

Basics of Electrochemistry

Objectives

- « Electrophysics »:
 - ions in solution
 - electrophoresis, ζ potential
 - solution in contact with a (metallic) electrode
- Electrochemistry:
 - ec cell at equilibrium (Nernst equation)
 - polarized ec cell (Faraday, Butler-Volmer)
 - three-electrode ec cell

Myself and ec

- Post-Doc (CNRS LPLE, Dr. Allongue):
 - Cu electroplating on n-Si(111)

- Currently (ETH LBB, Prof. Vörös):
 - modification of polymer coatings
 - metal 3D microprinting
 - electrophysiology

ec in Daily Life

batteries

fuel cells

solar cells

everywhere

metallic layers

corrosion

sensors

neurons

Electrochemistry

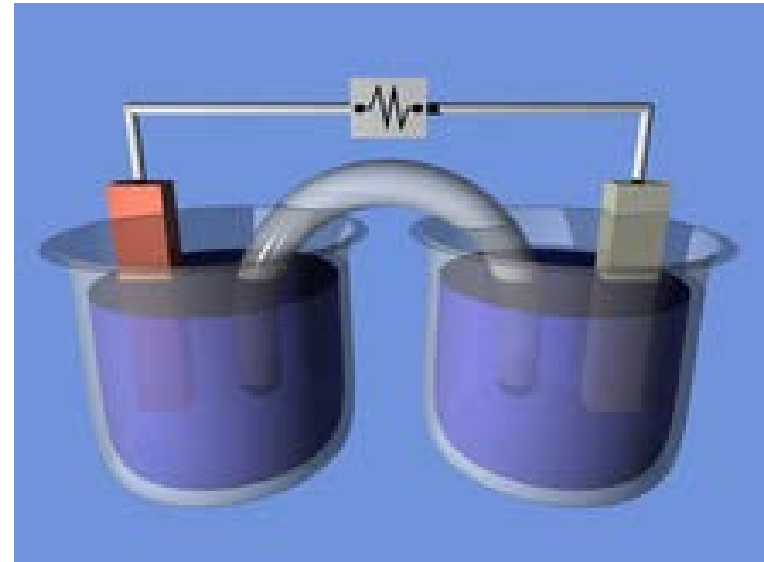
Electrochemistry is a discipline that deals with **chemical reactions** that involve **an exchange of electric charges** between two substances. Both chemical changes generating electric currents and chemical reactions triggered by the passage of electricity can be considered electrochemical reactions.

- **Electrolytic** processes

Reactions in which chemical changes occur on the passage of an electrical current

- **Galvanic or Voltaic** processes

Chemical reactions that result in the production of electrical energy



wikipedia.com

system: solution + electrodes

(solvent + solute) + electrodes (at least two)

(solvent (water?) + redox + salts + electrodes)

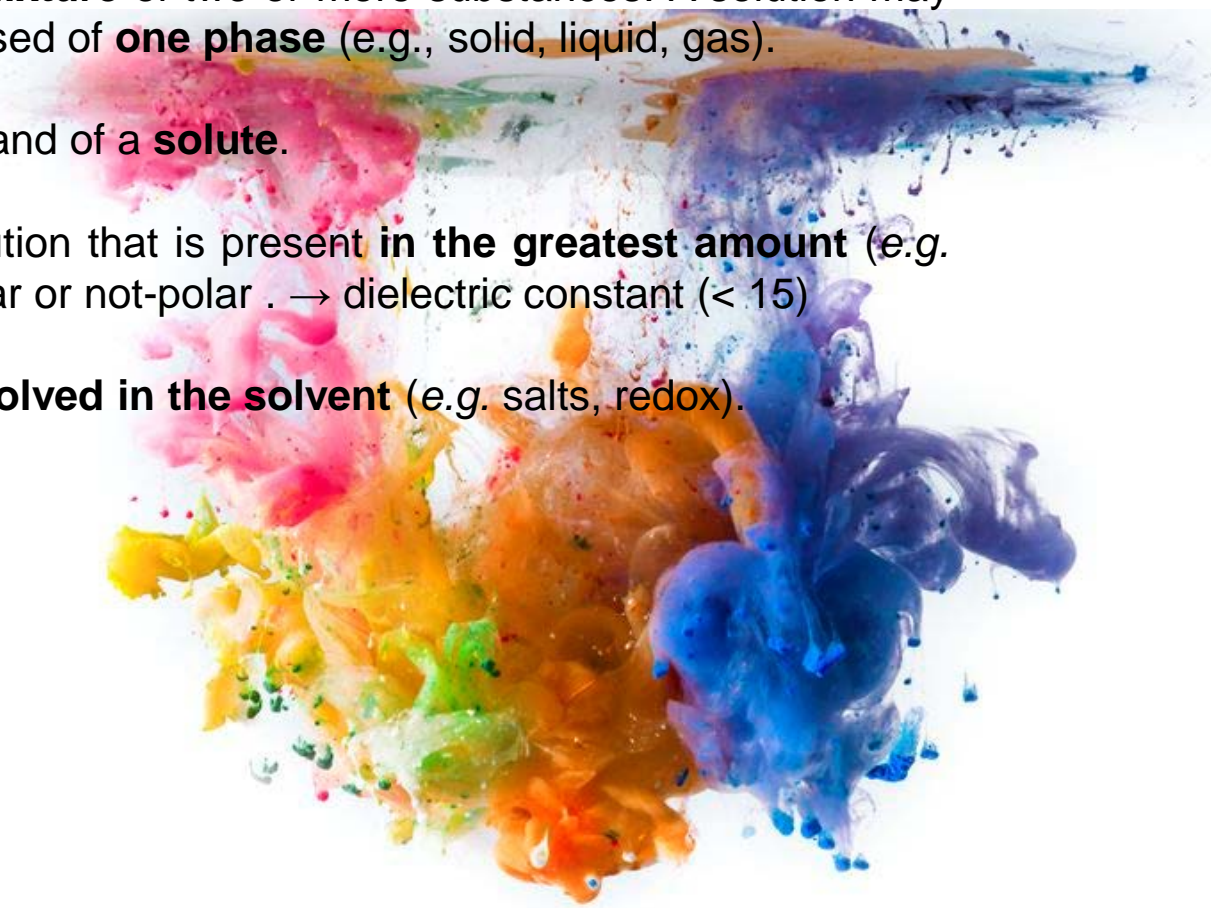
Solution

A **solution** is a homogeneous **mixture** of two or more substances. A solution may exist in any phase, but is composed of **one phase** (e.g., solid, liquid, gas).

A solution consists of a **solvent** and of a **solute**.

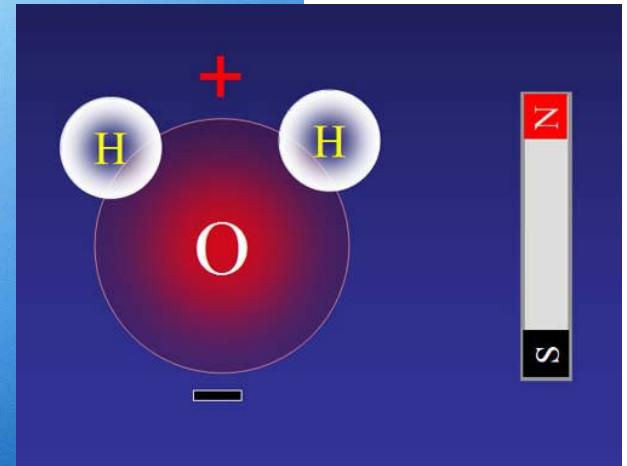
Solvent → component of a solution that is present **in the greatest amount** (e.g. water, organic chemicals) → polar or not-polar . → dielectric constant (< 15)

Solute → substance that is **dissolved in the solvent** (e.g. salts, redox).



Solvent

water is called the "universal solvent" because it dissolves more substances than any other liquid.



www.atceng.hk/

Salts

salt: acid + base \rightarrow salt + water (complete reaction!)

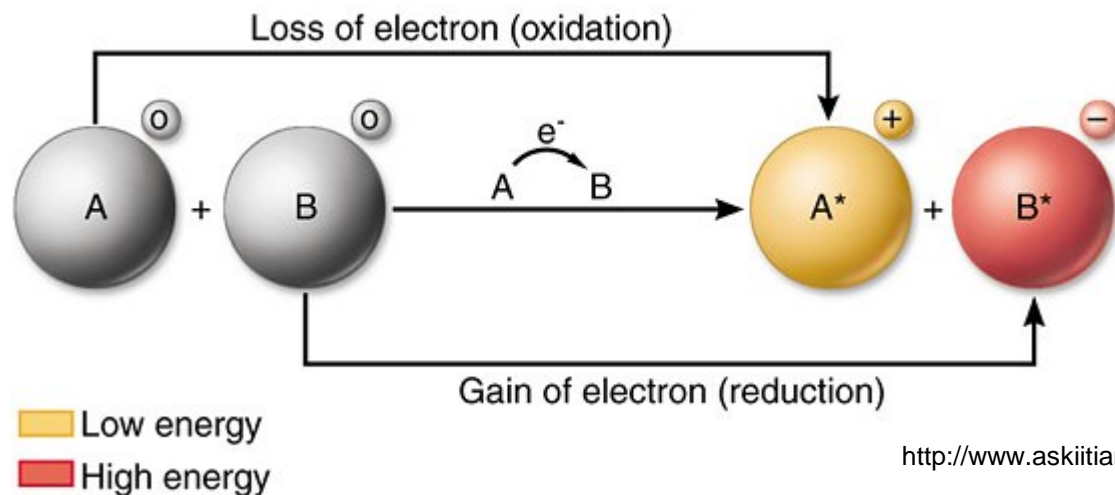
Why dissolution? Water can dissolve a salt because the positive part of water molecules attracts the negative ions and the negative part of water molecules attracts the positive ions.

The amount of a substance that can dissolve in a liquid (at a particular temperature) is called the solubility of the substance.

Solutions containing dissolved salts, **conduct electricity** because the released ions in the solution are capable of carrying an electric current.



RedOx



<http://www.askiitians.com/iit-jee-redox-reactions/>

An **oxidation-reduction (redox) reaction** is a type of chemical reaction that involves a **transfer of electrons** between two species. An oxidation-reduction reaction is any chemical reaction in which the oxidation number of a molecule, atom, or ion changes by gaining or losing an electron.

Redox reactions are common and vital to some of the basic functions of life, including photosynthesis, respiration, combustion, and corrosion or rusting.

Redox reactions are comprised of **two parts**, a reduced half and an oxidized half, that **always** occur together. The reduced half gains electrons and the oxidation number decreases, while the oxidized half loses electrons and the oxidation number increases.



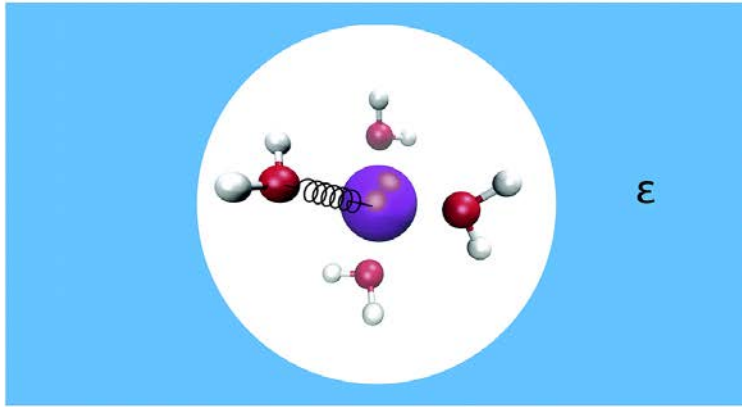
Now-Later.jpg

uzh | eth | zürich

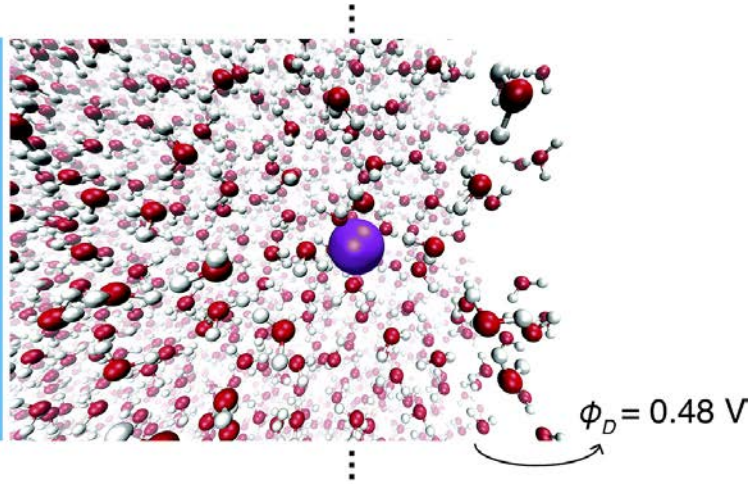
Electrodes



Solvation (Hydration) Shell

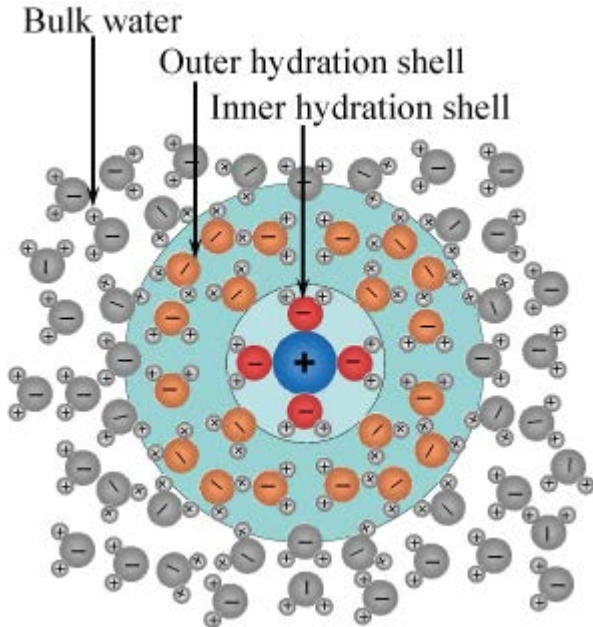


(a) Cluster Continuum



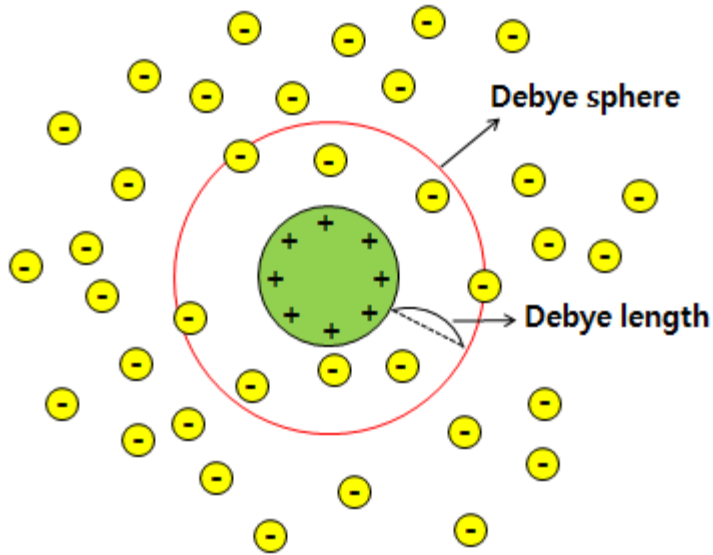
(b) DFT-MD

Chem. Sci. **2017** 8:6131



- electrostatic (dipolar) interactions
- hydrogen bonding
- thermal fluctuations

Debye (-Hückel) Length



$$\kappa^{-1} = \left(\frac{k_B T \epsilon_0 \epsilon}{2q^2 N_A I} \right)^{1/2}$$

$$= \frac{0.3 \text{ nm}}{\sqrt{I}} \quad I = \frac{1}{2} \sum_j [\text{ion}]_j Z_j^2$$

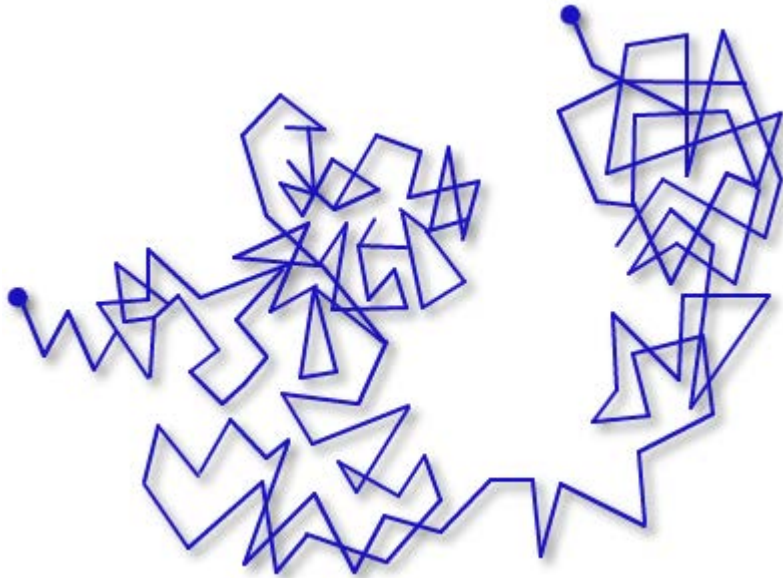
What we know now is quite important:

If you are some Debye lengths away from these fixed charges, you will not "see" them anymore; their effect on the equilibrium carrier distribution then is vanishingly small.

The Debye length resulting in any one of these situations thus is nothing but the typical distance **needed for screening** the surplus charge by the mobile carriers present in the material.

In other words, after you moved about one Debye length away from the surplus charge, its effects on the mobile charges of the material are no longer felt.

