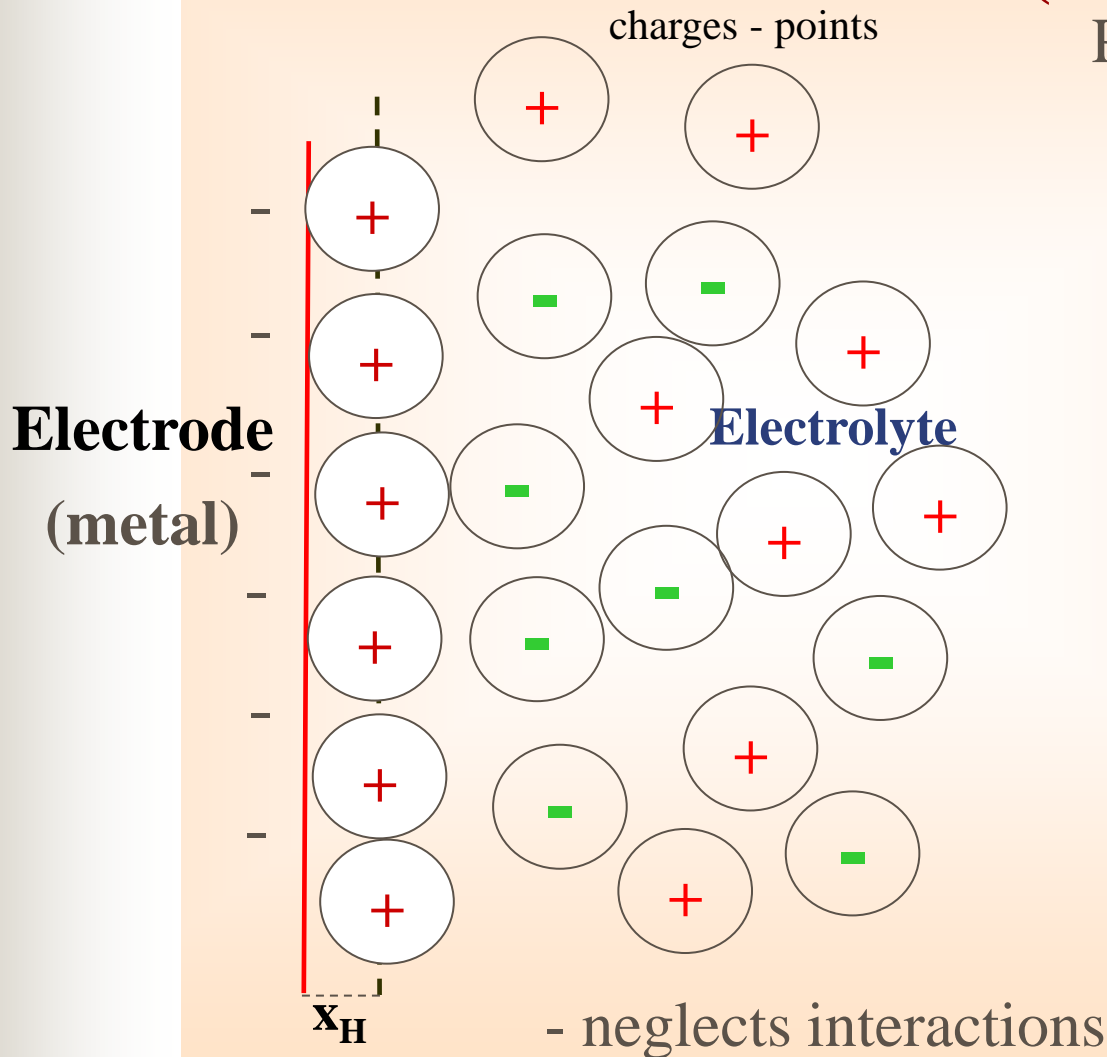
## **Chemical Models**

**Damaskin and Frumkin**

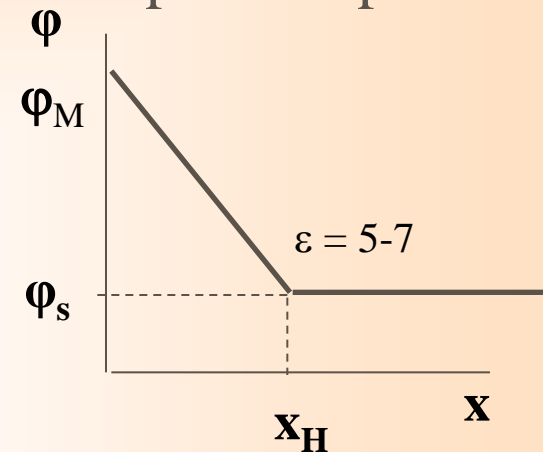
**Trasatti**

**Parsons**

# Helmholtz Model (1879)



Parallel-plate capacitor



$$C_d = \frac{\epsilon_r \epsilon_0}{x_H}$$

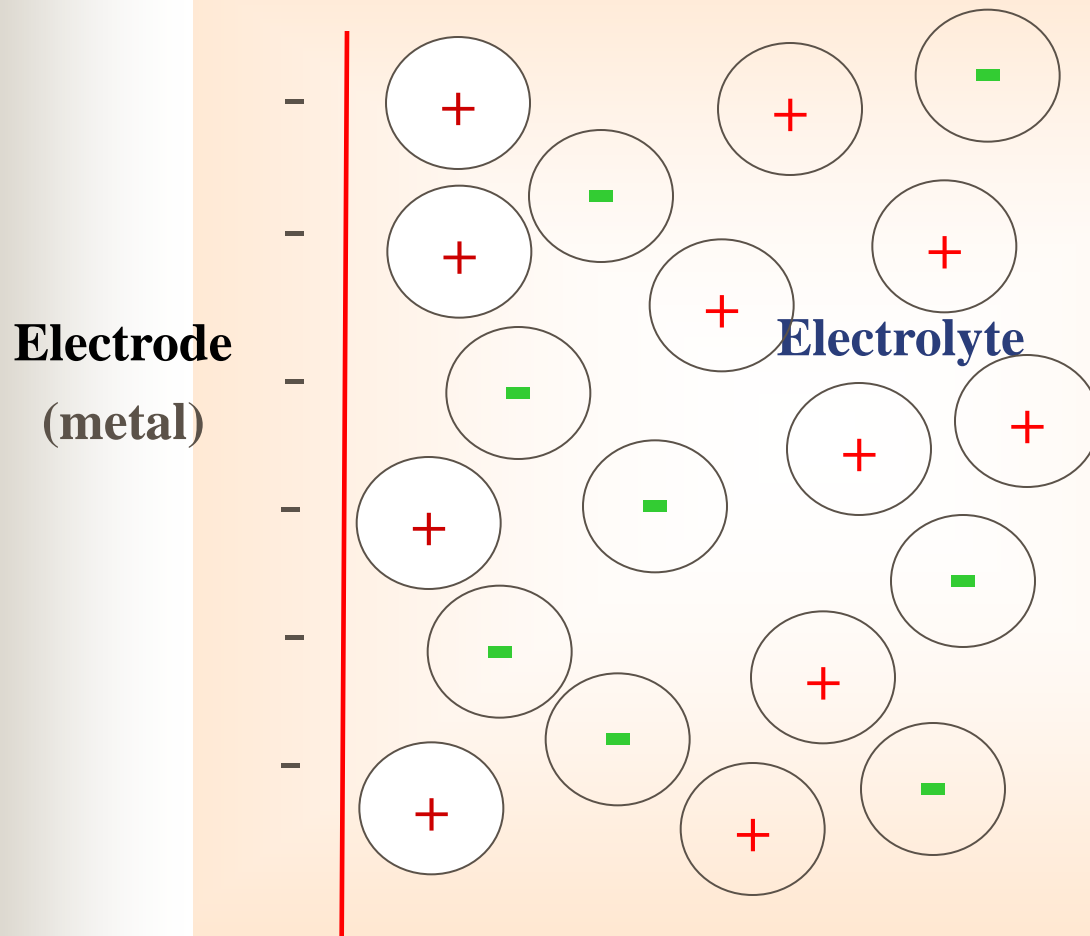
$C_d$

about 10-20  $\mu\text{F}/\text{cm}^2$

E

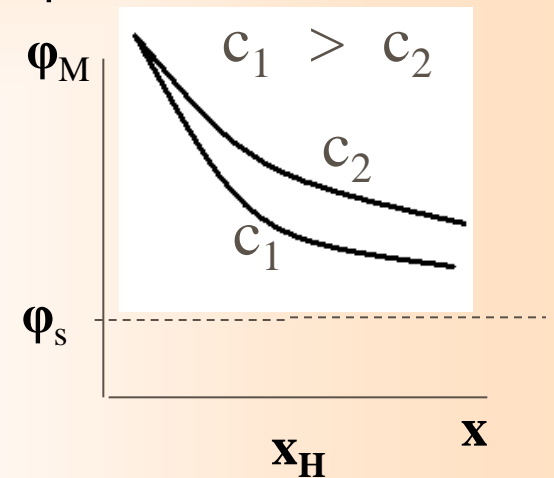
- does not take into account any concentration dependence

# Gouy-Chapman Model (1910-1913)

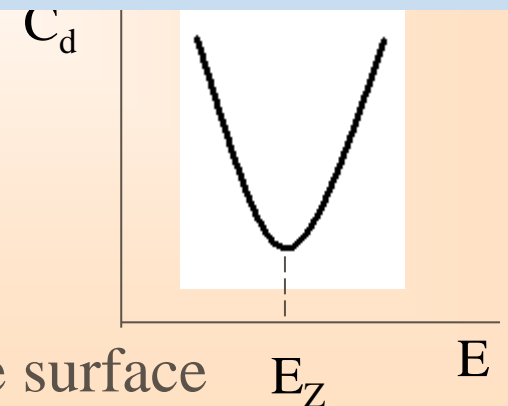


- neglects interactions
- ions are considered as point charges
- there is no concentration maximum of ions to the surface

$\phi$  diffuse double layer



$$C_{d,GC} = K \cosh \left( \frac{ze\phi_{\Delta,0}}{2k_B T} \right)$$





# Gouy-Chapman Model (1910-1913)

distribution of species with distance from electrode  
( $x_{DL}$  = distance characteristic of the diffuse layer)

$$n_i = n_i^0 \exp\left(\frac{-z_i e \varphi_{\Delta}}{k_B T}\right) \quad \text{Boltzmann's law}$$

$$\varphi_{\Delta} = \varphi - \varphi_s$$

$$\rho(x) = \sum_i n_i z_i e = \sum_i n_i^0 z_i e \exp\left(\frac{-z_i e \varphi_{\Delta}}{k_B T}\right)$$

$$\frac{\partial^2 \varphi_{\Delta}(x)}{\partial x^2} = \frac{-\rho(x)}{\epsilon_r \epsilon_0} \quad \text{Poisson's equation}$$

# Gouy-Chapman Model (1910-1913)

Poisson-Boltzmann equation

$$\frac{\partial^2 \varphi_{\Delta}(x)}{\partial x^2} = -\frac{e}{\varepsilon_r \varepsilon_0} \sum_i n_i^0 z_i \exp\left(\frac{-z_i e \varphi_{\Delta}}{k_B T}\right)$$

$x_{DL}$  = distance characteristic of the diffuse layer

$$x_{DL} = \left( \frac{\varepsilon_r \varepsilon_0 k_B T}{2 n_i^0 z^2 e^2} \right)^{1/2} \quad \text{diffuse layer thickness}$$

$x_{DL}$  for water at 298 K is  $3.04 \cdot 10^{-8} z^{-1} c^{-1/2}$  cm

if  $c = 1\text{M}$  and  $z = 1$ , then  $x_{DL}$  is 0.3 nm

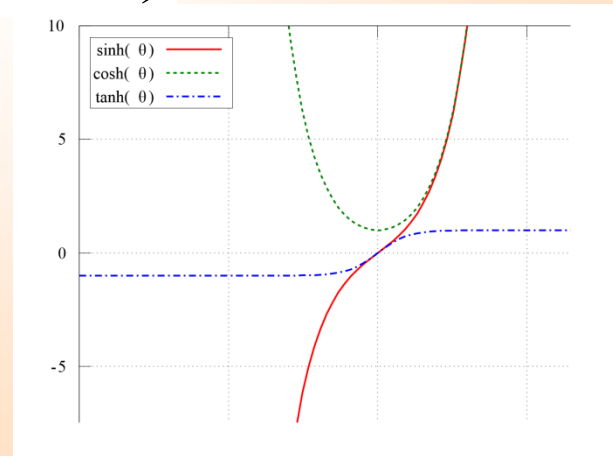
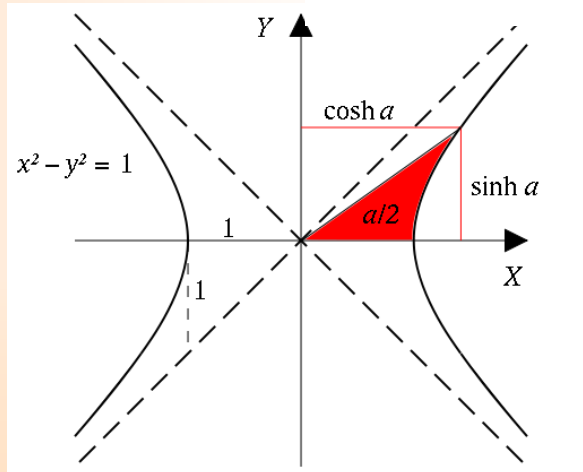
$$\sigma_M = \varepsilon_r \varepsilon_0 \left( \frac{\partial \varphi_{\Delta}}{\partial x} \right)_{x=0} = \left( 8 k_B T \varepsilon_r \varepsilon_0 n_i^0 \right)^{1/2} \sinh \left( \frac{z e \varphi_{\Delta,0}}{2 k_B T} \right)$$

