

Electrochemistry



[http://chen.chemistry.ucsc.edu/
teaching/chem269.htm](http://chen.chemistry.ucsc.edu/teaching/chem269.htm)

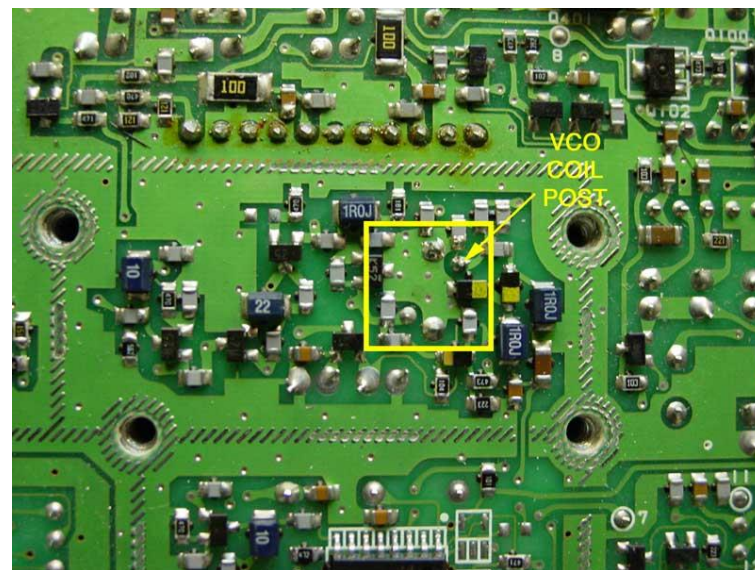
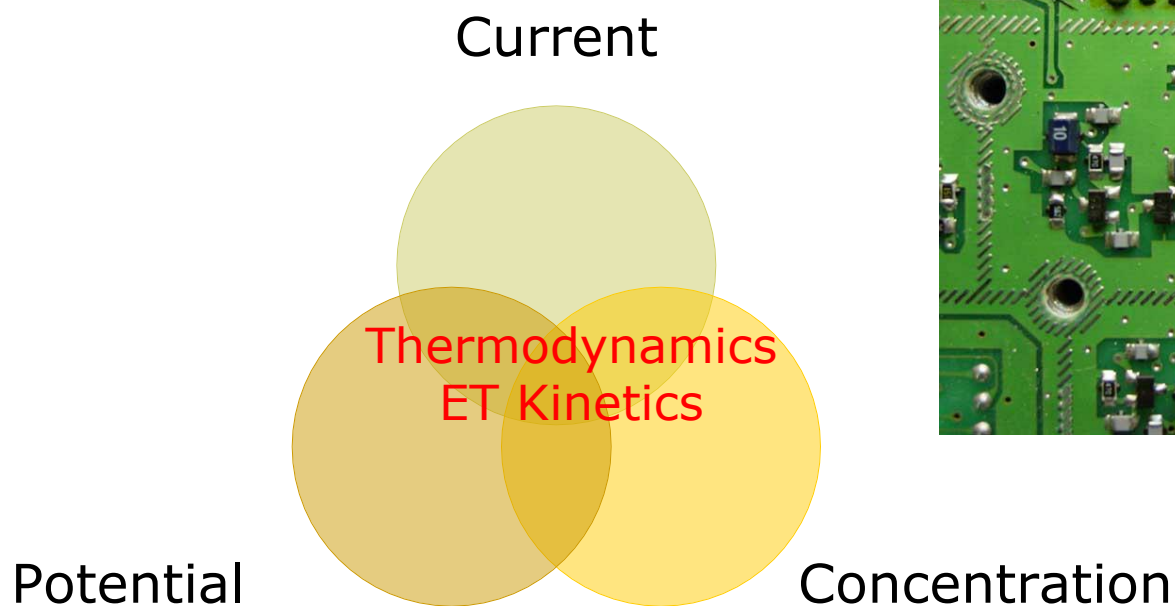
Course Content

- This course is designed to introduce the basics (**thermodynamics and kinetics**) and applications (**experimental techniques**) of electrochemistry to students in varied fields, including analytical, physical and materials chemistry. The major course content will include
 - **Part I Fundamentals**
 - Overview of electrode processes (Ch. 1)
 - Potentials and thermodynamics (Ch. 2)
 - Electron transfer kinetics (Ch. 3)
 - Mass transfer: convection, migration and diffusion (Ch. 4)
 - Double-layer structures and surface adsorption (Ch. 13)
 - **Part II Techniques and Applications**
 - Potential step techniques (Ch. 5): chronoamperometry
 - Potential sweep methods (Ch. 6): linear sweep, cyclic voltammetry
 - Controlled current microelectrode (Ch. 8): chronopotentiometry
 - Hydrodynamic techniques (Ch. 9): RDE, RRE, RRDE
 - Impedance based techniques (Ch. 10): electrochemical impedance spectroscopy, AC voltammetry
- **Grade:** 1 mid-term (30%); 1 final (50%); quizzes/homework (20%)