Brownian Motion



<http://physics.tutorcircle.com>

Brownian motion is the **random** motion of particles suspended in a fluid (a liquid or a gas) resulting from their collision with the fast-moving atoms or molecules in the gas or liquid.

$$\langle \Delta x(t) \rangle = 0$$

$$\langle \Delta y(t) \rangle = 0$$

$$\langle \Delta x^2(t) \rangle = 2Dt$$

$$\langle \Delta y^2(t) \rangle = 2Dt$$

$$\langle \Delta r^2(t) \rangle = 4Dt$$

Electrophoresis

$$j_{diffusion} = -|Z|D \frac{d[C]}{dt}$$

diffusion flux (Fick's law)
(C concentration, Z ion valence, D diffusion constant)

$$F_{ext} = eZ \cdot E$$

charge eZ in presence of an electric field E

$$F_{fr} = -f \cdot v$$

due to collisions between particles in solution

$$F_{ext} + F_{fr} = 0 \Rightarrow v_{drift} = -\mu E \rightarrow \mu, \text{ mobility!!!}$$

equilibrium

$$j_{drift} = v_{drift} |Z| F [C]$$

Farady constant

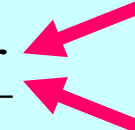
$$= -\mu |Z| F [C] E$$

$$= -\mu |Z| F [C] \frac{dV}{dx}$$

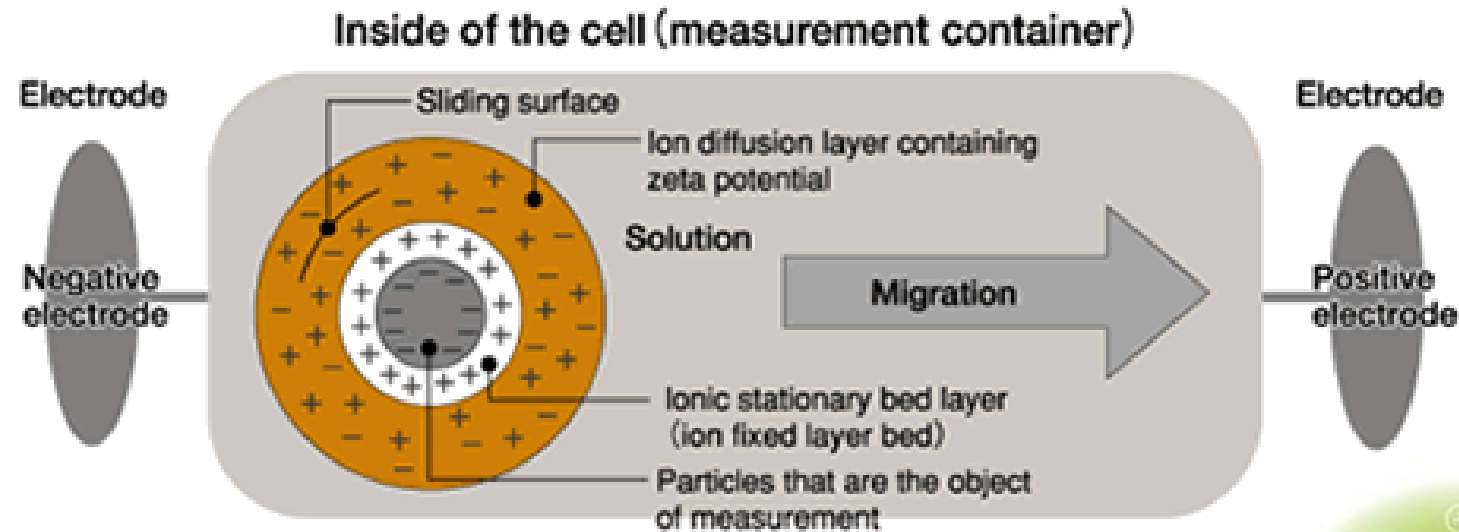
flux within E in a solution (Ohm's law)

$$v_{drift} = \frac{eZE}{f}$$

$$\mu \equiv \frac{v_{drift}}{E} = \frac{eZ}{f}$$

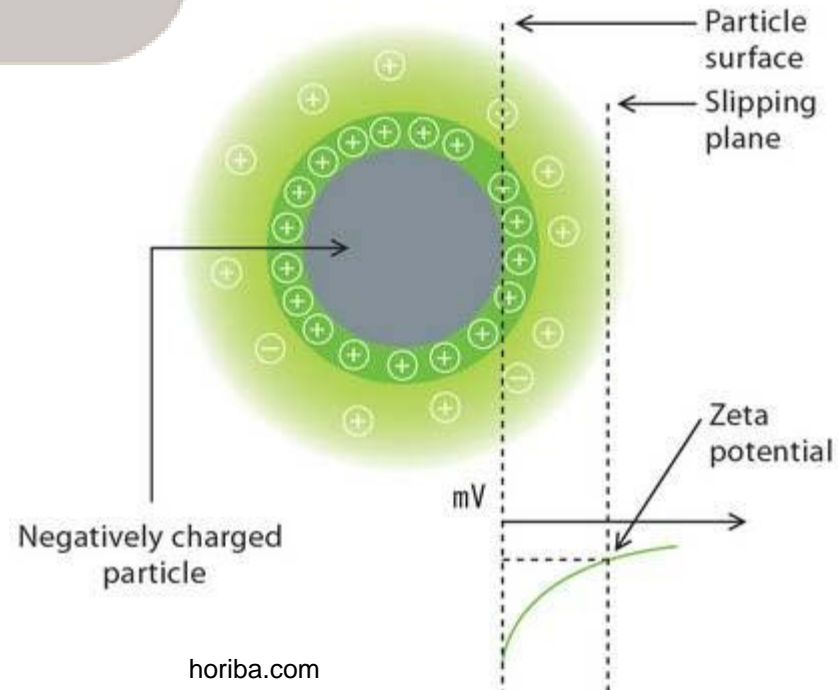
$$\equiv \frac{\epsilon_r \epsilon_0 \zeta}{\eta}$$


zeta ζ Potential



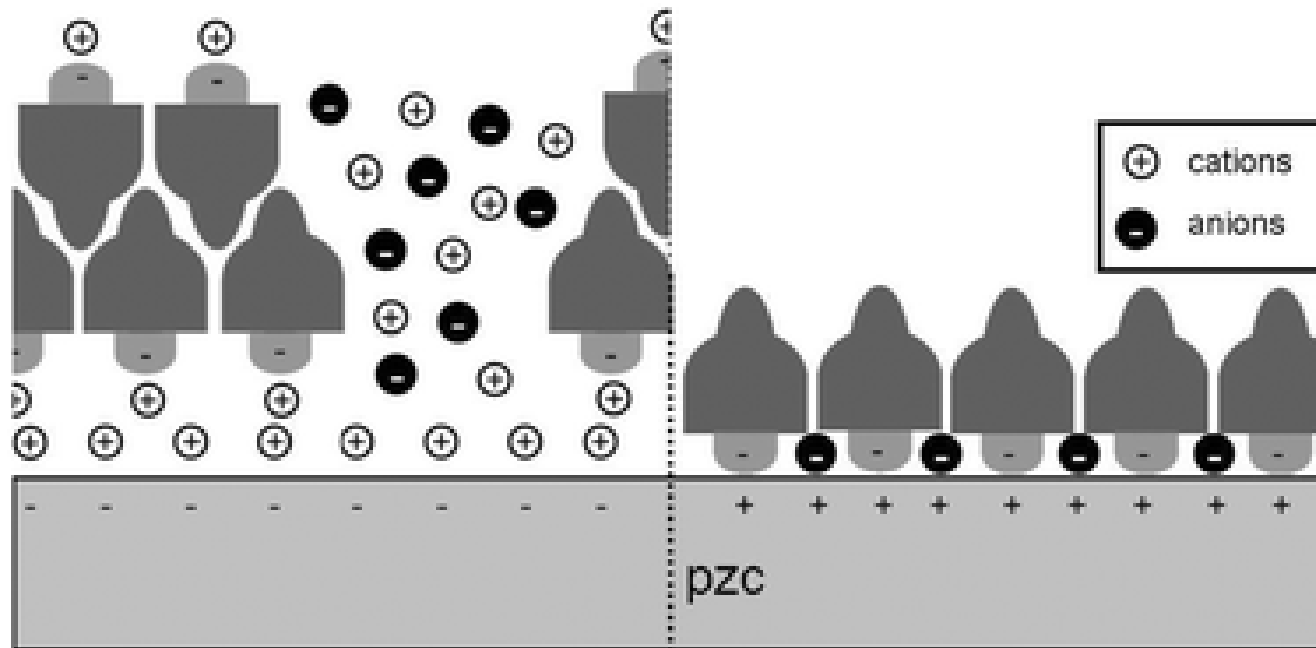
When a colloidal particle moves in the dispersion medium, **a layer of the surrounding liquid** remains attached to the particle. The boundary of this layer is called **slipping plane** (or **shear plane**). → the solvent molecules outside of the slipping plane DO NOT travel with the particle!

The Zeta potential cannot be directly measured.



The DLVO Theory (Derjaguin, Landau, Verwey and Overbeek) tries to explain why some colloidal systems agglomerate while others do not.

Point of Zero Charge



Phys. Chem. Chem. Phys. 2011 13:13232

The point of zero charge (pzc), in physical chemistry, is a concept relating to the phenomenon of adsorption, and it describes the condition when the electrical charge density on a surface is zero.

Point of zero charge is of fundamental importance in surface science. For example, in the field of environmental science, it determines how easily a substrate is able **to adsorb potentially harmful ions**. It also has countless applications in technology of colloids, e.g., flotation of minerals.

At pzc, the colloidal system exhibits **zero zeta potential** (i.e., the particles remain stationary in an electric field), minimum stability (i.e., exhibits maximum coagulation/flocculation rate), maximum solubility of the solid phase, maximum viscosity of the dispersion, and other peculiarities.



Solution Conductivity

η , applied overpotential

$$I = \frac{\eta}{R_S}$$

R_S , solution resistance

ohmic behaviour

η

+ve -ve

Na+ Cl- Na+

Cl- Na+ Na+

Cl- Na+ Cl-

Cl- Cl- Cl-

Na+ Na+

Cl- Cl- Na+

Cl- Na+

Cl- Na+

Conductivity probe

Ions (e.g. Na⁺ & Cl⁻) are drawn towards the opposite charged platinum electrode. This generates a very small current through the solution. The meter measures this current and, as the distance between the electrodes is known, the conductivity can be calculated in S/cm. Once a temperature compensation has been applied.

In an ideal system this follows a known equation. In reality, fringe field effects mean that the probe must be calibrated especially as the platinum electrodes age.

Fringe field effects

Square electrode

+ve -ve

Field lines

@andyjconnelly

<https://andyjconnelly.wordpress.com/2017/07/14/conductivity-of-a-solution/>



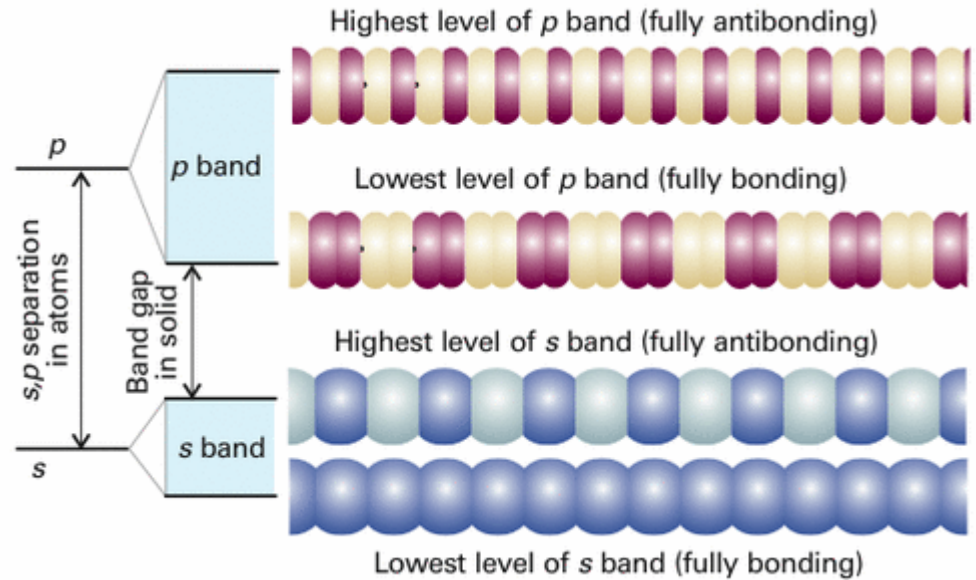
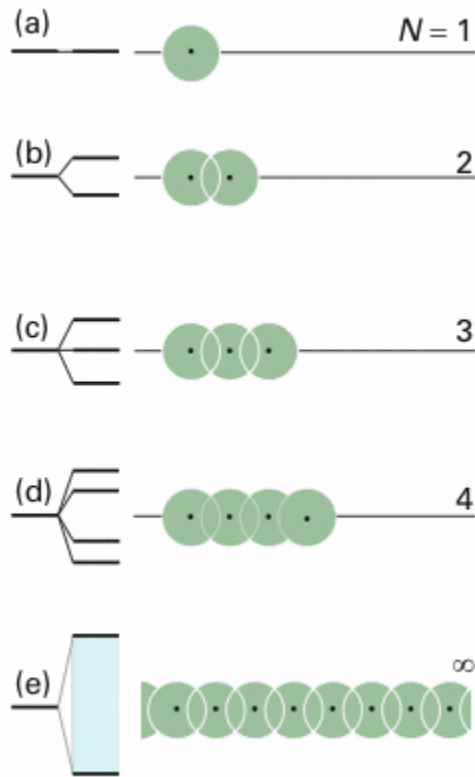
(Metallic) Electrodes



Nutrition for Optimal Wellness™

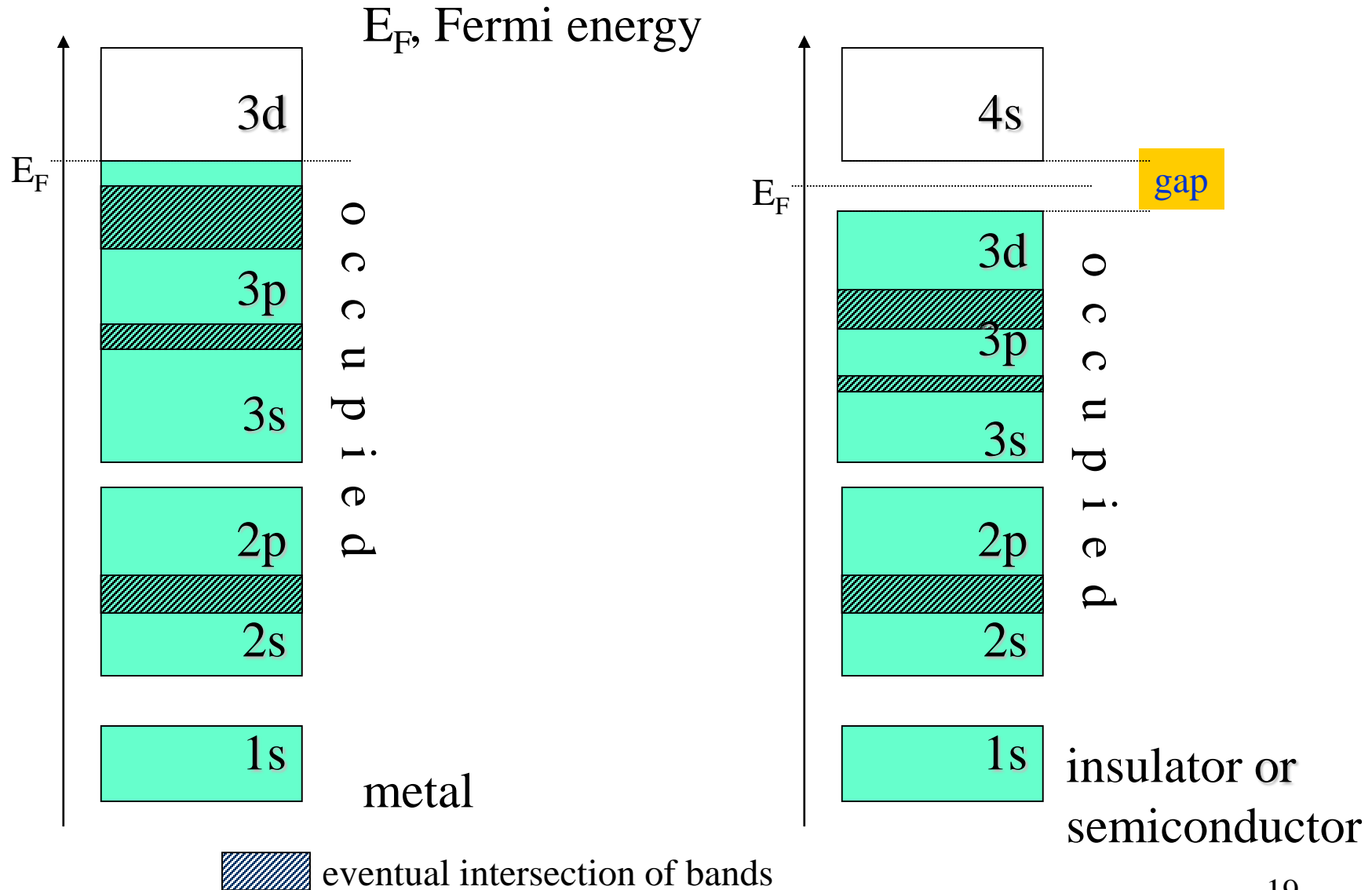
totalnutritionconcepts.com

Formation of Crystal Bands

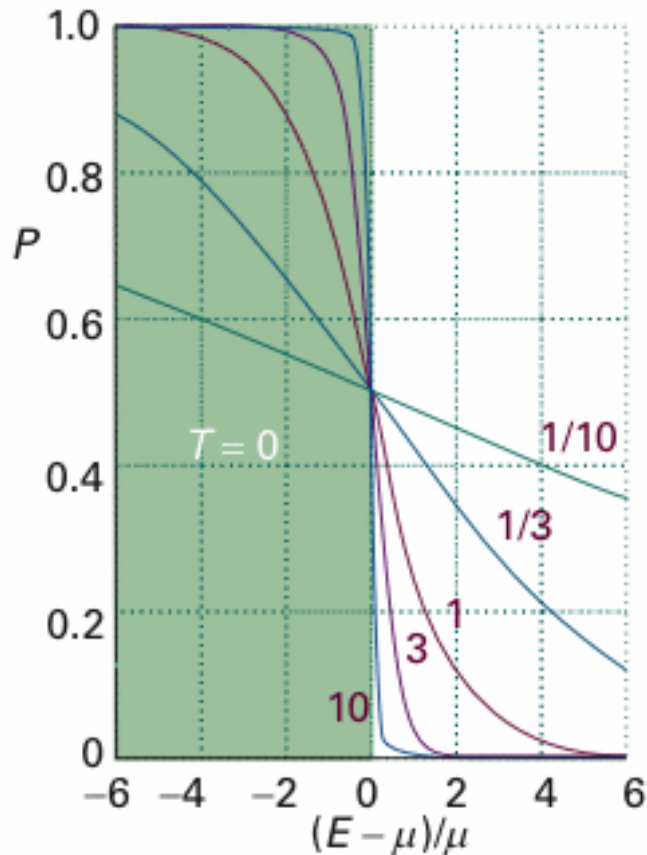


(from Atkins-dePaula)