# Gouy-Chapman Model (1910-1913)

$$\sigma_M = \varepsilon_r \varepsilon_0 \left( \frac{\partial \varphi_{\Delta}}{\partial x} \right)_{x=0} = \left( 8k_B T \varepsilon_r \varepsilon_0 n_i^0 \right)^{1/2} \sinh \left( \frac{ze\varphi_{\Delta,0}}{2k_B T} \right)$$

$$C_{d,GC} = \left( \frac{\partial \sigma_M}{\partial \varphi_{\Delta,0}} \right) = \left( \frac{2z^2 e^2 \varepsilon_r \varepsilon_0 n_i^0}{k_B T} \right)^{1/2} \cosh \left( \frac{ze\varphi_{\Delta,0}}{2k_B T} \right)$$

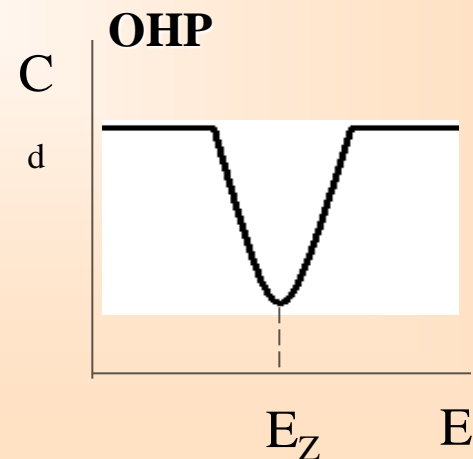
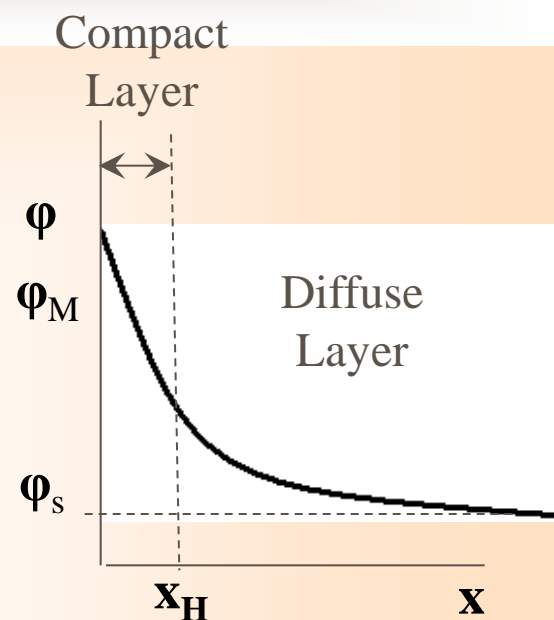
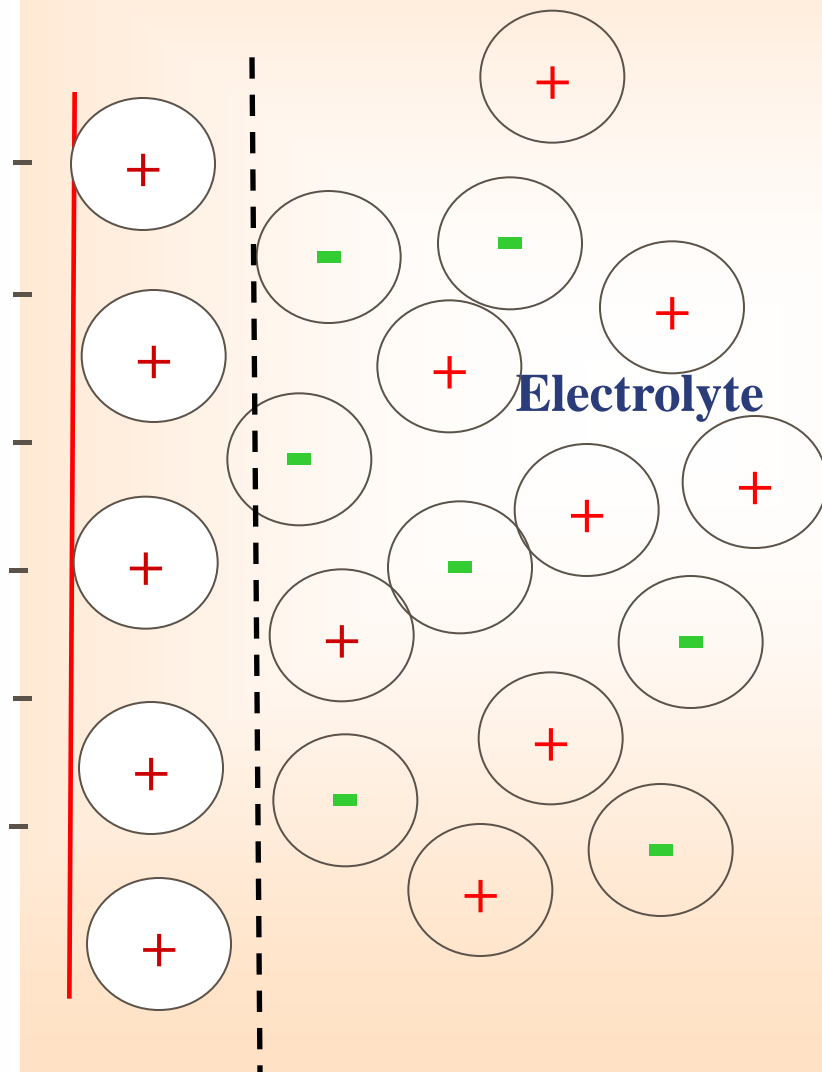
$$C_{d,GC} = K \cosh \left( \frac{ze\varphi_{\Delta,0}}{2k_B T} \right)$$



$$C_{d,GC} = 228 z c_{\infty}^{1/2} \cosh(19.5 z \varphi_{\Delta,0}) \mu F . cm^{-2}$$

# Stern Model (1924)

Electrode  
(metal)



# Stern Model (1924)

$$\frac{1}{C_d} = \frac{1}{C_H} + \frac{1}{C_{GC}}$$
$$= \frac{x_H}{\varepsilon_r \varepsilon_0} + \frac{1}{\left(2\varepsilon_r \varepsilon_0 z^2 e^2 n_i^2 / k_B T\right)^{1/2} \cosh(z e \varphi_{\Delta 0} / 2 k_B T)}$$

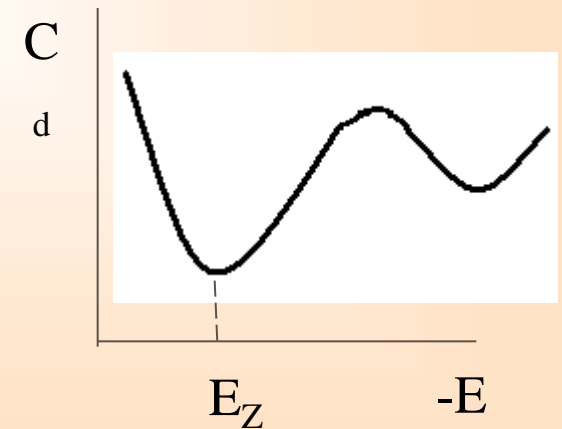
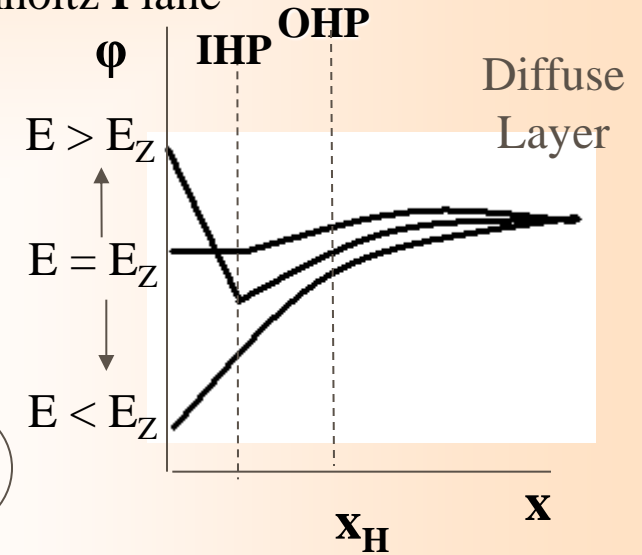
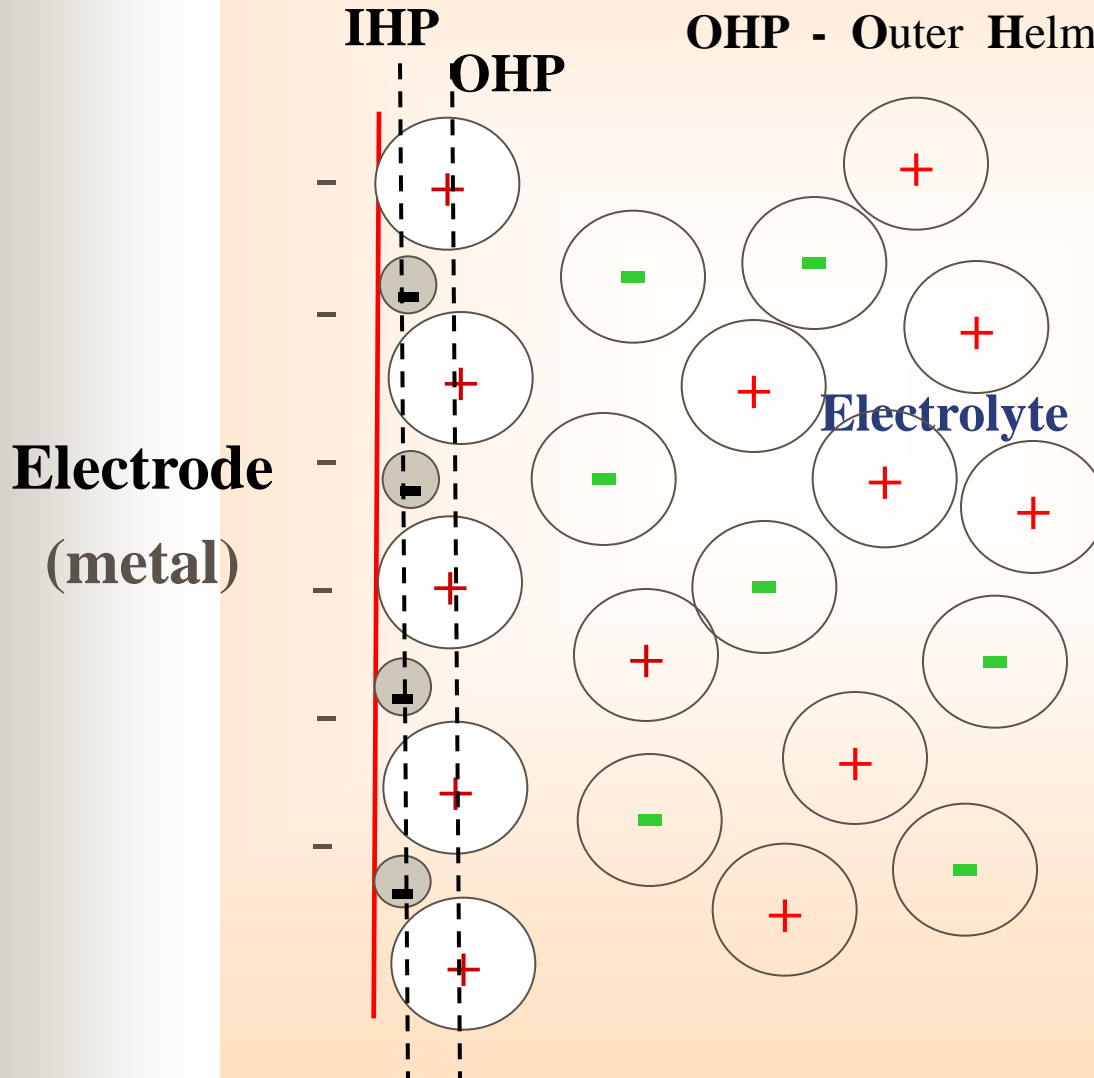
close to  $E_Z$ ,  $C_H \gg C_{GC}$  and so  $C_d \sim C_{GC}$

far from  $E_Z$ ,  $C_H \ll C_{GC}$  and so  $C_d \sim C_H$

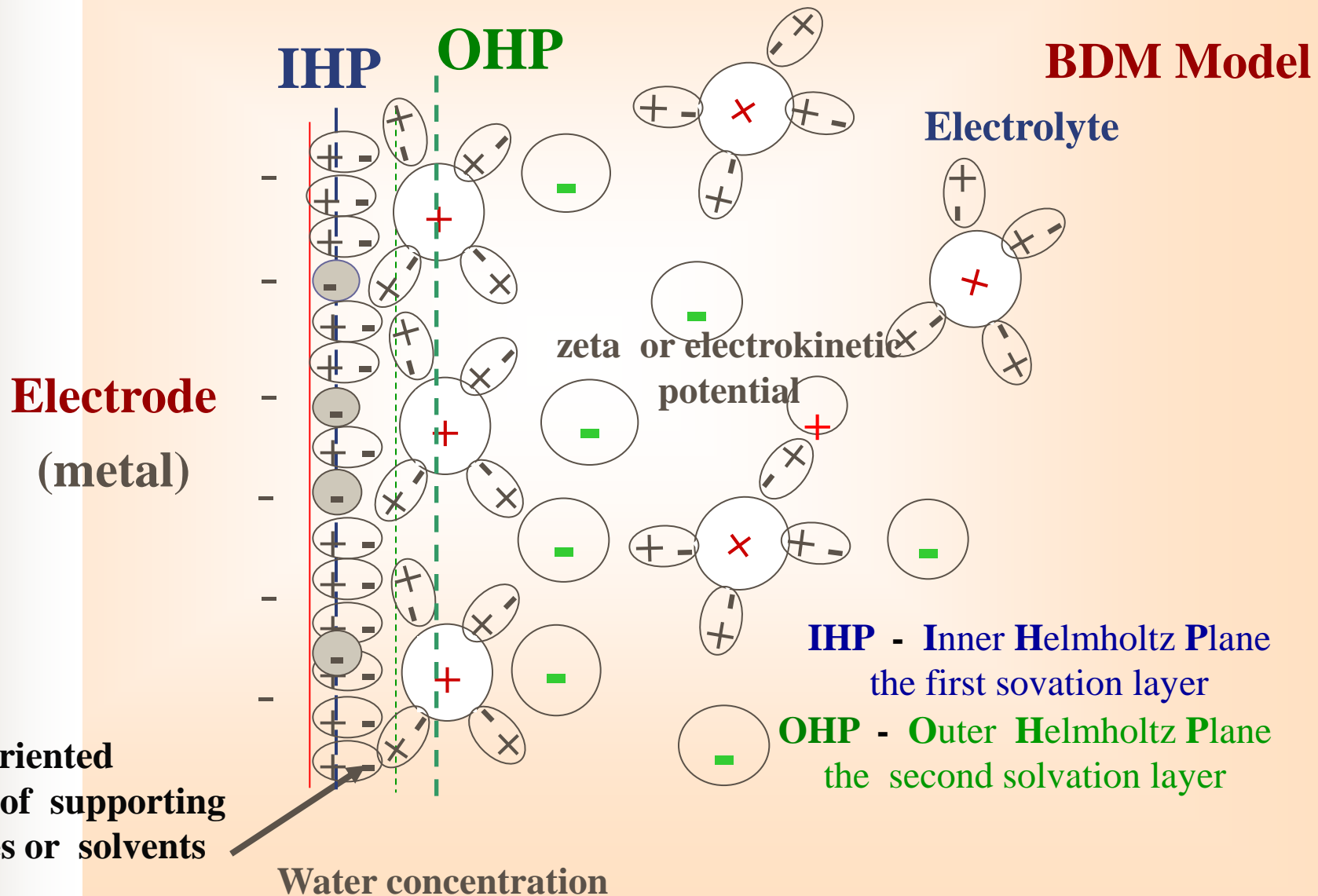
separation plane between the two zones is called the  
**outer Helmholtz plane (OHP)**

