



BASIC PRINCIPLES OF ELECTRODE PROCESSES

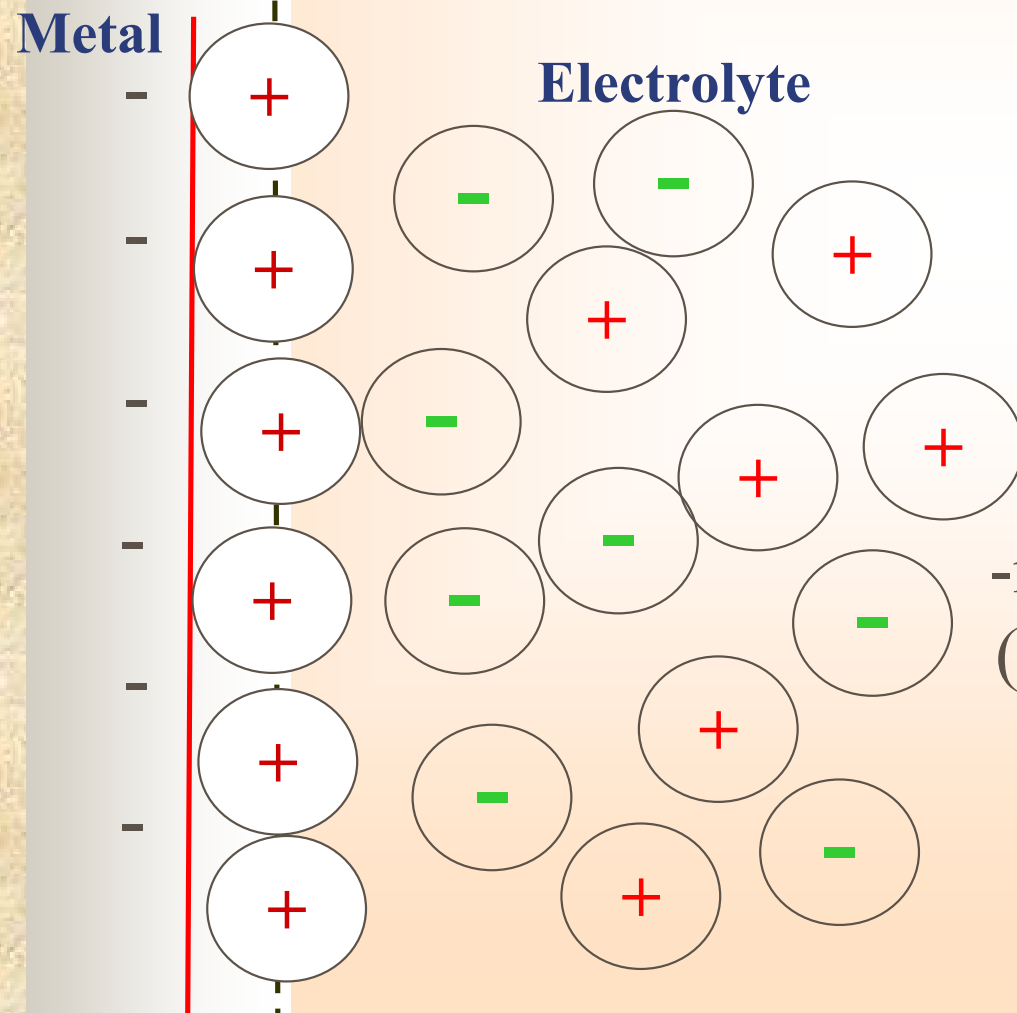
Heterogeneous kinetics

I

Charged interfaces

Ions and dipoles in the volume element :

- solutions (random distribution, isotropic) (charge $Q = 0$)
- charged interface: electrode/electrolyte (anisotropic) ($Q \neq 0$)



*Electric (electrode) double layer
(EDL):*

- metals/electrolytes (Ag/Ag^+) ;
(Hg/NaF) ; (Hg/KI)

- non-metallic elements/ electrolyte
(gas, glass, polymers, membranes,
colloides...)

- liquid I/liquid II

Potential creation on interface

Heterogeneous system



solid conductive phase – interface – liquid conductive phase



1. Ag (Ag⁺)

2. Pt (Pt-Ir, graphite)



Ag⁺ NO₃⁻

Fe²⁺, Fe³⁺ (SO₄²⁻)

spontaneous ion crossing 1. or electron transfer 2.

⇒ spontaneous interface charging:



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: $\mu_i = \mu_i^o + RT \ln a_i$

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

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

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

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

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 ⇒

impolarizedable interface

(impolarizedable electrode, Ag / Ag⁺)

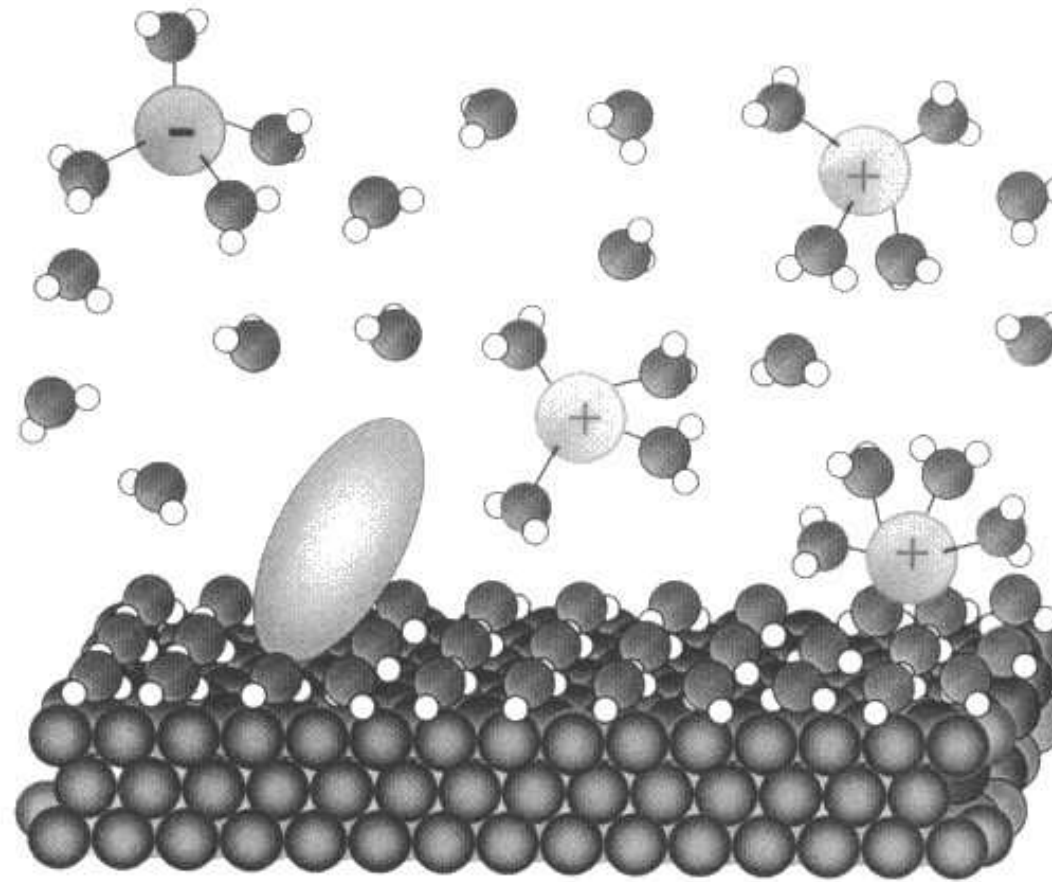
↪ **charge doesn't go through an interface**