Prerequisites

- Differential equation
- Thermodynamics
- Chemical kinetics

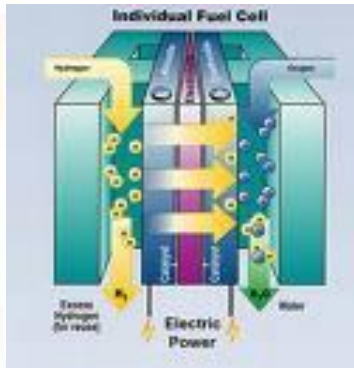
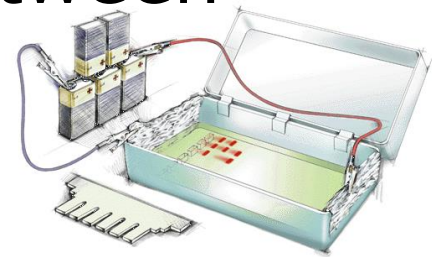
Electrochemistry in a Nutshell



Overview of Electrochemical Processes

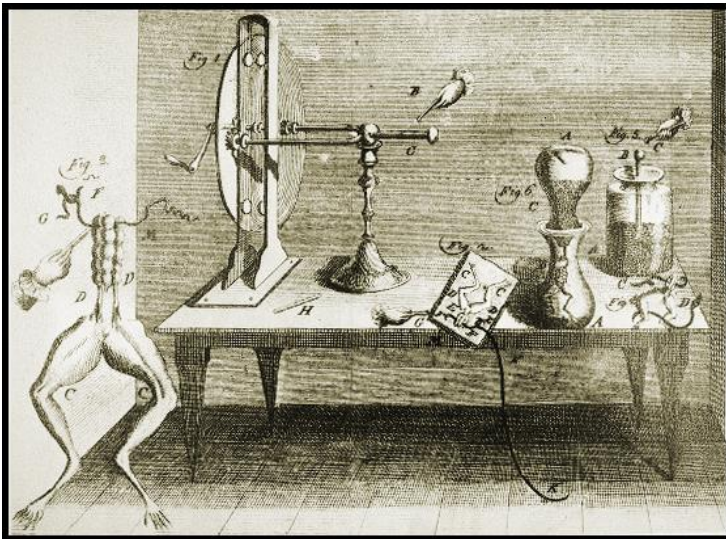
□ Electrochemistry: interrelation between electrical and chemical effects

- Electrophoresis
- Corrosion and electroplating
- Electrochromic display
- Electrochemical sensor
- Batteries, fuel cells, so



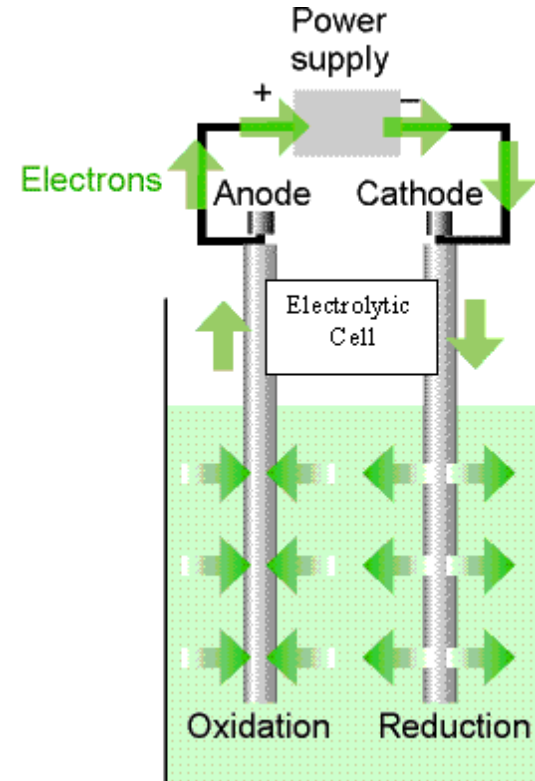
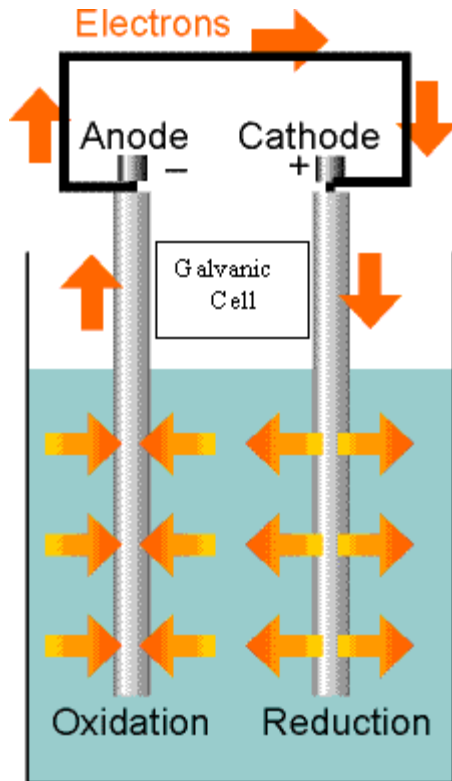
Cell Definition