# Grahame Model (1947)

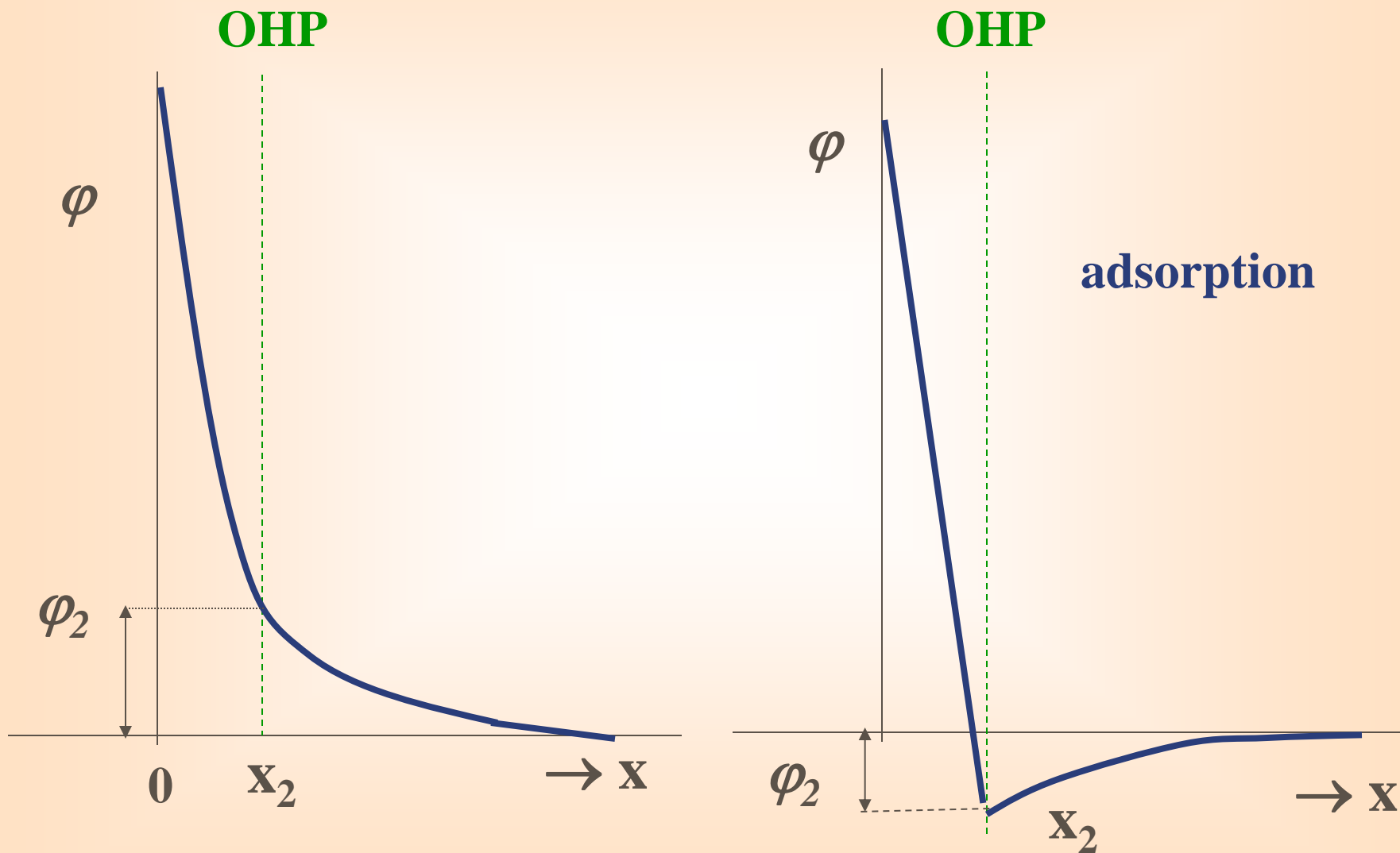
IHP - Inner Helmholtz Plane  
 OHP - Outer Helmholtz Plane



# Bockris, Devanathan, Müller Model (1963)



# CHARACTERISTIC OF ELECTRODE POTENTIAL IN DOUBLE LAYER

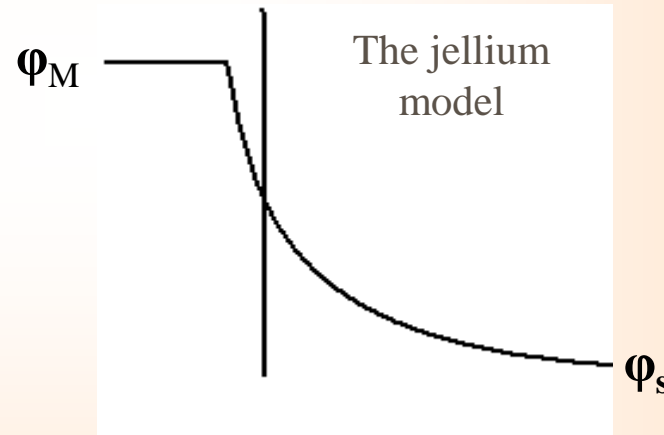
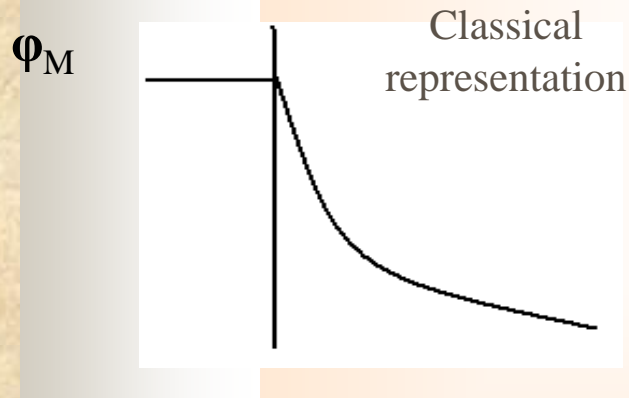




# ELECTRODE DOUBLE LAYER STRUCTURE ON INTERFACE ELECTRODE - ELECTROLYTE

## Chemical Models

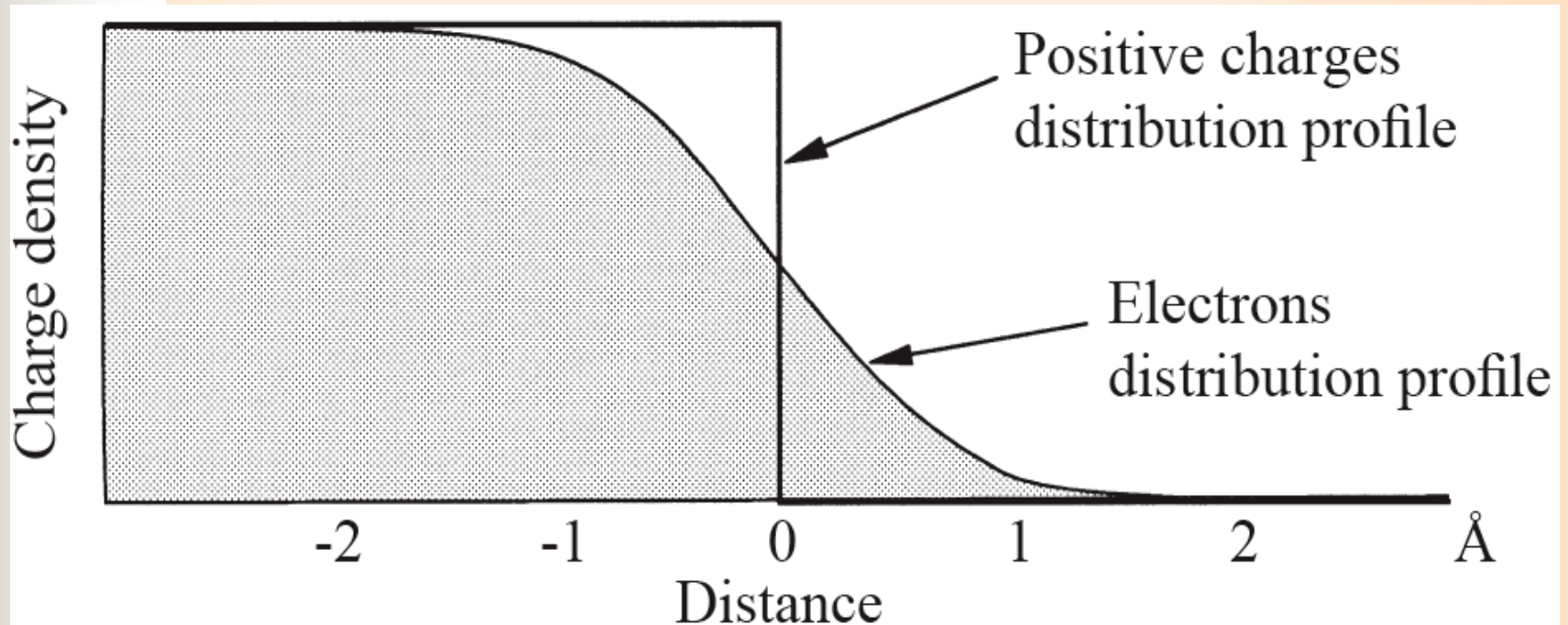
- the electronic distribution of the atoms in electrodes (not only electrostatic forces)
- difference between (sp) metals and transition (d)metals
- IHP as an electronic molecular capacitor
- jellium model Raman spectra, EXAFS:Extended X-Ray Absorption Fine Structure



Variation of the electrostatic potentials with distance from a metallic electrode

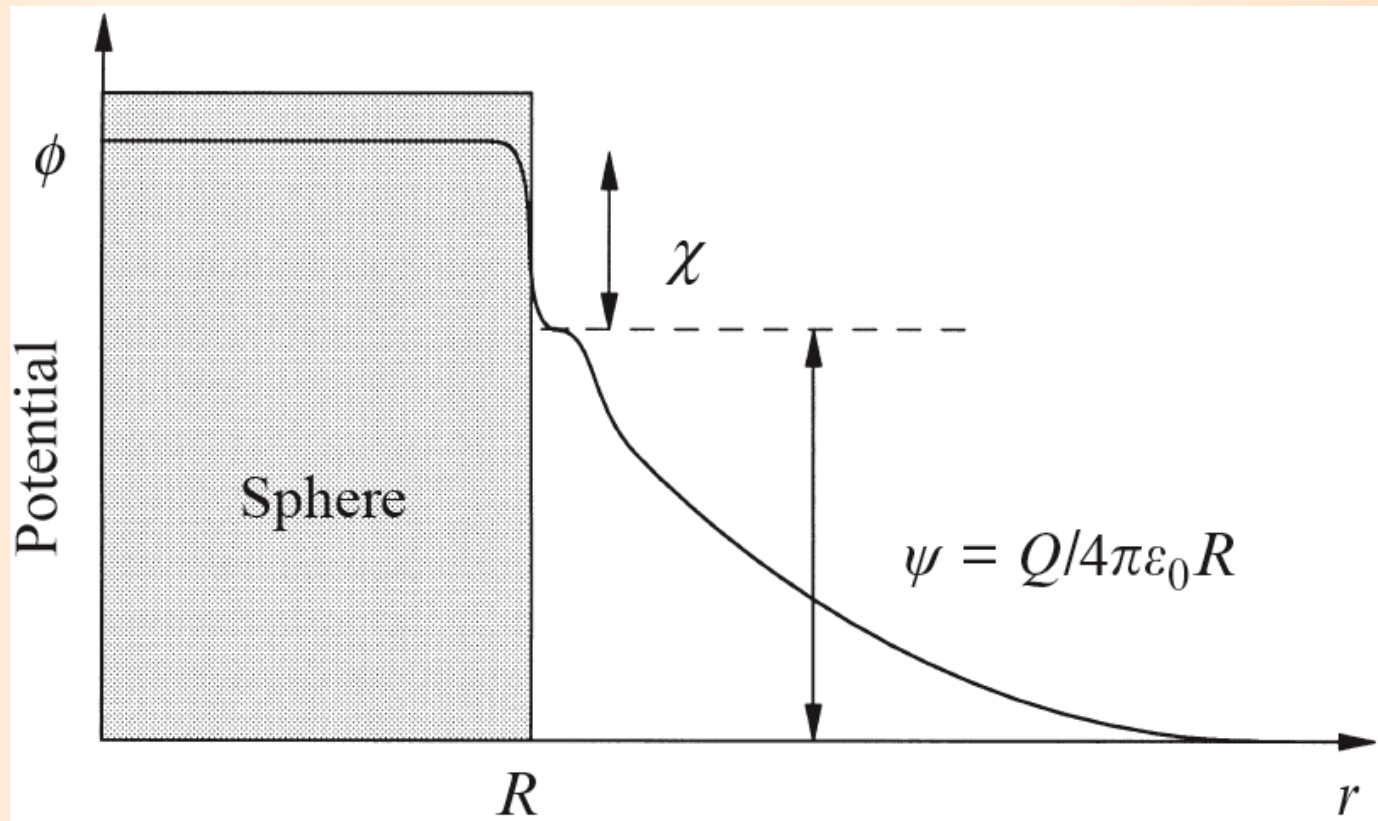
**Chemical Model (Damaskin and Frumkin)**  
**(Trasatti)**  
**(Parsons)**

## ELECTRODE DOUBLE LAYER STRUCTURE ON INTERFACE ELECTRODE - ELECTROLYTE



Electron spill-over at the surface of a metal according to the Jellium model.

