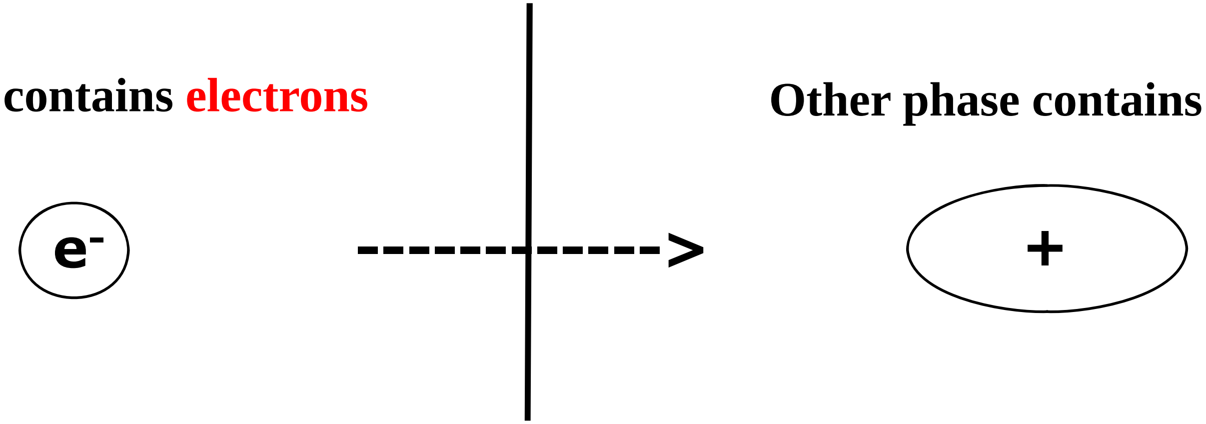
Understanding the Electrochemistry: Some Distinctive Concepts

Prof. Byungwoo Park

Seoul National University
Electromaterials and Nanomaterials Group

http://bp.snu.ac.kr

Introduction



One phase contains electrons

Other phase contains ions

Fundamental act in electrochemistry

"Passage of Current Caused by Chemical Changes"

Broad Field: sensors, electro-analysis, electro-synthesis,
electrodeposition, corrosion, and
dye-sensitized solar cell (DSC), fuel cell, and battery.

Electrochemistry is the Study of Phenomena at the Electrode/Electrolyte Interfaces.

Introduction

Electrode reactions such as (1), (2), and (3) can only happen at the interface.

$$2H^{+} + 2e \rightarrow H_2 \qquad (1)$$

$$Cu^{2+} + 2e \rightarrow Cu \qquad (2)$$

$$FeCp_2 \rightarrow FeCp_2^{+} + e \qquad (3)$$

Electrode reactions tend to make the composition in the nearby solution different from that further away.

There is a tendency for the system to transport **reactants** from remote points and the depleted zone widens as the reaction proceeds (Fig.1(b)).

Just as the **reactants** is depleted near the interface, the **product** accumulates nearby as shown in Fig. 1(c).

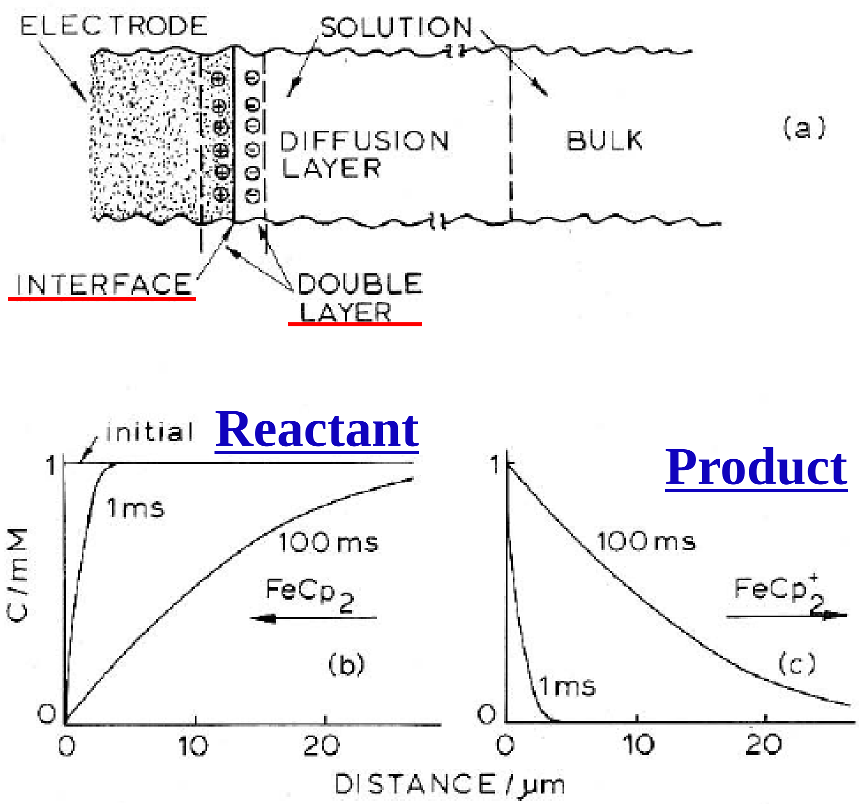


Figure 1. (a) Spatial structure of an electrochemical system. (b) Concentration profiles of ferrocene undergoing oxidation at the electrode. Distance is measured from the electrode toward the bulk. Times are elapsed periods from start of electrolysis. (c) Concentration profiles of ferricenium produced by oxidation of ferrocene.

Faulkner, Journal of Chem., Education, 1983

Potential is an Expression of Electron Energy.

Standard potential: oxidation/reduction possible.

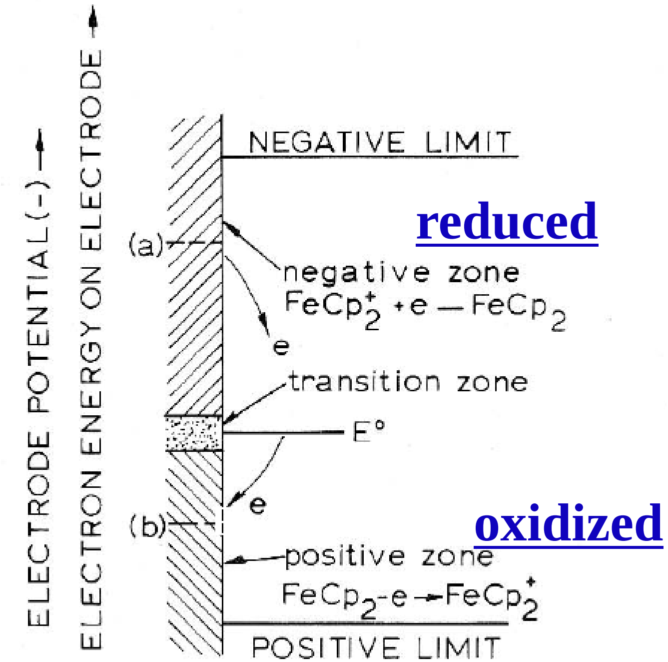


Figure 3. Illustration of potential as an expression of electron energy. At potential (a) ferricenium at the surface would be reduced to ferrocene. At potential (b) ferrocene at the surface is oxidized to ferricenium. The potential limits correspond to values for which the solvent, supporting electrolyte, or electrode material are oxidized or reduced.

The energy required to add or subtract an electron from the electrode can also be expressed in this potential.

Any electrode process is characterized by its own standard potential E^0.

On the positive side of E^0, the oxidized form of the redox couple is stable, whereas the reduced form is stable on the potential more negative than E^0.

In the zone ~100 mV wide centered on E^0, statistical equilibrium of electrons on the electrode and species in the solution permits mixtures of oxidized and reduced forms with appreciable amounts (transition zone).

Potential is an expression of electron energy.

Faulkner, Journal of Chem., Education, 1983

Work Function (not real)

Ashcroft, Solid State Physics

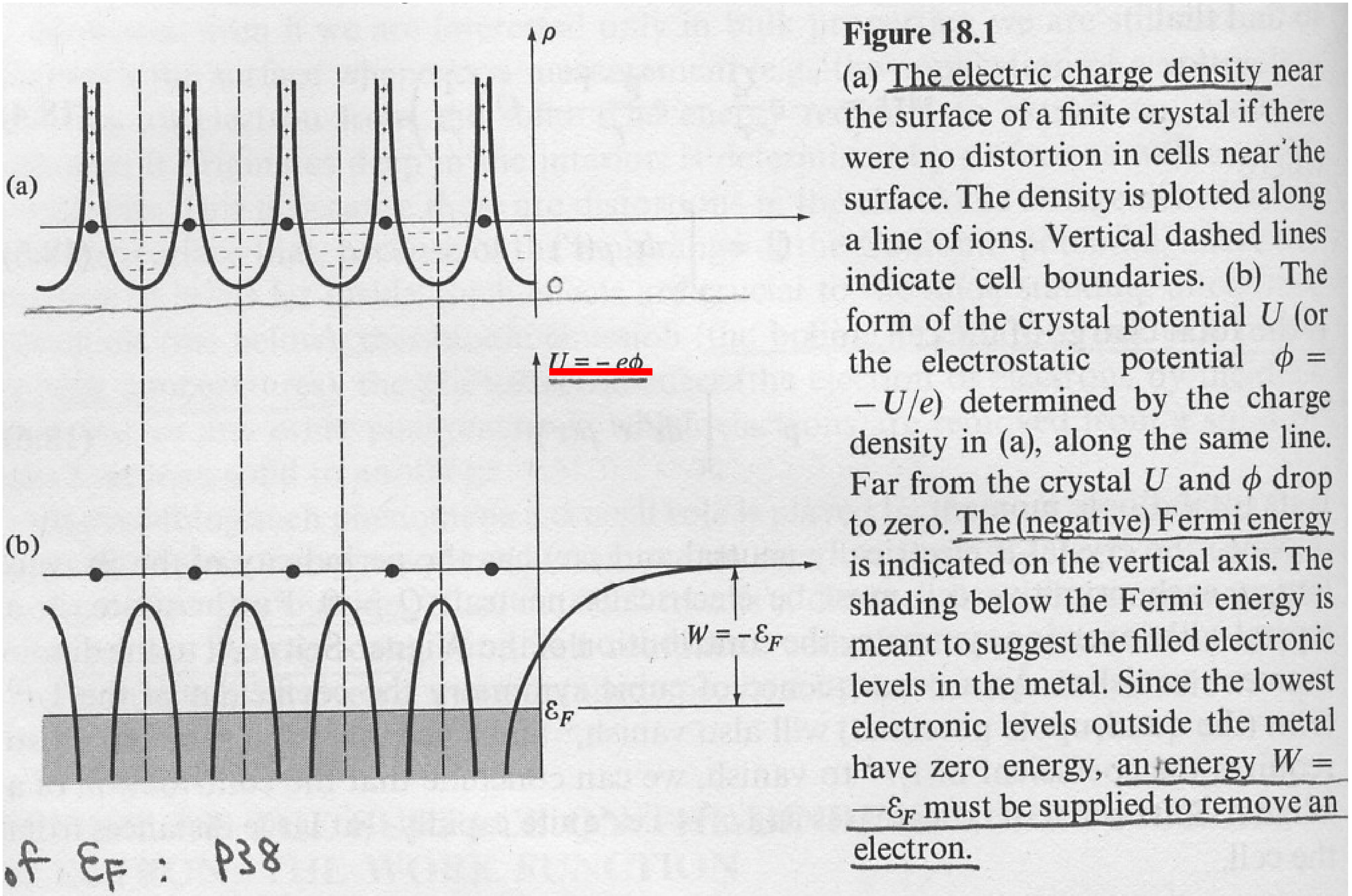


Figure 18.1
(a) The electric charge density near the surface of a finite crystal if there were no distortion in cells near the surface. The density is plotted along a line of ions. Vertical dashed lines indicate cell boundaries. (b) The form of the crystal potential U (or the electrostatic potential $\phi = -U/e$) determined by the charge density in (a), along the same line. Far from the crystal U and ϕ drop to zero. The (negative) Fermi energy is indicated on the vertical axis. The shading below the Fermi energy is meant to suggest the filled electronic levels in the metal. Since the lowest electronic levels outside the metal have zero energy, an energy $W = -\mathcal{E}_F$ must be supplied to remove an electron.