- ❑ Galvanic cell [Galvanic cell.flv](#)
 - Chemical energy → electrical energy
 - Fuel cell, battery
- ❑ Electrolytic cell [Electrolysis Splitting Water Animation.flv](#)
 - Electrical energy → chemical energy
 - Corrosion, electroplating



Luigi Galvani (9 September 1737 – 4 December 1798) was an [Italian physician](#) and [physicist](#) who lived and died in [Bologna](#). In 1771, he discovered that the muscles of dead frogs twitched when struck by a spark. He was a pioneer in modern [obstetrics](#), and discovered that [muscle](#) and [nerve cells](#) produce [electricity](#).

Electrode Definition



- Anode: oxidation
- Cathode: reduction

Electrochemical Cells

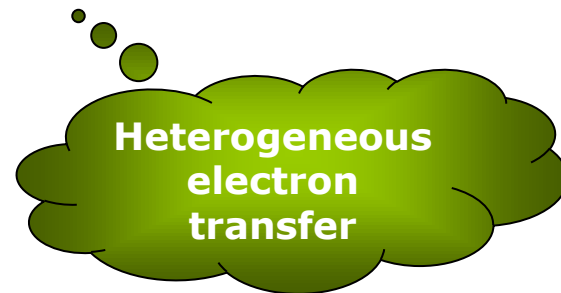
□ Charge transfer across the electrode/electrolyte interface

■ Electrode materials

- Solid metals (Pt, Au, Ag, ...)
- Liquid metals (Hg, amalgam, ...)
- Carbons (graphite, diamond, ...)
- Semiconductors (ITO, Si, ...)

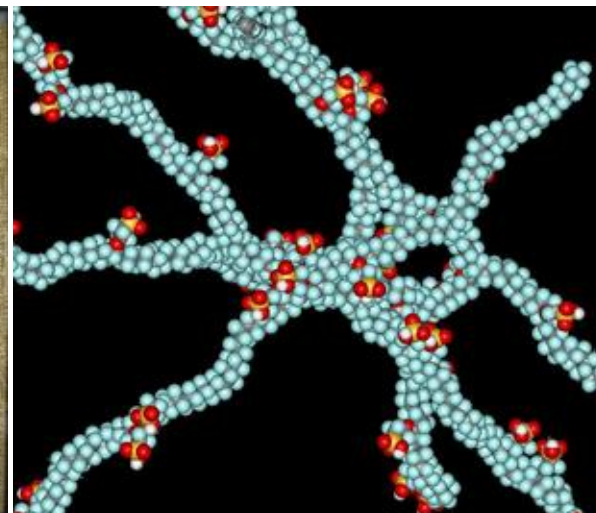
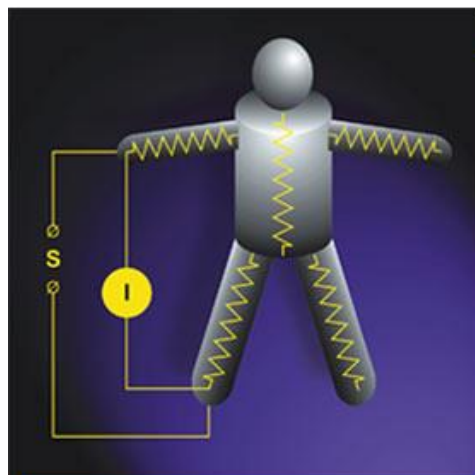
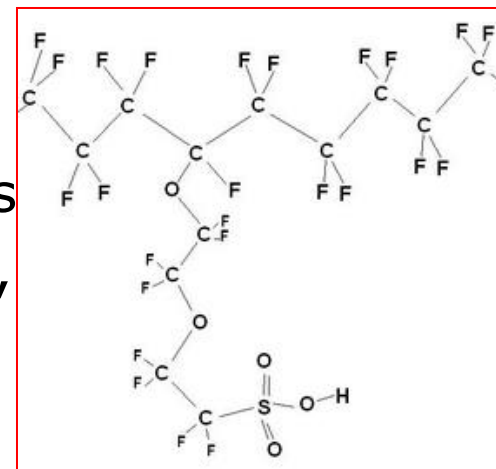
■ Electrode geometry