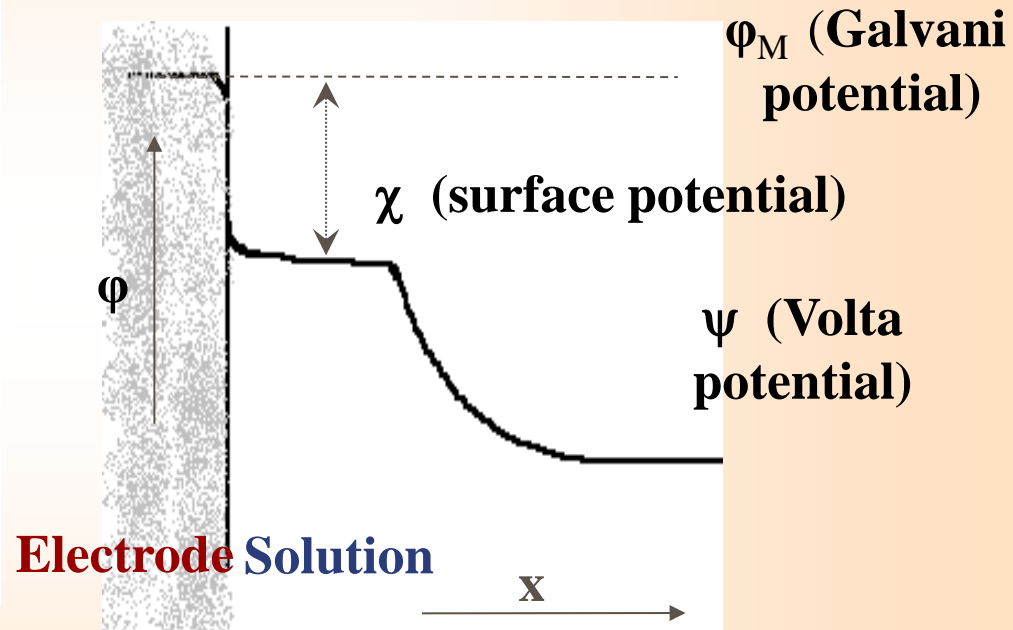
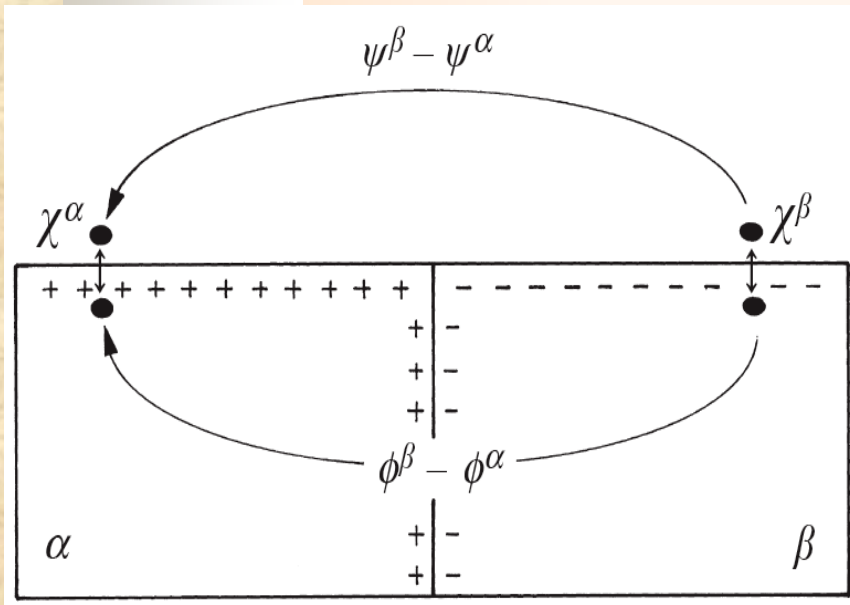
## ELECTRODE DOUBLE LAYER STRUCTURE ON INTERFACE ELECTRODE - ELECTROLYTE



Radial distribution of potential for a metal sphere of radius  $R$  carrying a positive charge  $Q$ , illustrating the contributions of the outer potential and the surface potential. The inner potential is constant inside the sphere.

# ELECTRODE DOUBLE LAYER STRUCTURE ON INTERFACE ELECTRODE - ELECTROLYTE

## Solid metallic electrodes



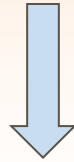
Surface potential, the Volta potential and the Galvani potential differences for two phases in contact.

# Solid metallic electrodes

mercury



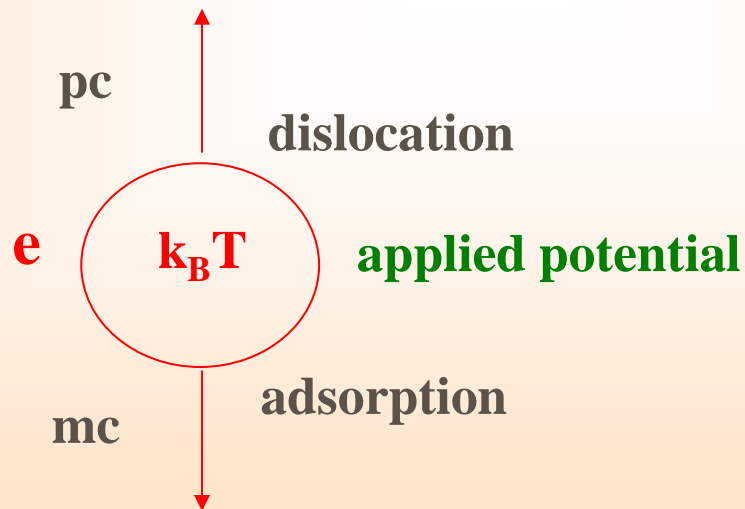
solid electrode



a well defined structure

pc (polycrystal)

mc (monocrystal)

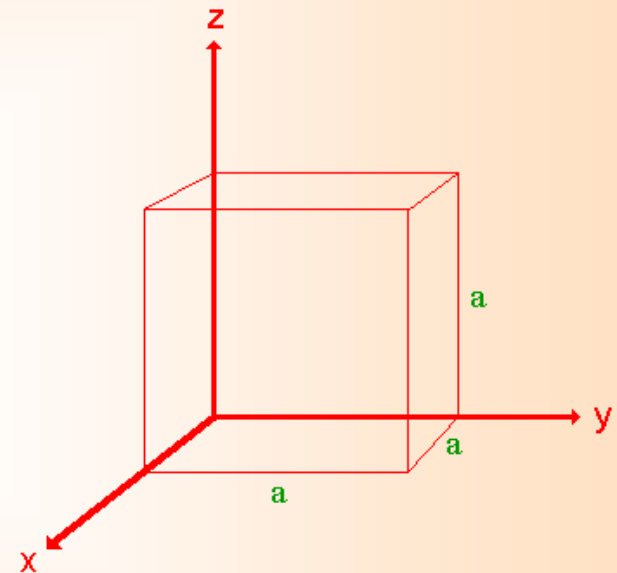



# Solid metallic electrodes (monocrystals)

The orientation of a surface or a crystal plane may be defined by considering how the plane (or indeed any parallel plane) intersects the main crystallographic axes of the solid. The application of a set of rules leads to the assignment of the **Miller Indices**,  $(hkl)$ ; a set of numbers which quantify the intercepts and thus may be used to uniquely identify the plane or surface.

The following treatment of the procedure used to assign the **Miller Indices** is a simplified one (it may be best if you simply regard it as a "recipe") and only a cubic crystal system (one having a cubic unit cell with dimensions  $a \times a \times a$ ) will be considered.

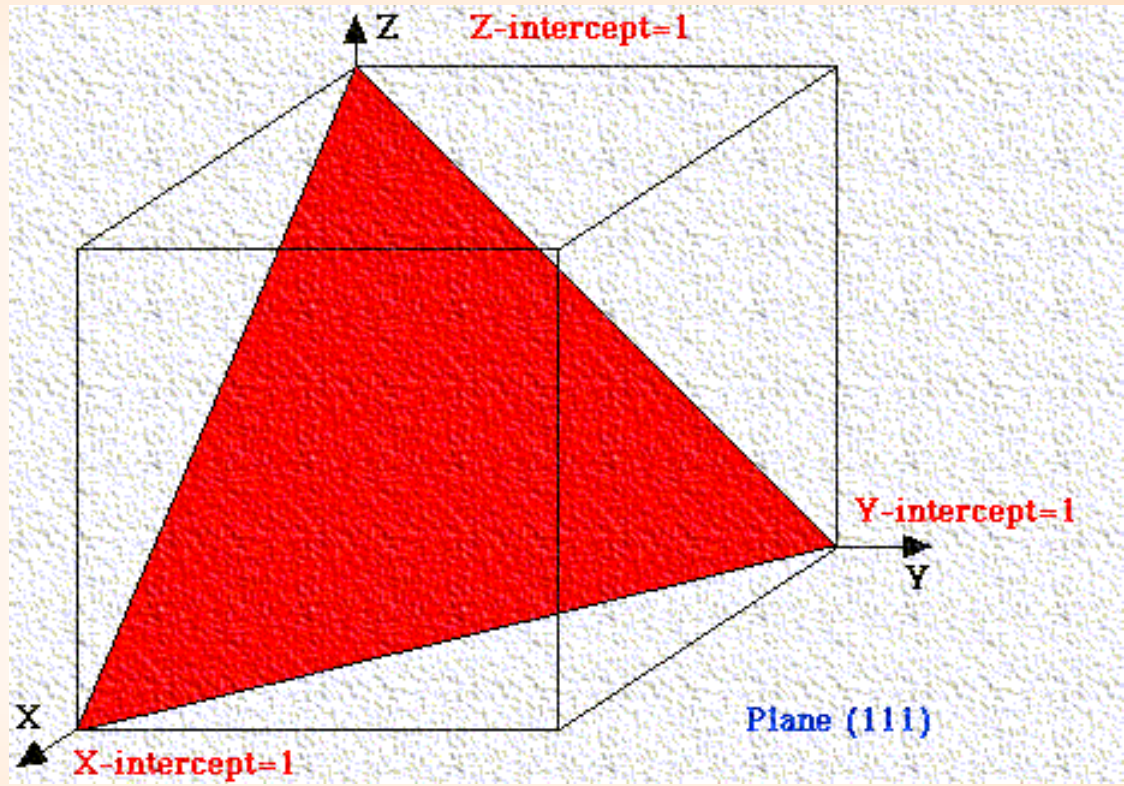
## Miller Index $(hkl)$



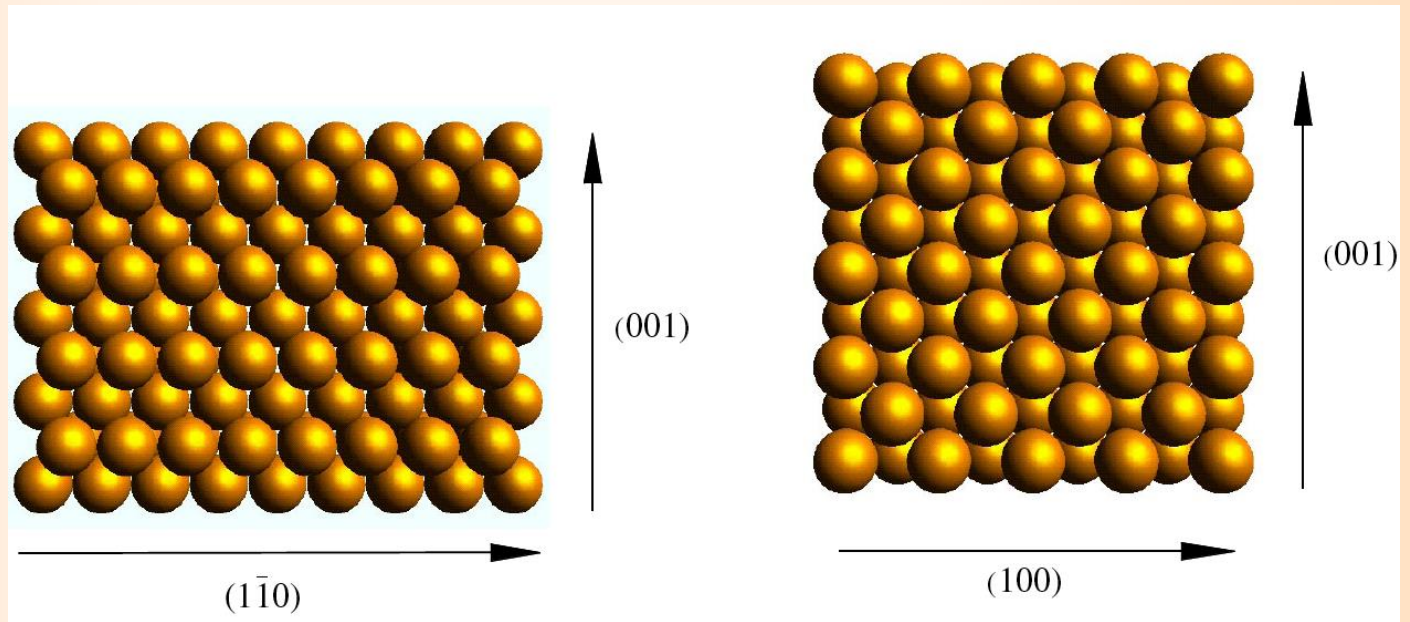


The Miller indices are found by determining the points at which a given crystal plane intersects the three axes, say at  $(a,0,0)$ ,  $(0,b,0)$ , and  $(0,0,c)$ . If the plane is parallel an axis, it is given an intersection  $\infty$ . The **Miller index** for the face is then specified by  $(1/a, 1/b, 1/c)$ , where the three numbers are expressed as the smallest integers, and negative quantities are indicated with an overbar. A face, when given with the crystal class, determines a set of faces known as a form and is denoted  $\{a,b,c\}$ . The vector normal to a face is specified as  $[a,b,c]$ .