of $\mathcal{E}_F$: P38

Double Layer – Work Function

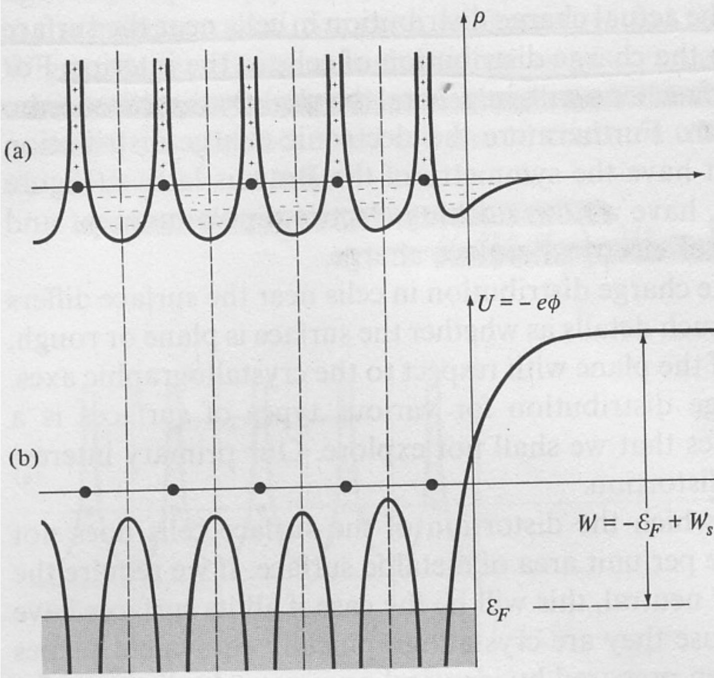


Figure 18.2
(a) The actual form of the electric charge density near the surface of a crystal (neglecting possible slight displacements of the ions near the surface from their sites in the infinite crystal). Note the electron deficiency in the two cells nearest the surface and the presence of electronic charge in the first "cell" on the vacuum side of the surface. It is this kind of distortion that produces the "double layer" described below. (b) The form of the crystal potential U determined by the charge density in (a). If the additive constant is chosen so that U resembles the potential of Fig. 18.1b far inside the crystal, then outside of the crystal U will not approach zero, but the value W_s equal to the work that must be done to carry an electron through the electric field in the double layer. The lowest levels outside the crystal now have an energy W_s, and therefore an energy $W = -\mathcal{E}_F + W_s$ must be supplied to remove an electron.

Ashcroft
Solid State Physics

Work Function

C. Kittel, Solid State Physics, 8th edition

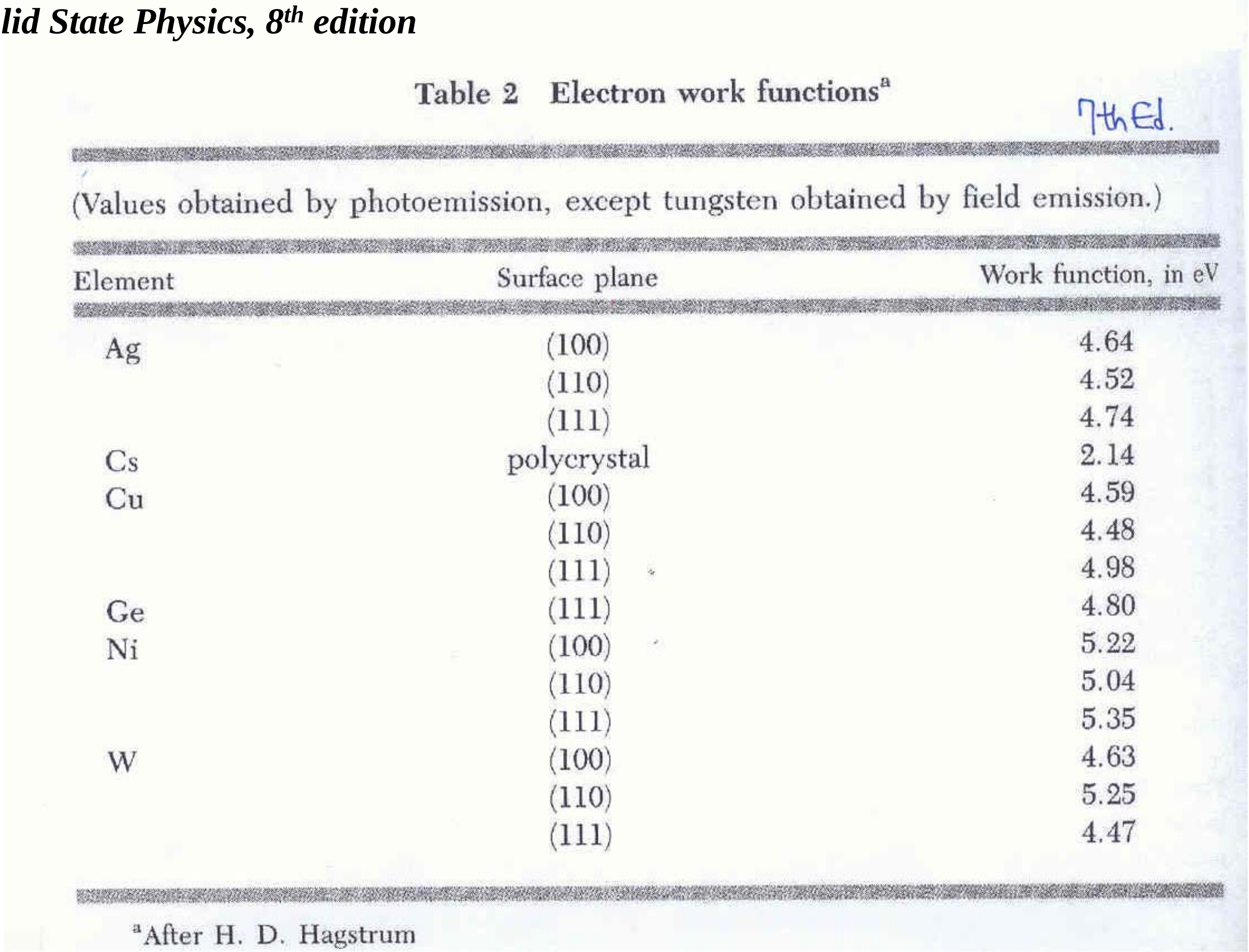


Table 2 Electron work functions[a]

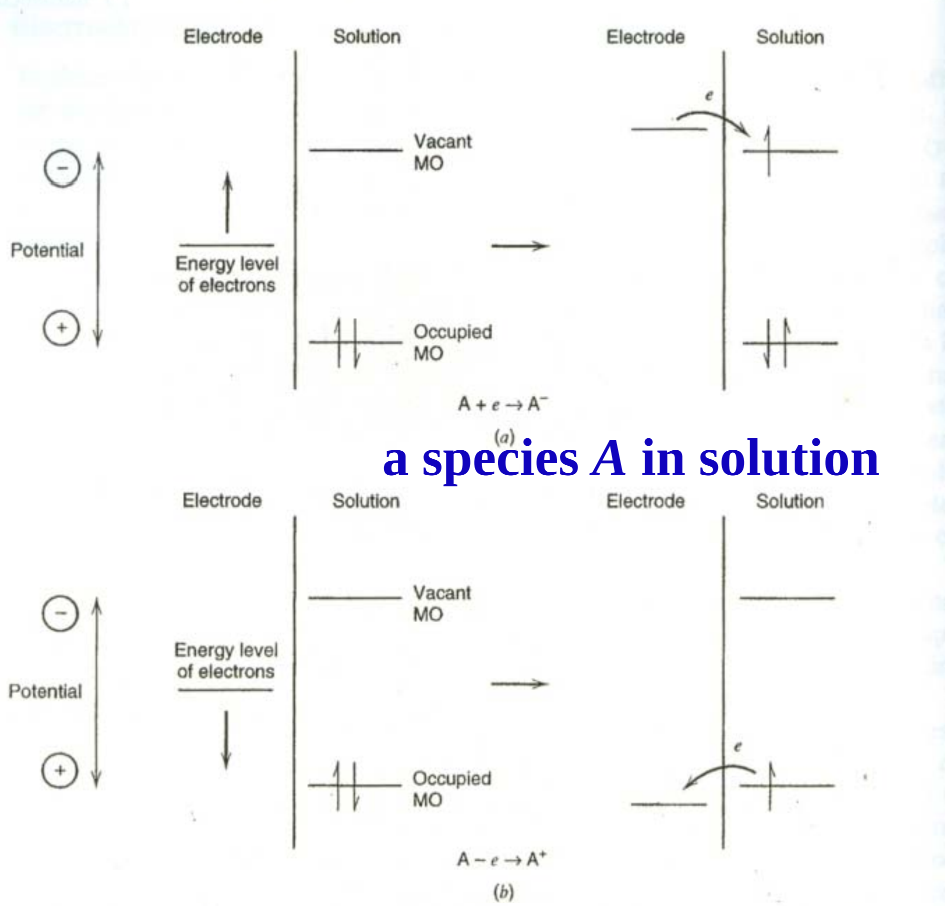
7th Ed.

(Values obtained by photoemission, except tungsten obtained by field emission.)

Element	Surface plane	Work function, in eV
Ag	(100)	4.64
	(110)	4.52
	(111)	4.74
Cs	polycrystal	2.14
Cu	(100)	4.59
	(110)	4.48
	(111)	4.98
Ge	(111)	4.80
Ni	(100)	5.22
	(110)	5.04
	(111)	5.35
W	(100)	4.63
	(110)	5.25
	(111)	4.47

[a] After H. D. Hagstrum

Electron Transfer at Interface



a species *A* in solution

Figure 1.1.2 Representation of (*a*) reduction and (*b*) oxidation process of a species, A, in solution. The molecular orbitals (MO) of species A shown are the highest occupied MO and the lowest vacant MO. These correspond in an approximate way to the E^0s of the A/A$^-$ and A$^+$/A couples, respectively. The illustrated system could represent an aromatic hydrocarbon (e.g., 9,10-diphenylanthracene) in an aprotic solvent (e.g., acetonitrile) at a platinum electrode.

Magnitude of the potential controls the direction and rate of charge transfer.

As a potential is moved negative, the species that will be reduced first (assuming all are rapid) is the oxidant (acceptor) in the couple with the least negative E^0.