possible of charging ⇒

polarizedable interface

(polarizedable electrode, Pt, graphite, Hg, without Hg^{z+} in solution)

ELECTRODE DOUBLE LAYER (EDL)



●●● electrode surface

●● water molecule

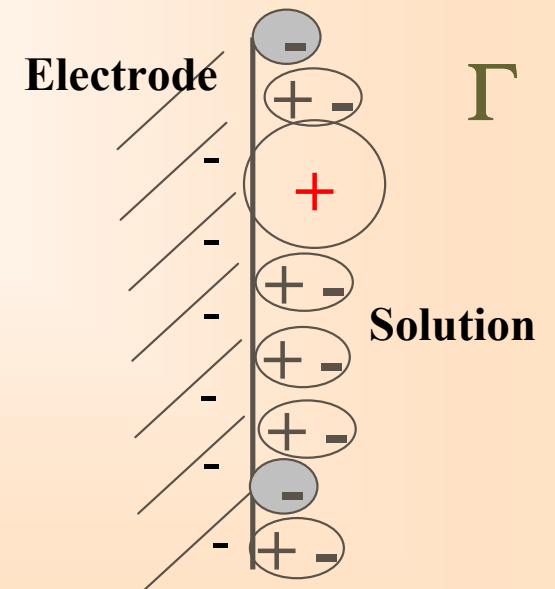
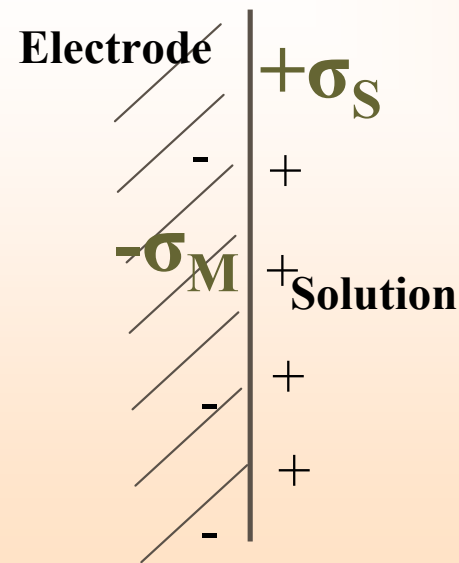
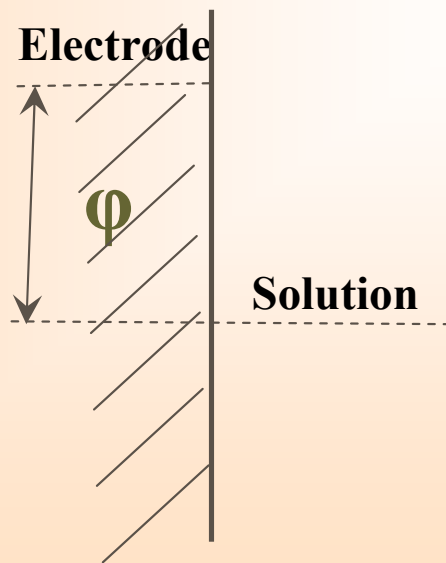
⊕ cation

⊖ anion

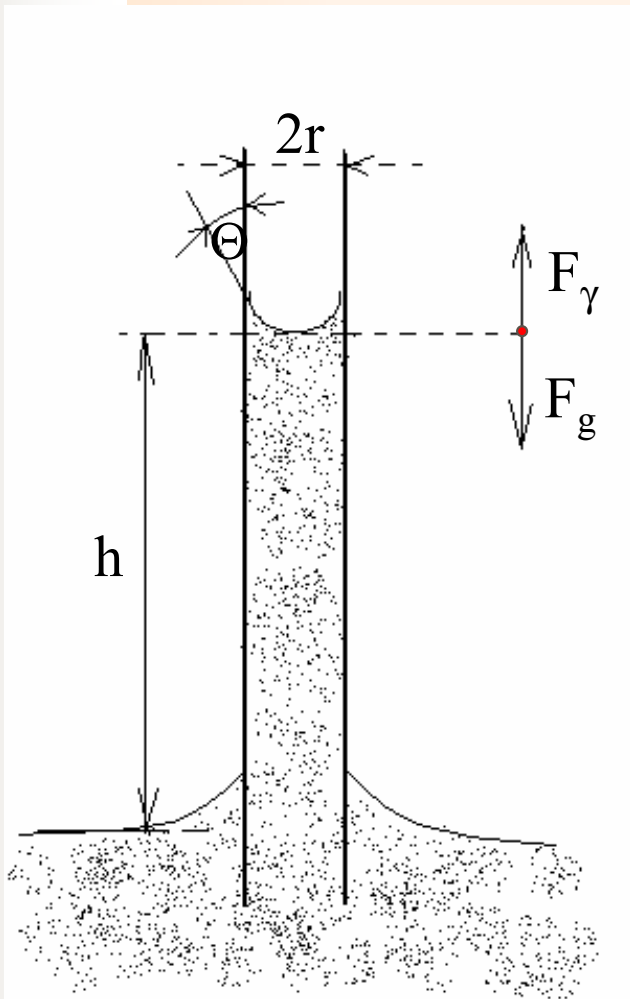
○ adsorbed neutral species

ELECTRODE DOUBLE LAYER (EDL)

electrostatic potential ϕ
charge density σ
surface tension γ
capacity C
adsorption Γ



surface tension γ



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 σ

$$\frac{\partial \gamma}{\partial E_{\Delta}} = -\sigma_M \quad \text{Lippman equation}$$