Occupation of Crystal Bands



Fermi-Dirac Distribution



Fermi-Dirac distribution

$$f(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1}$$

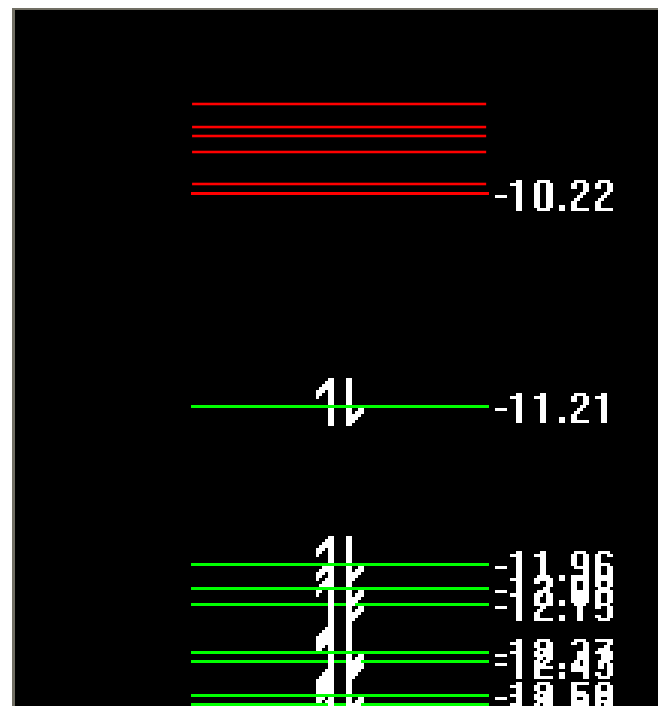
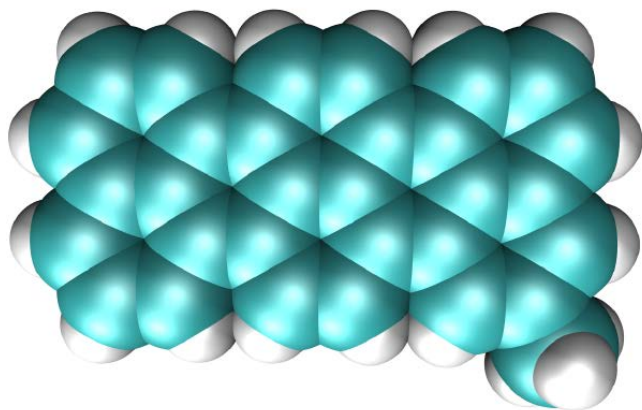
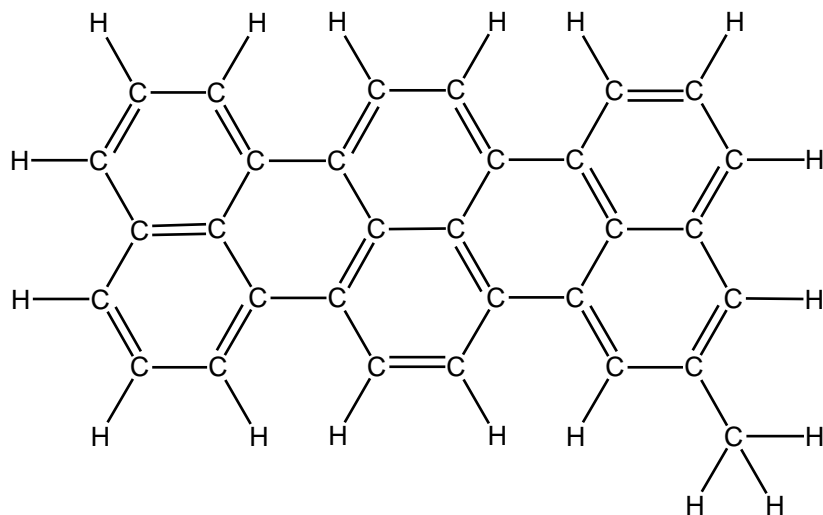
(from Atkins-dePaula)

$$k_B = 1.380658 \times 10^{-23} \text{ J/K} = 8.6 \times 10^{-5} \text{ eV/K}$$

Boltzmann constant

HOMO - LUMO

Highest Occupied MO
 Lowest Unoccupied MO

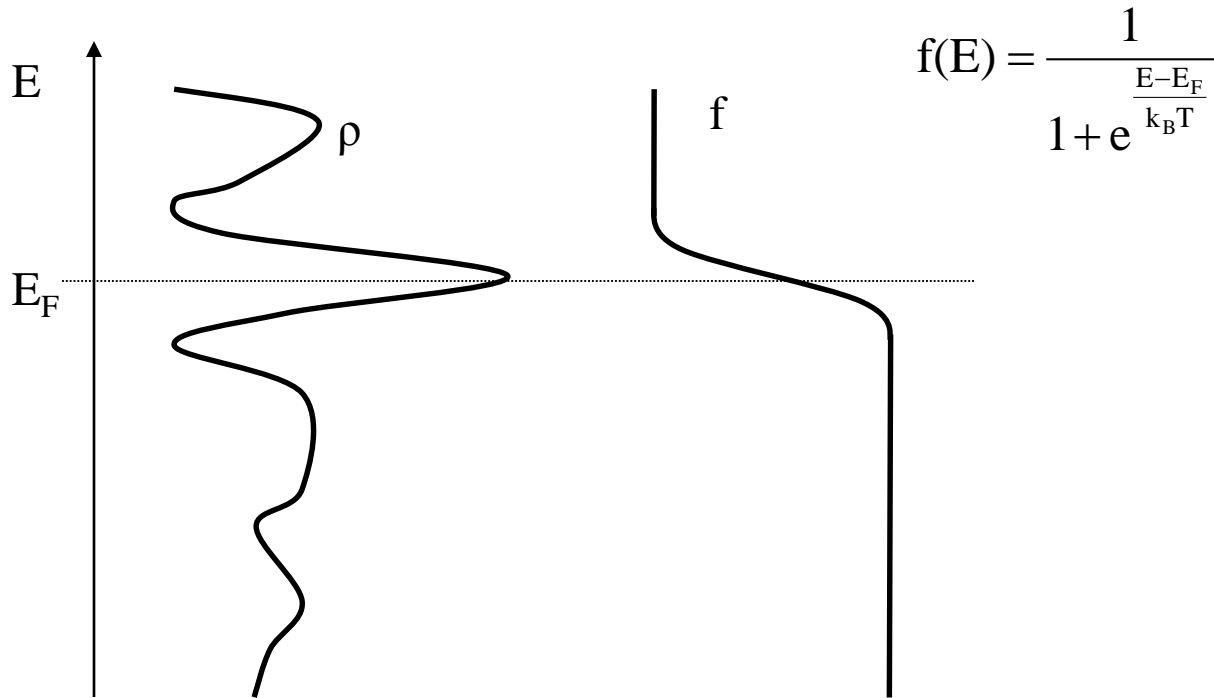


methylterrylene_iso2

the metallic electrode

$\rho(E)$, density of states (band theory)

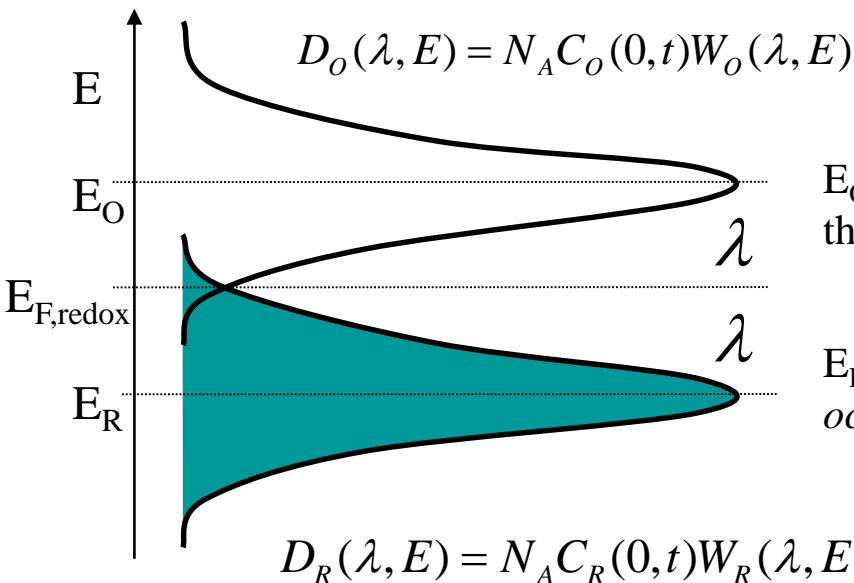
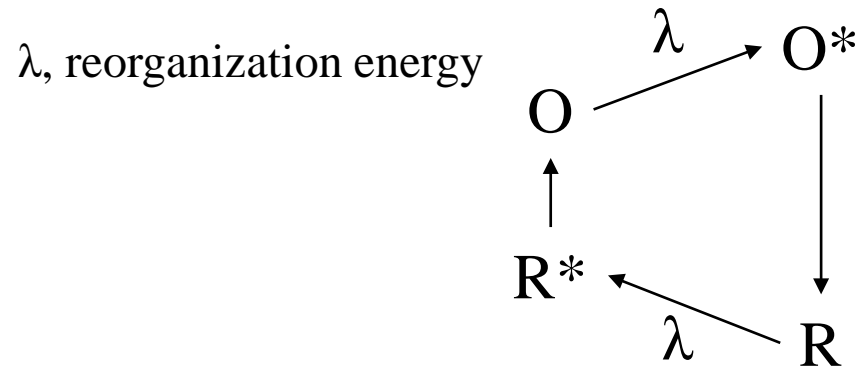
$f(E)$, Fermi-Dirac distribution



$$N_{\text{occ}}(E) = f(E)\rho(E)$$

$$N_{\text{unocc}}(E) = [1 - f(E)]\rho(E)$$

Redox Energy Levels



E_O , energy obtained adding an electron from the infinity to the *unoccupied* state of the oxidized form

E_R , energy spent removing an electron from the *occupied* state of the reduced form to the infinity

$E_O \neq E_R$ because different solvation shell

E_O and E_R fluctuating because of the fluctuations of the solvent molecules around the O and r species

$$W_O(\lambda, E) = \frac{1}{\sqrt{4\pi\lambda k_B T}} e^{-\frac{(E-E_F-\lambda)^2}{4\lambda k_B T}}$$

$$W_R(\lambda, E) = \frac{1}{\sqrt{4\pi\lambda k_B T}} e^{-\frac{(E-E_F+\lambda)^2}{4\lambda k_B T}}$$

Equilibrium (in words)

In a chemical process, **chemical equilibrium** is the state in which the chemical activities or concentrations of the reactants and products have **no net change over time**. Usually, this state results when the forward chemical process proceeds at the same rate as their reverse reaction. The reaction rates of the forward and reverse reactions are generally not zero but, being equal, there are no net changes in any of the reactant or product concentrations. This process is known as **dynamic** equilibrium.

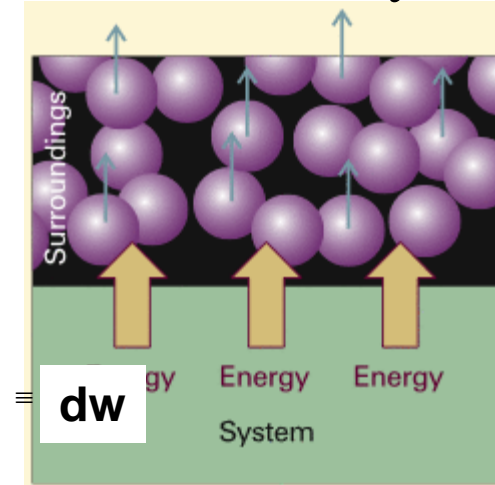
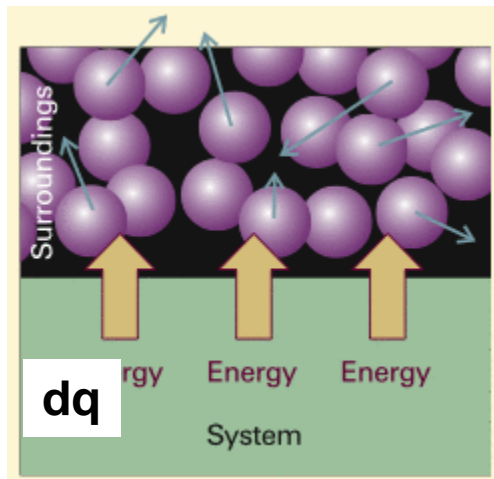
From Wikipedia

activity → *slide 14*

Chemical Potential

$$dU = dq + dw$$

(1st law of thermodynamics)



Atkins

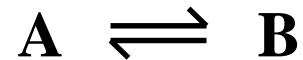
$$G \equiv U + pV - TS$$

(definition of Gibbs free energy)

$$\mu_j \equiv \left(\frac{\partial U}{\partial n_j} \right)_{S, V, n'}$$

$$\mu_j \equiv \left(\frac{\partial G}{\partial n_j} \right)_{p, T, n'}$$

Equilibrium (formula)



$$d\xi_A \rightleftharpoons d\xi_B \quad d\xi \equiv \text{extent of reaction}$$

$$dn_A = -d\xi \quad dn_B = +d\xi$$

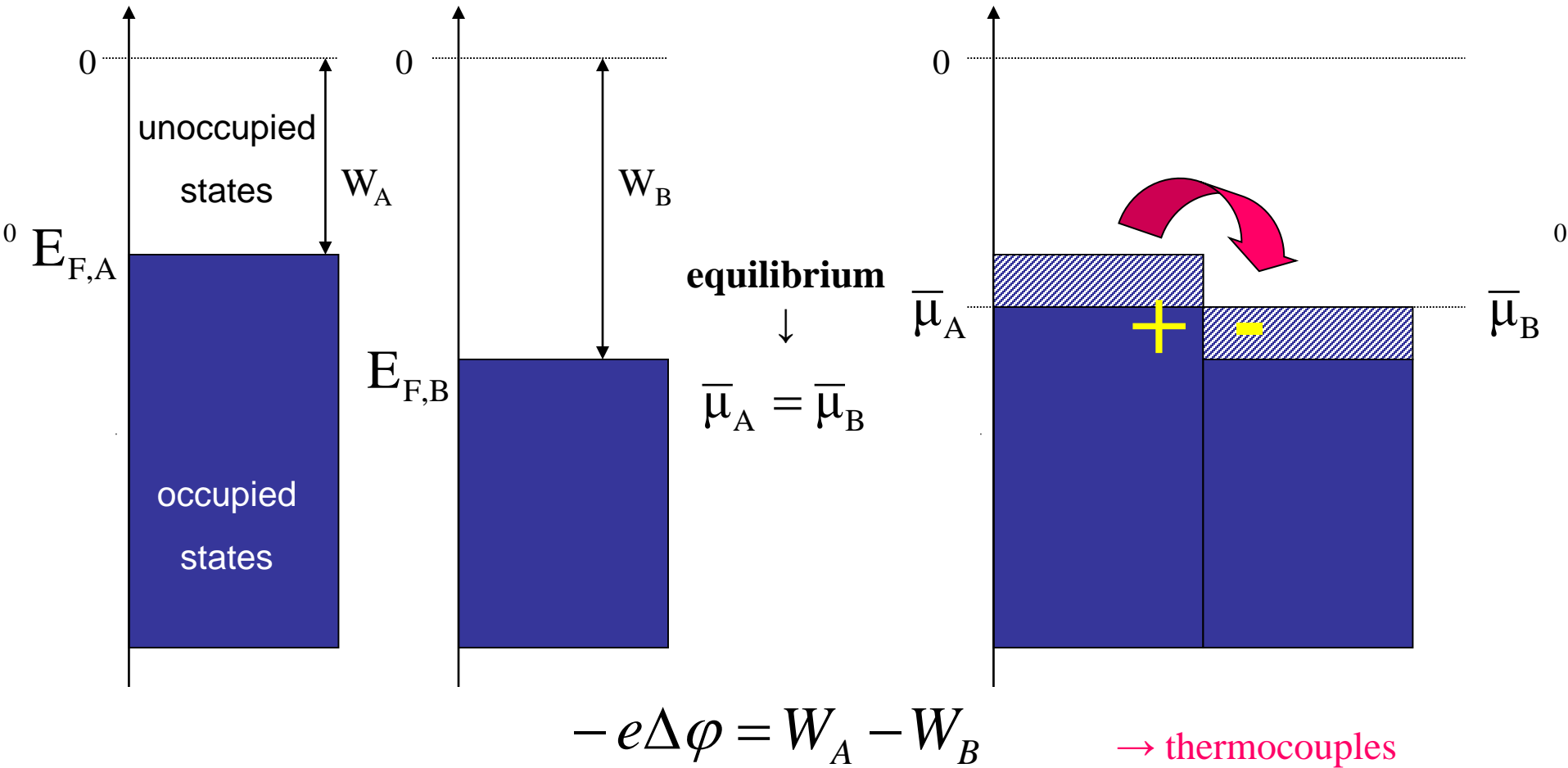
$$\begin{aligned} dG|_{p,T} &= \mu_A dn_A + \mu_B dn_B \\ &= (\mu_B - \mu_A) d\xi \end{aligned}$$


 equilibrium $\rightarrow dG|_{p,T} = 0 \Rightarrow \mu_B = \mu_A$


$$\Delta_r G \equiv \left. \frac{dG}{d\xi} \right|_{p,T} = \sum_j \nu_j \mu_j \quad (\text{prod} - \text{react}) = 0 \quad (\text{Gibbs-Duhem})$$

ν_j , stoichiometric coefficient

Contact Potential



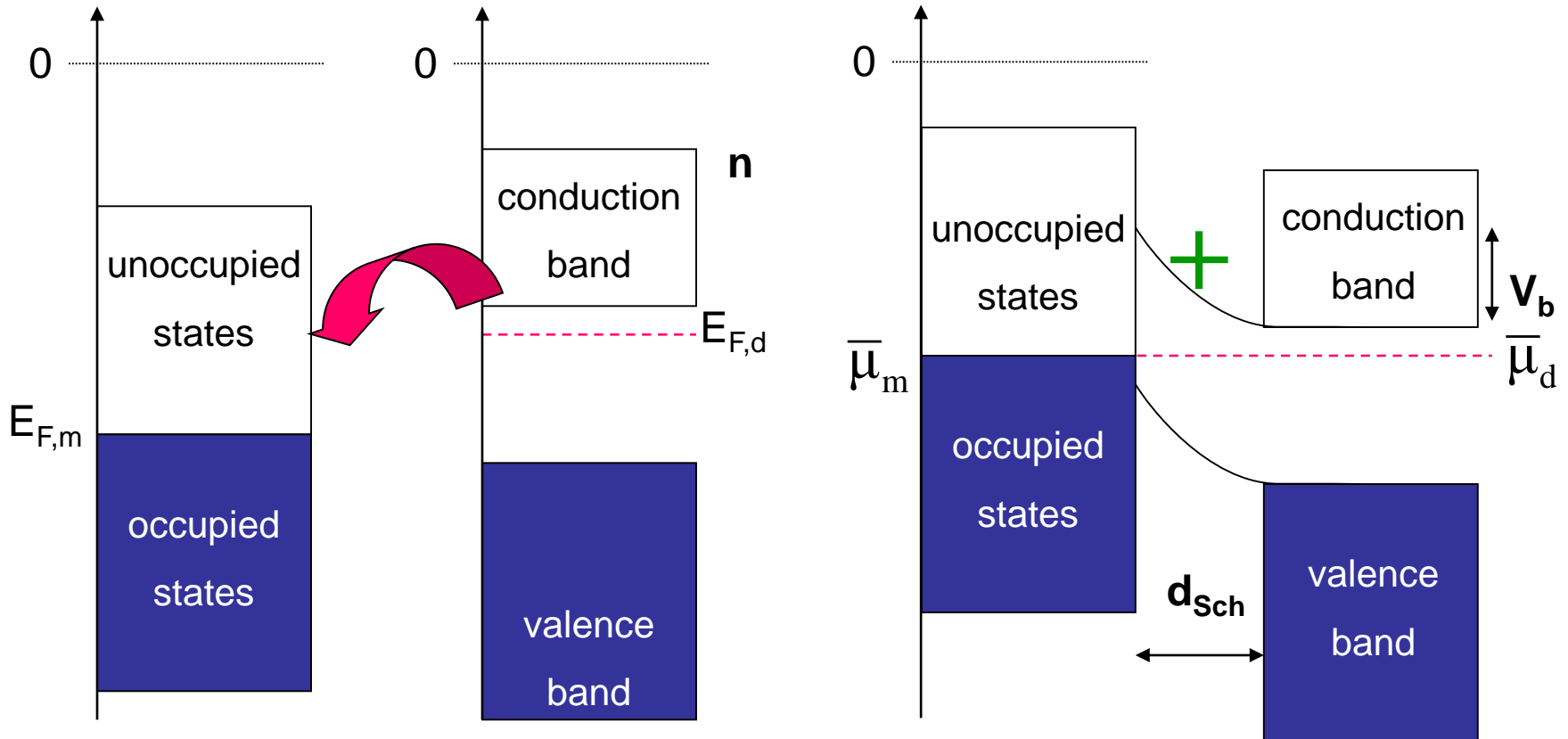
$$\bar{\mu} \equiv \mu_0 + ZF\Delta\phi$$