A. J. Bard, Electrochemical Methods, 2nd edition

Standard Electrode Potential

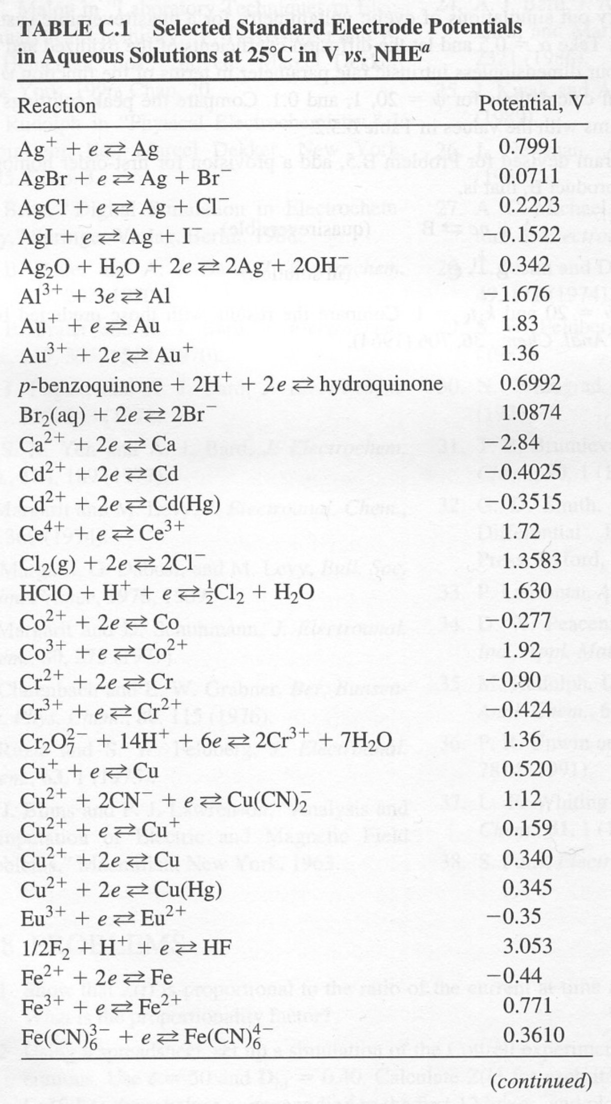


TABLE C.1 Selected Standard Electrode Potentials in Aqueous Solutions at 25°C in V *vs.* NHE[a]

Reaction	Potential, V
$Ag^+ + e \rightleftarrows Ag$	0.7991
$AgBr + e \rightleftarrows Ag + Br^-$	0.0711
$AgCl + e \rightleftarrows Ag + Cl^-$	0.2223
$AgI + e \rightleftarrows Ag + I^-$	−0.1522
$Ag_2O + H_2O + 2e \rightleftarrows 2Ag + 2OH^-$	0.342
$Al^{3+} + 3e \rightleftarrows Al$	−1.676
$Au^+ + e \rightleftarrows Au$	1.83
$Au^{3+} + 2e \rightleftarrows Au^+$	1.36
p-benzoquinone + $2H^+ + 2e \rightleftarrows$ hydroquinone	0.6992
$Br_2(aq) + 2e \rightleftarrows 2Br^-$	1.0874
$Ca^{2+} + 2e \rightleftarrows Ca$	−2.84
$Cd^{2+} + 2e \rightleftarrows Cd$	−0.4025
$Cd^{2+} + 2e \rightleftarrows Cd(Hg)$	−0.3515
$Ce^{4+} + e \rightleftarrows Ce^{3+}$	1.72
$Cl_2(g) + 2e \rightleftarrows 2Cl^-$	1.3583
$HClO + H^+ + e \rightleftarrows \frac{1}{2}Cl_2 + H_2O$	1.630
$Co^{2+} + 2e \rightleftarrows Co$	−0.277
$Co^{3+} + e \rightleftarrows Co^{2+}$	1.92
$Cr^{2+} + 2e \rightleftarrows Cr$	−0.90
$Cr^{3+} + e \rightleftarrows Cr^{2+}$	−0.424
$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftarrows 2Cr^{3+} + 7H_2O$	1.36
$Cu^+ + e \rightleftarrows Cu$	0.520
$Cu^{2+} + 2CN^- + e \rightleftarrows Cu(CN)_2^-$	1.12
$Cu^{2+} + e \rightleftarrows Cu^+$	0.159
$Cu^{2+} + 2e \rightleftarrows Cu$	0.340
$Cu^{2+} + 2e \rightleftarrows Cu(Hg)$	0.345
$Eu^{3+} + e \rightleftarrows Eu^{2+}$	−0.35
$1/2F_2 + H^+ + e \rightleftarrows HF$	3.053
$Fe^{2+} + 2e \rightleftarrows Fe$	−0.44
$Fe^{3+} + e \rightleftarrows Fe^{2+}$	0.771
$Fe(CN)_6^{3-} + e \rightleftarrows Fe(CN)_6^{4-}$	0.3610

(continued)

NHE (= SHE)

Normal Hydrogen Electrode

- Neglect any orientational dependence
- 298 K
- Acid solution with
  an activity of H^+ = 1 mol/liter (pH 0)

A. J. Bard, Electrochemical Methods, 2nd edition

$$E^M_{(abs)} \cong E^M_{(SHE)} + 4.44\ \mathrm{eV}$$

Current is an Expression of Rate.

Usually we focus attention on a single electrode called the *working electrode*

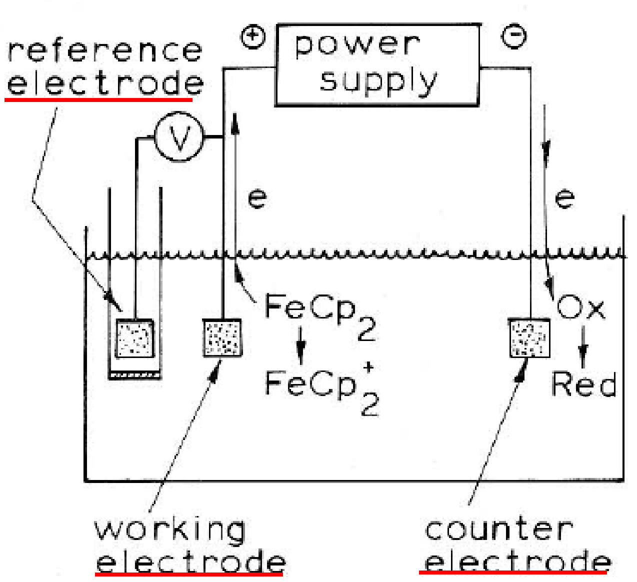


Figure 2. Structure of an electrochemical cell. The voltmeter has a high impedance, so current does not flow in the circuit between the working and reference electrodes.

Suppose ferrocene is being oxidized.

$FeCp_2 \rightarrow FeCp_2^+ + e$ (3)

Each molecule that is oxidized gives up electrons to the working electrode.

The electron will pass through the external circuit, and back into the solution at a second electrode called the *counter electrode.*

Electrons at either electrode can flow into or out of the electrode by way of external circuit which can be

oxidizing or reducing current

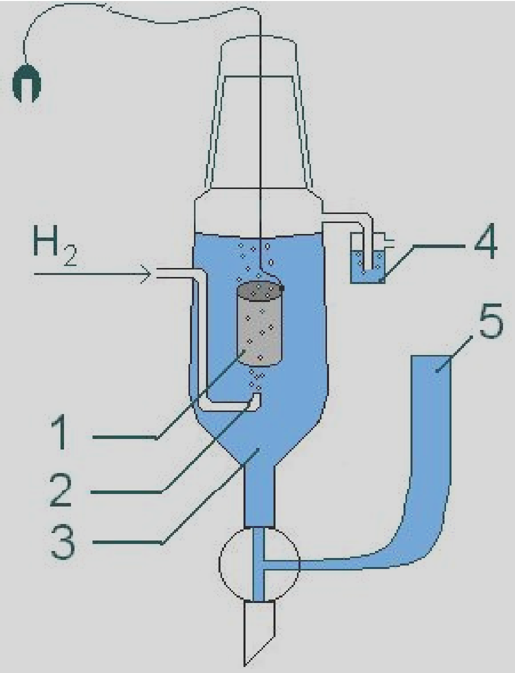
(*anodic or cathodic*).

The flow of electrons is directly proportional to the rate of reaction there. So, **the current is an expression of rate.**

Faulkner, Journal of Chem., Education, 1983

Reference Electrode

Standard Hydrogen Electrode = NHE



(image from Wikipedia)

1. Platinized platinum electrode.
2. Hydrogen gas.
3. **Acid solution with an activity of H^+ = 1 mol/liter.**
4. Hydroseal for prevention of oxygen interference.
5. Reservoir via which the second half-element of the galvanic cell should be attached.

Potentials actually mean the voltage differences between a working electrode and a reference electrode.

The reference electrode is arranged so that it does not pass current, and is in equilibrium.

The reference electrode is constructed so that it contains both forms of redox couple

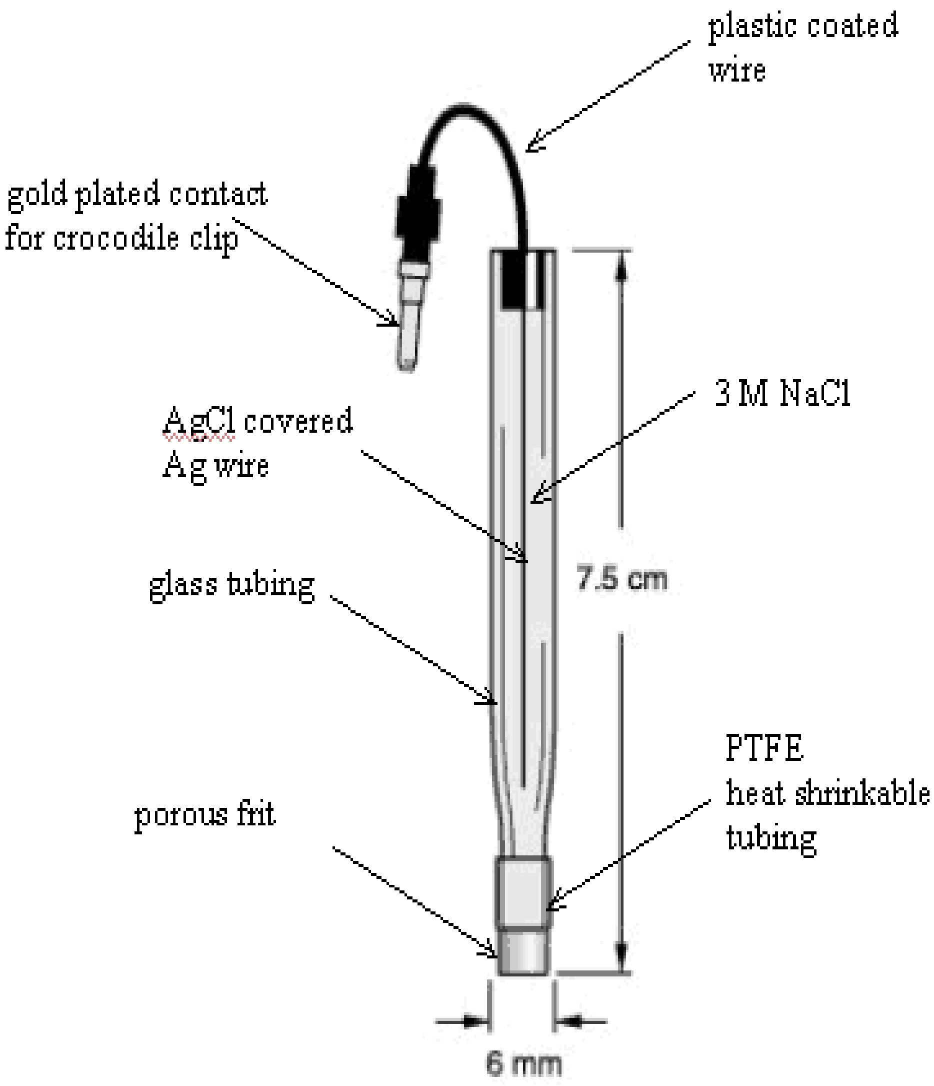
(e.g., H^+/H_2, Hg/Hg_2SO_4, or Ag/AgCl)

at fixed composition.