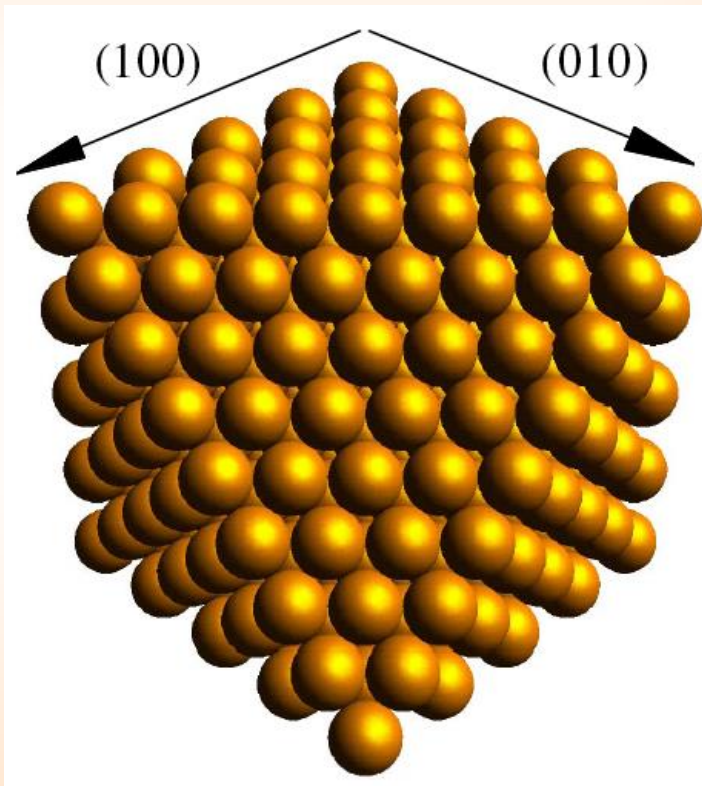
<http://onsager.bd.psu.edu/~jircitano/Miller.html>





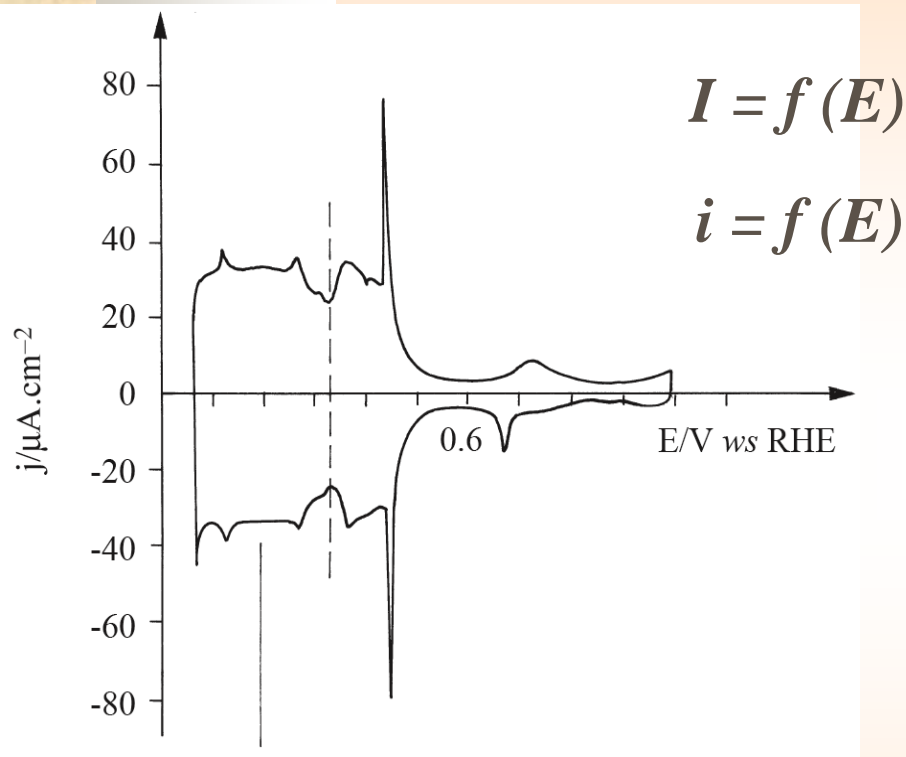


Surface of a monocrystal  $(110)$  and  $(100)$



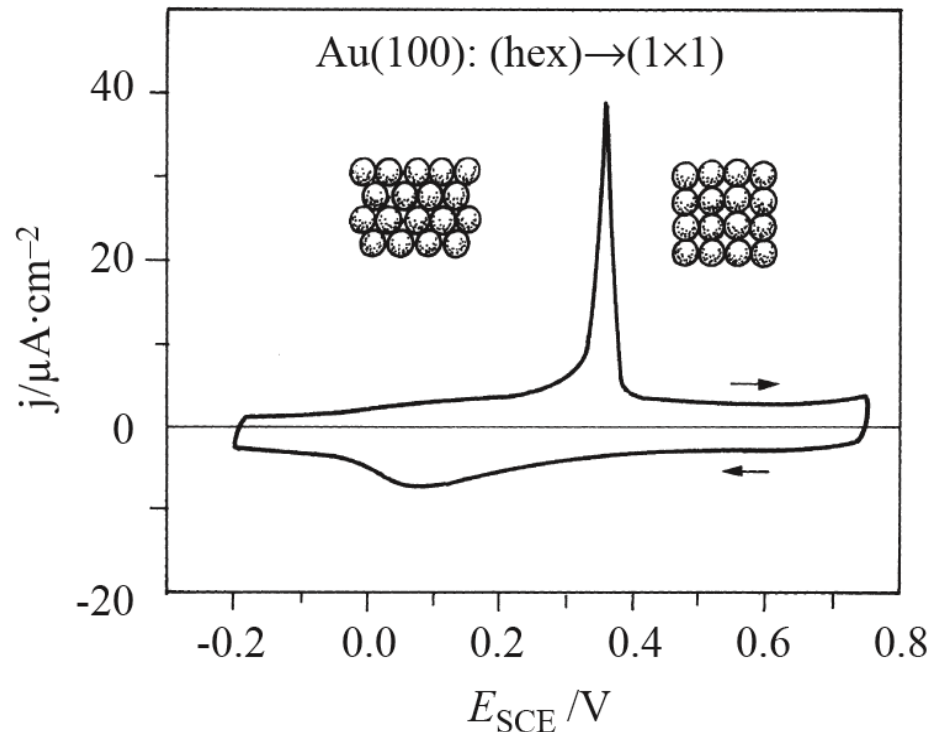
Surface of a monocrystal (111)

# Cyclic Voltammetry



Cyclic voltammogram of a Pt(111) electrode having just been polished, flame-treated and cooled in air. Solution: 0.5 M  $\text{H}_2\text{SO}_4$ . Sweep rate  $50 \text{ mV} \cdot \text{s}^{-1}$

[Clavilier, *J. Electroanal. Chem.*, 107(1980)205].



CV curve for Au(100) in 0.1 M  $\text{H}_2\text{SO}_4$ , starting with a freshly prepared reconstruction surface at  $-0.2 \text{ V}$  vs. SCE. Scan rate:  $50 \text{ mV} \cdot \text{s}^{-1}$ . Lifting of the (hex) reconstruction during the positive scan is seen by a pronounced current peak. The subsequent scan in negative direction reflects the electrochemical behaviour of Au(100)-(1 $\times$ 1).

[Dakkouri & Kolb, in *Interfacial Electrochemistry*, Marcel Dekker, 1999]



# Solid metallic electrodes

Electrons

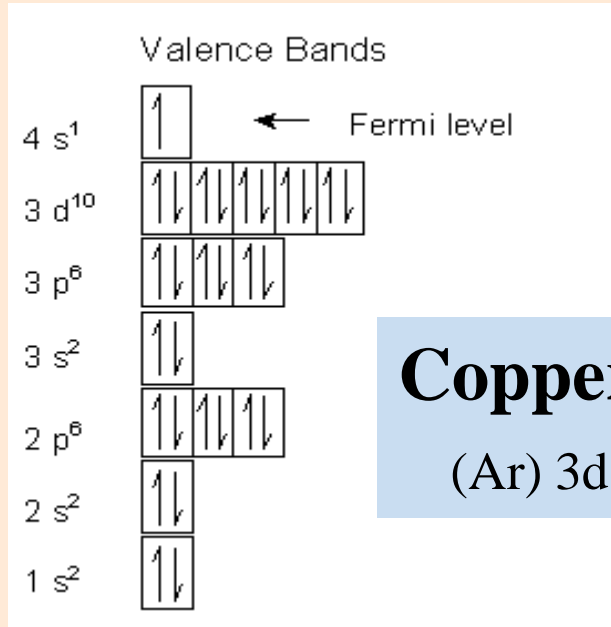
Fermions

valence band, valence energy, Fermi energy level

the highest occupied  
molecular orbital in the  
valence band at 0 K

„Fermi sea“

# Solid metallic electrodes



**Copper Cu**

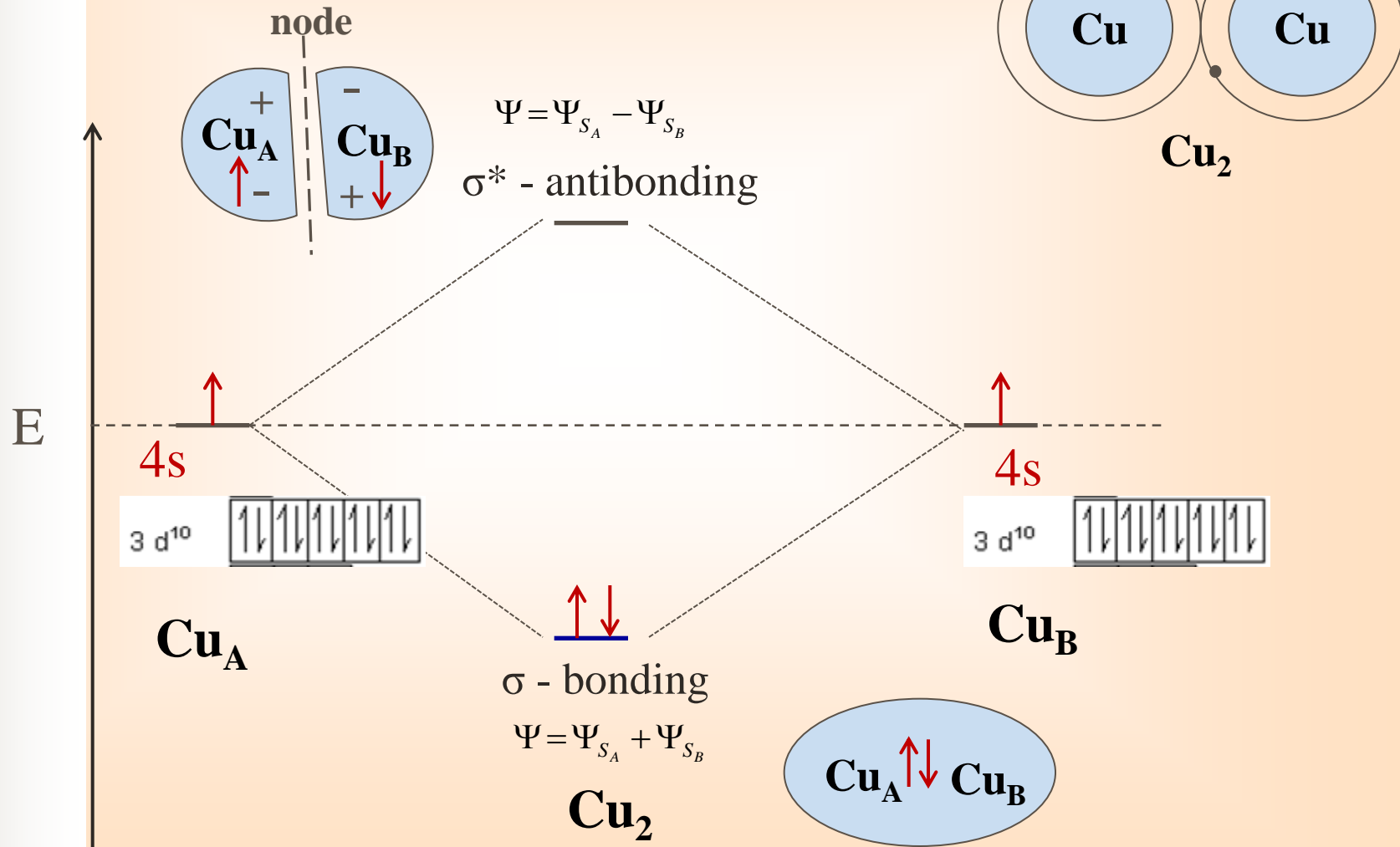
(Ar) 3d<sup>10</sup>, 4s<sup>1</sup>

The density of states occupied by electrons in a metal in the region of the Fermi level  $E_F$  at different T