→ for a metal, $\mu^0 = E_F$ at $T = 0K$

Schottky Barrier

Siemens, 1938

→ diodes



metal

n-semicon

d , donor

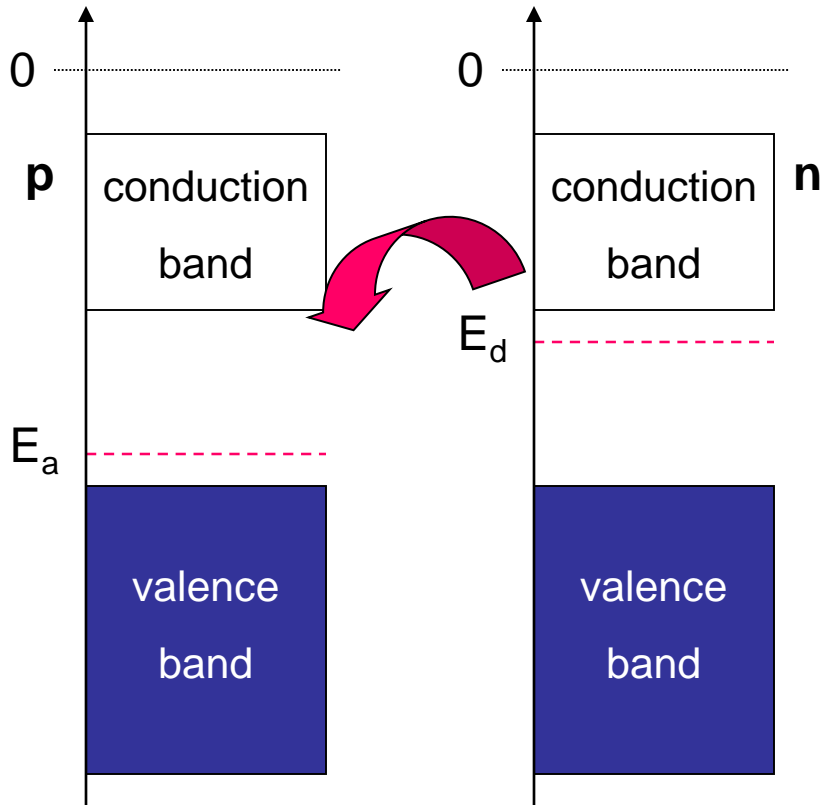
d_{Sch} , depletion region (→ because of the very low charge mobility in semiconductors)²⁸

V_b , energy barrier generated at the interface

p-n Junction

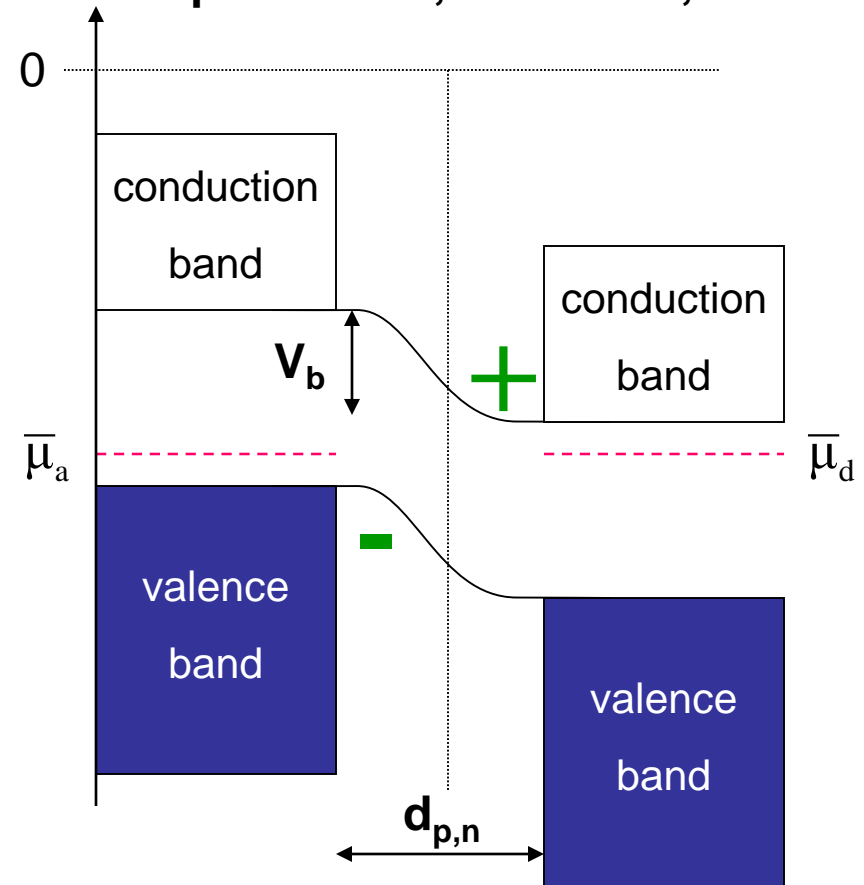
Russel Ohl, Bell Laboratories, 1939

→ p-n diodes, transistors, etc.



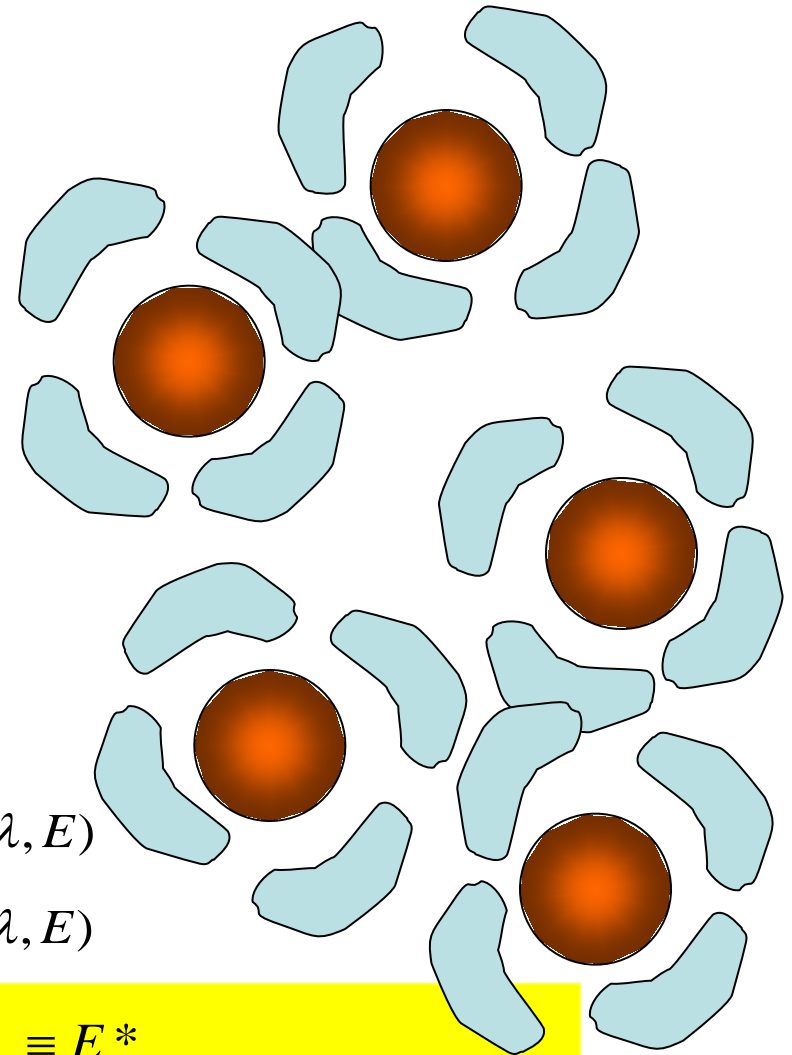
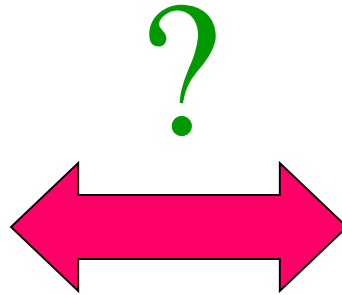
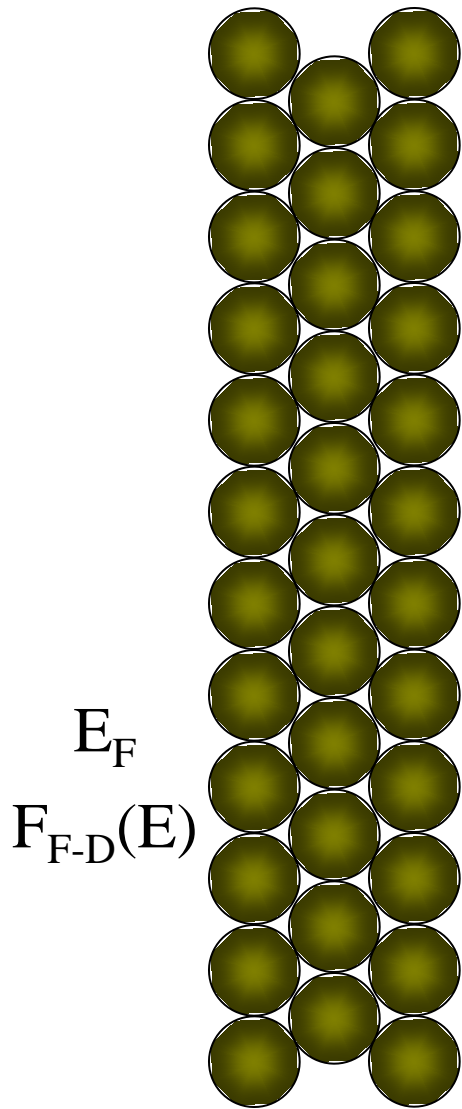
d , donor

a , acceptor



$d_{p,n}$, depletion region

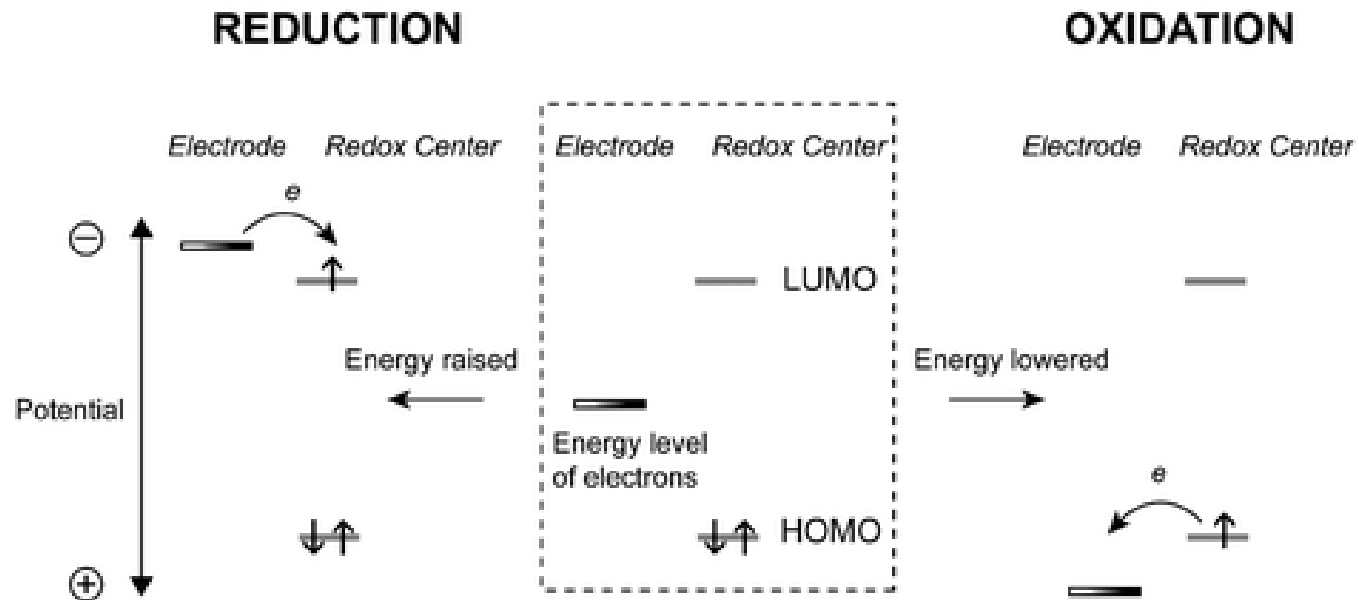
μ_{redox}



$$\mu_{\text{redox}} \equiv E^*$$

$$\text{where } D_O(\lambda, E^*) = D_R(\lambda, E^*)$$

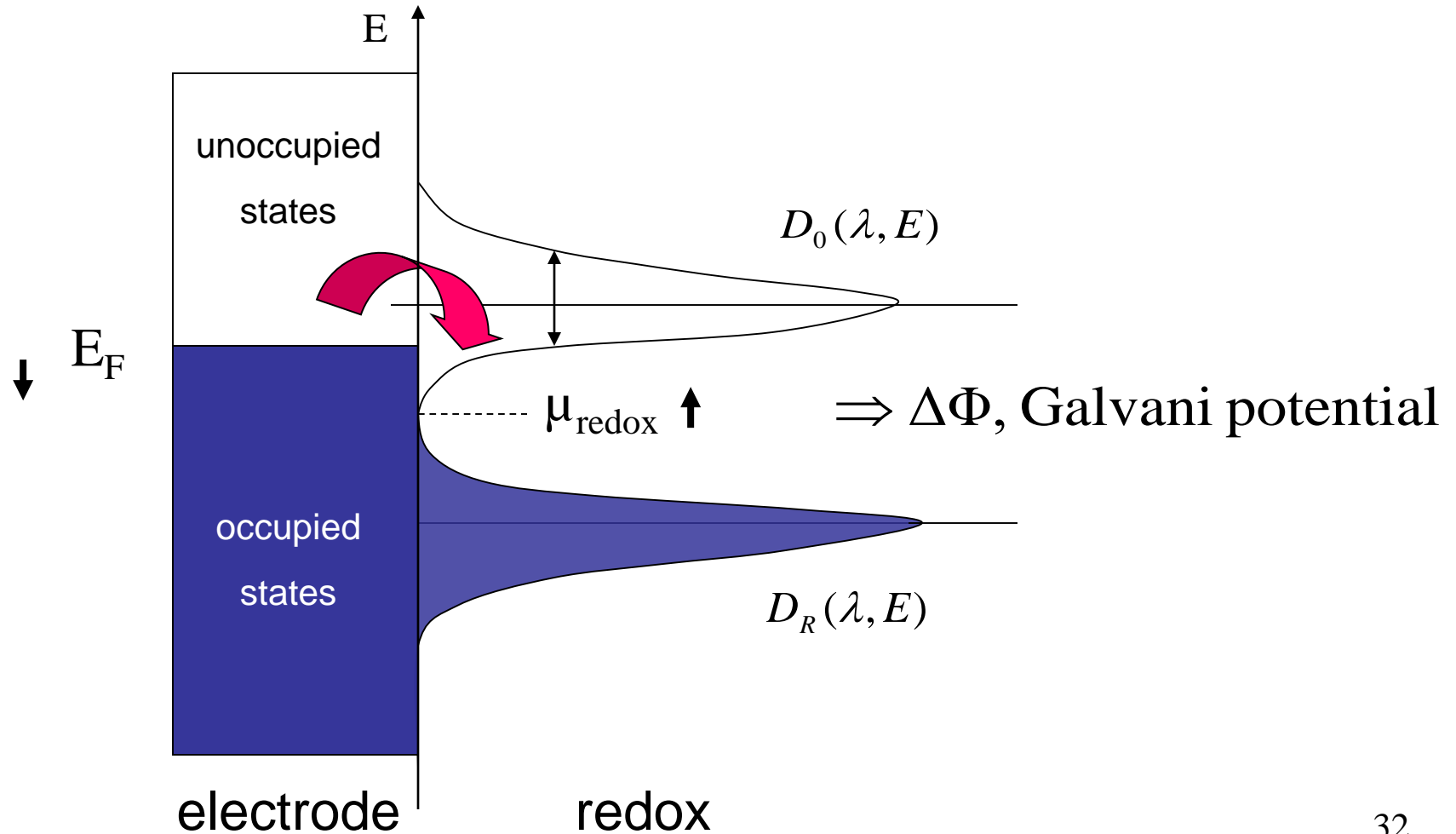
Energy Levels



Faraday Disc 2006 131:197

Electrode-Solution Interface

equilibrium $\rightarrow \bar{\mu}_{\text{metal}} = \bar{\mu}_{\text{redox}}$



$\Delta\varphi$ and μ

$$\bar{\mu}_j = \mu_j \pm Z_j F \Delta\varphi$$

$$\Delta_r G = \sum_{prod} \nu_i \mu_i - \sum_{react} \nu_i \mu_i$$

Ox + ne → Red

$$\Delta_r G_{redox} = \sum_{red} \nu_j \bar{\mu}_j - \sum_{ox} \nu_j \bar{\mu}_j - n \bar{\mu}_e$$

$$= \sum_{red} \nu_j \mu_j - \sum_{ox} \nu_j \mu_j - n \mu_e + n F \Delta\varphi$$

$e \rightarrow \varphi_{(M)}$

$ions \rightarrow \varphi_{(S)}$

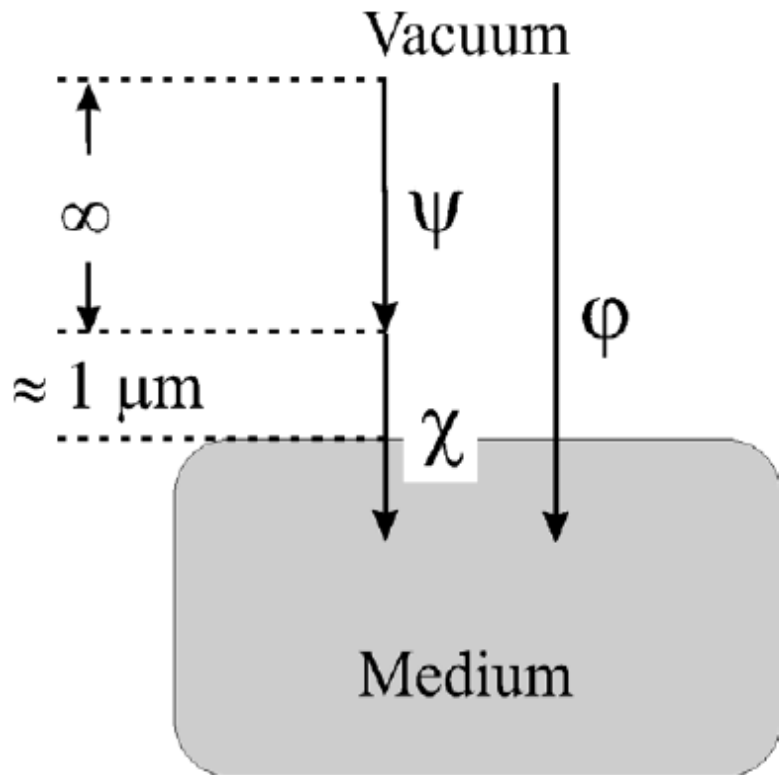
0 at equilibrium!

$$\sum_{red} \nu_j Z_j - \sum_{ox} \nu_j Z_j = n$$

charge conservation

$$\Delta\varphi = \frac{1}{nF} \left(\sum_{ox} \nu_j \mu_j - \sum_{red} \nu_j \mu_j + n \mu_e \right)$$

How Many Potentials!