Electron energies in the metallic part of the electrode are fixed at a value near the E^0.

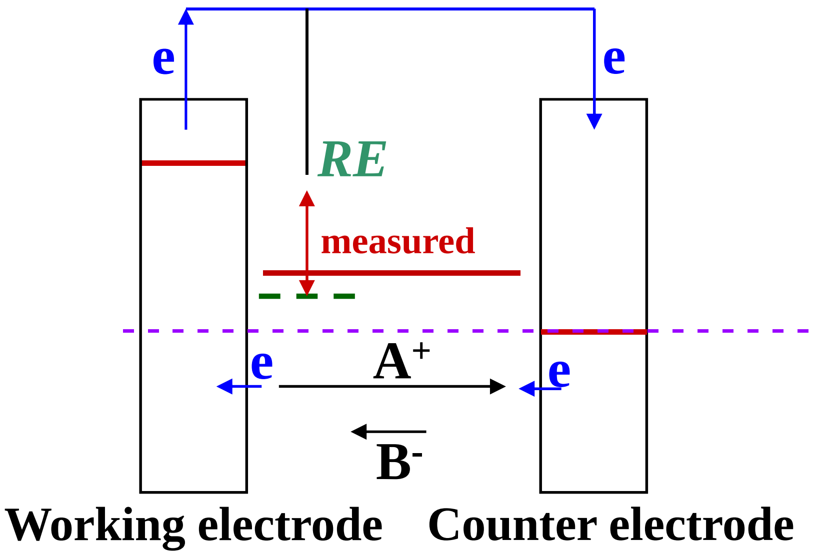
Reference Electrode

Adrian W. Bott's Group, Current Separations 14:2 (1995)
Bioanalytical Systems West Lafayette

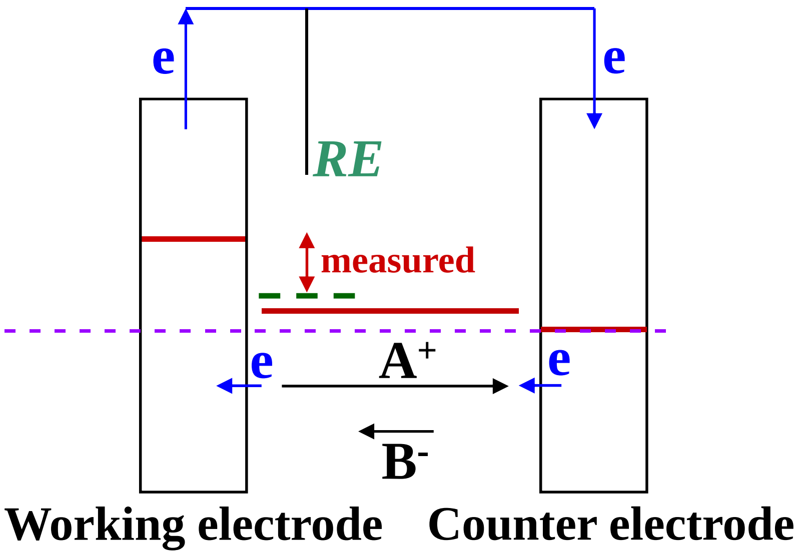


Vycor® **porous glass**
- modest leak rate
- possible contamination of solution
- ionic conducting pathway

Counter Electrode >> Working Electrode



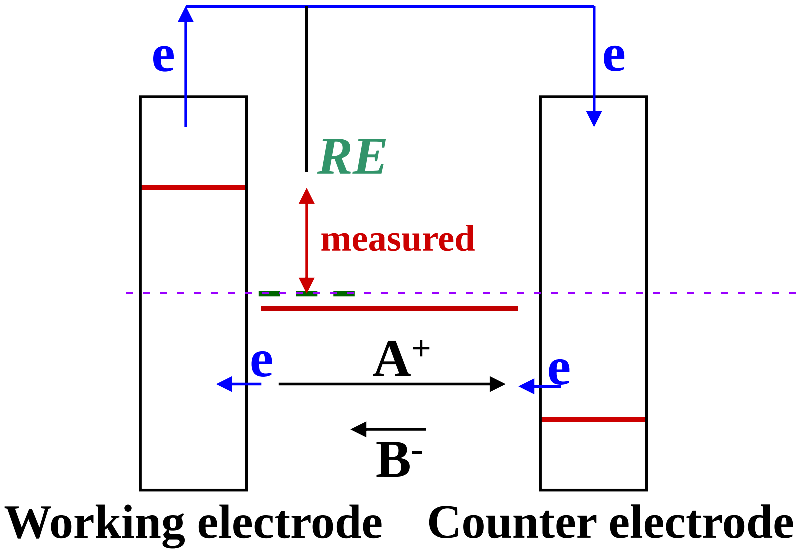
RE: Reference electrode



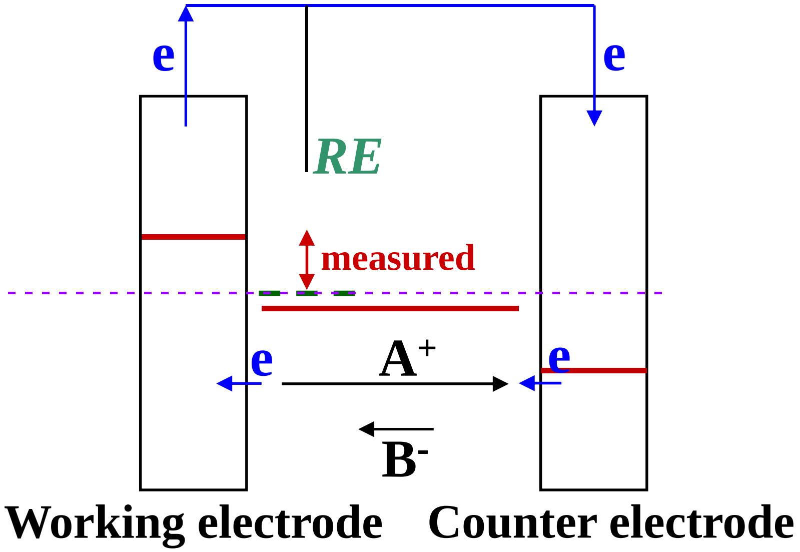
RE: Reference electrode

- Surface area:
  Working electrode << Counter electrode
- For different potential at working electrode,
  approximately the same potential at counter electrode.

Counter Electrode ~ Working Electrode



RE: Reference electrode



RE: Reference electrode

- Surface area:
  Working electrode ~ Counter electrode
- For different potential at working electrode,
  different potential at counter electrode

Electrochemical Cells and Reactions

Conduction

1. Metals
2. Solution (ion migration)
3. Electrode rxns (at interfaces)

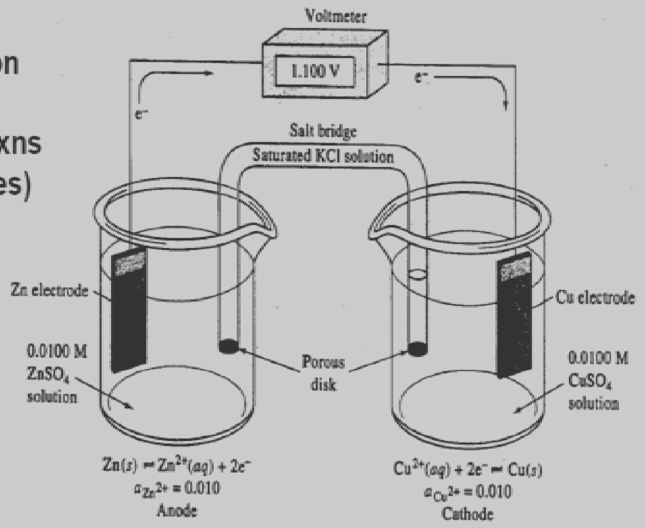


Figure 22-1 A galvanic electrochemical cell with a salt bridge.

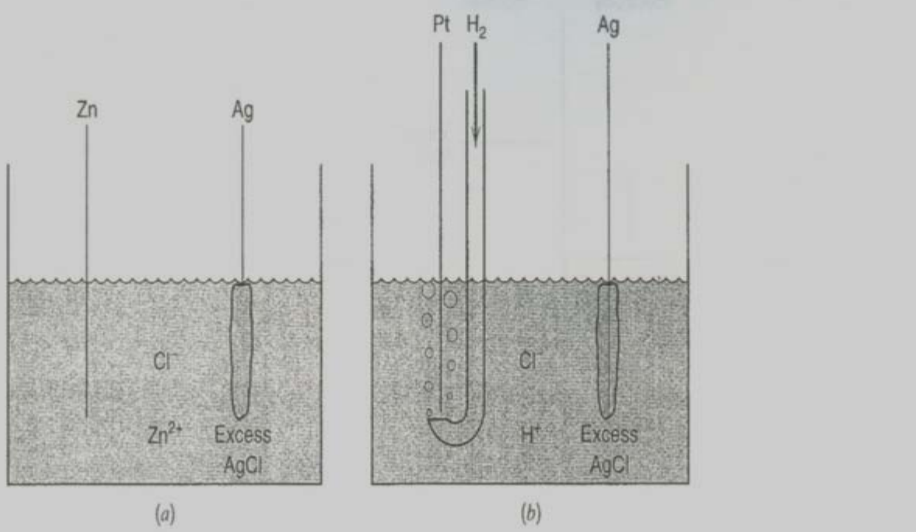


Figure 1.1.1 Typical electrochemical cells. (*a*) Zn metal and Ag wire covered with AgCl immersed in a $ZnCl_2$ solution. (*b*) Pt wire in a stream of H_2 and Ag wire covered with AgCl in HCl solution.

A potential difference between two electrodes represents a tendency for the reaction to occur.