Copper Cu  
(Ar) 3d<sup>10</sup>, 4s<sup>1</sup>

# Band Theory

Based on Quantum Molecular Orbital Theory



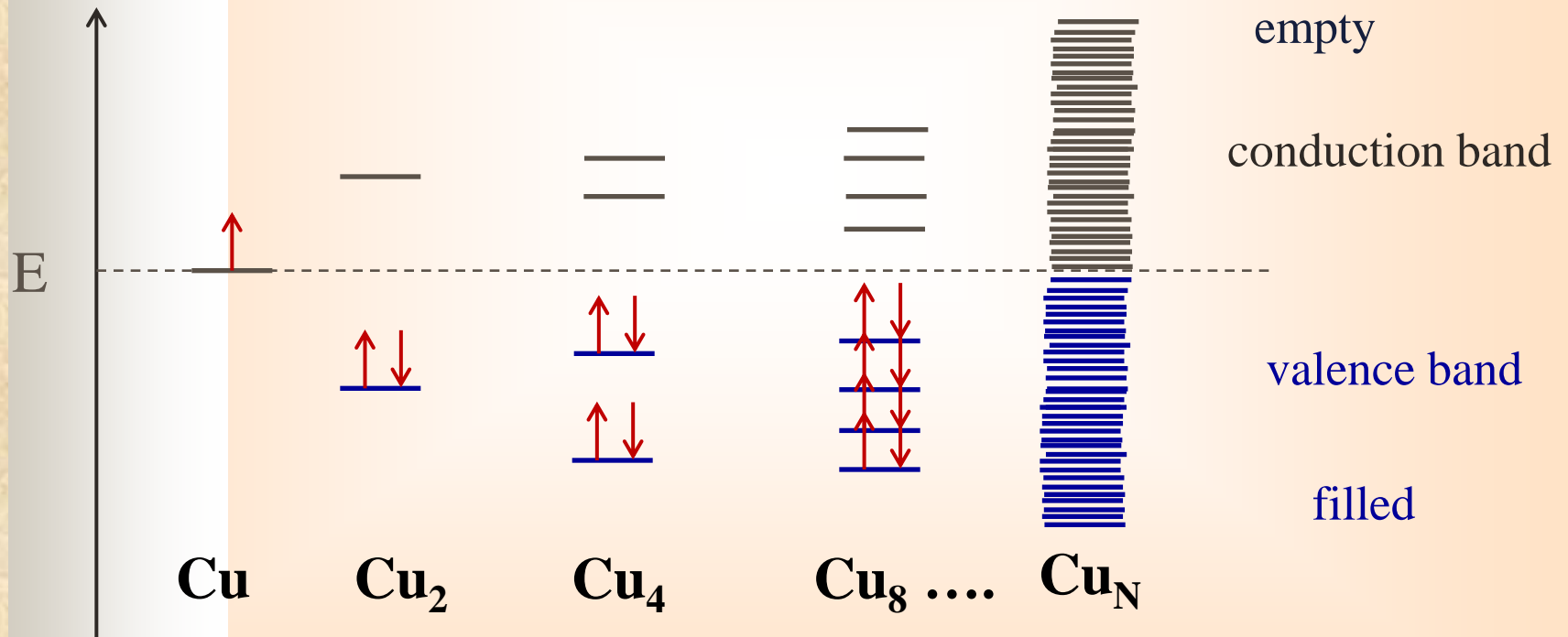
# Band Theory

Based on Quantum Molecular Orbital Theory

from  $\text{Cu}_2$  to  $\text{Cu}(s)$

**Copper Cu**  
(Ar)  $3d^{10}, 4s^1$

S - bands

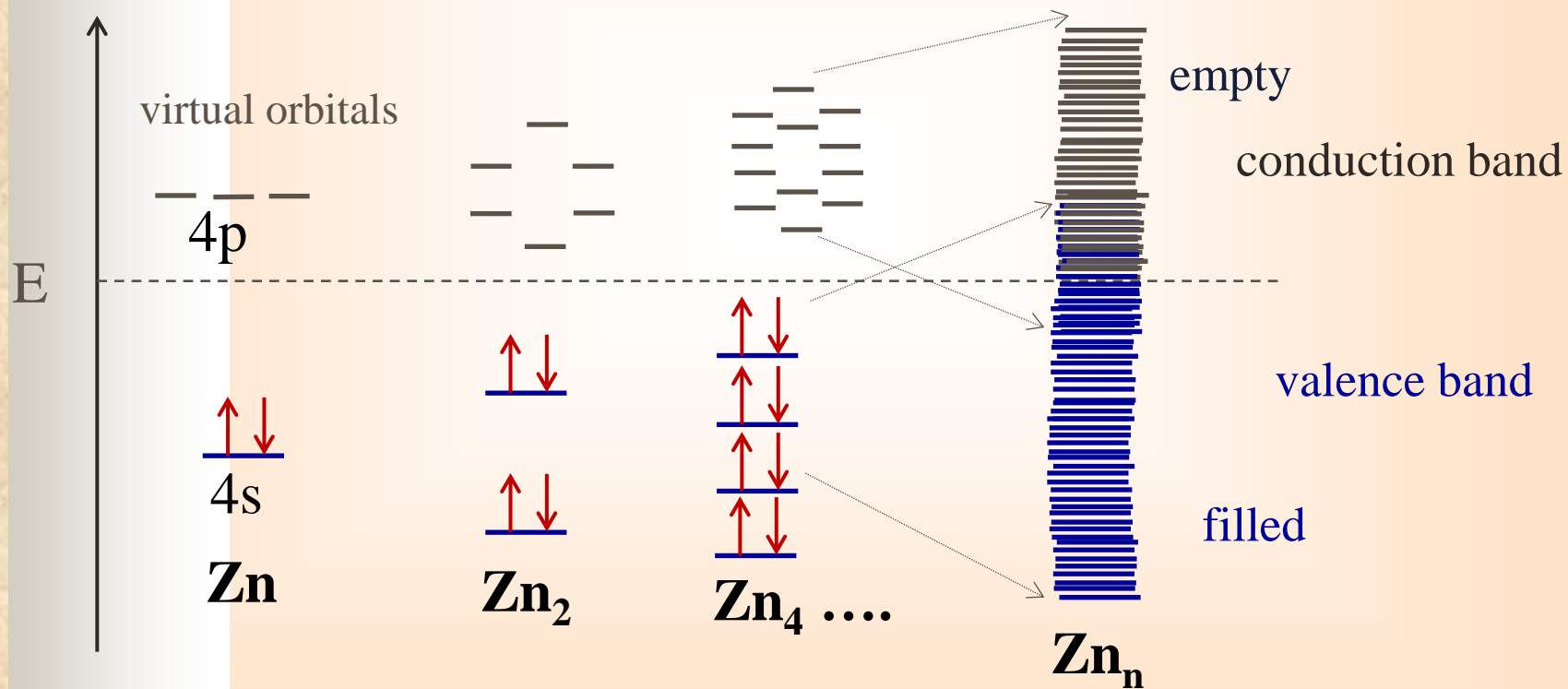


**Zinc**  
(Ar) 3d<sup>10</sup>, 4s<sup>2</sup>

# Band Theory

Based on Quantum Molecular Orbital Theory

from Zn<sub>2</sub> to Zn(s)



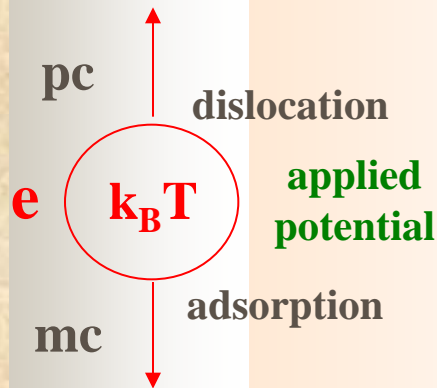


# Solid metallic electrodes

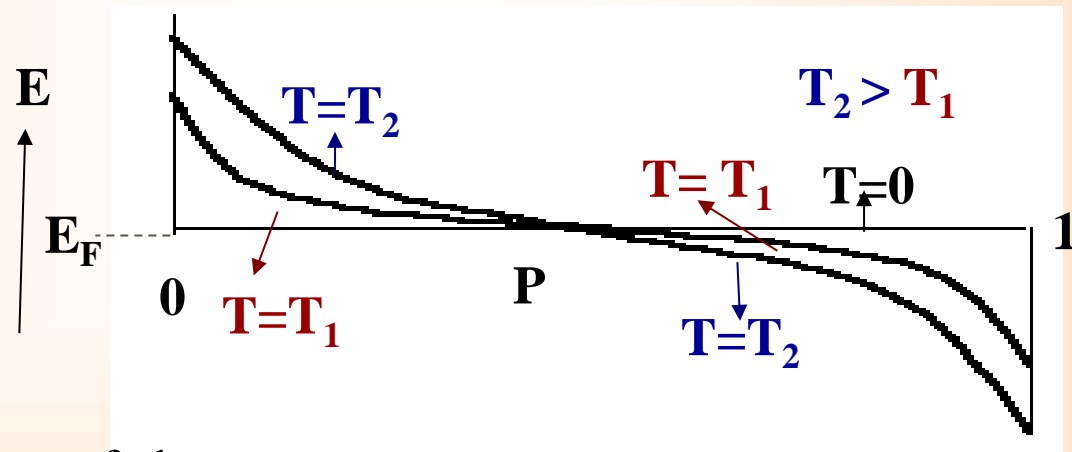
$$P = \frac{1}{1 + \exp \left[ (E - E_F) / k_B T \right]}$$

$E_F$  Fermi energy level

Fermi energy is the electrochemical potential of the electrons in the metal electrode



↑T ↑*smearred occupation*



$E$  .... energy of electron

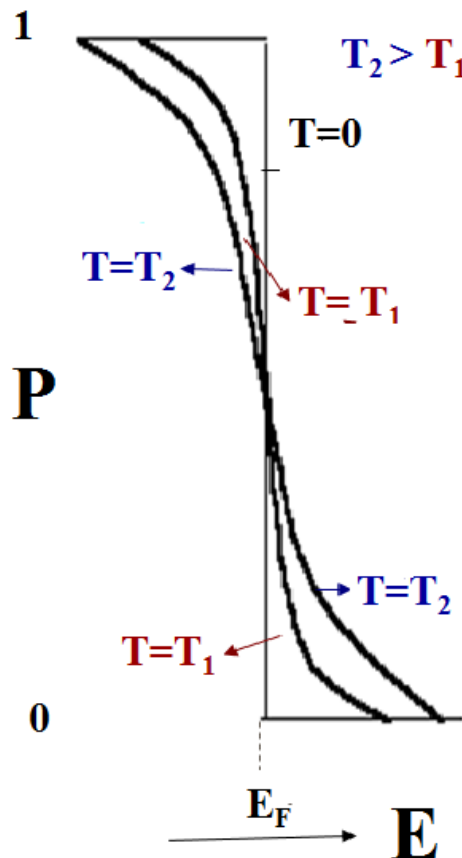
$E_F$  .... energy of the Fermi level (electrochemical potential)

$P$  .... probability of occupation of a level of energy  $E$

$E = E_F \dots\dots P = 0.50$        $E = E_F + k_B T \dots P = 0.27$        $E = E_F - k_B T \dots P = 0.73$

# Solid metallic electrodes

**P** .... probability of occupation of a level of energy **E**



$$P = \frac{1}{1 + \exp \left[ \frac{(E - E_F)}{k_B T} \right]}$$

**E** .... energy of electron

$E_F$  .... Fermi energy level

$$E = E_F \dots\dots P = 0.50$$

$$E = E_F + k_B T \dots\dots P = 0.27$$

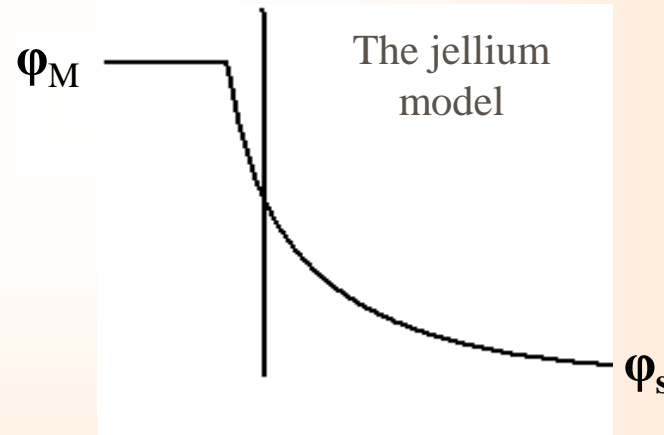
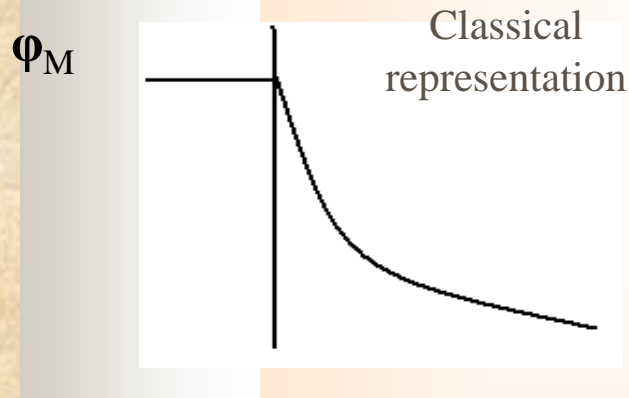
$$E = E_F - k_B T \dots\dots P = 0.73$$

$\uparrow T$   $\uparrow$  *smearred occupation*

# ELECTRODE DOUBLE LAYER STRUCTURE ON INTERFACE ELECTRODE - ELECTROLYTE

## Chemical Models

- the electronic distribution of the atoms in electrodes (not only electrostatic forces)
- difference between (sp) metals and transition (d)metals
- IHP as an electronic molecular capacitor
- jellium model Raman spectra, EXAFS:Extended X-Ray Absorption Fine Structure