The internal potential is defined by the **work**, which is required to bring a test charge from an infinite distance and from a vacuum into the interior of the phase far from the phase boundary.

DOI: 10.1109/JSEN.2008.918758

Figure 5.15: Illustration of the Galvani φ , Volta ψ , and surface potential χ .

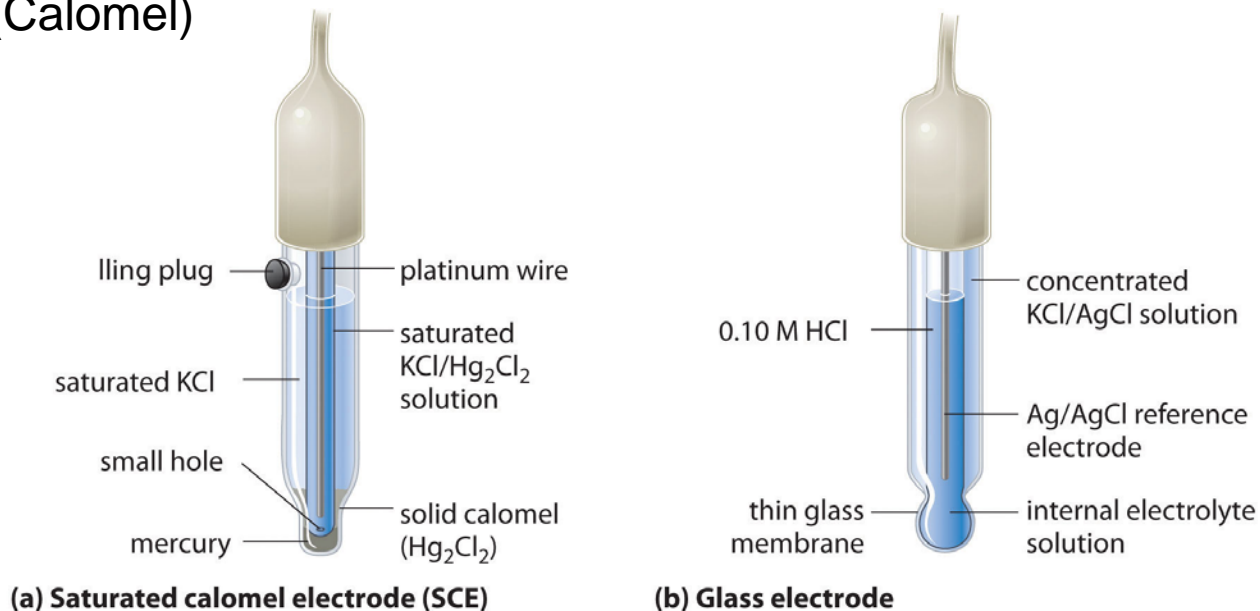
Reference Electrode

Galvani potential cannot be measured in an **absolute** way!

⇒ need of a **second** electrode, the reference electrode

- NHE (hydrogen)
- Ag/AgCl
- SCE (Calomel)

stable! ⇒ according to the chosen solution



Nernst Equation

1888

$$\Delta\varphi = \frac{1}{nF} \left(\sum_{ox} \nu_j \mu_j - \sum_{red} \nu_j \mu_j + n\mu_e \right)$$

$$\mu_j = \mu_j^0 + RT \ln a_j$$

0 = standard conditions

a_{ion} = activity

$$\Delta\varphi = \Delta\varphi_c^0 + \frac{RT}{nF} \left(\sum_{ox} \ln a_{ox,j} - \sum_{red} \ln a_{red,j} \right)$$

$$= \Delta\varphi_c^0 - \frac{RT}{nF} \ln Q$$

$$Q = \left(\prod_j a_j^{\nu_j} \right)_{equilibrium}$$

$$\nu_{prod} > 0$$

$$\nu_{react} < 0$$

gas constant R , $R = 8.31 \frac{J}{molK}$ $R = N_A k_B$

$\Delta\varphi$ and Ion Concentration

$$\Delta\varphi = \Delta\varphi_c^\circ - \frac{RT}{nF} \ln Q$$

$$= C_1 + C_2 \ln a_{ion}$$

for pure phases, $a = 1$

$$\Delta\varphi = C_1 + C_2 \ln(r[ion])$$

$$= (C_1 + C_2 \ln r) + C_2 \ln[ion]$$

$$= C' + C_2 \ln[ion]$$

Debye-Hückel theory

$$a_{ion} = r[ion]$$

$$r_{ion} = \frac{AZ^2 \sqrt{I}}{1 + Ba\sqrt{I}}$$

$$I = \frac{1}{2} \sum_j [ion]_j Z_j^2$$

A, B → constants from theory

a → ion size parameter

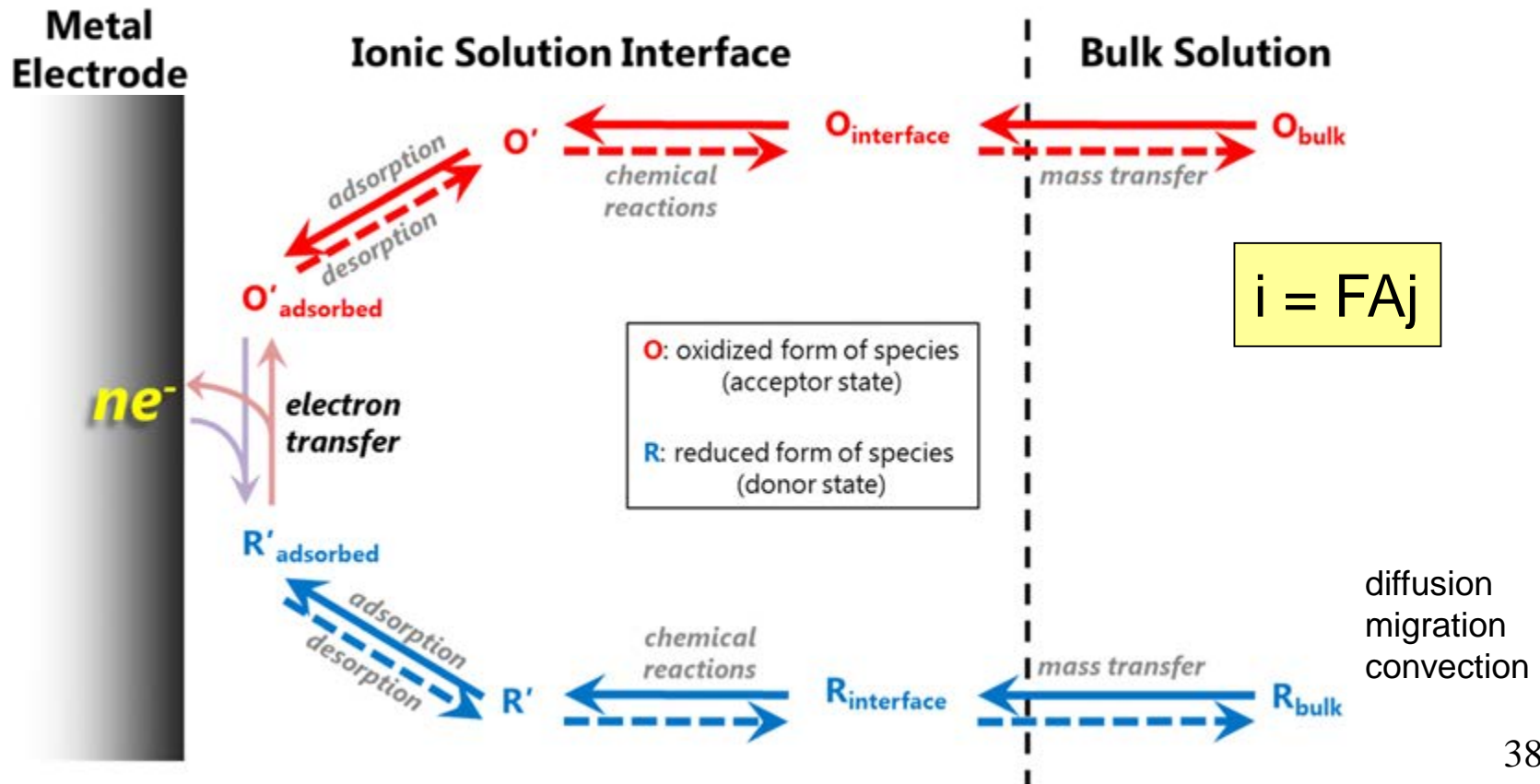
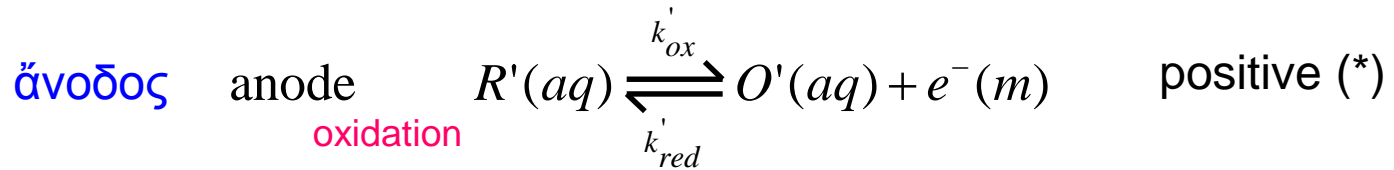
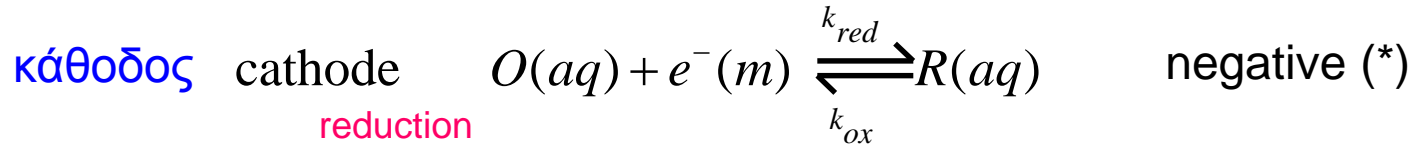
Z → number of ion charges

I → ionic strength

$C_2 = 59 \text{ mV}$ when "log" instead of "ln", $n = 1$, $T = 25 \text{ }^\circ\text{C}$

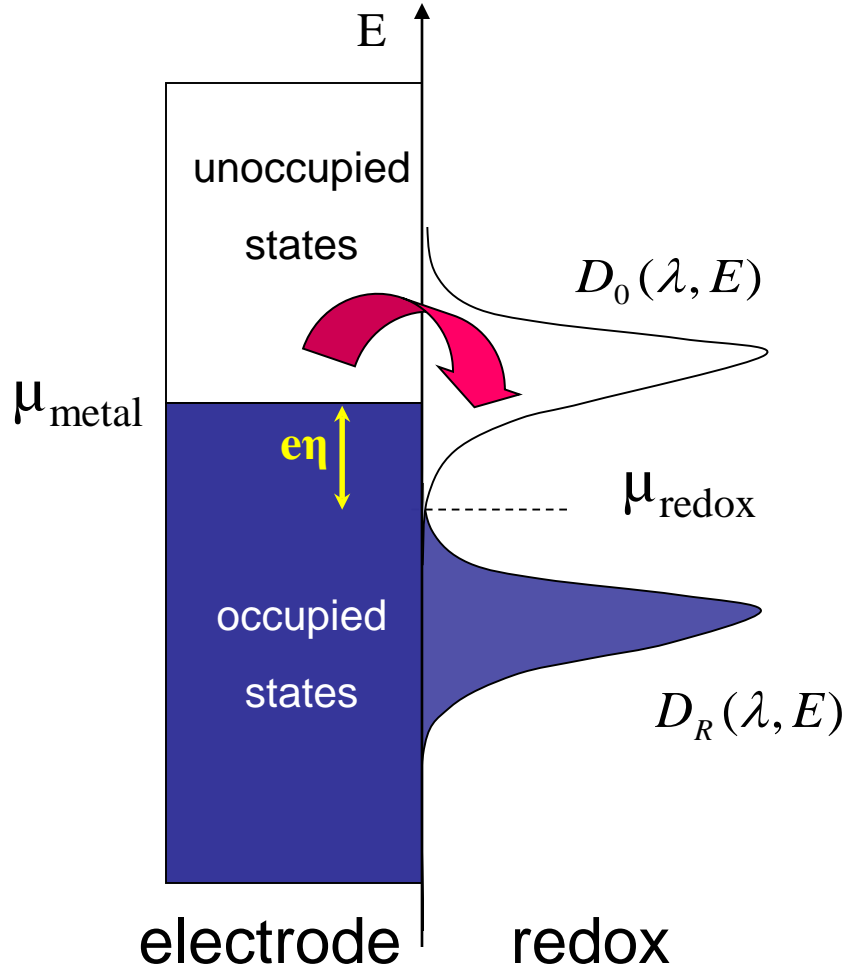


RedOx Current



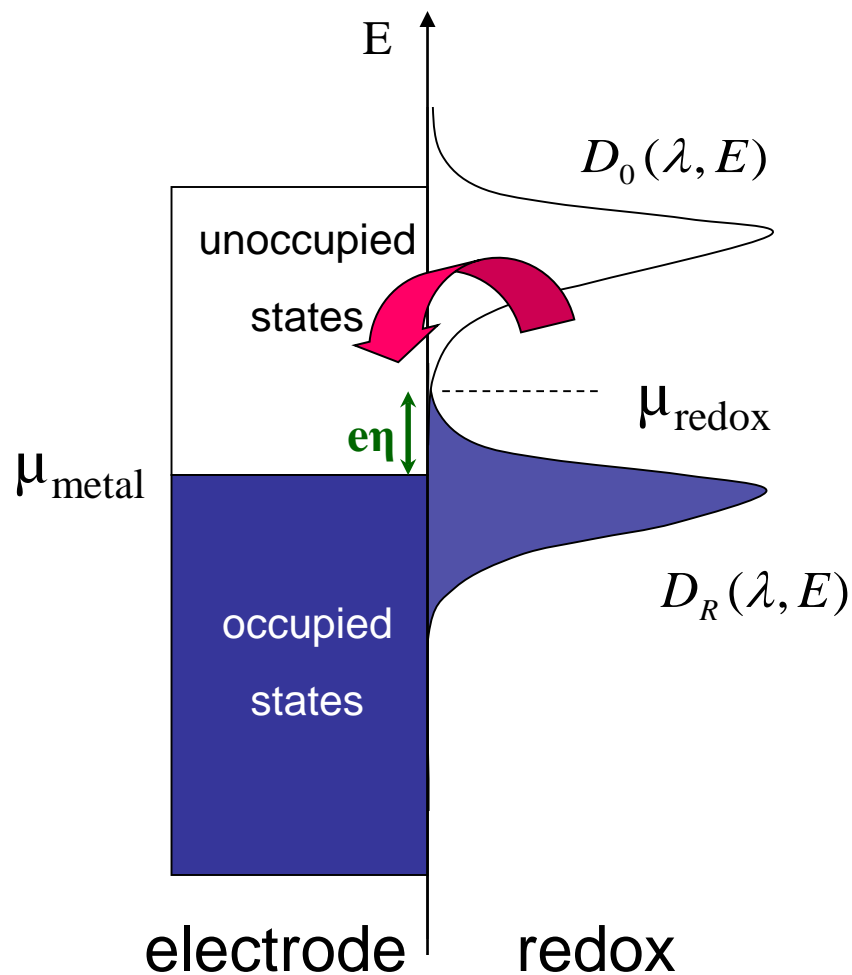


η in the Gerischer's View



cathodic polarization

$$i^+ \gg i^-$$



anodic polarization

$$i^- \gg i^+$$



Faraday's Laws

1833

First law: In electrolysis, the quantities of substances involved in the chemical change are proportional to the quantity of electricity which passes through the electrolyte.

Second law: The masses of different substances set free or dissolved by a given amount of electricity are proportional to their chemical equivalents.

$$m = \frac{q \times EW}{F} = \frac{i \times t \times EW}{F}$$

$$EW = \frac{\text{molecular weight}}{\text{valency}}$$

The mass of a compound which will combine with 8 g of oxygen or 1 g of hydrogen is said to be the equivalent weight of the compound.