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 Γ

Langmuir isotherm

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

Θ fraction of coverage

Γ, Γ_{∞} surface or maximum surface excess

β_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

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

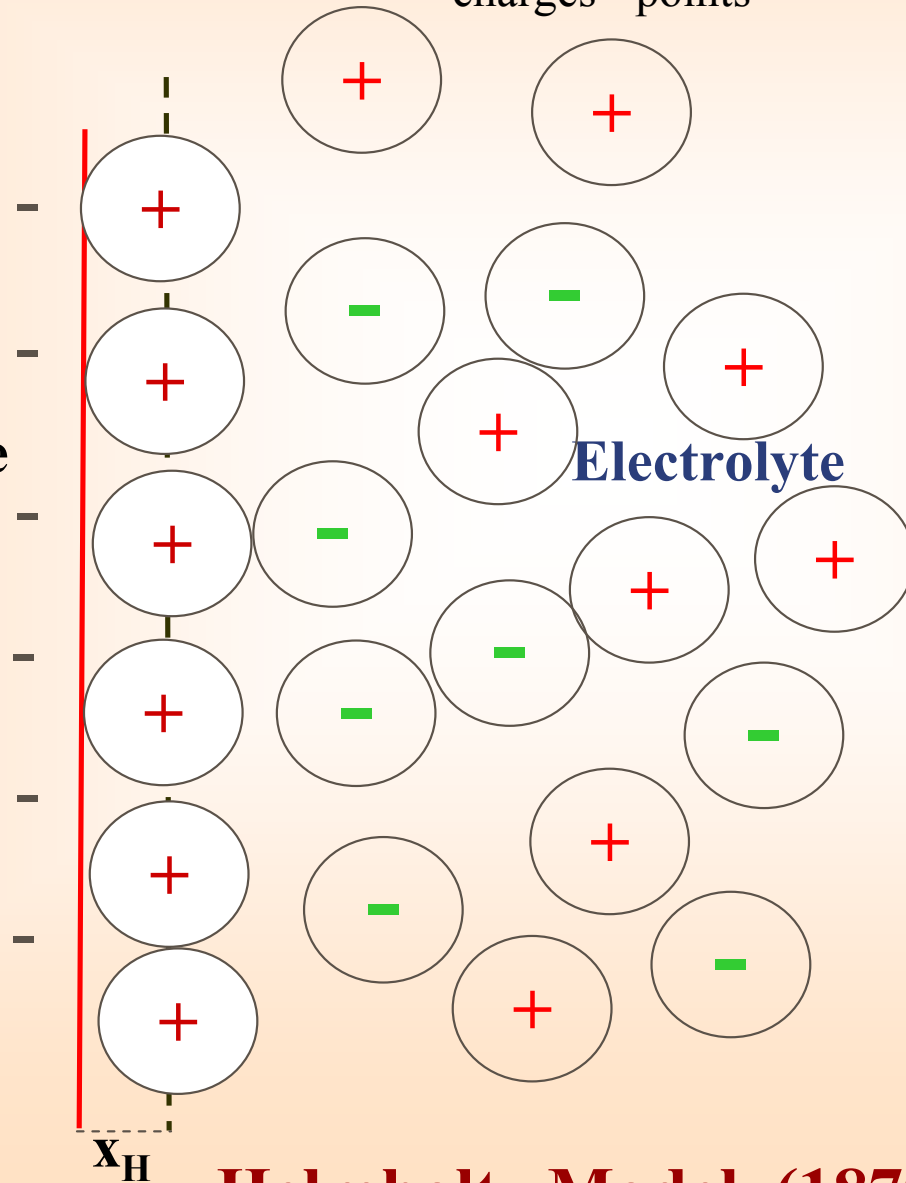
electrostatic
models

ELECTRODE DOUBLE LAYER STRUCTURE ON INTERFACE ELECTRODE - ELECTROLYTE

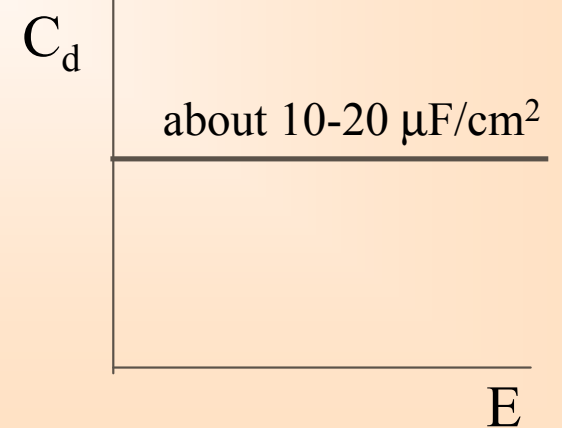
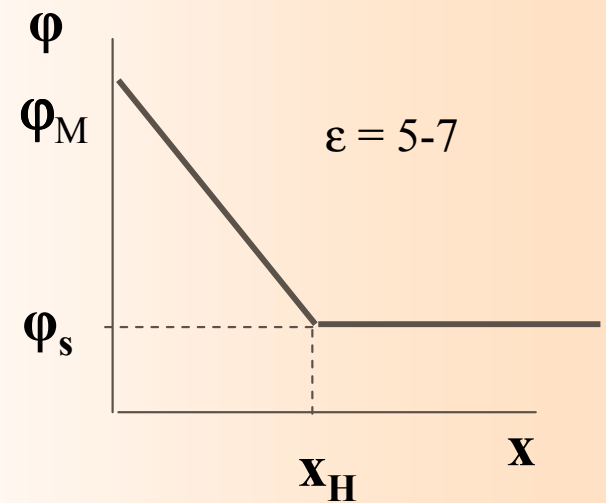
history