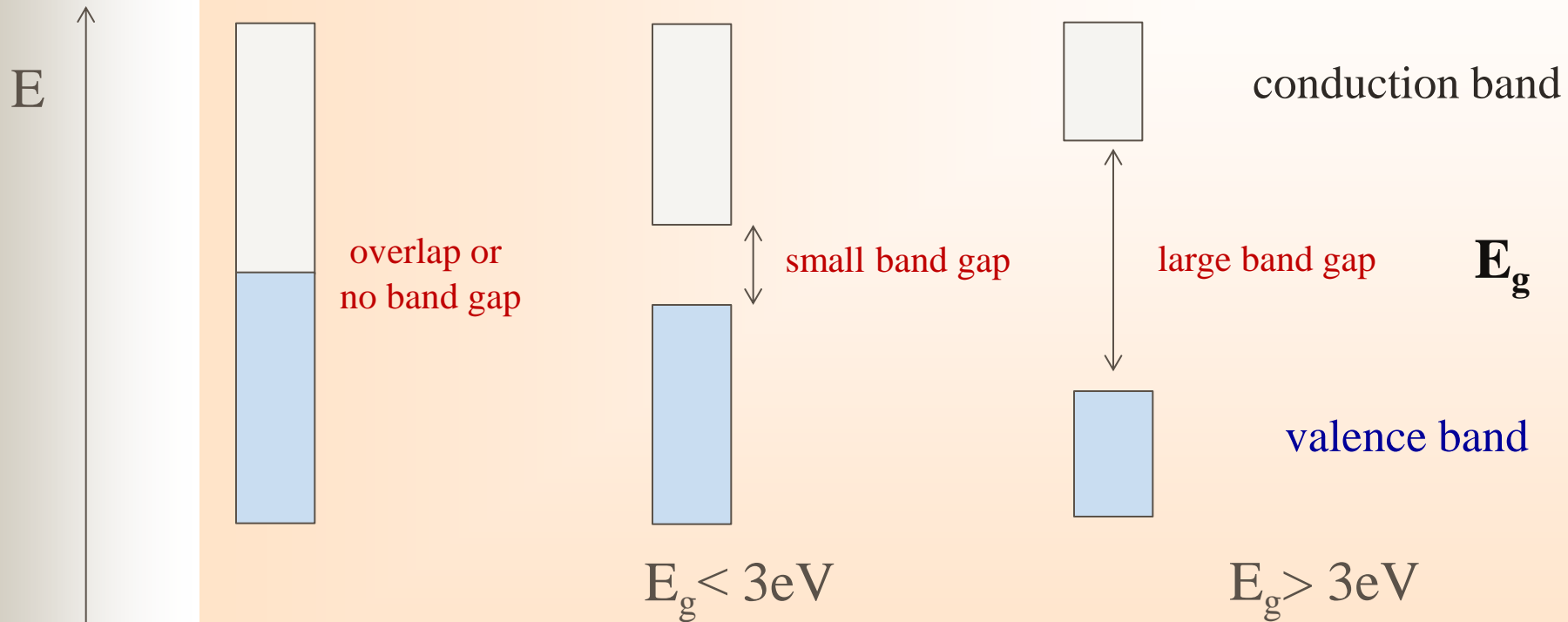


Variation of the electrostatic potentials with distance from a metallic electrode

**Chemical Model (Damaskin and Frumkin)**  
**(Trasatti)**  
**(Parsons)**

# Conductor, semiconductor, insulator

*B, Si, Ge, As* metalloids,



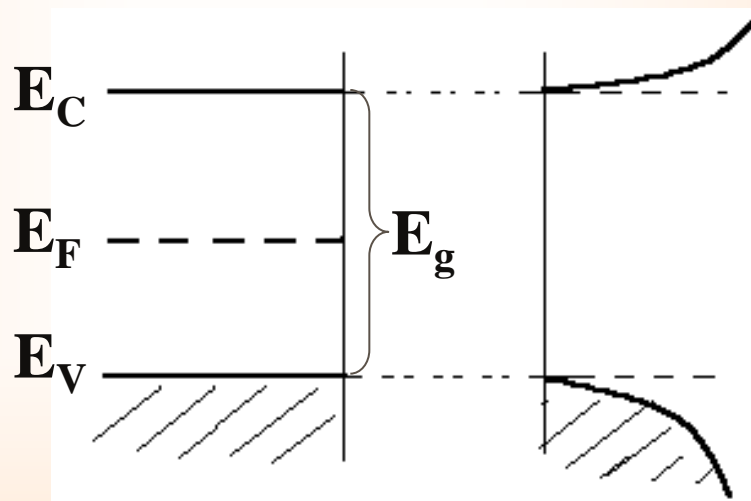
conduct electricity – but not well

yes or not, 0 or 1

# Semiconductor electrodes

- accessible electronic levels are more restricted
- separation between the occupied valence band and the unoccupied conduction band (smaller than 3 eV)  
(greater than 4 eV - insulator, for example diamond 5.4 eV)

The valency band is totally filled and the conduction band is empty



Variation of density of available states with energy

## band model for a semiconductor

Conductivity – movement of electrons or holes in the valence band.

Electron promotion to conductivity band – T,  $h\nu$  excitation

$$\text{The Fermi energy} - E_F \approx (E_V + E_C)/2 = E_V + E_g/2$$

# The number of excited electrons $n$

(considering the case  $E_g \gg k_B T$ )

$$n \propto \exp\left(\frac{-E_g}{2k_B T}\right)$$

Other electronic levels (surface states) can exist on the semiconductor surface due to adsorbed species or surface reorganization.

<b>semiconductor</b>	<b><math>E_g</math>/eV</b>	<b><math>\lambda</math> /nm</b>
SnO <sub>2</sub>	3.5	350
TiO <sub>2</sub>	3.0	410
Si	1.1	1130

**n - type semiconductor (Si doped P, As)**

**p - type semiconductor (Si doped B)**



# Semiconductor electrodes (SemiCEs)

The major interest in semiCEs is due to:

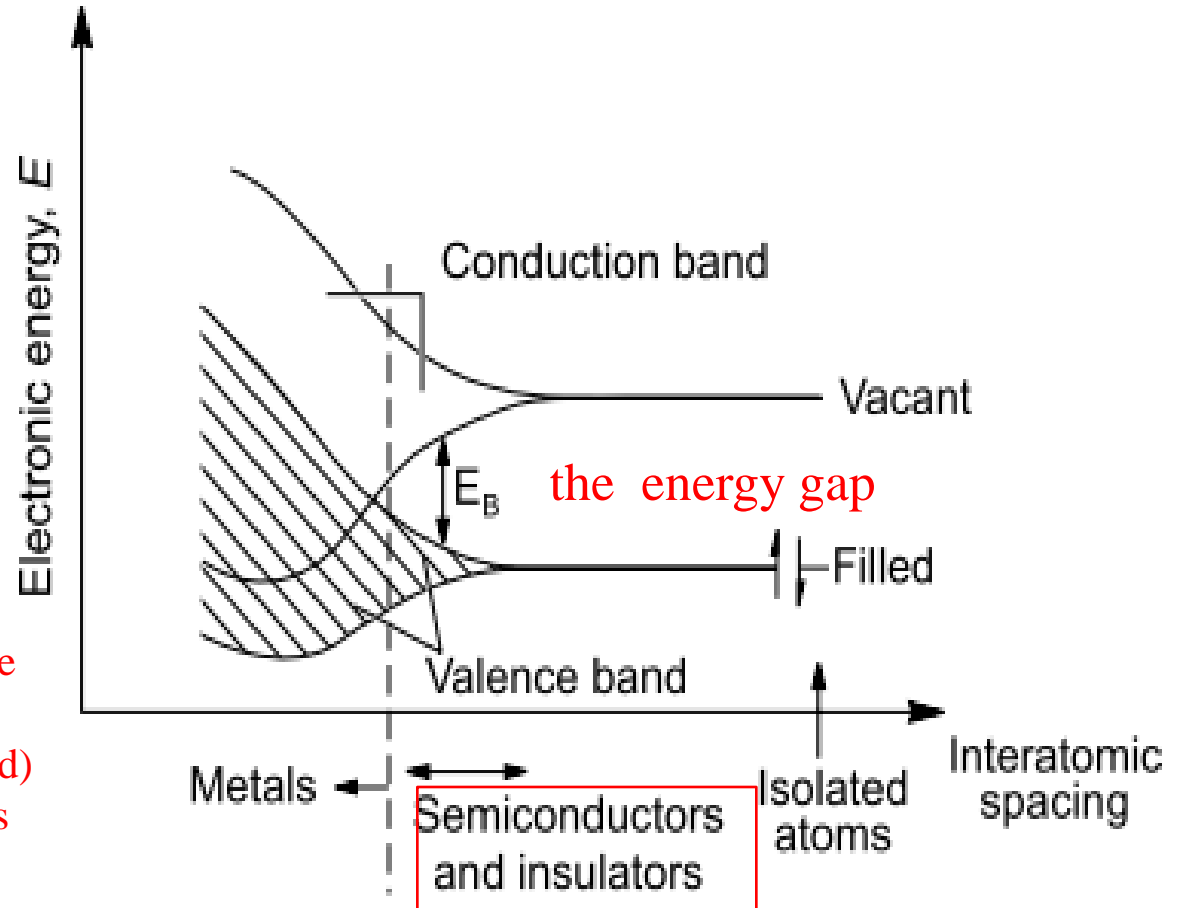
- 1) the photoelectrochemical properties of the semiCE/electrolyte interface,
- 2) the generation of currents following exposure to elmg radiation (e.g., solar energy conversion),
- 3) optically transparent semiCEs are available for electrochromic displays and spectroelectrochemistry.

The properties of semiCEs - their differences from those of metallic electrodes (the electronic structures) - energy bands, which are made up of the atomic orbitals of the individual atoms

# Semiconductor electrodes (SemiCEs)

**F1**

Generation of bands in solids from atomic orbitals of isolated atoms (adapted from ref. 1).



between the upper edge of the valence band and the lower edge of the conduction band) that determines the properties of the material

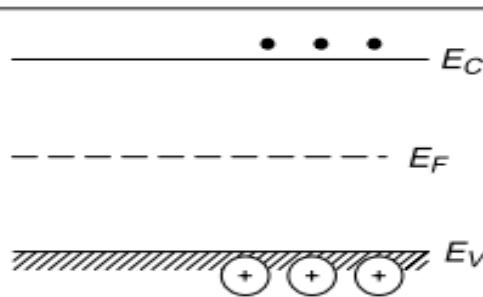
Electrons can be excited to the conduction band either thermally or photochemically.



# Semiconductor electrodes (SemiCEs)

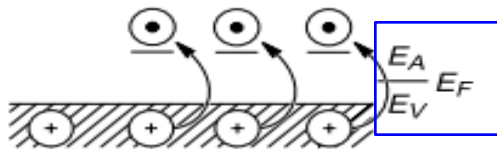
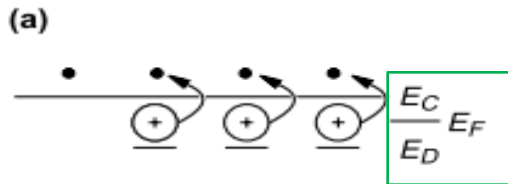
F2

Schematic diagram of the energy levels of an intrinsic semiconductor.



F3

Schematic diagram of the energy levels of an n-type semiconductor (a) and a p-type semiconductor (b).



the vacancy

**n-type: negative (electrons)**

**p-type: positive (holes)**

Doping involves the addition of a different element into the semiconductor (group V element, e.g., P or a group III element, e.g., Al) into a group IV element, e.g., Si). The addition of P (V) into Si (IV) introduces occupied energy levels into the band gap close to the lower edge of the conduction band, thereby allowing facile promotion of electrons into the conduction band. The addition of Al (III) introduces vacant energy levels into the band gap close to the upper edge of the valence band, which allows facile promotion of electrons from the valence band.

Holes are considered to be mobile

# Semiconductor electrodes (SemiCEs)

Another important concept in discussion of solid state materials is the **Fermi level**. This is defined as the energy level at which the probability of occupation by an electron is  $\frac{1}{2}$ ; for an intrinsic semiconductor the Fermi level lies at the mid-point of the band gap. Doping changes the distribution of electrons within the solid, and hence changes the Fermi level. For a **n-type semiconductor**, the Fermi level lies just **below the conduction band**, whereas for a **p-type semiconductor** it lies **just above the valence band**.

- 1) The Fermi level of a semiCE varies with the applied potential
- 2) The redox potential of a semiCE is determined by the Fermi level
- 3) In order for the two phases to be in equilibrium, their electrochemical potential must be the same

# Semiconductor electrodes (SemiCEs)

The excess charge that is now located on the semiconductor does not lie at the surface, as it would for a metallic electrode, but extends into the electrode for a significant distance (100-10,000 Å). This region is referred to as **the space charge region**, and has an associated electrical field. Hence, there are two double layers to consider:

- 1) **the interfacial (electrode/electrolyte) double layer**
- 2) **the space charge double layer.**

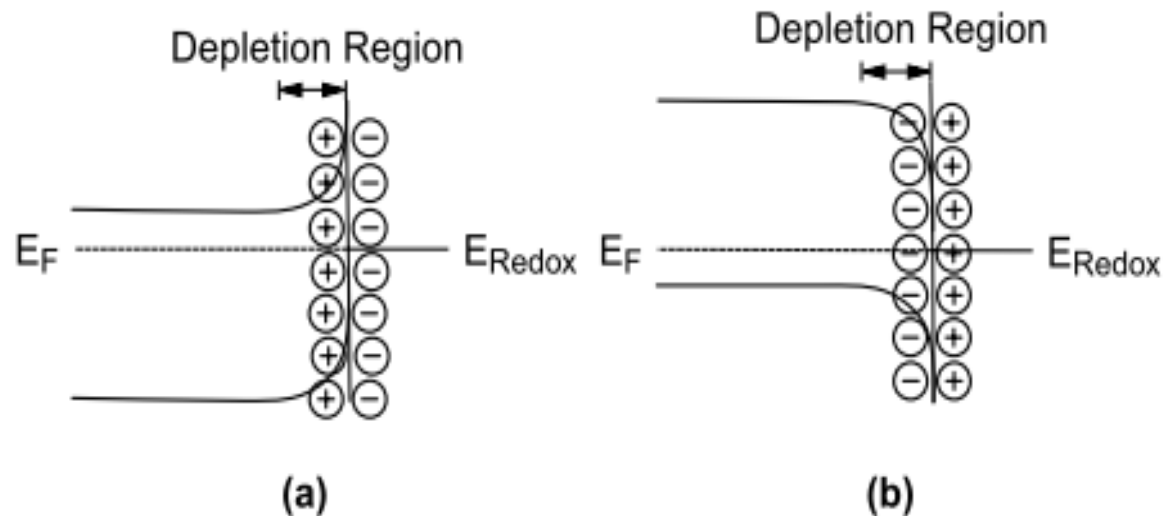
# Semiconductor electrodes (SemiCEs)

For an n-type semiCE at open circuit, the Fermi level is typically higher than the redox potential of the electrolyte, and hence electrons will be transferred from the electrode into the solution. Therefore, there is a positive charge associated with the space charge region, and this is reflected in an upward bending of the band edges

For a p-type semiconductor, the Fermi level is generally lower than the redox potential, and hence electrons must transfer from the solution to the electrode to attain equilibrium. This generates a negative charge in the space charge region, which causes a downward bending in the band edges

## F4

Band bending for an n-type semiconductor (a) and a p-type semiconductor (b) in equilibrium with an electrolyte.