- Disk
- (hemi)sphere
- Cylinder
- (ultra)microelectrode or nanoelectrode



Electrochemical Cells

- Electrolyte (a.k.a. salt solution)
 - Charge carried by ions
 - Liquid solutions containing ionic species
 - Molten salts (melted salts (ionic liquid), fused salts, room-temperature glass)
 - Ionically conductive polymer (e.g., Nafion)



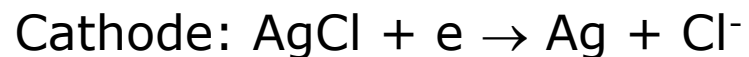
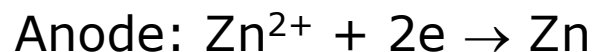
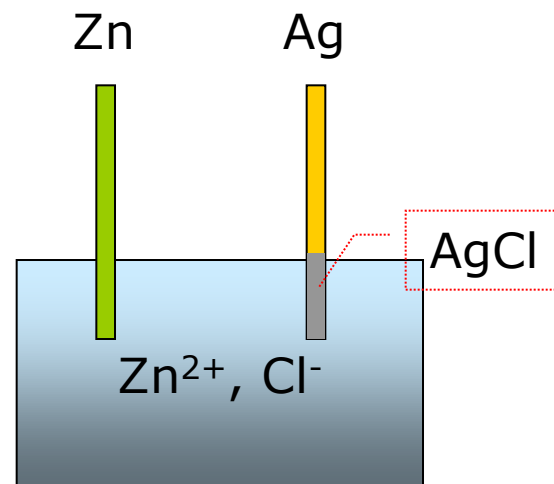
Cell Notation

□ Cell notation



□ Procedure

- Identify electrodes (anode and cathode)
- Starting from anode to cathode
- Vertical bars represent phase boundaries



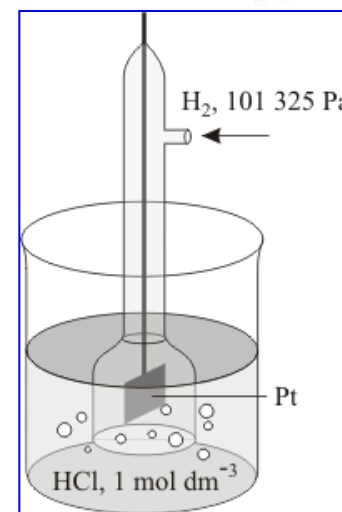
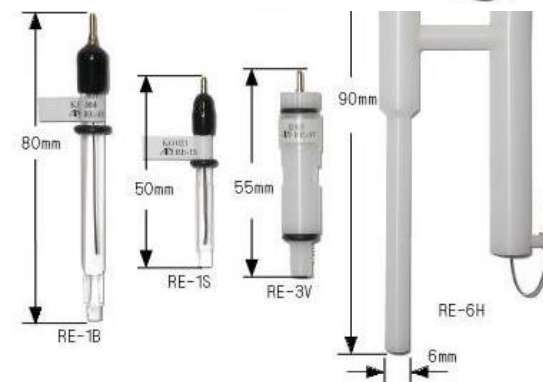
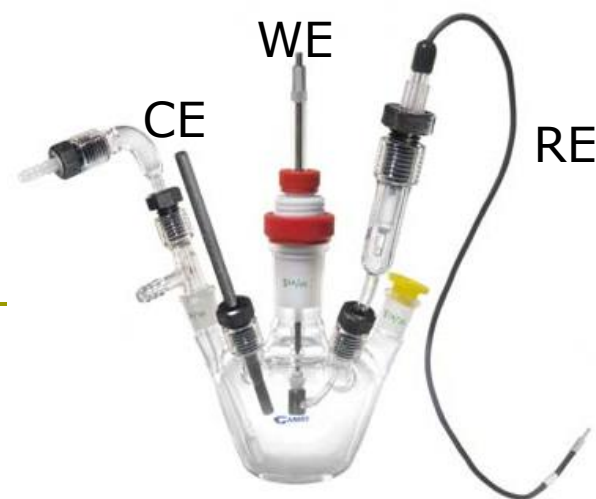
Two half cells:
Half reactions in
reduction format

Exercises

- $\text{Zn}|\text{ZnCl}_2(\text{aq})||\text{CuCl}_2(\text{aq})|\text{Cu}$
- $\text{Pt}|\text{FeSO}_4(\text{aq}), \text{Fe}_2(\text{SO}_4)_3(\text{aq})||\text{K}_2\text{Cr}_2\text{O}_7(\text{aq}), \text{H}_2\text{SO}_4(\text{aq})|\text{Pt}$