Electrode
(metal)

charges - points

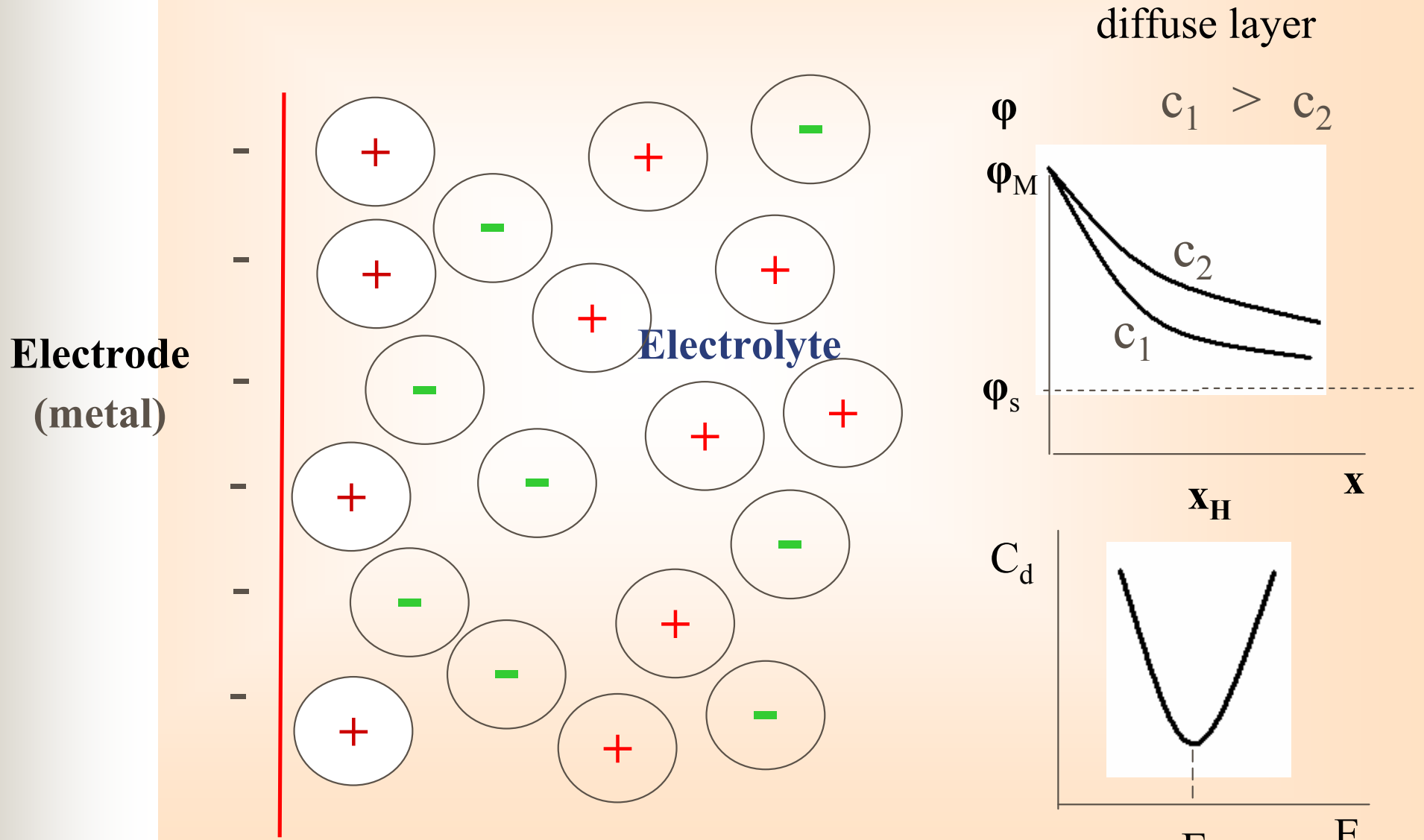


$$C_d = \frac{\epsilon_r \epsilon_0}{x_H}$$



Helmholtz Model (1879)

ELECTRODE DOUBLE LAYER STRUCTURE ON INTERFACE ELECTRODE - ELECTROLYTE



Gouy-Chapman Model (1910-1913)

Gouy-Chapman Model (1910-1913)

distribution of species with distance from electrode

(x_{DL} = distance characteristic of the diffuse layer)

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

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

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

$$\frac{\partial^2 \varphi_{\Delta}(x)}{\partial x^2} = \frac{-\rho(x)}{\epsilon_r \epsilon_0}$$