A. J. Bard, Electrochemical Methods, 2nd edition

Electrochemical Cells and Reactions

The potential that develops in a cell is a measure of the tendency for a reaction to proceed toward equilibrium.

$$E = E^{o\prime} + \frac{2.303\,RT}{nF} \log \frac{[Ox]}{[Red]}$$

Measured
E vs. Ref

Nernst Equation

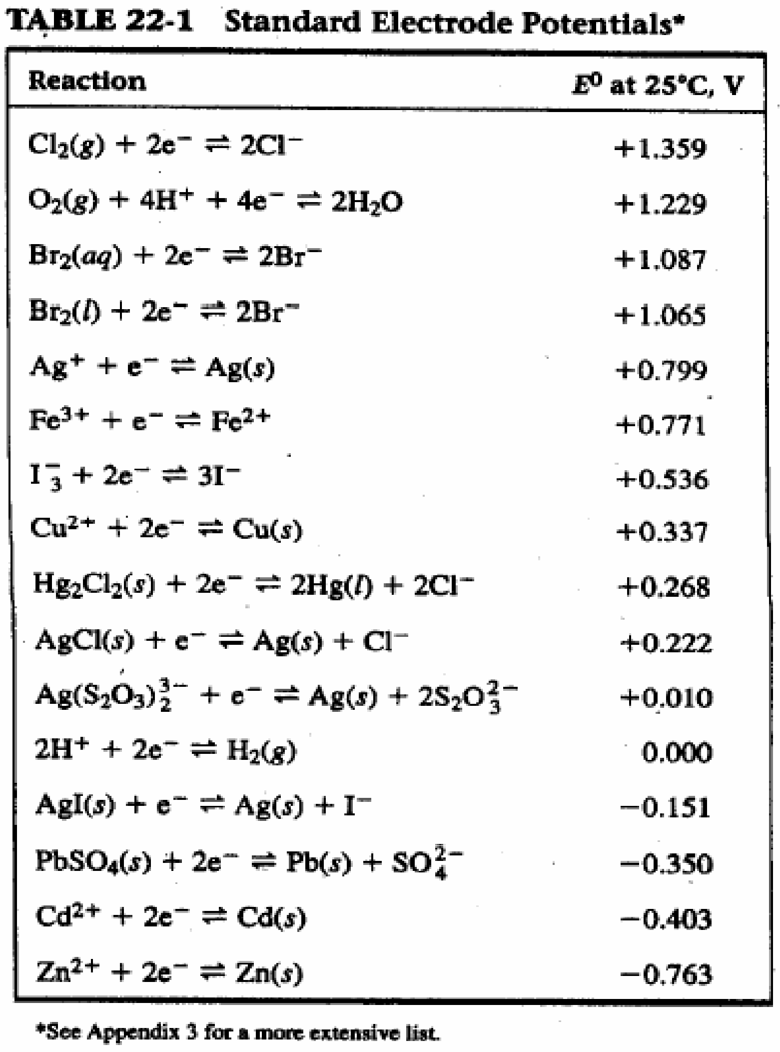


TABLE 22-1 Standard Electrode Potentials*

Reaction	E^0 at 25°C, V
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$	+1.359
$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-$	+1.087
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-$	+1.065
$Ag^+ + e^- \rightleftharpoons Ag(s)$	+0.799
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.771
$I_3^- + 2e^- \rightleftharpoons 3I^-$	+0.536
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	+0.337
$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$	+0.268
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$	+0.222
$Ag(S_2O_3)_2^{3-} + e^- \rightleftharpoons Ag(s) + 2S_2O_3^{2-}$	+0.010
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	0.000
$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-$	−0.151
$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}$	−0.350
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$	−0.403
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	−0.763

*See Appendix 3 for a more extensive list.

Standard oxidation/reduction reactions:

All relative to the H_2/H^+ reaction, 298 K, unit activities for all species, and pH 0.

A. J. Bard, Electrochemical Methods, 2nd edition

Double Layer

A. J. Bard, Electrochemical Methods, 2nd edition

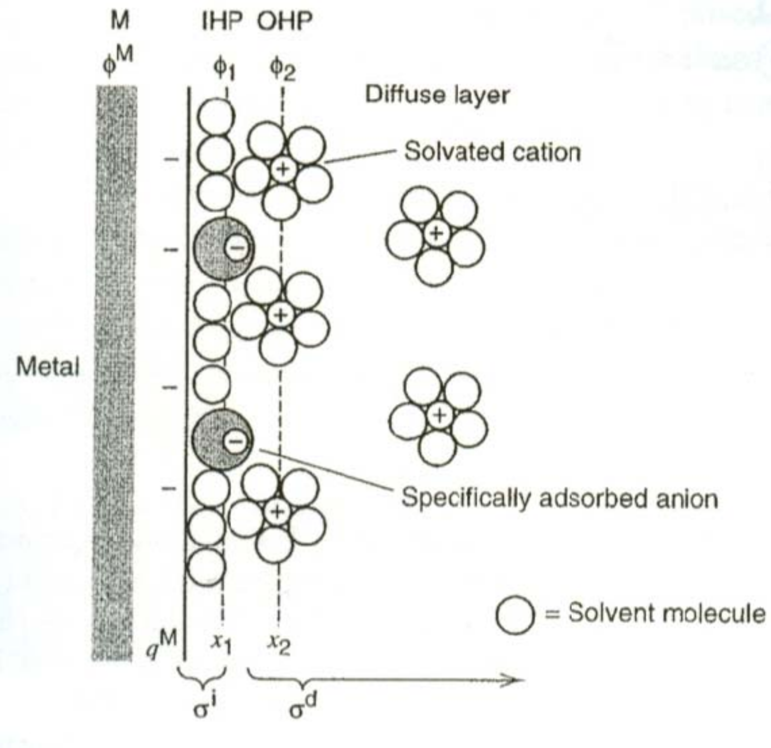


Figure 1.2.3 Proposed model of the double-layer region under conditions where anions are specifically adsorbed.

$q^{\text{metal}} = -q^{\text{solution}}$ charge neutrality!

compact layer = inner and outer Helmholtz planes (electrostatic forces are very strong!)

diffuse layer = gradient of charge accumulation (thermal agitation)

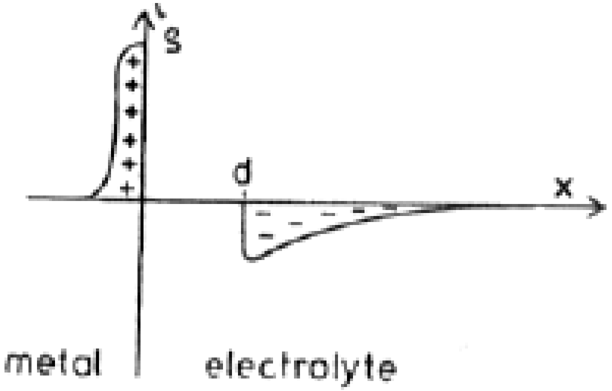
$\sigma^{\text{metal}} = q^{\text{metal}}/\text{area}$ ($\mu C/cm^2$)

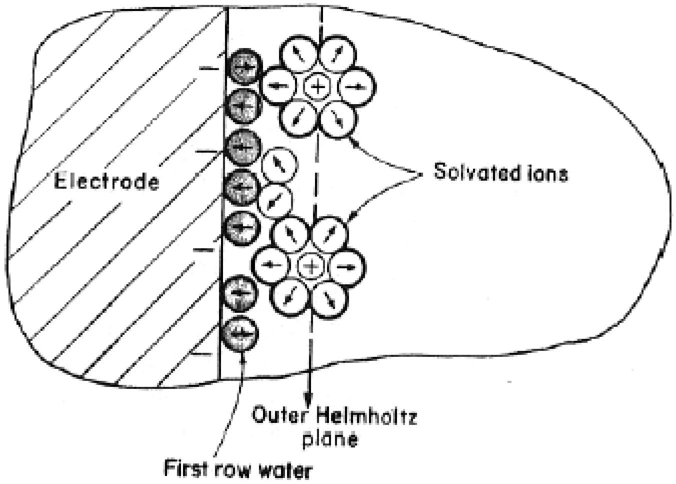
- The excess charge on a metal is confined to the near surface region.
- However, the balancing charge on the solution side of the interface extends out into the solution with some thickness (ionic zones in solution).

Double Layer

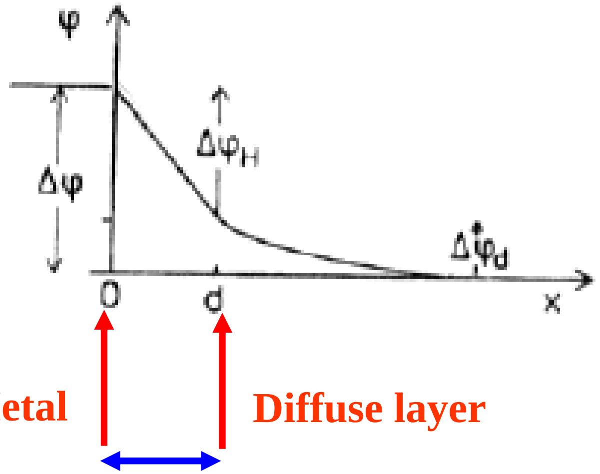
The CRC Handbook of Solid State Electrochemistry
H. J. M. Bouwmeester, p. 27

Charge distribution





Potential distribution



Metal

Diffuse layer

Double layer

Helmholtz Layer and Diffuse Layer

A. J. Bard, Electrochemical Methods, 2nd edition

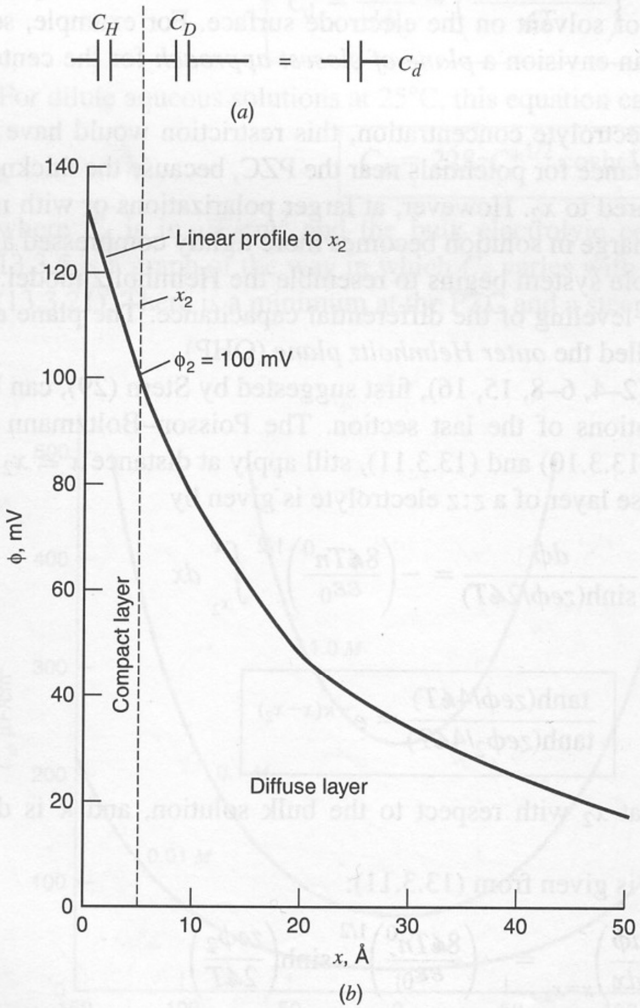


Figure 13.3.6 (*a*) A view of the differential capacitance in the Gouy–Chapman–Stern (GCS) model as a series network of Helmholtz-layer and diffuse-layer capacitances. (*b*) Potential profile through the solution side of the double layer, according to GCS theory. Calculated from (13.3.23) for 10^{-2} *M* 1:1 electrolyte in water at 25°C.