Electrodes

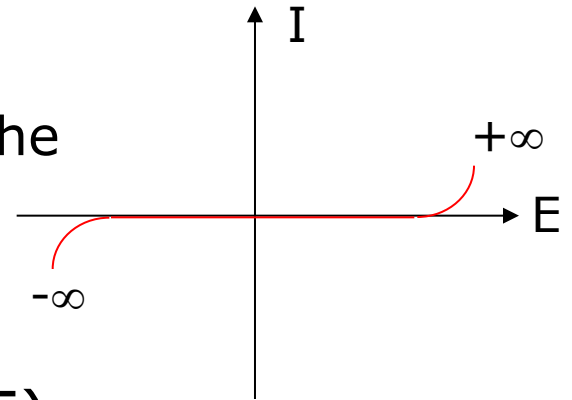
- ❑ Working electrode
 - Reactions of our interest
- ❑ Reference electrode
 - Controlling the working electrode potential
 - Standard hydrogen electrode (**SHE**):
 $\text{Pt}|\text{H}_2(1 \text{ atm})|\text{H}^+ (a = 1, \text{aq}), E^\circ = 0 \text{ V}$
 - Secondary reference electrodes
 - ❑ Saturated calomel electrode (**SCE**)
 $\text{Hg}|\text{Hg}_2\text{Cl}_2|\text{KCl} (\text{sat'd}), E^\circ = 0.242 \text{ V}$
 - ❑ $\text{Ag}|\text{AgCl}|\text{KCl} (\text{sat'd}), E^\circ = 0.197 \text{ V}$
- ❑ Counter electrode
 - To separate current and potential control



Electrode Polarization

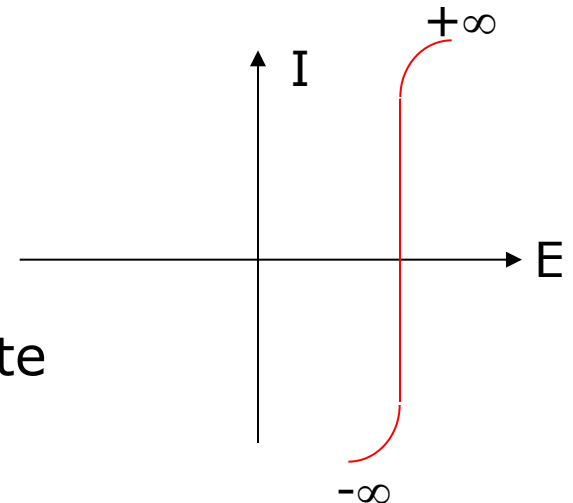
□ Ideal polarized electrode (IPE)

- No charge transfer can occur across the metal-solution interface regardless of the potential imposed by an outside source of voltage



□ Ideal nonpolarized electrode (InPE)

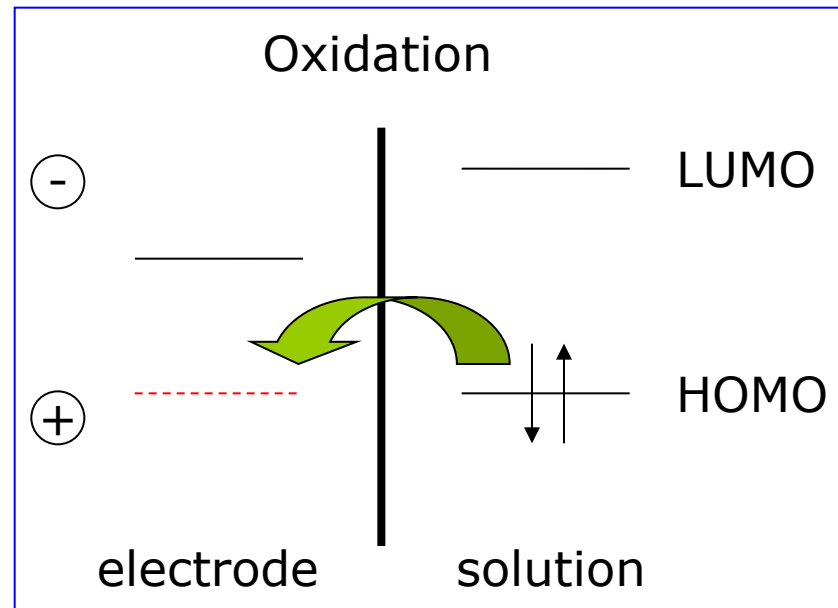
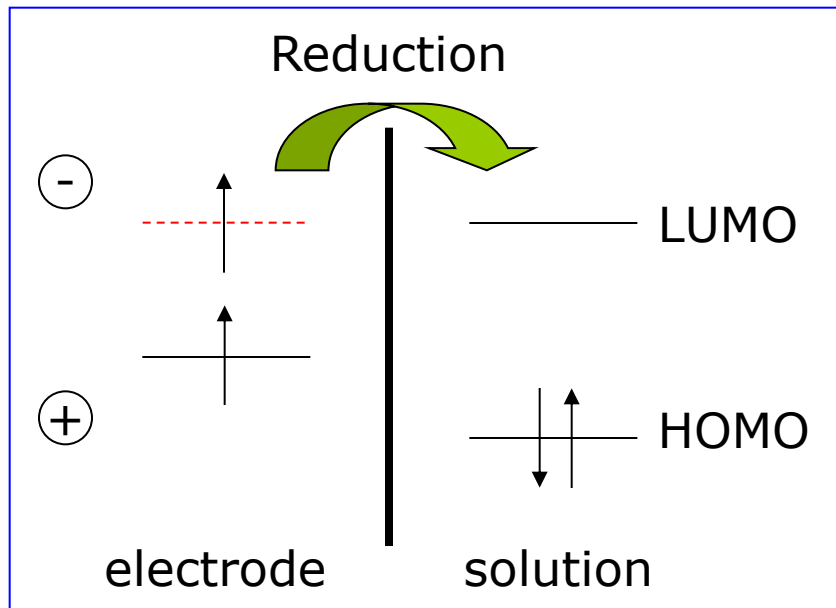
- The potential of the electrode will not change from its equilibrium potential with the application of even a large current density. The reason for this behavior is that the electrode reaction is extremely fast (has an almost infinite exchange current density).