Poisson's equation

Poisson-Boltzmann equation

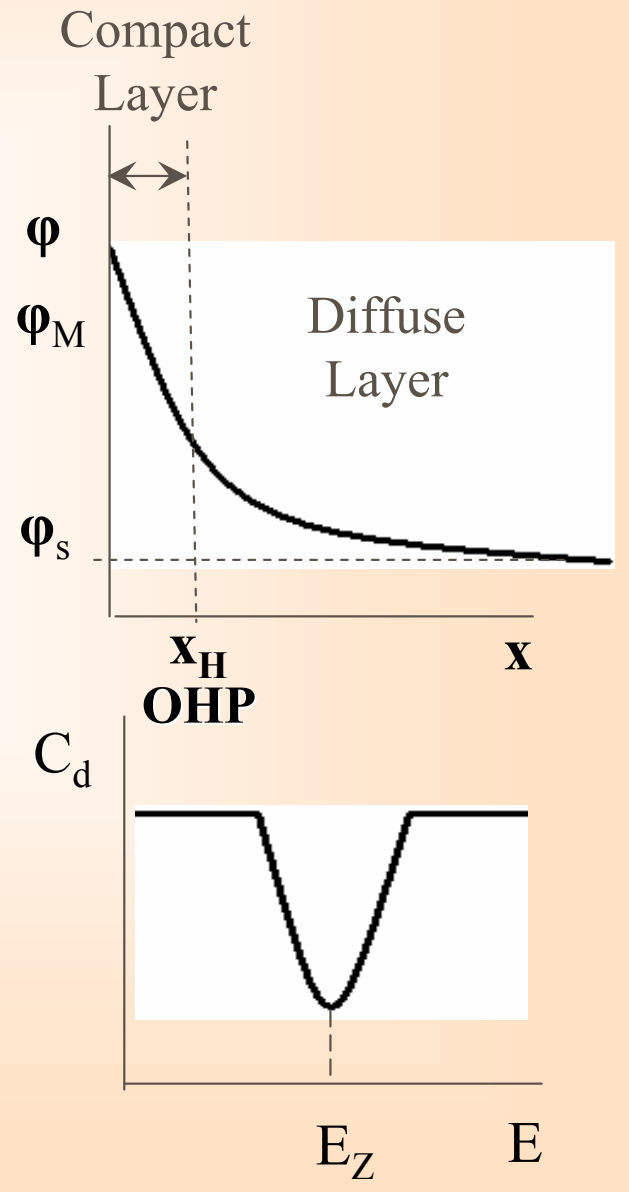
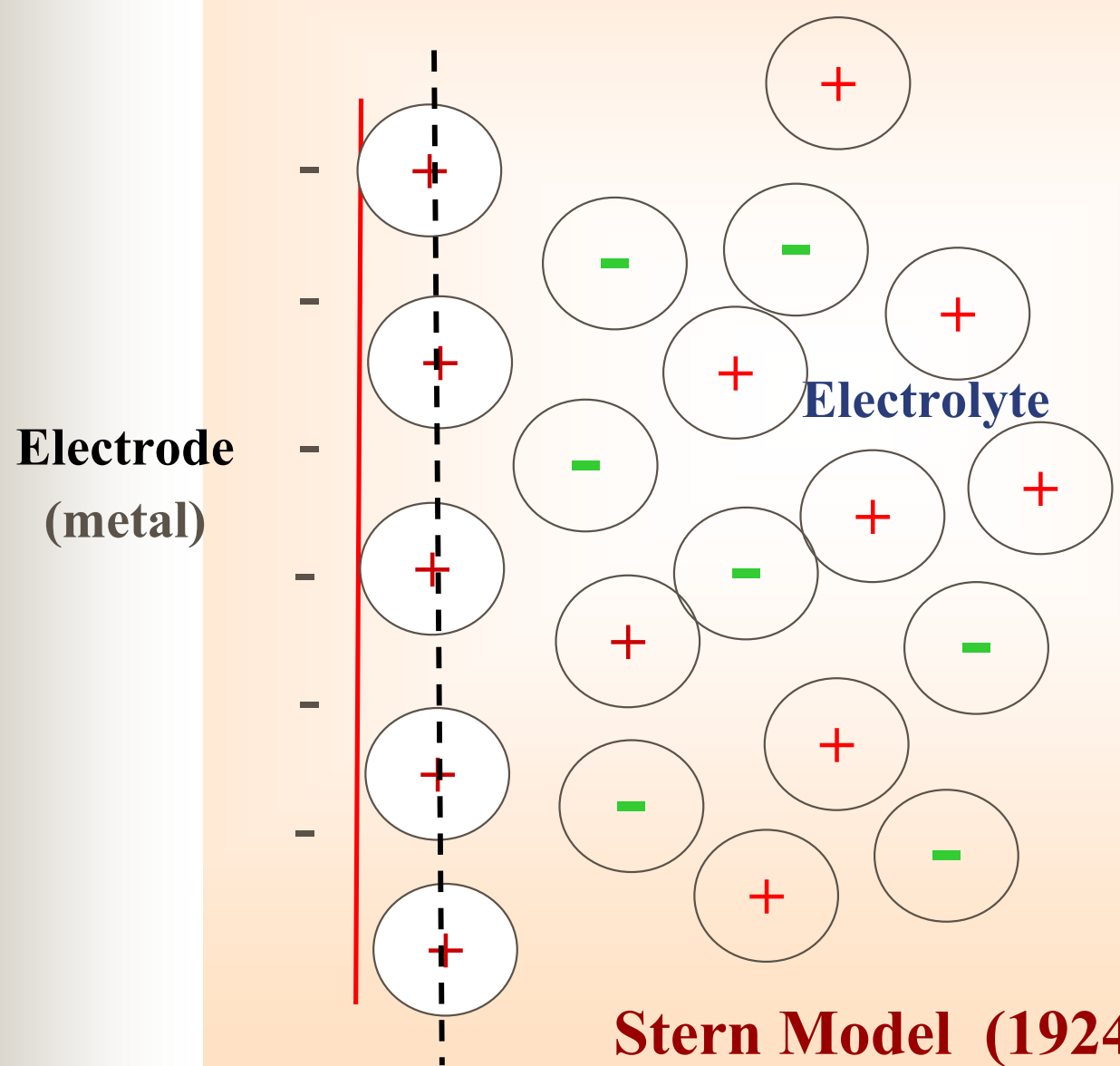
$$\frac{\partial^2 \varphi_{\Delta}(x)}{\partial x^2} = -\frac{e}{\epsilon_r \epsilon_0} \sum_i n_i^0 z_i \exp\left(\frac{-z_i e \varphi_{\Delta}}{k_B T}\right)$$

x_{DL} = distance characteristic of the diffuse layer

$$x_{DL} = \left(\frac{\epsilon_r \epsilon_0 k_B T}{2 n_i^0 z^2 e^2} \right)^{1/2} \quad \text{diffuse layer thickness}$$

x_{DL} for water at 298 K is $3.04 \cdot 10^{-8} z^{-1} c^{-1/2}$ cm
if $c = 1M$ and $z = 1$, then x_{DL} is 0.3 nm.