Potential Profile Across the Double-Layer

A. J. Bard, Electrochemical Methods, 2nd edition

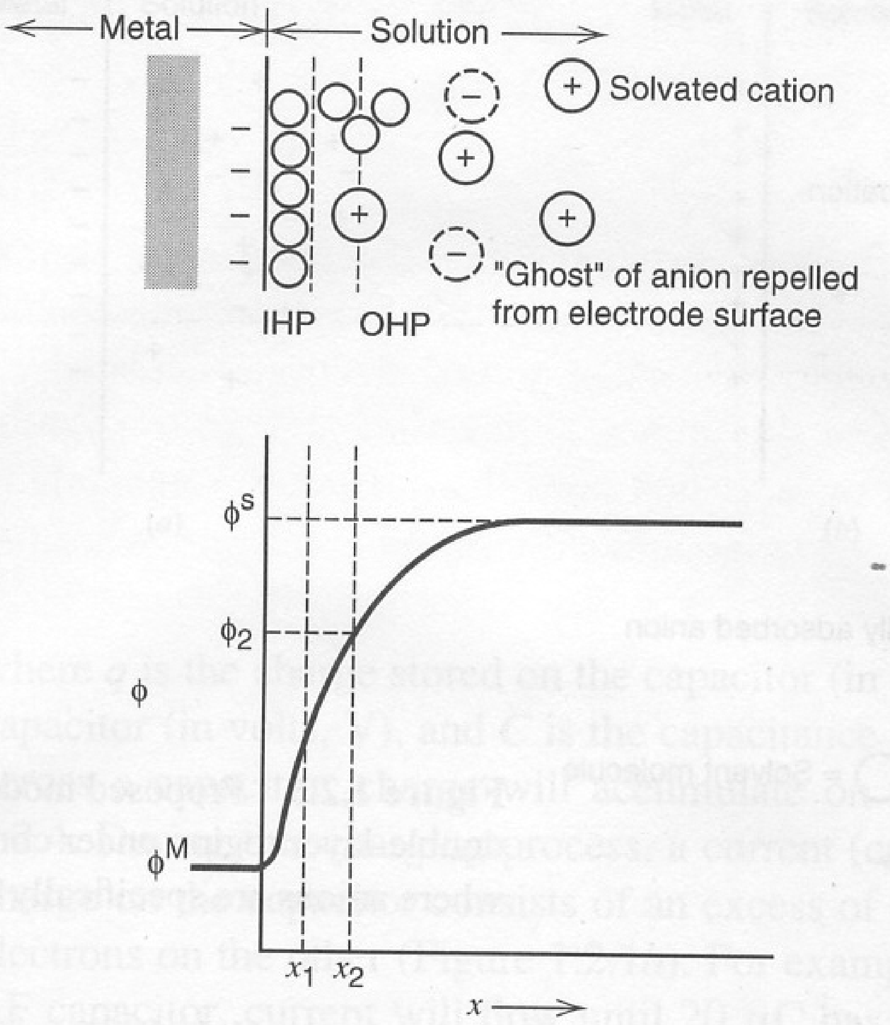
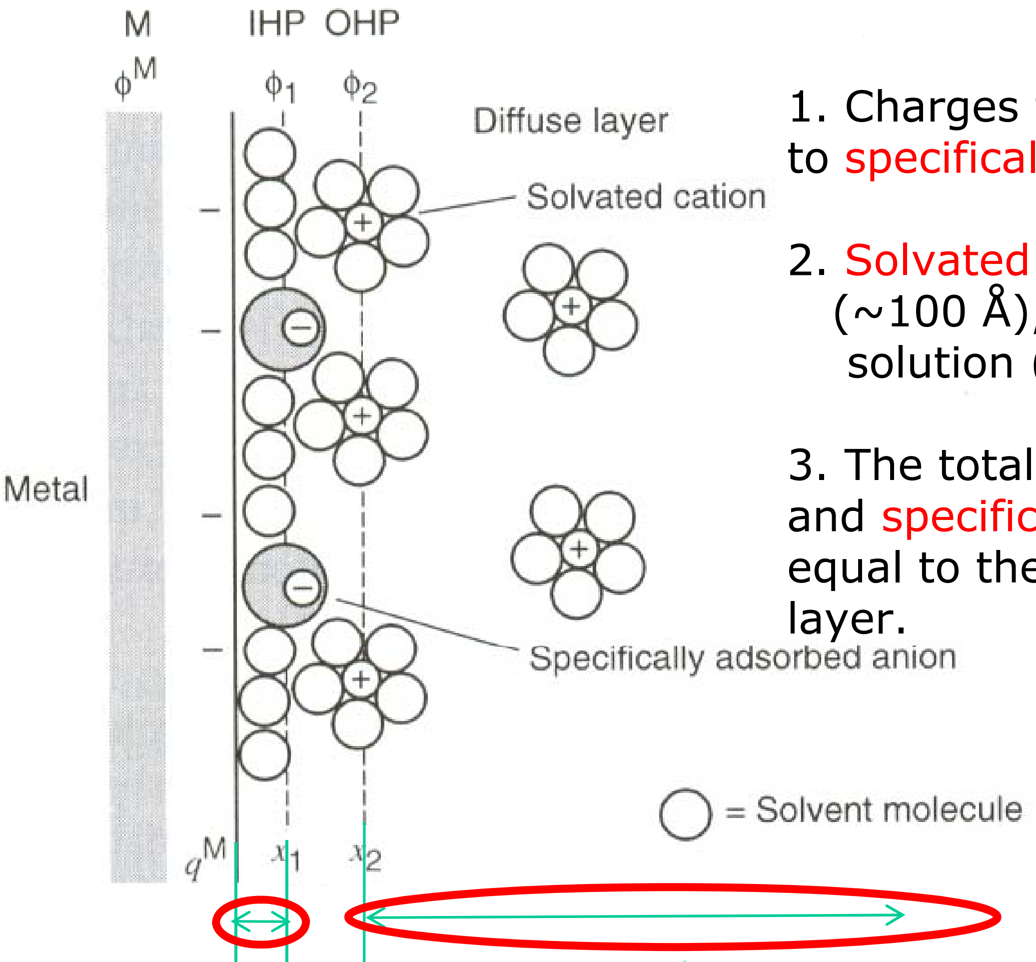


Figure 1.2.4 Potential profile across the double-layer region in the absence of specific adsorption of ions. The variable ϕ, called the *inner potential*, is discussed in detail in Section 2.2. A more quantitative representation of this profile is shown in Figure 12.3.6.



1. Charges from inner Helmholtz layer is attributed to specifically adsorbed anions (σ^{inner}).

2. Solvated ions are distributed in diffuse layer (~100 Å), because of thermal agitation in the solution ($\sigma^{diffuse}$).

3. The total charge density from the metal surface and specifically adsorbed anions in inner layer is equal to the charge from solvated ions in diffuse layer.

$$\sigma^{metal} + \sigma^{inner} = -\sigma^{diffuse}$$

Inner Helmholtz Layer

Diffuse Layer (~100 Å)

①

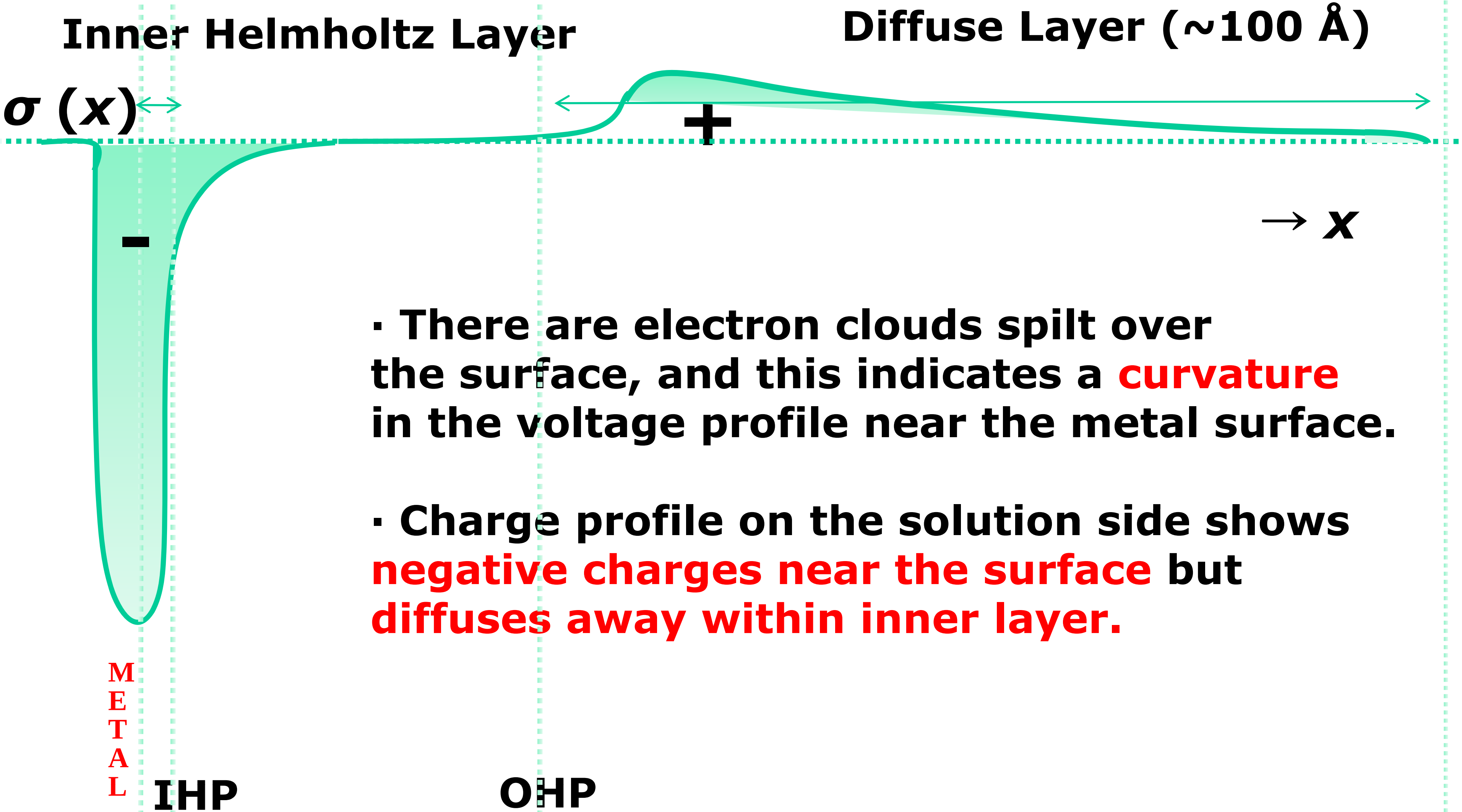
① Inner Helmholtz Plane

②

② Outer Helmholtz Plane

Bard, A. J., and Faulkner, L. R.
Electrochemical Methods
Wiiey, New York. 1980, Chap. 1