Cell Resistance

- ❑ Most electrodes are neither IPE nor InPE. For reference electrodes, any deviation from InPE will cause fluctuation in potential control
- ❑ Introduction of a CE minimizes the current passage through RE. But it is still nonzero, therefore producing a nonzero resistance (iR_s), which may distort the voltammetric data.

Electrode Reactions



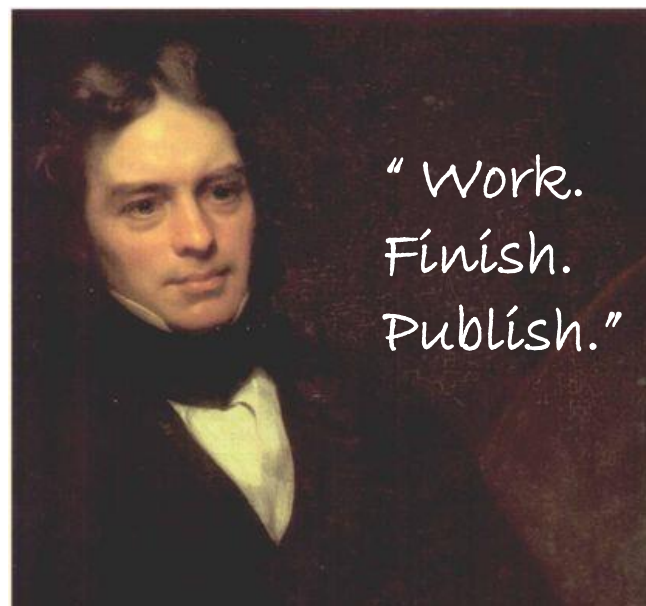
- Electrochemical reactions are all **adiabatic**
 - the donor level and the acceptor level must be at the same energy state
- Faraday's law $F = 96,485 \text{ C/mol}$

Michael Faraday

- ❑ **Michael Faraday**, FRS (22 September 1791 – 25 August 1867) was an English chemist and physicist who contributed to the fields of electromagnetism and electrochemistry.
- ❑ As a chemist, Faraday discovered **benzene**, investigated the clathrate hydrate of chlorine, invented an early form of the bunsen burner and **the system of oxidation numbers, and popularized terminology such as anode, cathode, electrode, and ion.**
- ❑ The SI unit of capacitance, the farad, is named after him, as is the Faraday constant, the charge on a mole of electrons (about 96,485 coulombs). Faraday's law of induction states that a magnetic field changing in time creates a proportional electromotive force.