Gibbs Free Energy G

1873

$$G = U + pV - TS$$

T, temperature

U, internal energy

P, pressure

V, volume

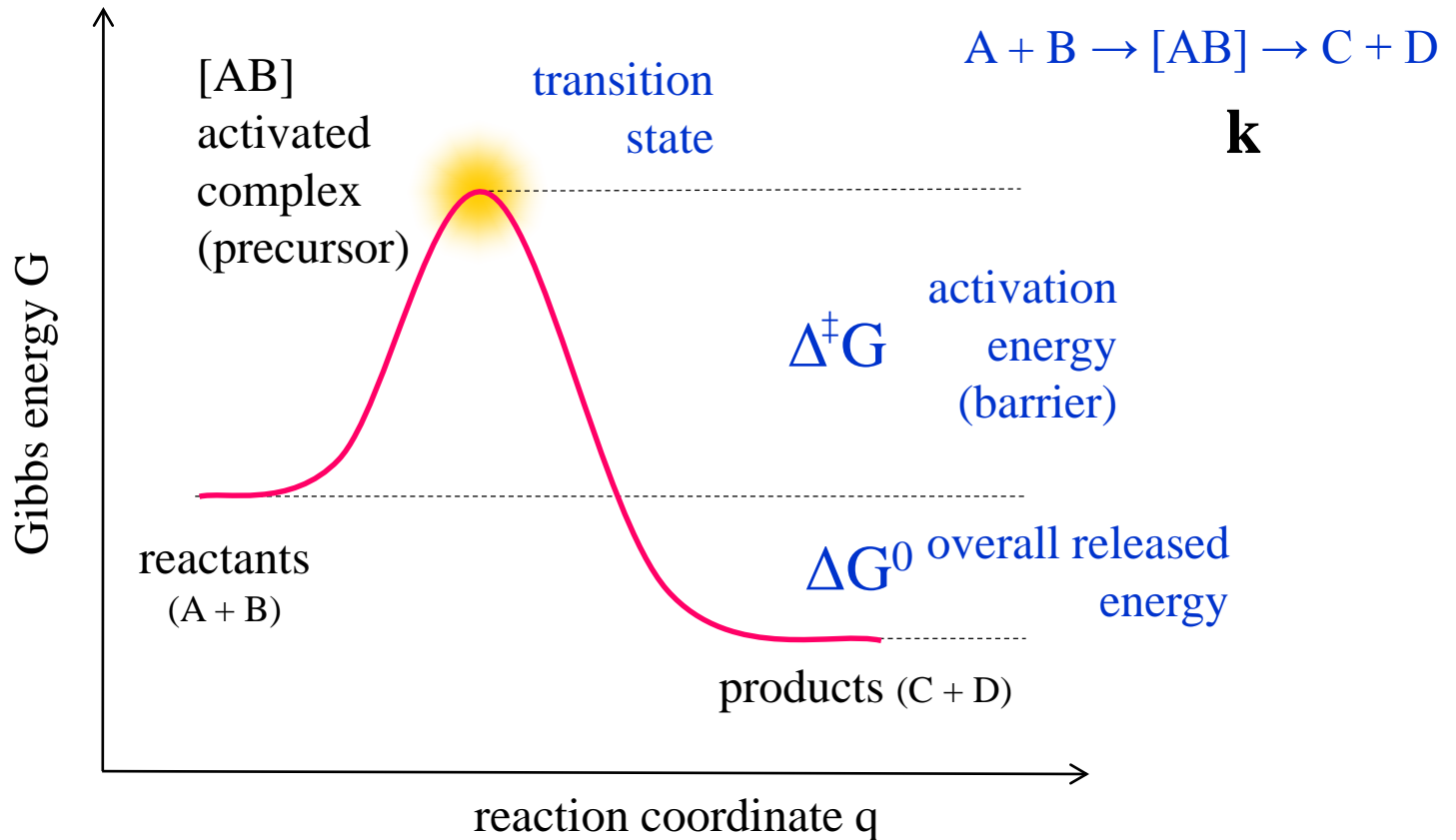
S, entropy

Every system (*T, p constant!*) seeks to achieve a *minimum* of free energy



chemical reactions in a laboratory

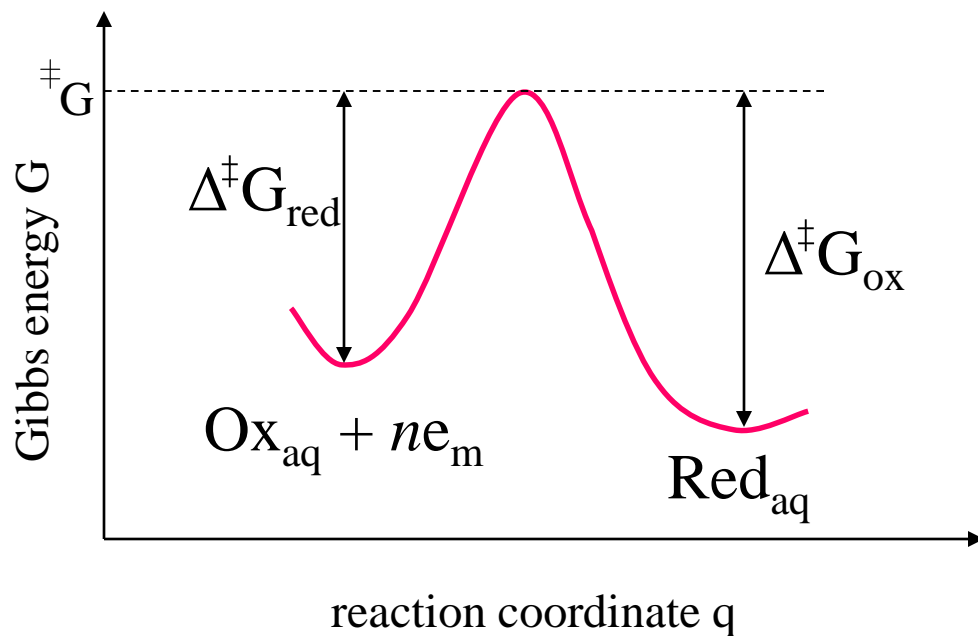
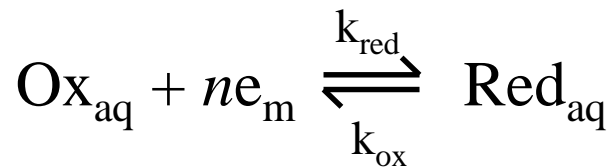
Transition State Theory



$$k \propto e^{-\frac{\Delta^\ddagger G}{RT}}$$

$$R = \frac{k_B}{N_A} = 8.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Energy Barrier



$$k_{\text{red}} = \nu_{\text{red}} e^{\frac{-\Delta^{\ddagger}G_{\text{red}}}{RT}}$$

$$k_{\text{ox}} = \nu_{\text{ox}} e^{\frac{-\Delta^{\ddagger}G_{\text{ox}}}{RT}}$$

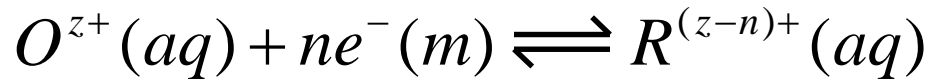
$$\Delta^{\ddagger}G_{\text{red}} = \ddagger G - G_{\text{ox}, \text{min}}$$

$$\Delta^{\ddagger}G_{\text{ox}} = \ddagger G - G_{\text{red}, \text{min}}$$



η effect on G - 1

interfacial potential



F, Faraday constant!

$$\begin{aligned} G_{\text{react}} &= G'_{\text{react}} + zF\varphi_S - nF\varphi_M \\ &= G'_{\text{react}} + (z - n)F\varphi_S - nF(\varphi_M - \varphi_S) \end{aligned}$$

$$G_{\text{prod}} = G'_{\text{prod}} + (z - n)F\varphi_S$$

overpotential

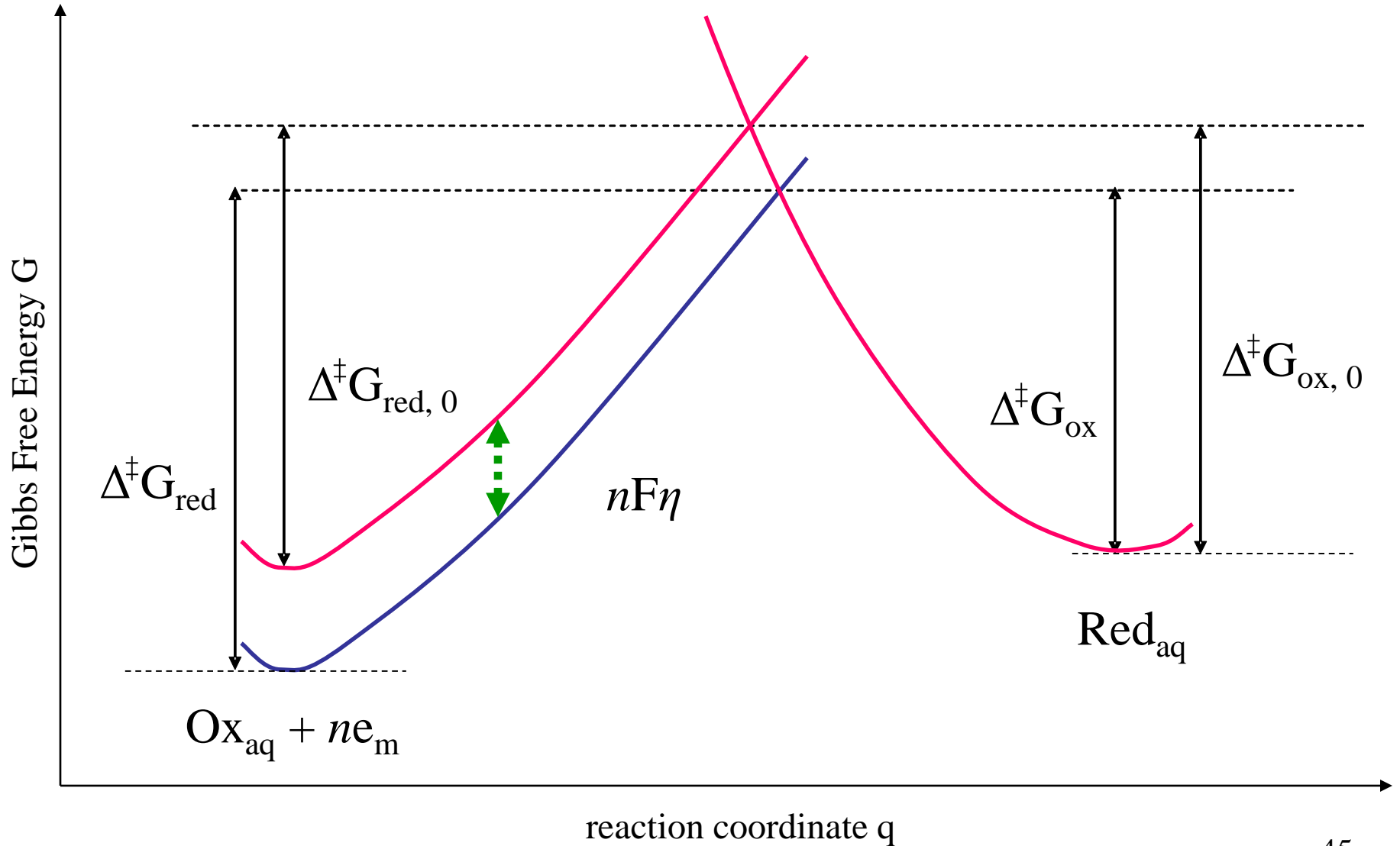
$$\eta \equiv \varphi_S - \varphi_M$$

$$\equiv \Delta\varphi|_{\text{appl}} - \Delta\varphi|_{\text{equil}}$$

$$\Delta\varphi|_{\text{equil.}} \stackrel{\text{Nernst}}{=} \Delta\varphi^0 + \frac{RT}{nF} \ln \frac{[O]}{[R]}$$

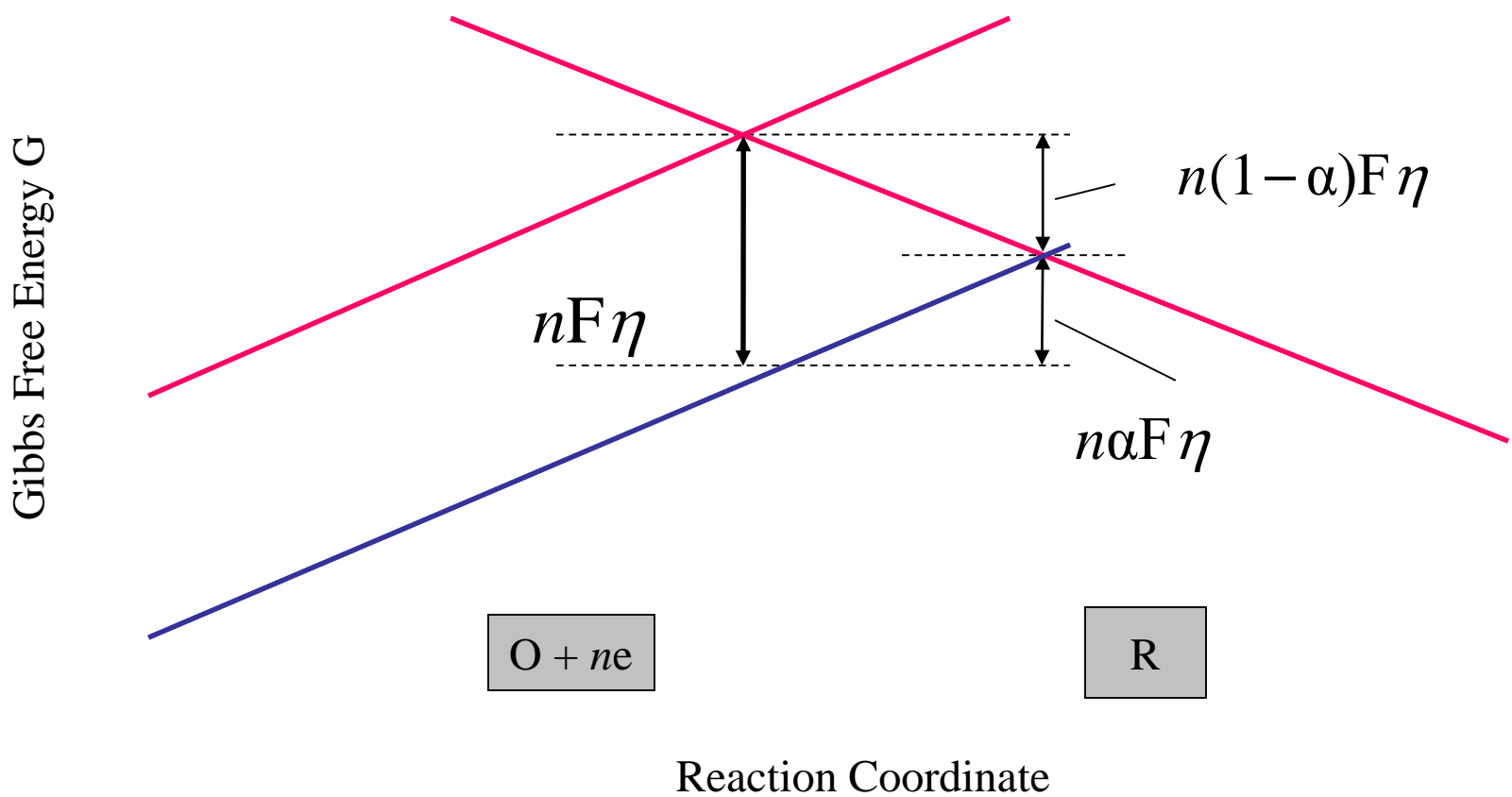


η effect on G - 2



Transfer Coefficient α

$\alpha \equiv$ *transfer* coefficient





Butler-Volmer Equation - 1

1930

$$\Delta^\ddagger G_{\text{red}} = \Delta^\ddagger G_{\text{red},0} + n\alpha F \eta$$

$$\Delta^\ddagger G_{\text{ox}} = \Delta^\ddagger G_{\text{ox},0} - n(1-\alpha)F \eta$$

$$k_{\text{red}} = A_{\text{red}} e^{-\frac{\Delta^\ddagger G_{\text{red}}}{RT}}$$

$$k_{\text{ox}} = A_{\text{ox}} e^{-\frac{\Delta^\ddagger G_{\text{ox}}}{RT}}$$

$$k_{\text{red}} = A_{\text{red}} e^{-\frac{\Delta^\ddagger G_{\text{red},0}}{RT}} e^{-n\alpha f \eta}$$

$$k_{\text{ox}} = A_{\text{ox}} e^{-\frac{\Delta^\ddagger G_{\text{ox},0}}{RT}} e^{n(1-\alpha)f \eta}$$

$$f \equiv \frac{F}{RT}$$



Butler-Volmer Equation - 2

zero net current! (\rightarrow corrosion!)

at equilibrium with $C(0, t) = C^*$, $\eta = 0 \Rightarrow k_{\text{ox}} = k_{\text{red}} \equiv k_0$

$$k_{\text{red}} = k_0 e^{-n\alpha f \eta}$$

$$k_{\text{ox}} = k_0 e^{n(1-\alpha) f \eta}$$

$$i = nFAk_0 [C_{\text{ox}}(0, t)e^{-\alpha n f \eta} - C_{\text{red}}(0, t)e^{(1-\alpha) n f \eta}]$$