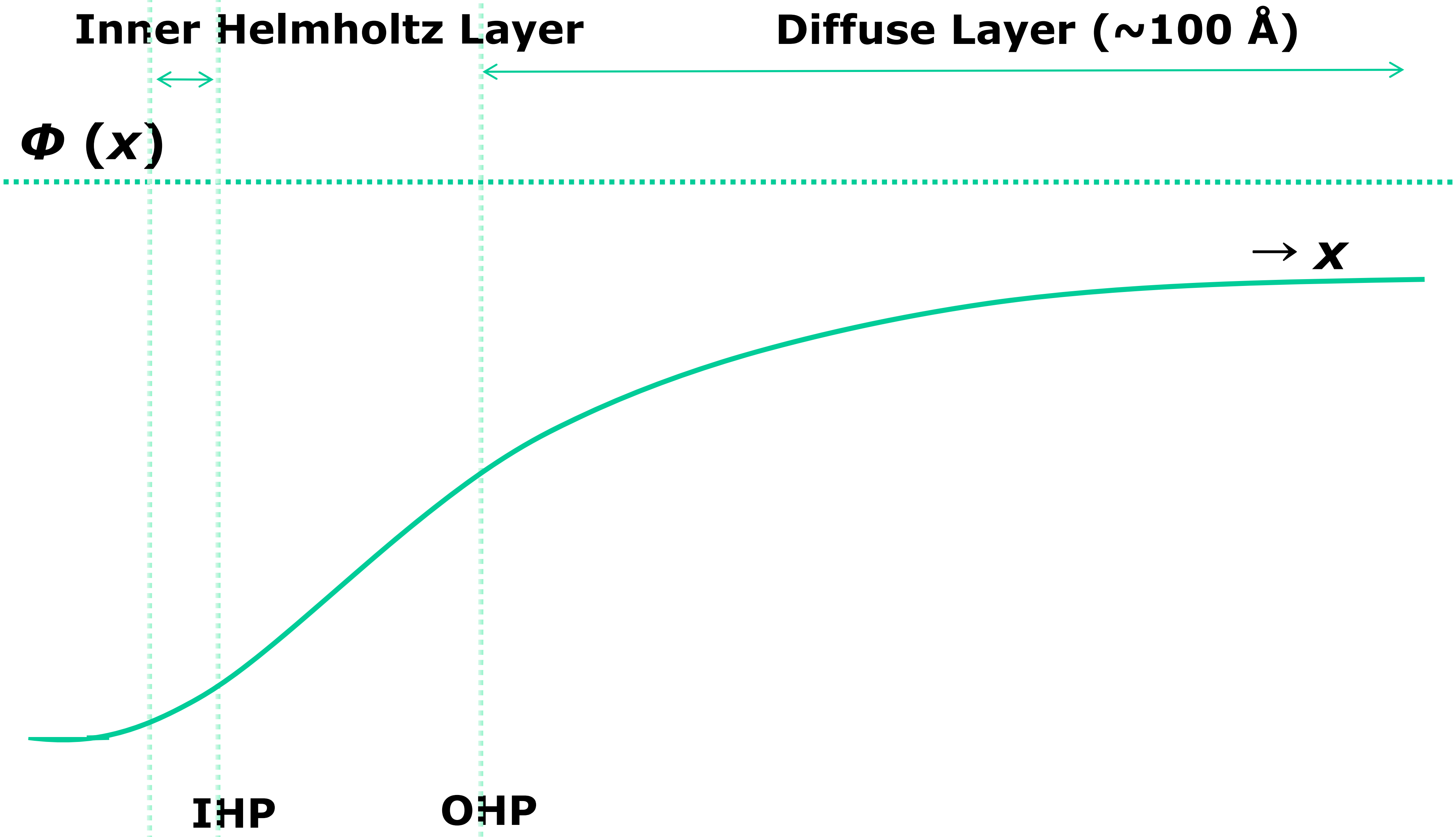
Charge Profile in the Vicinity of Interface



- There are electron clouds spilt over the surface, and this indicates a **curvature** in the voltage profile near the metal surface.

- Charge profile on the solution side shows **negative charges near the surface** but **diffuses away within inner layer.**

Voltage Profile in the Vicinity of Interface



Inner Helmholtz Layer

Diffuse Layer (~100 Å)

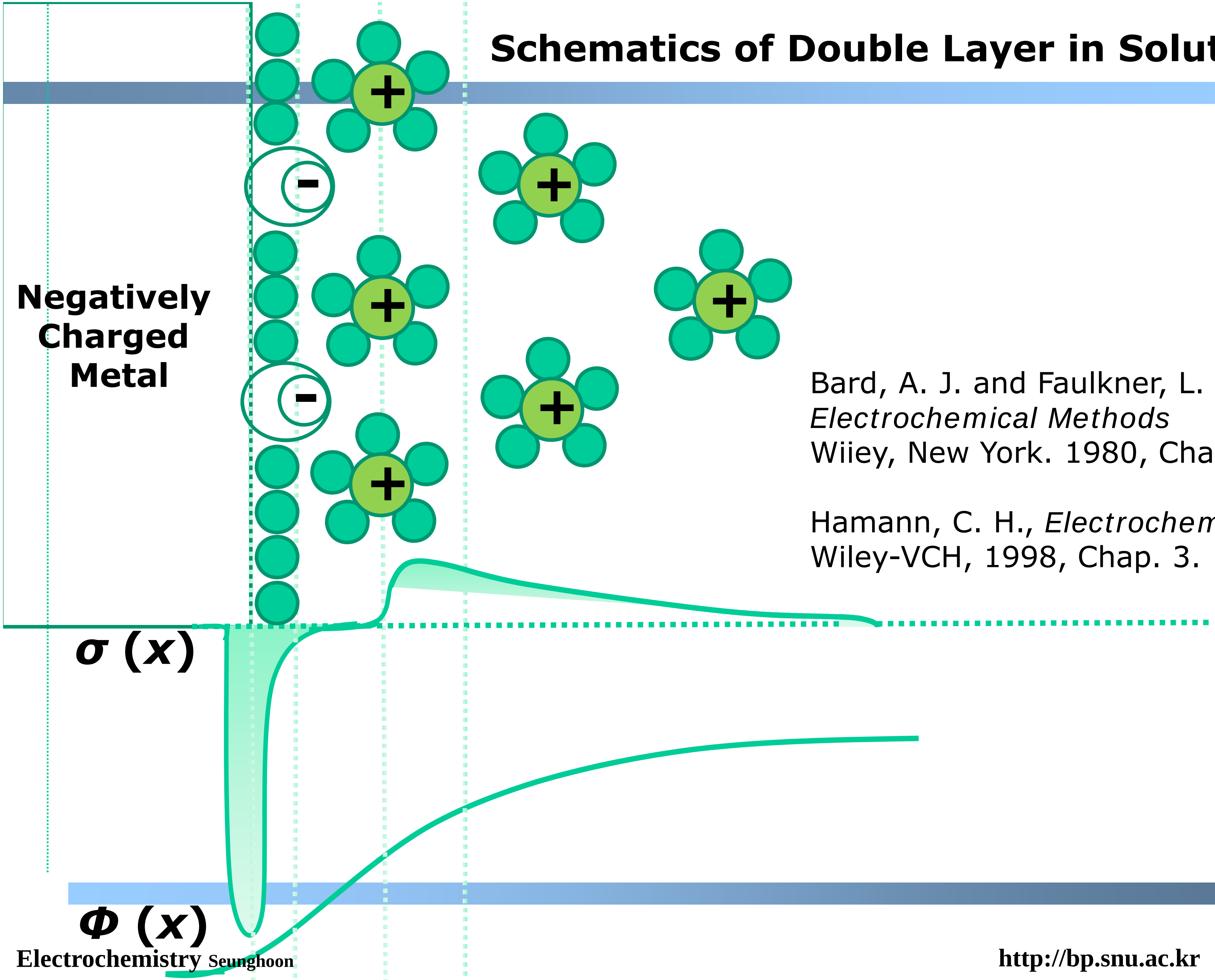
$\Phi\ (x)$

$\rightarrow x$

IHP

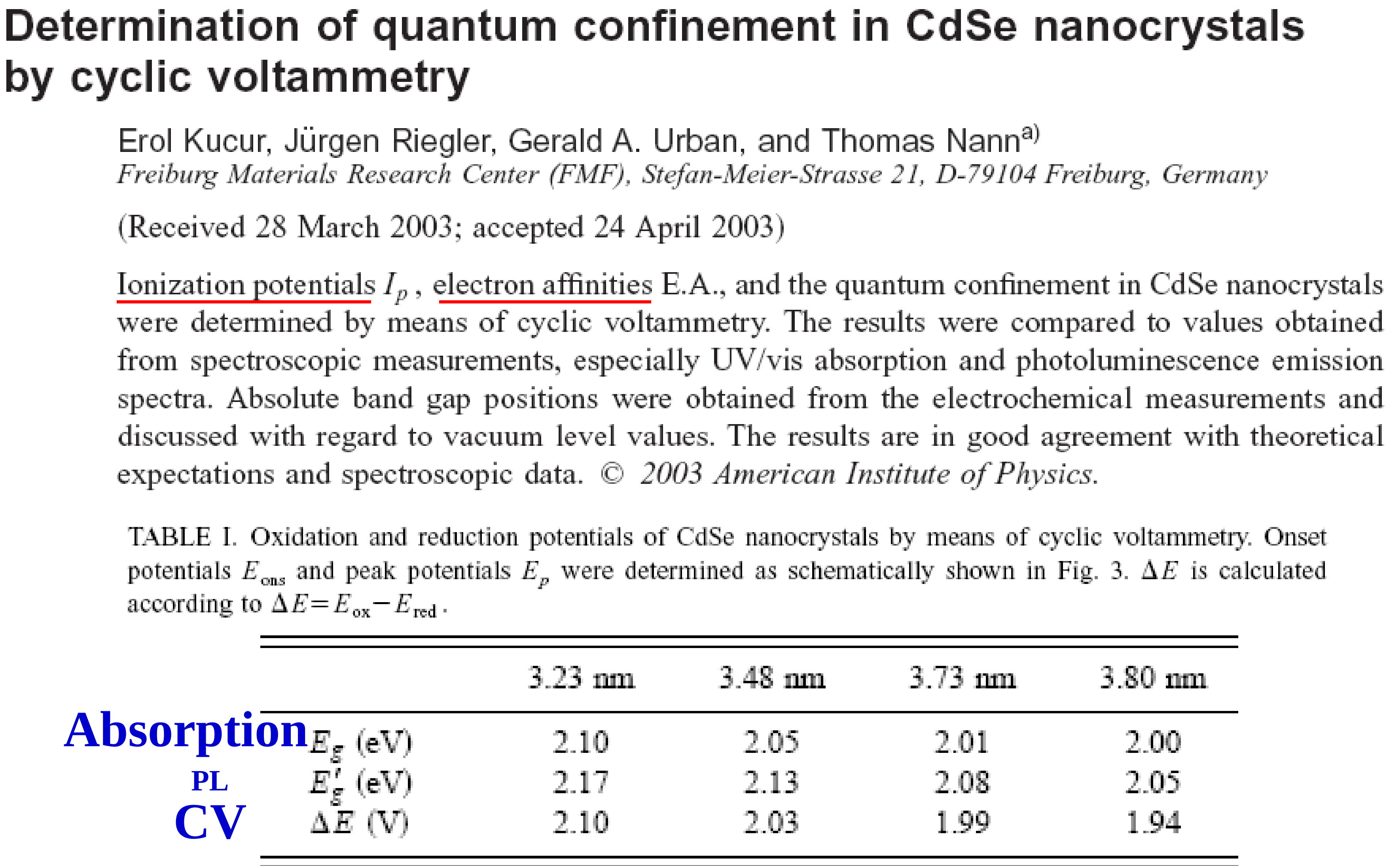
OHP

Schematics of Double Layer in Solution



Bard, A. J. and Faulkner, L. R.
Electrochemical Methods
Wiiey, New York. 1980, Chap. 1.

Hamann, C. H., *Electrochemistry*
Wiley-VCH, 1998, Chap. 3.