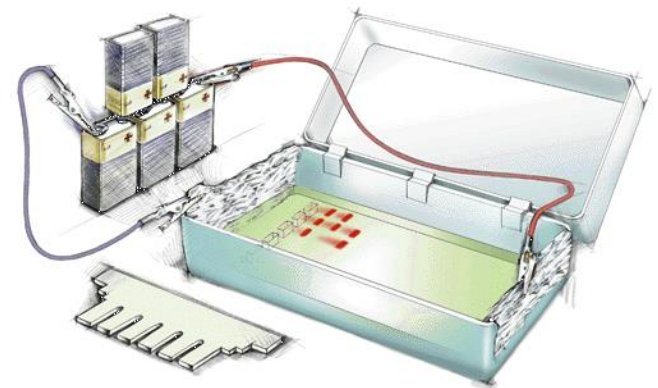


Slide that Faraday used in his lecture on gold sols, in 1858

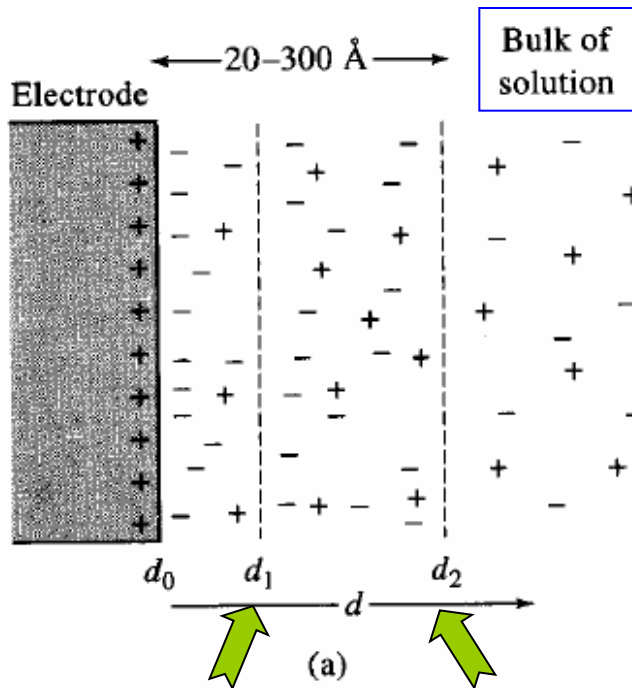


Faradaic and Non-Faradaic Processes

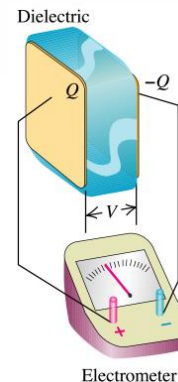
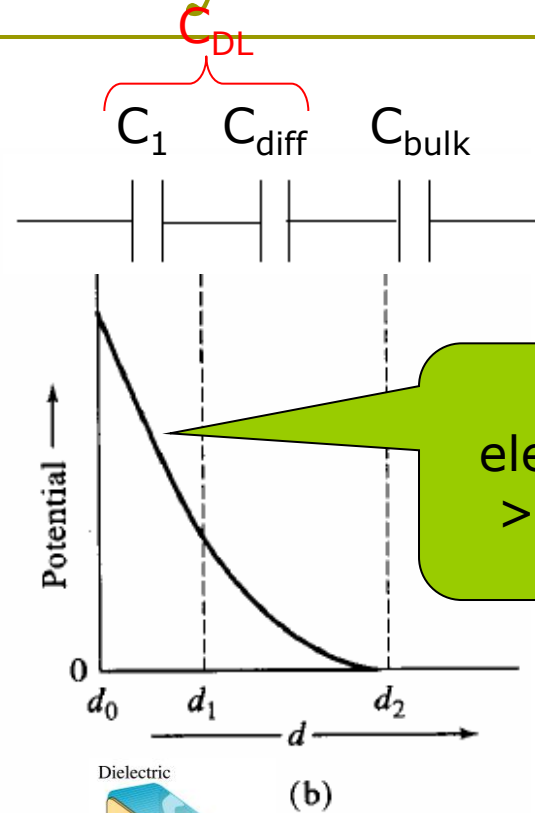
- **Faradaic** process: charge transfer across the electrode|electrolyte interface, a.k.a. the double-layer (Faraday's Law)
- **Non-Faradaic** process: no charge transfer across the electrode|electrolyte interface but the structure at the double-layer may vary (double-layer charging) [Ions in electric field](#)



Electrode Double Layer

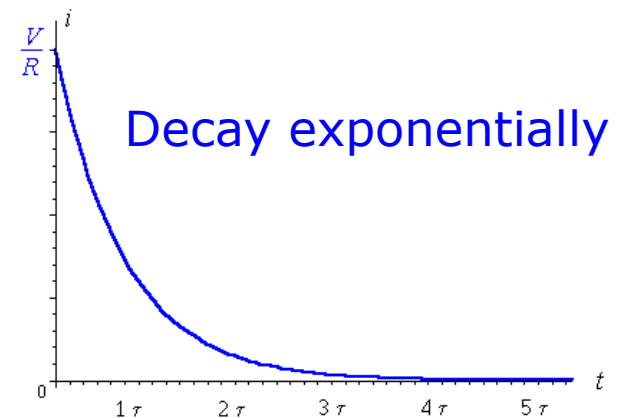
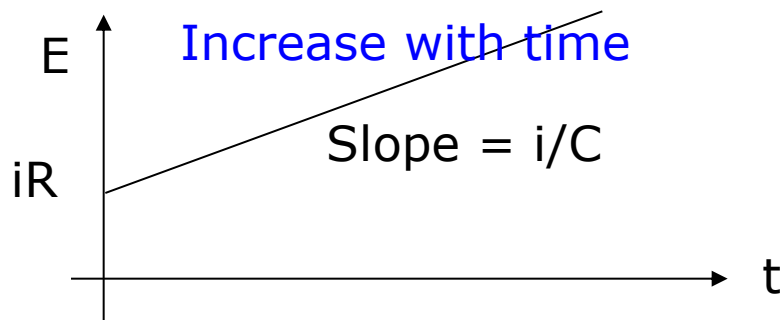
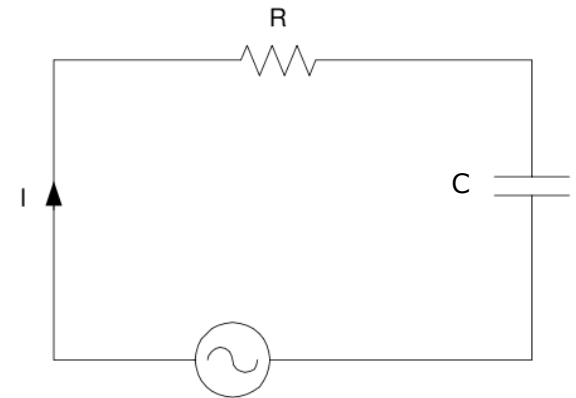