$n \equiv$ number of e^- exchanged

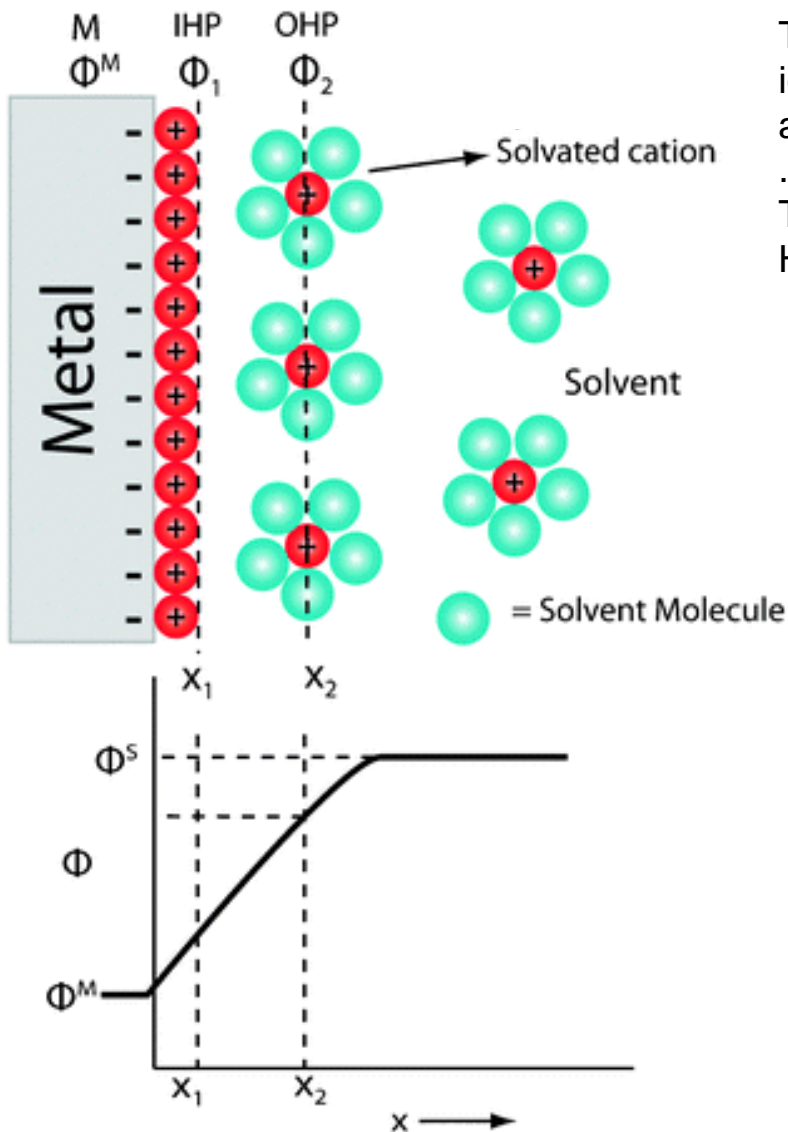
$\eta \equiv$ overpotential

$$f = \frac{F}{RT} = \frac{1}{25.69 \text{ mV}} \text{ (at 298 K)}$$

$$F = 9.6485 \times 10^4 \text{ C mol}^{-1}$$

$$R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$$

Helmholtz double layer



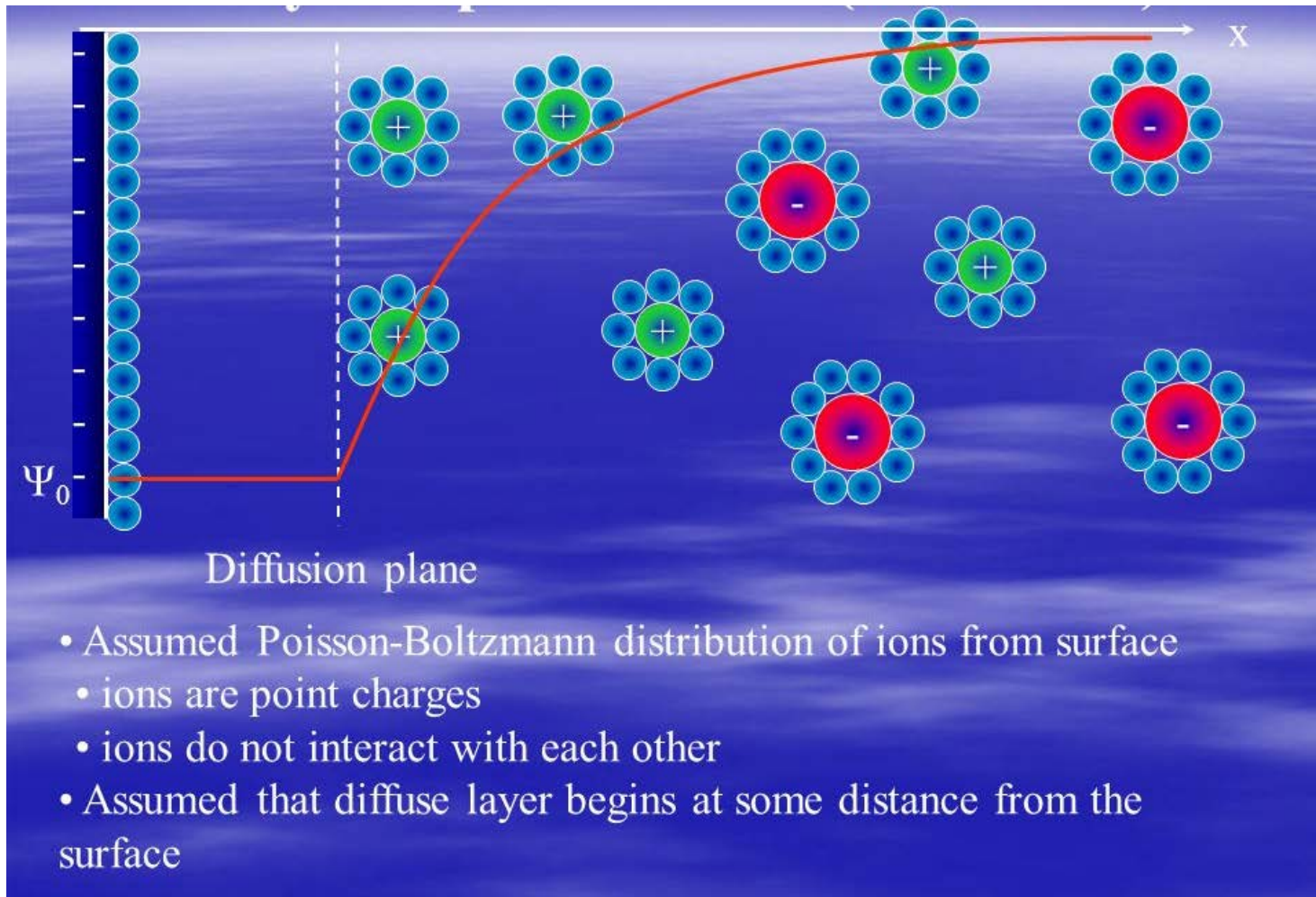
The inner-most or compact layer is composed of solvent, ions, and molecules that are **not fully** solvated, and which are said to be specifically adsorbed to the electrode surface.

The center of this adsorbed layer defines the inner Helmholtz plane (IHP).

OHP represents the closest approach of solvated ions to the surface of the electrode. These solvated ions interact with the surface of the electrode in a long-range electrostatic fashion only, and are said to be non-specifically adsorbed. The center of this second layer defines the outer Helmholtz plane



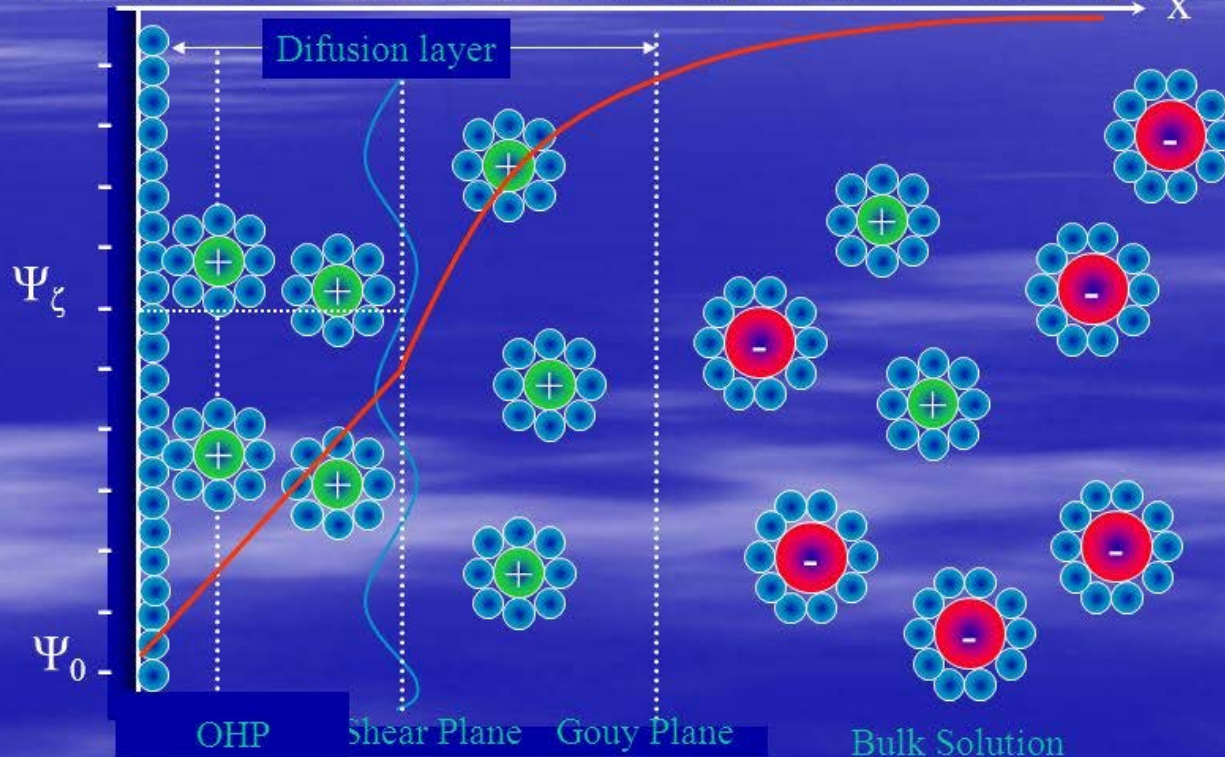
Gouy-Chapman (diffuse)

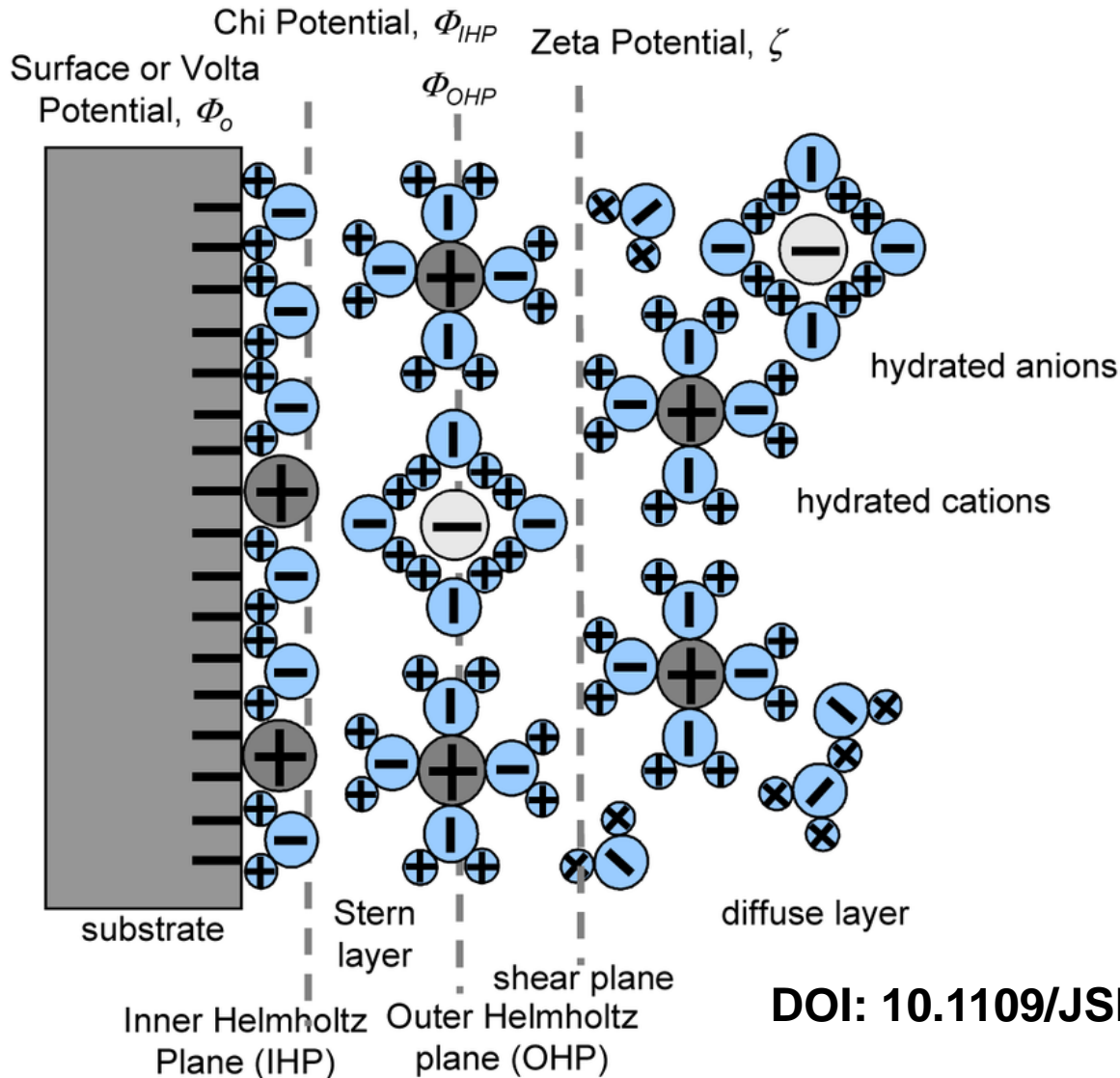


<http://slideplayer.com>

Stern (1924) / Grahame (1947) Model

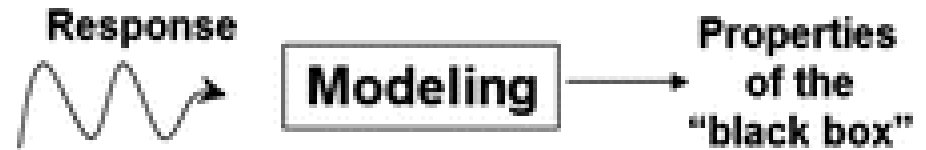
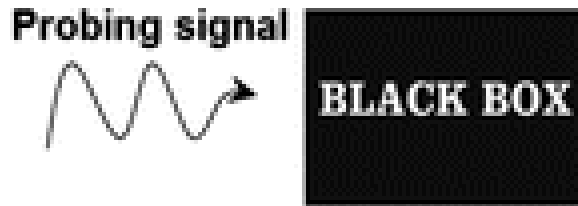
In different approaches the linear decay is assumed to be until the shear plane, since there is the barrier where the charges considered static. In this course however we will assume that the decay is linear until the Stern plane.



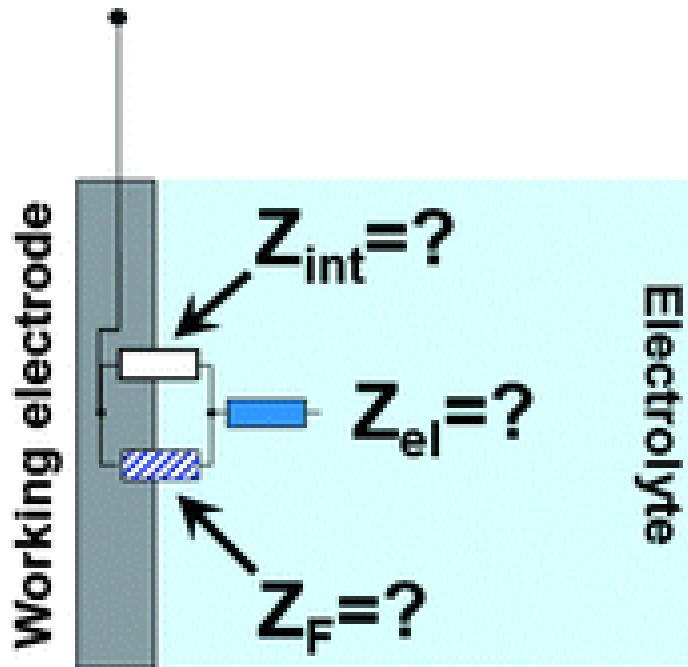


DOI: 10.1109/JSEN.2008.918758

equivalent circuit

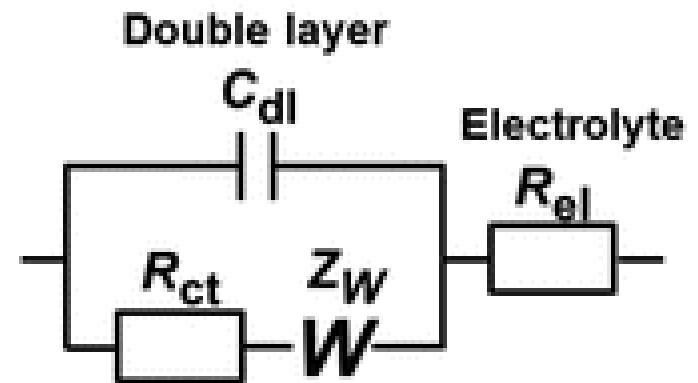


(B)



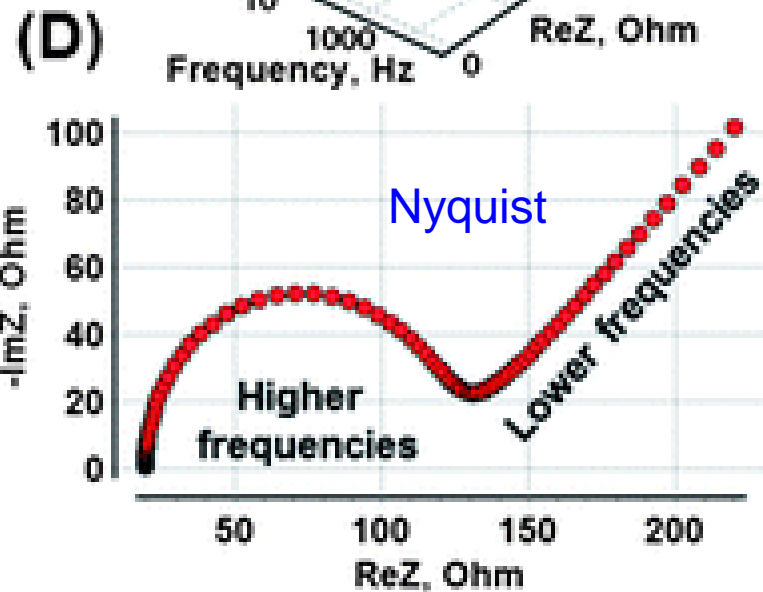
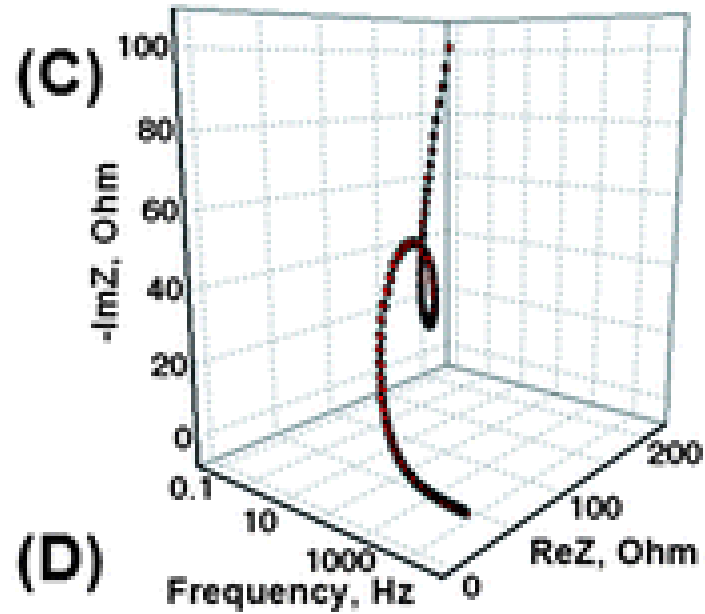
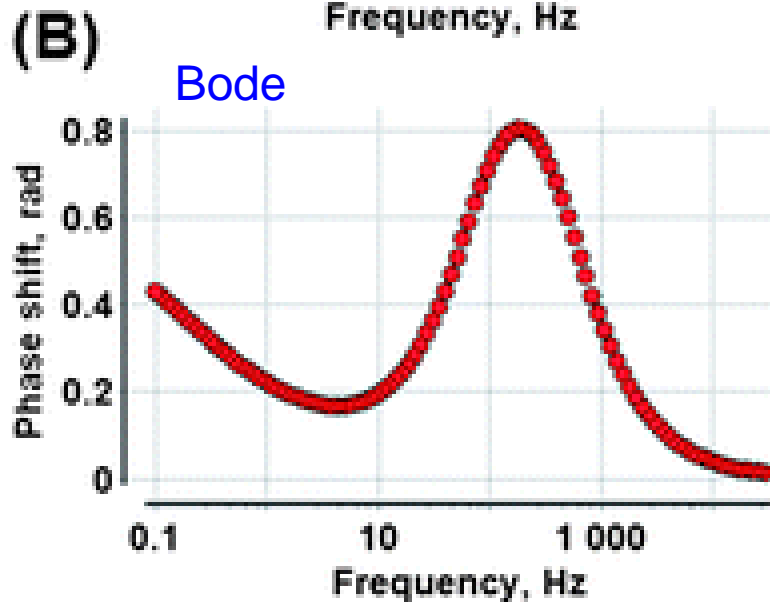
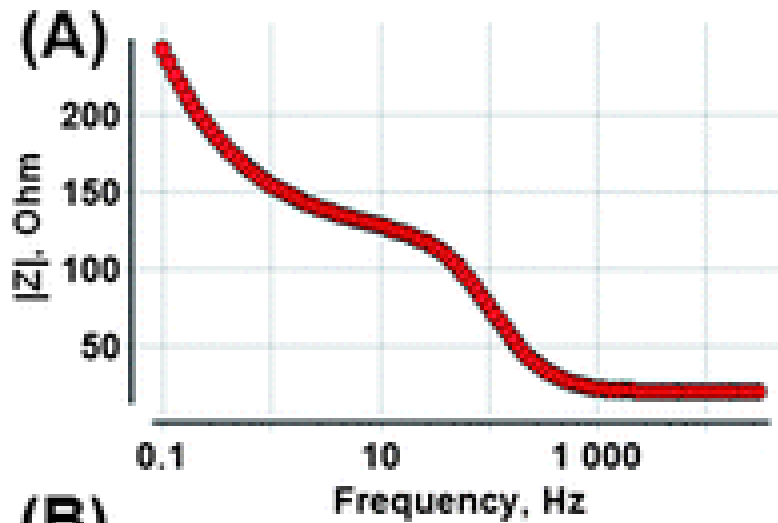
(C)