ELECTRODE DOUBLE LAYER STRUCTURE ON INTERFACE ELECTRODE - ELECTROLYTE



Stern Model (1924)

$$\frac{1}{C_d} = \frac{1}{C_H} + \frac{1}{C_{GC}}$$
$$= \frac{x_H}{\epsilon_r \epsilon_0} + \frac{1}{\left(2\epsilon_r \epsilon_0 z^2 e^2 n_i^2 / k_B T\right)^{1/2} \cosh(z e \varphi_{\Delta 0} / 2 k_B T)}$$

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

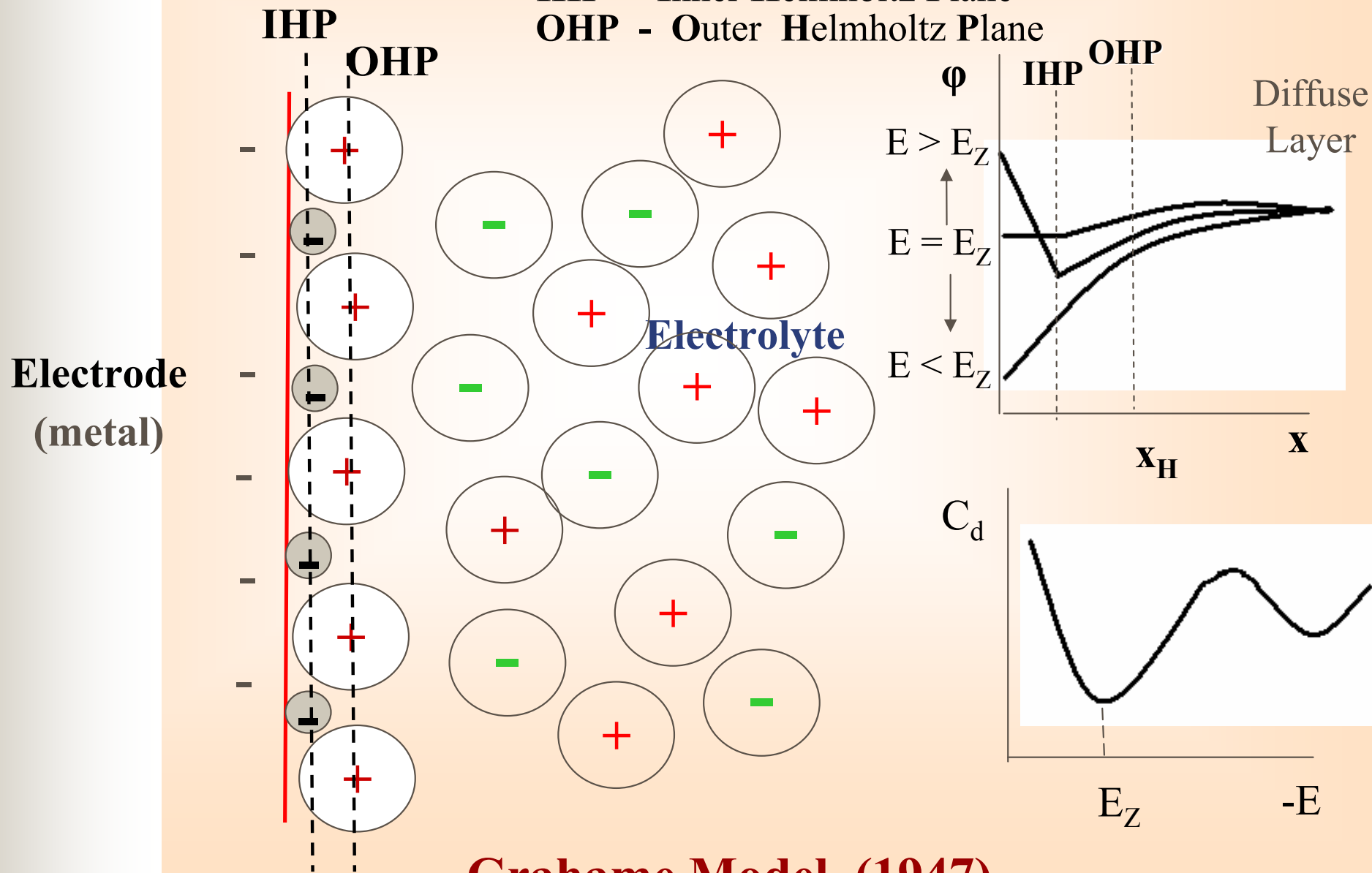
far from E_Z , $C_H \ll C_{GC}$ and so $C_d \sim C_H$