Determination of quantum confinement in CdSe nanocrystals by cyclic voltammetry

Erol Kucur, Jürgen Riegler, Gerald A. Urban, and Thomas Nann[a)]
Freiburg Materials Research Center (FMF), Stefan-Meier-Strasse 21, D-79104 Freiburg, Germany

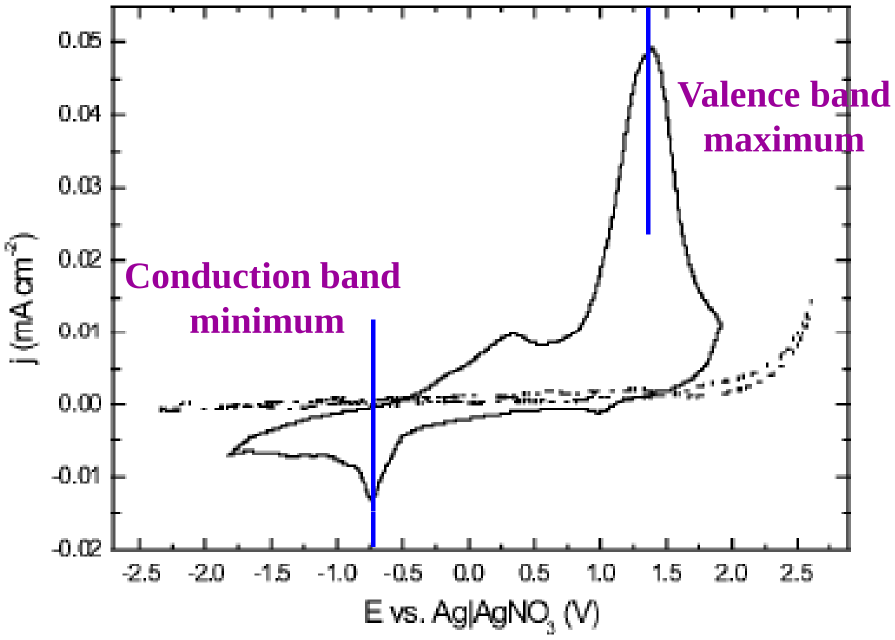
(Received 28 March 2003; accepted 24 April 2003)

Ionization potentials I_p, electron affinities E.A., and the quantum confinement in CdSe nanocrystals were determined by means of cyclic voltammetry. The results were compared to values obtained from spectroscopic measurements, especially UV/vis absorption and photoluminescence emission spectra. Absolute band gap positions were obtained from the electrochemical measurements and discussed with regard to vacuum level values. The results are in good agreement with theoretical expectations and spectroscopic data. © *2003 American Institute of Physics.*

TABLE I. Oxidation and reduction potentials of CdSe nanocrystals by means of cyclic voltammetry. Onset potentials E_{ons} and peak potentials E_p were determined as schematically shown in Fig. 3. ΔE is calculated according to $\Delta E = E_{\text{ox}} - E_{\text{red}}$.

		3.23 nm	3.48 nm	3.73 nm	3.80 nm
Absorption	E_g (eV)	2.10	2.05	2.01	2.00
PL	E_g' (eV)	2.17	2.13	2.08	2.05
CV	ΔE (V)	2.10	2.03	1.99	1.94

Band Structure Determined by Cyclic Voltammetry for CdSe Nanocrystals



Valence band maximum

Conduction band minimum

FIG. 2. Cyclic voltammogram of monodisperse CdSe nanocrystals (3.73 nm diameter) adsorbed on a gold disk microelectrode (400 μm radius) in acetonitrile+0.1 M TBAPF$_6$ at 20 mV/s at room temperature. Dotted line: voltammogram of bare gold electrode.

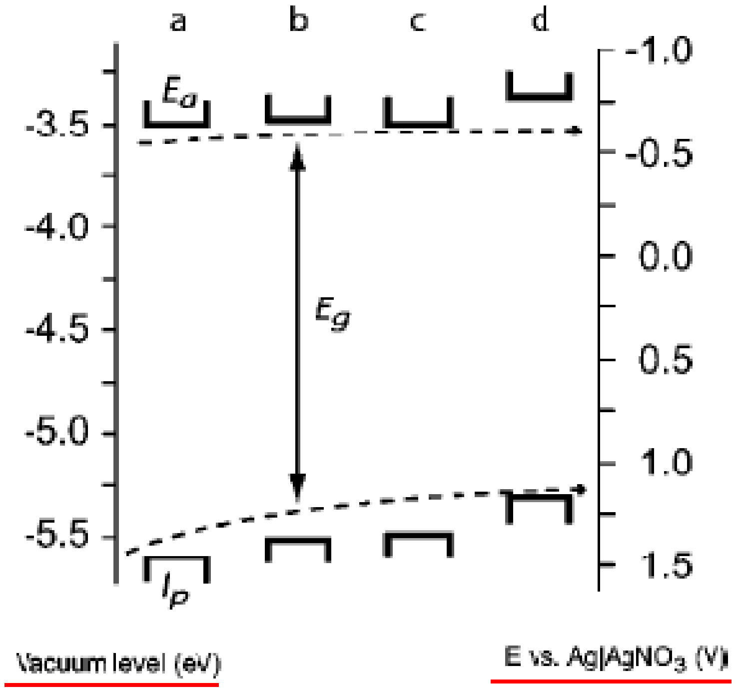


FIG. 7. Schematic diagram of the electrochemically determined ionization potentials I_p and electron affinities E.A. of four different sizes of CdSe nanocrystals. Dashed arrows: Approach of the confined I_p and E_a values to the bulk band edges with growing particle size (CdSe bulk band gap =1.74 eV).

$$I_p = -(E_{\mathrm{ox}} + 4.14)\ \mathrm{eV},$$

$$\mathrm{E.A.} = -(E_{\mathrm{red}} + 4.14)\ \mathrm{eV},$$

Thomas Nann's Group, Journal of Chemical Physics (2003)
Freiburg Materials Research Center (Germany)

Experiment and Variables in Electrochemical Cell

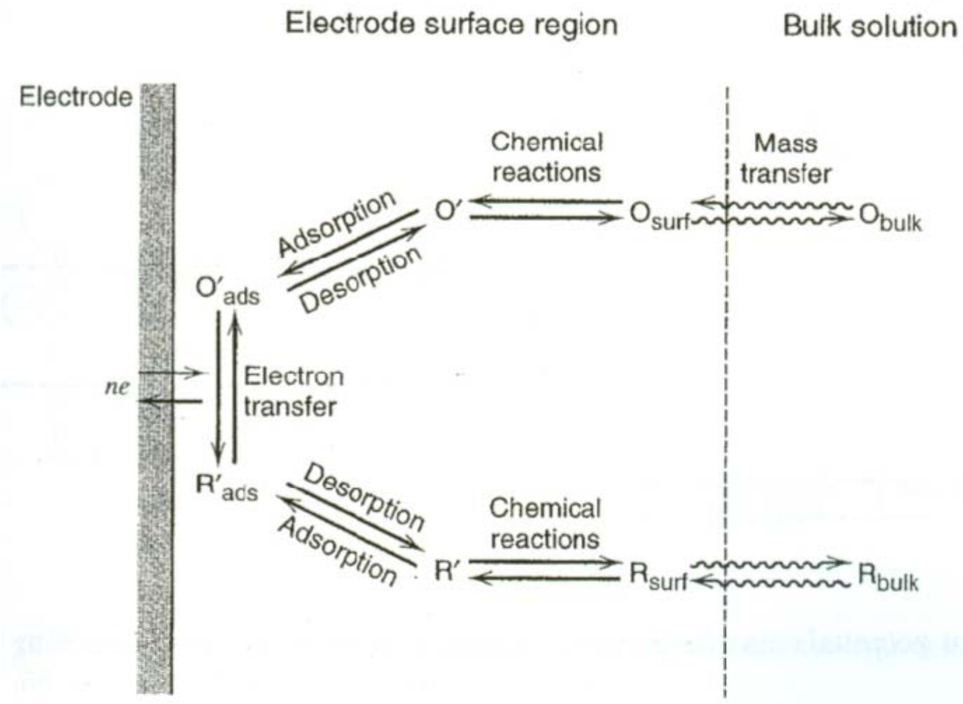


Figure 1.3.6 Pathway of a general electrode reaction.

1. Mass transfer of reactant/product to and away from the electrode interface.

2. Electron transfer at the interface.

3. Preceeding or follow-up chemical reactions.

4. Surface processes (adsorption/desorption)

Working Electrode (Indicator Electrode)

A. J. Bard, Electrochemical Methods, 2nd edition

Mass Transport

A. J. Bard, Electrochemical Methods, 2nd edition

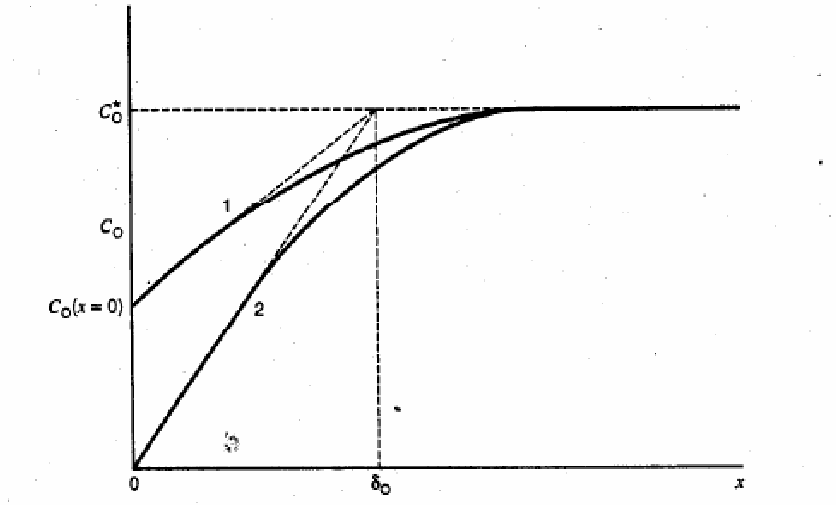


Figure 1.4.1 Concentration profiles (solid lines) and diffusion layer approximation (dashed lines). $x = 0$ corresponds to the electrode surface and δ_O is the diffusion layer thickness. Concentration profiles are shown at two different electrode potentials: (*1*) where $C_O(x = 0)$ is about $C_O^*/2$, (*2*) where $C_O(x = 0) \approx 0$ and $i = i_l$.

Modes of Mass Transport:

Migration
– movement of ions by an electric field

Diffusion
– by a concentration gradient

Convection
– by stirring or hydrodynamic transport

$$\boxed{J_i(x) = -D_i \frac{dC_i(x)}{dx} - \frac{z_iF}{RT} D_iC_i \frac{d\Phi(x)}{dx} - C_i\upsilon(x)}$$

$J_i(x)$ = flux of I (mol/s-cm^2)

D = diffusion coeff. (cm^2/s)

C = conc. (mol/cm^3)

$\frac{d\Phi(x)}{dx}$ = potential gradient

z = charge on species

$\upsilon(x)$ = velocity (cm/s)

The Scope of Electrochemistry

1. Investigation of chemical phenomena associated with a charge-transfer reaction.

2. To assure electro-neutrality,
   two (or more) half reactions take place in opposite directions
   (oxidation and reduction).

3. If the change of total Gibbs free energy is negative,
   the corresponding electrical energy gets released.