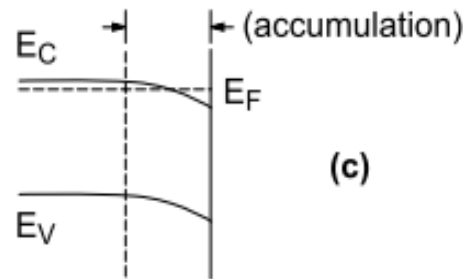
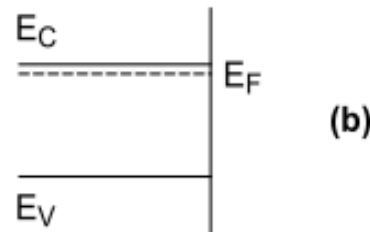
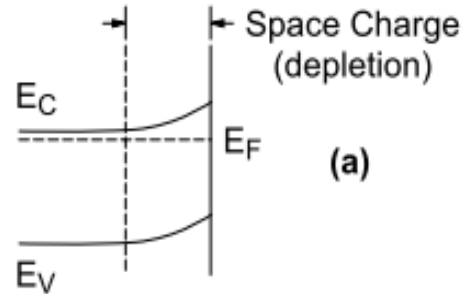


# Semiconductor electrodes (SemiCEs)

## F5

Effect of varying the applied potential ( $E$ ) on the band edges in the interior of an n-type semiconductor.

- a)  $E > E_{fb}$ , b)  $E = E_{fb}$ ,  
c)  $E < E_{fb}$ .

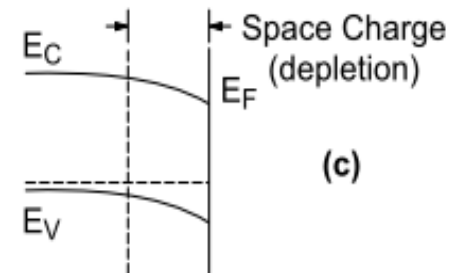
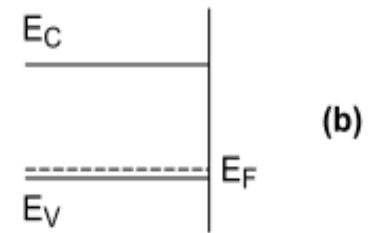
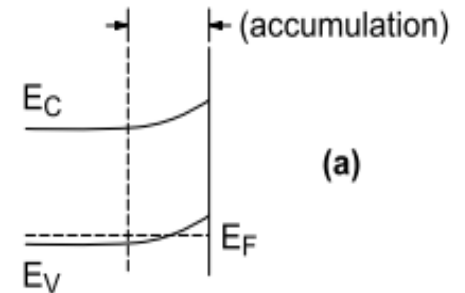


Electrode      Solution

## F6

Effect of varying the applied potential ( $E$ ) on the band edges in the interior of a p-type semiconductor.

- a)  $E > E_{fb}$ , b)  $E = E_{fb}$ ,  
c)  $E < E_{fb}$ .



Electrode      Solution

# Semiconductor electrodes (SemiCEs)

Since the holes in the space charge region are removed by this process, this region is again a depletion layer. As for metallic electrodes, changing the potential applied to the electrode shifts the Fermi level. The band edges in the interior of the semiconductor (i.e., away from the depletion region) also vary with the applied potential in the same way as the Fermi level.

The charge transfer abilities of a semiconductor electrode depend on whether there is an accumulation layer or a depletion layer. If there is an accumulation layer, the behavior of a semiconductor electrode is similar to that of a metallic electrode, since there is an excess of the majority of charge carrier available for charge transfer. In contrast, if there is a depletion layer, then there are few charge carriers available for charge transfer, and electron transfer reactions occur slowly, if at all. However, if the electrode is exposed to radiation of sufficient energy, electrons can now be promoted to the conduction band. If this process occurs in the interior of the semiconductor, recombination of the promoted electron and the resulting hole typically occurs, together with the production of heat. However, if it occurs in the space charge region, the electric field in this region will cause the separation of the charge. For example, for an n-type semiconductor at positive potentials, the band edges curve upwards, and hence the hole moves towards the interface, and the electron moves to the interior of the semiconductor. The hole is a high energy species that can extract an electron from a solution species; that is, the n-type semiconductor electrode acts as a photoanode.

# Semiconductor electrodes (SemiCEs)

Ideal behavior for an n-type semiconductor electrode in the dark and under irradiation is shown in F7. At the flatband potential ( $E_{fb}$ ), there is no current, either in the dark or upon irradiation (Region II), since there is no electric field to separate any generated charge carriers. At potentials negative of the flatband potential (Region I), an accumulation layer exists, and the electrode can act as a cathode, both in the dark and upon irradiation (the electrode is referred to as a dark cathode under these conditions). At potentials positive of the  $E_{fb}$  (Region III), a depletion layer exists, so there can be no oxidative current in the dark. However, upon irradiation, a photocurrent can be observed at potentials negative of the redox potential of the analyte (which lies at  $E_0$ ), since some of the energy required for the oxidation is provided by the radiation (via the high energy hole). Using similar reasoning, it can be shown that p-type semiconductor electrodes are dark anodes and photocathodes.

There are a number of experiments used to measure the various parameters discussed above. The  $E_{fb}$  can be determined by measuring the photopotential as a function of radiation intensity, the onset of the photocurrent, or the capacitance of the space charge region. The simplest method is to measure the open-circuit potential (photopotential) of the electrochemical cell under radiation of varying intensity. For a system under equilibrium, the photopotential is the change in the Fermi level due to the promotion of electrons to the conduction band, and it reaches a maximum at the  $E_{fb}$ .

## Semiconductor electrodes (SemiCEs)

Therefore, a plot of photopotential versus light intensity will attain a limiting plateau at the flatband potential. For the second method, although the onset of the photocurrent might be simplistically considered to be the flatband potential, it is actually the potential at which the dark current and photocurrents are equal. Therefore, such measurements should be used with caution. The third method involves measuring the apparent capacitance as a function of potential under depletion condition and is based on the Mott-Schottky relationship:

$$\frac{1}{C_{sc}^2} = \frac{2}{e\epsilon\epsilon_0 N} \left( E - E_{FB} - \frac{kT}{e} \right)$$

$C_{sc}$  = capacitance of the space charge region

$\epsilon$  = dielectric constant of the semiconductor

$\epsilon_0$  = permittivity of free space

$N$  = donor density (electron donor concentration for an *n*-type semiconductor or hole acceptor concentration for a *p*-type semiconductor)

$E$  = applied potential

$E_{fb}$  = flatband potential





## Semiconductor electrodes (SemiCEs)

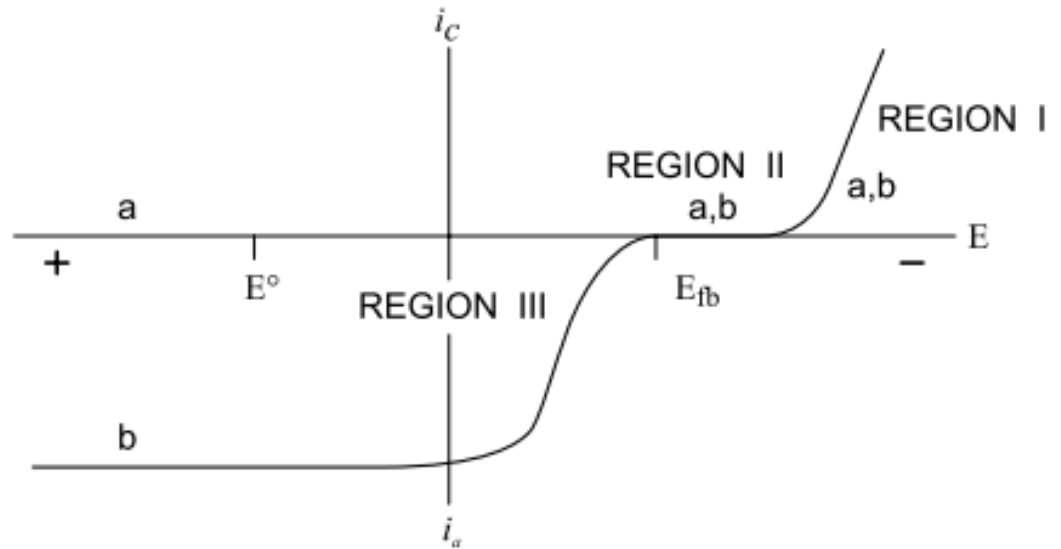
Mott-Schottky plots ( $1/C^2$  vs.  $E$ ) are shown for a p-type silicon semiconductor and an n-type silicon semiconductor in F8 and F9, respectively (2). The donor density can be calculated from the slope, and the flatband potential can be determined by extrapolation to  $C = 0$ . The capacitance values are calculated from impedance measurements. The model required for the calculation is based on two assumptions:

1. There are two capacitances to be considered, that of the space charge region and that of the double layer. Since these capacitances are in series, the total capacitance is the sum of their reciprocals. As the space charge capacitance is much smaller than double layer capacitance (2-3 orders of magnitude), the contribution of the double layer capacitance to the total capacitance is negligible. Therefore, the capacitance value calculated from this model is assumed to be the value of the space charge capacitance.
2. The equivalent circuit used in this model is a series combination of a resistor and a capacitance (the space charge capacitance). The capacitance is calculated from the imaginary component of the impedance ( $Z''$ ) using the relationship  $Z'' = 1/2 \pi fC$ . The model is adequate provided the frequency is high enough (on the order of kHz).

# Ideal behavior of n-type conductor on the dark and under irradiation

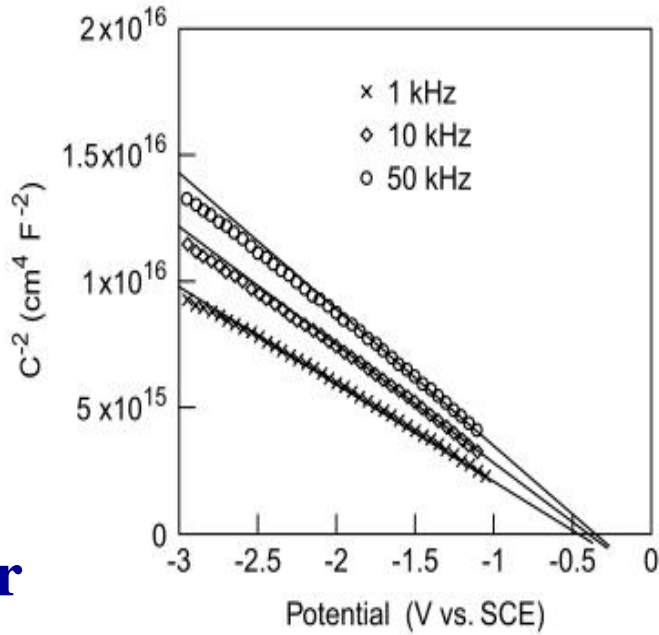
**F7**

*Ideal behavior for an n-type semiconductor in the dark (a) and under irradiation.*



F8

Mott-Schottky plot for a p-type semiconductor (figure adapted from ref. 2).

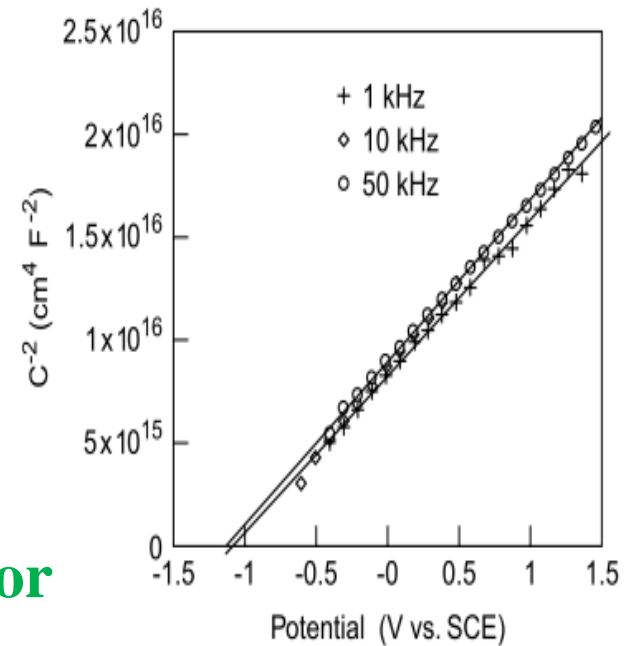


**p-type  
semiconductor**

**Mott-Schottky plot**

F9

Mott-Schottky plot for an n-type semiconductor (figure adapted from ref. 2).



**n-type  
semiconductor**