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

ELECTRODE DOUBLE LAYER STRUCTURE ON INTERFACE ELECTRODE - ELECTROLYTE

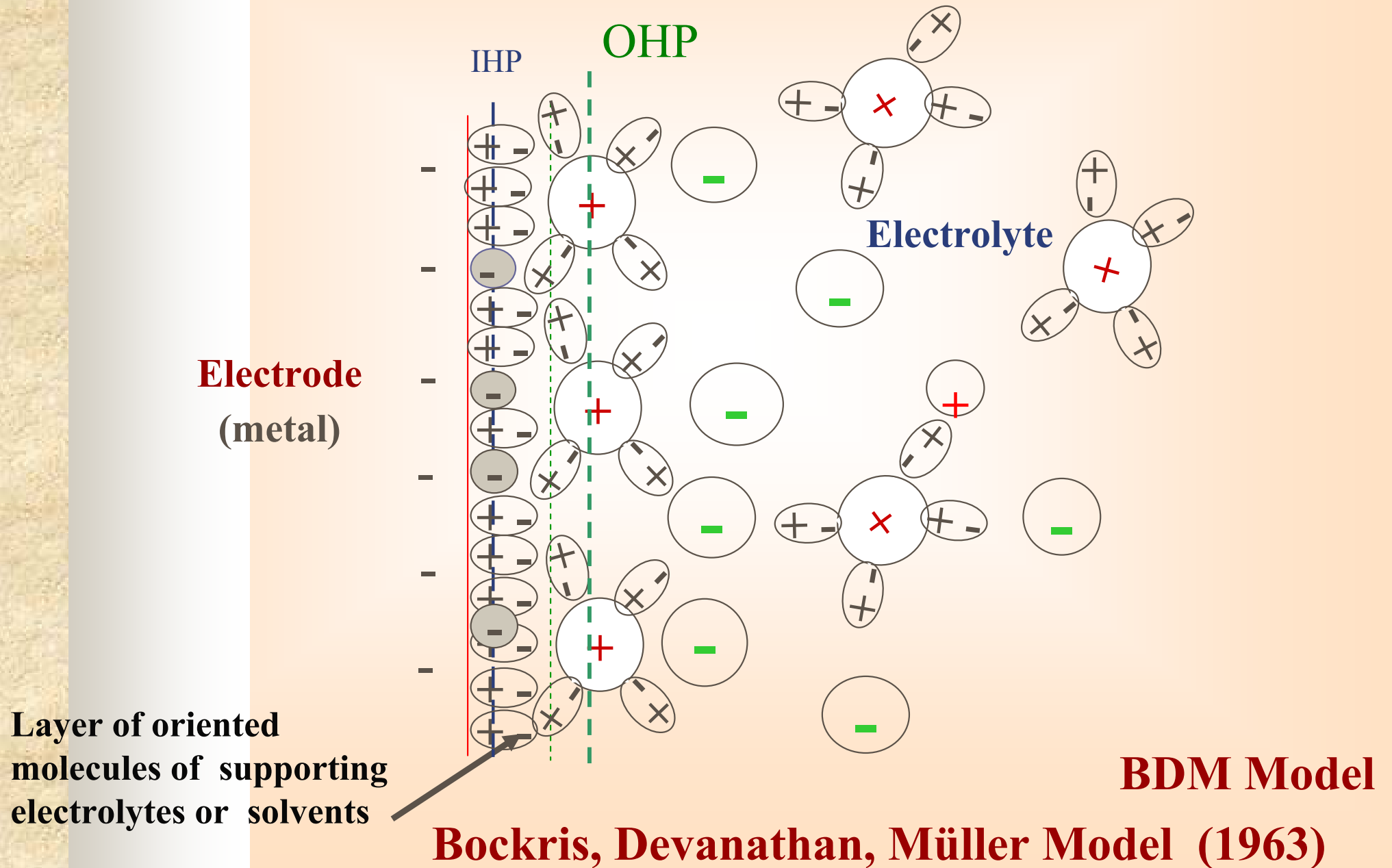
IHP - Inner Helmholtz Plane

OHP - Outer Helmholtz Plane

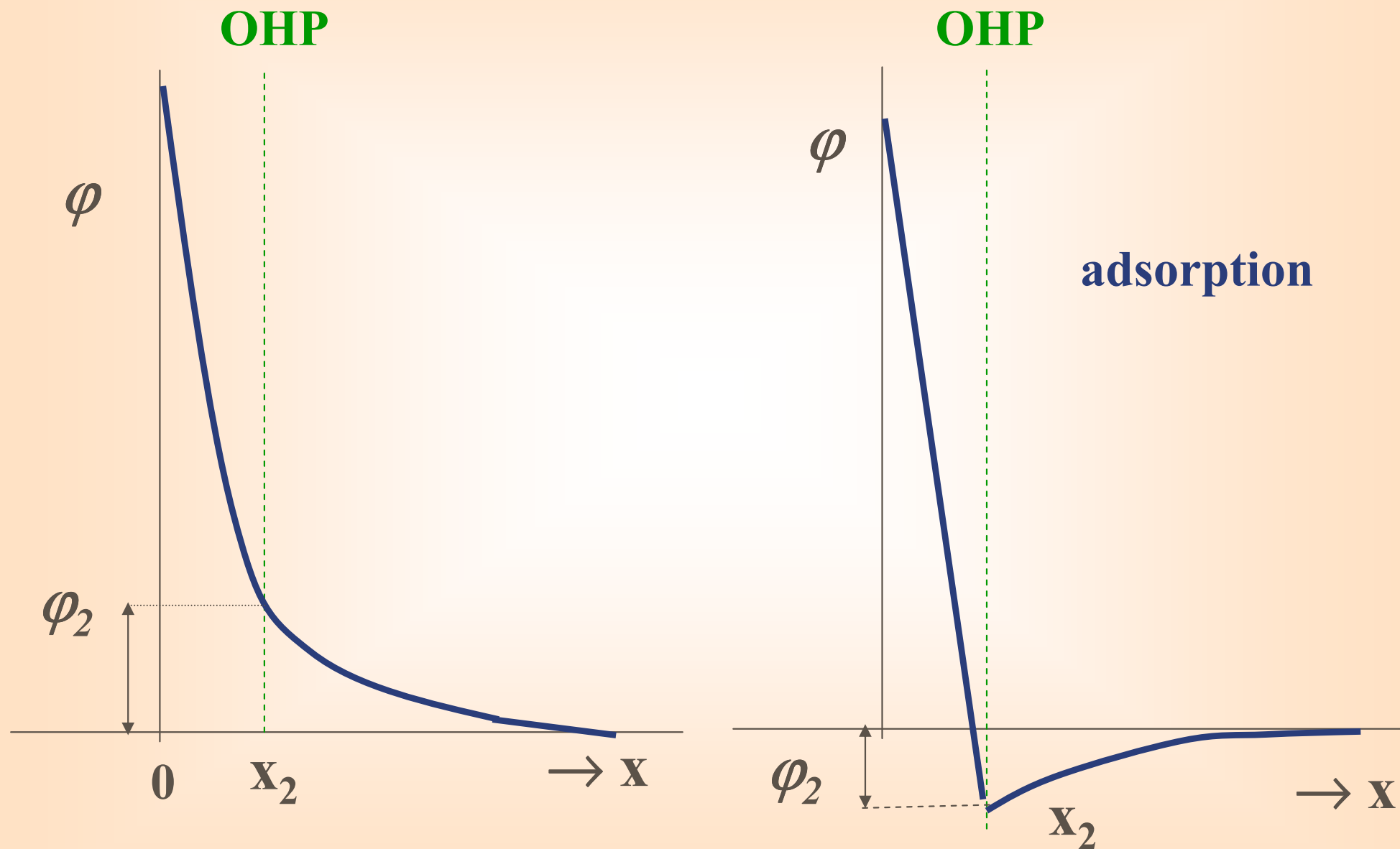


Grahame Model (1947)