A common equivalent electric circuit

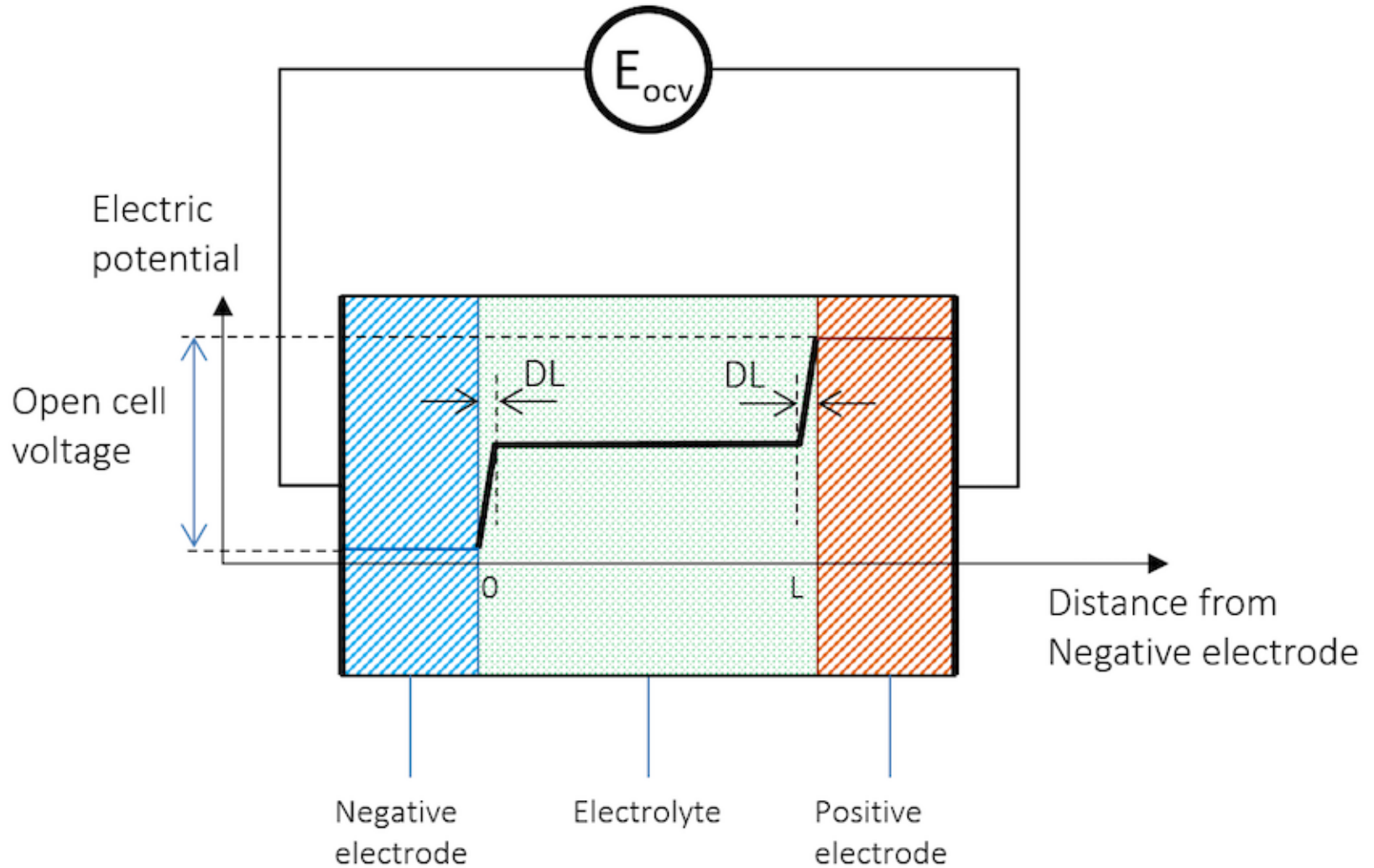


Diffusion and charge transfer

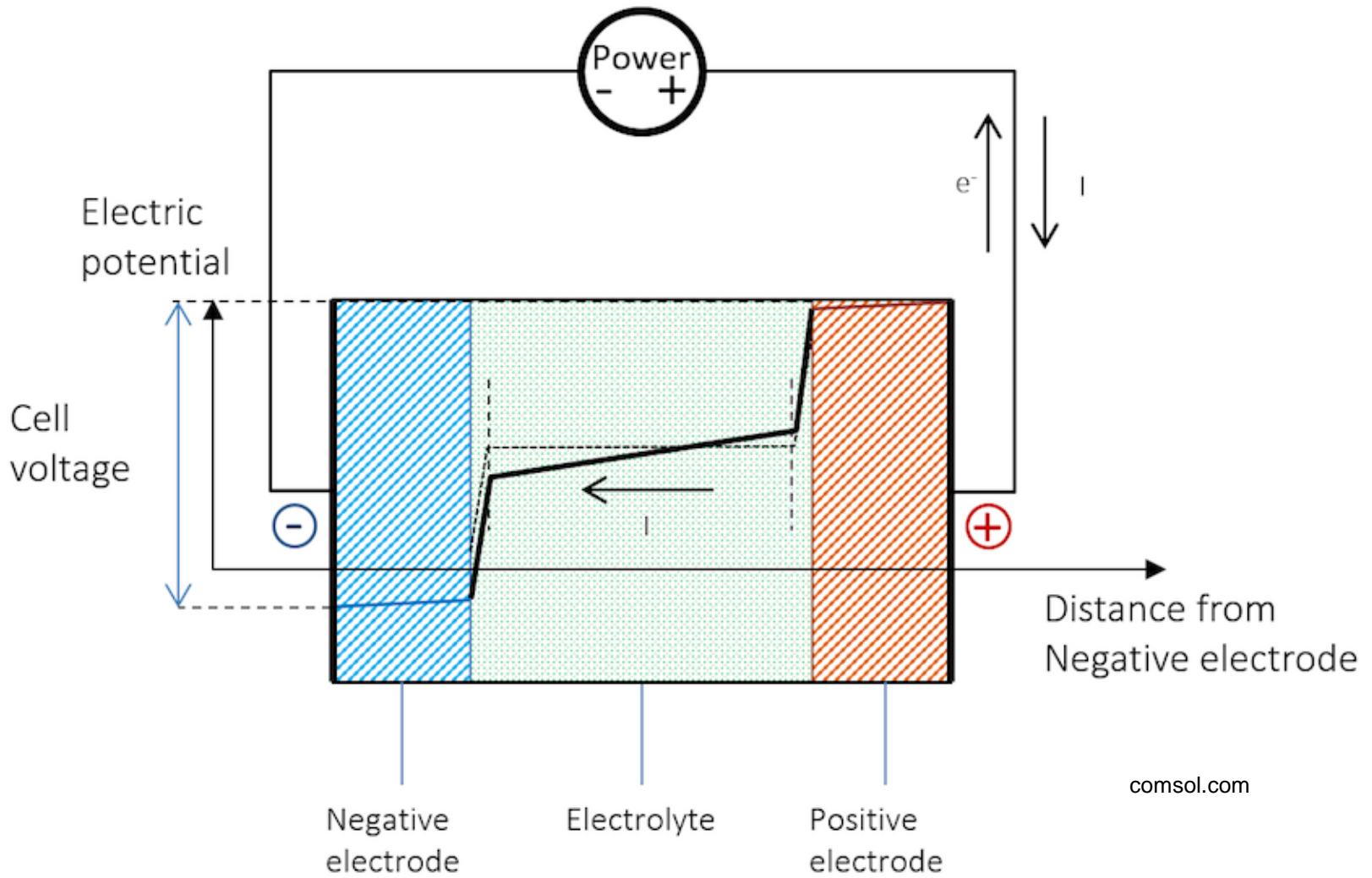
EIS



Open Circuit Potential



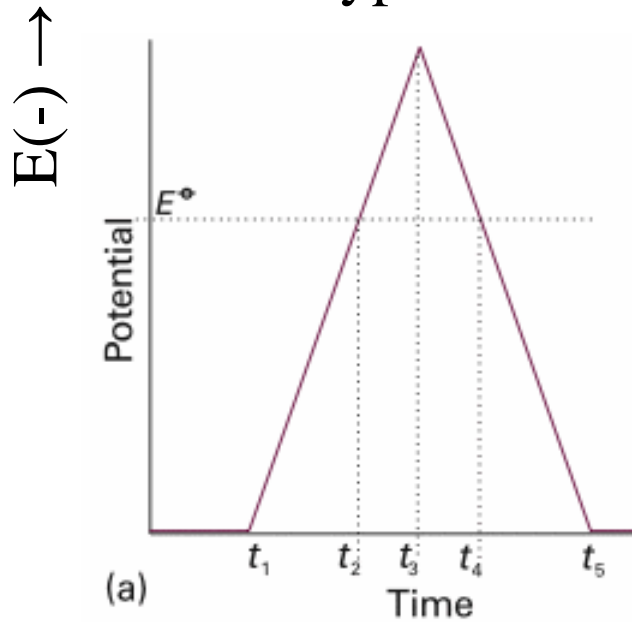
2 electrodes? better 3!



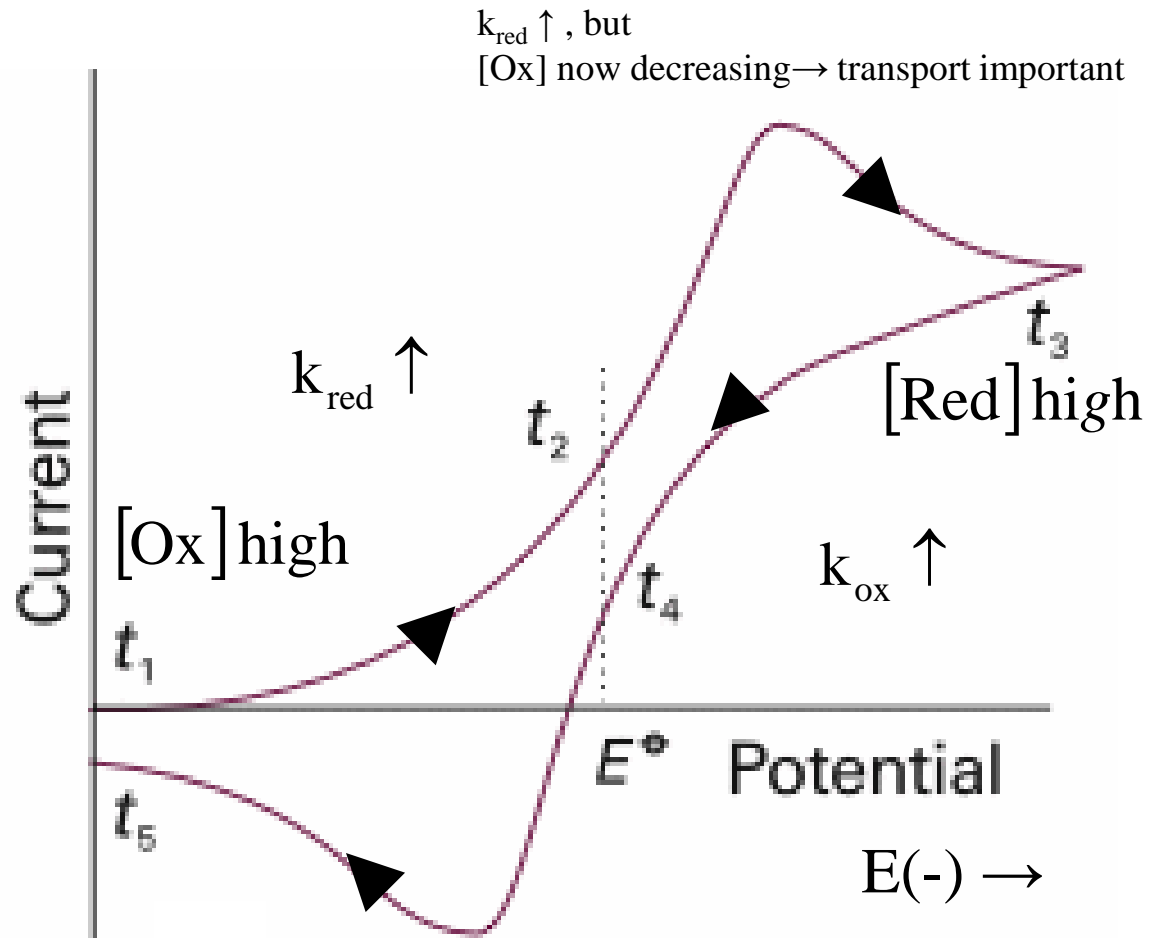
comsol.com

Cyclic Voltammetry

hypothesis → at t_1 only Ox in solution

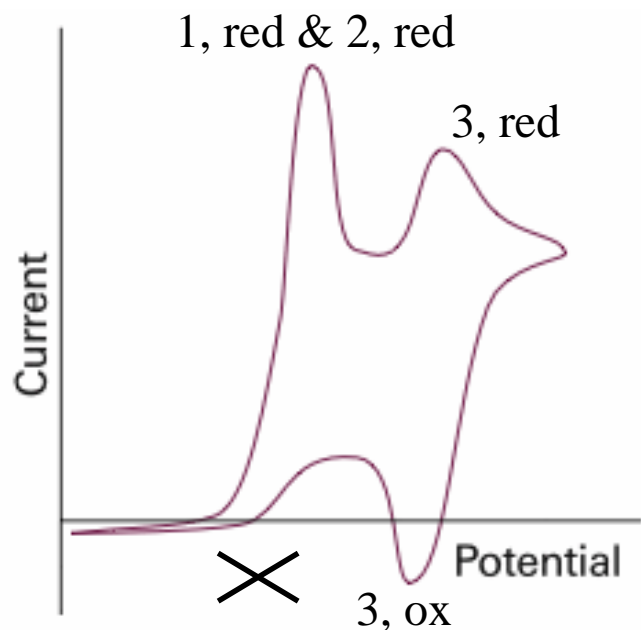


- concentrations
- diffusion constants
- reaction mechanism



$k_{\text{ox}} \uparrow$, but
[Red] now decreasing → transport important

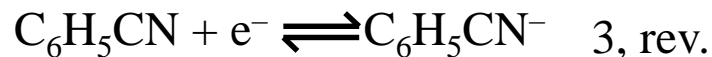
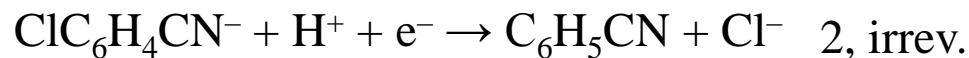
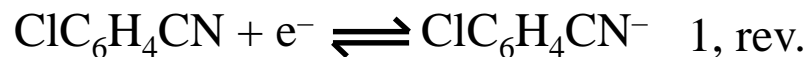
CV, irreversible step



Atkins 25.47

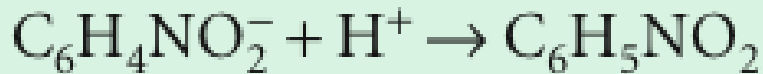
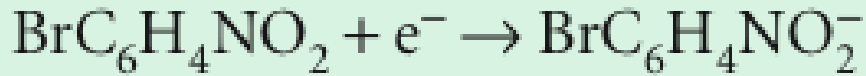
irreversible step → NO reverse peak 1!!!

p-chlorobenzonitrile



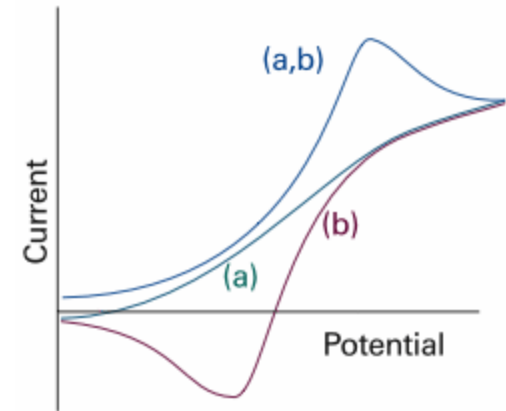
CV, sweep rate

p-bromonitrobenzene



1, rev.

2, irrev.

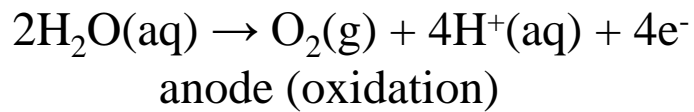
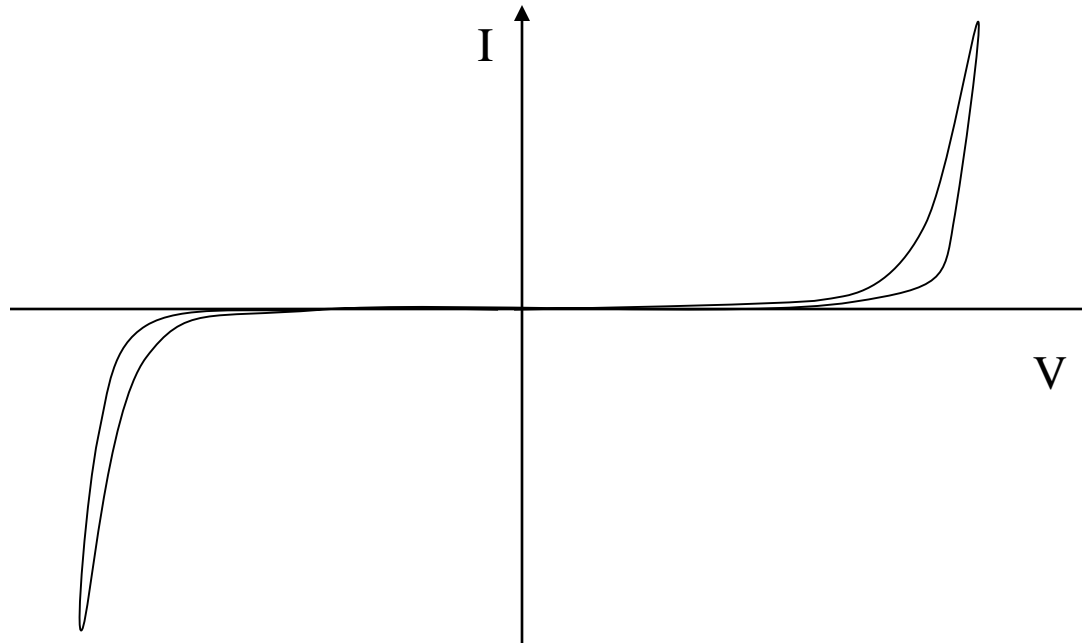
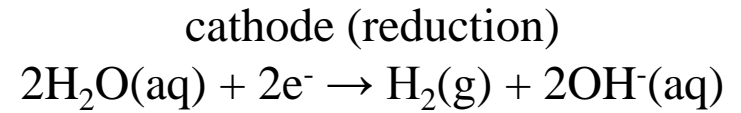


Atkins 25.46

irreversible step \rightarrow NO reverse peak!!!

...but if CV faster than irreversible step \rightarrow reversible CV!!!

Water Electrolysis





bibliography

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- A.J. Bard, L.R. Faulkner, *Electrochemical Methods*, Wiley