ELECTRODE DOUBLE LAYER STRUCTURE ON INTERFACE ELECTRODE - ELECTROLYTE



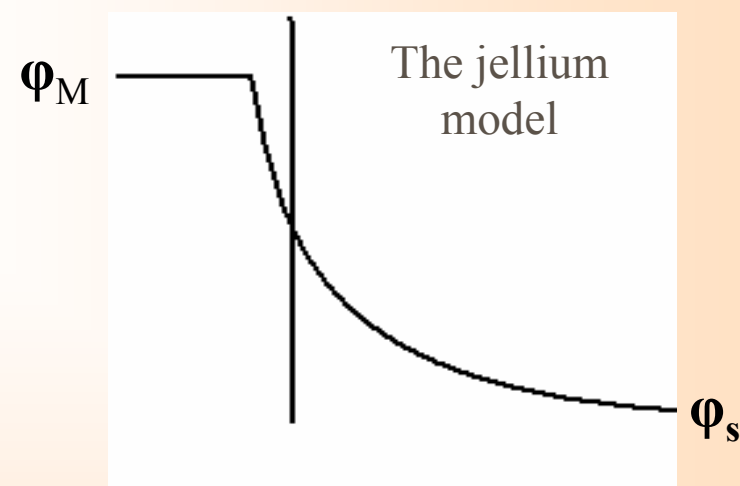
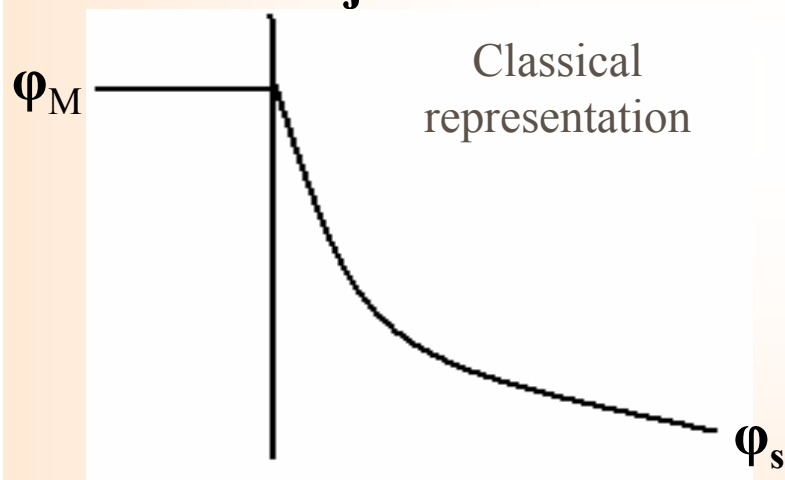
CHARACTERISTIC OF ELECTRODE POTENTIAL IN DOUBLE LAYER



ELECTRODE DOUBLE LAYER STRUCTURE ON INTERFACE ELECTRODE - ELECTROLYTE

**Chemical Models - the electronic distribution of the atoms in the electrode
(not only electrostatic forces)**

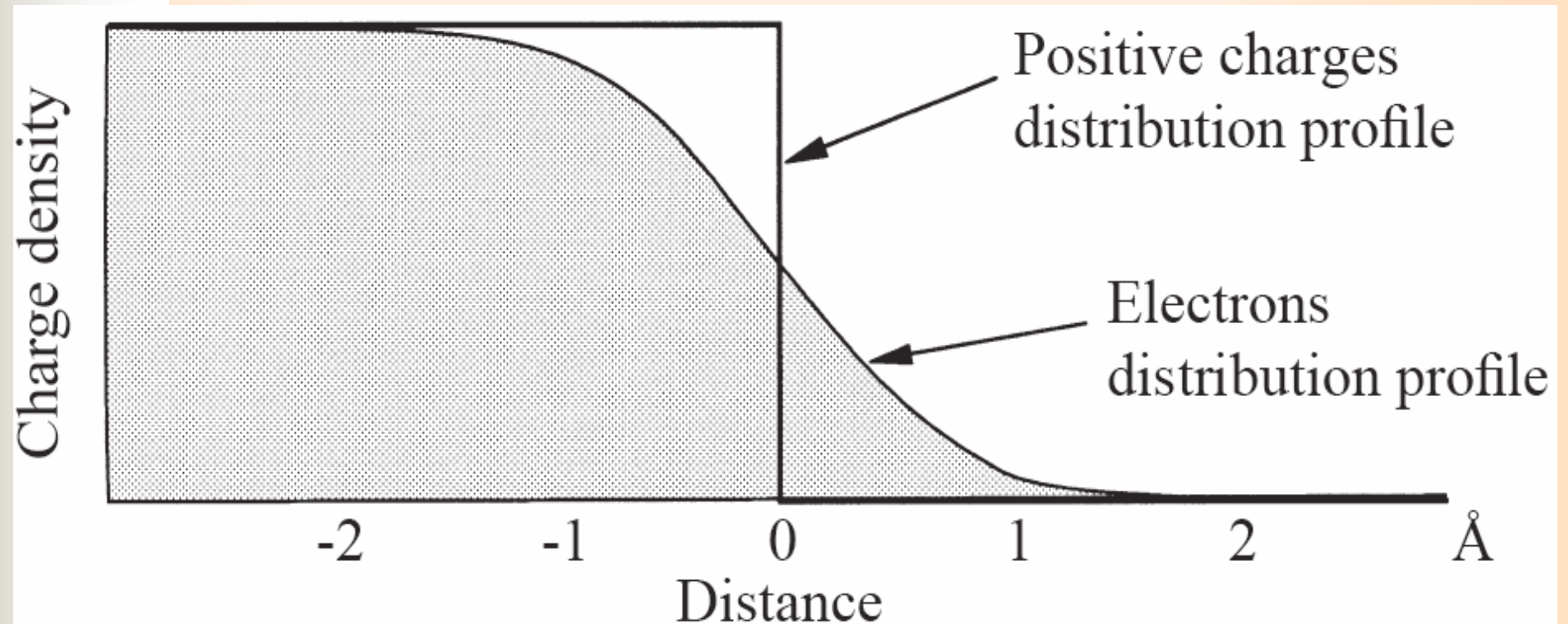
- difference between (sp) metals and transition (d)metals
- IHP as an electronic molecular capacitor
- jellium model



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.