IHP/OHP Diffuse layer


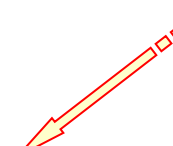


Double-Layer Charging


- Voltage step (chronoamperometry)
 - $i = (E/R)e^{-t/RC}$
 - $\tau = RC$
- Current step (Chronopotentiometry)
 - $E = i(R + t/C)$



First-Order Differential Equation

$$\frac{dy}{dx} + p(x)y = q(x)$$

$$y = \frac{\int \boxed{u(x)} q(x) dx + \textcircled{C}}{\boxed{u(x)}}$$


constant

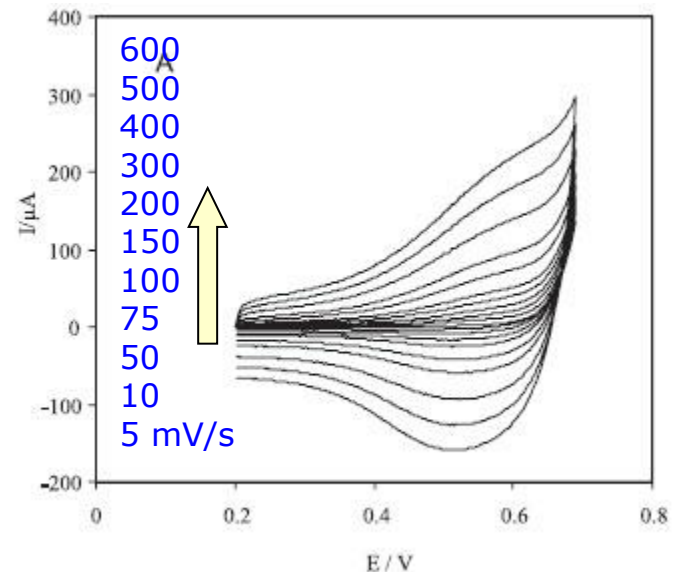
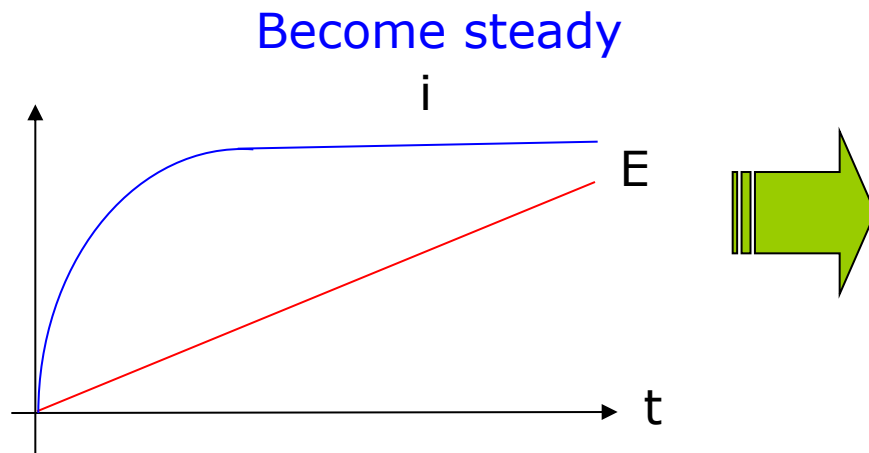

$$u(x) = \exp \left(\int p(x) dx \right)$$

Double-Layer Charging

□ Voltage ramp (cyclic voltammetry, Tafel plot)

- $E = vt$

- $i = vC(1 - e^{-t/RC})$

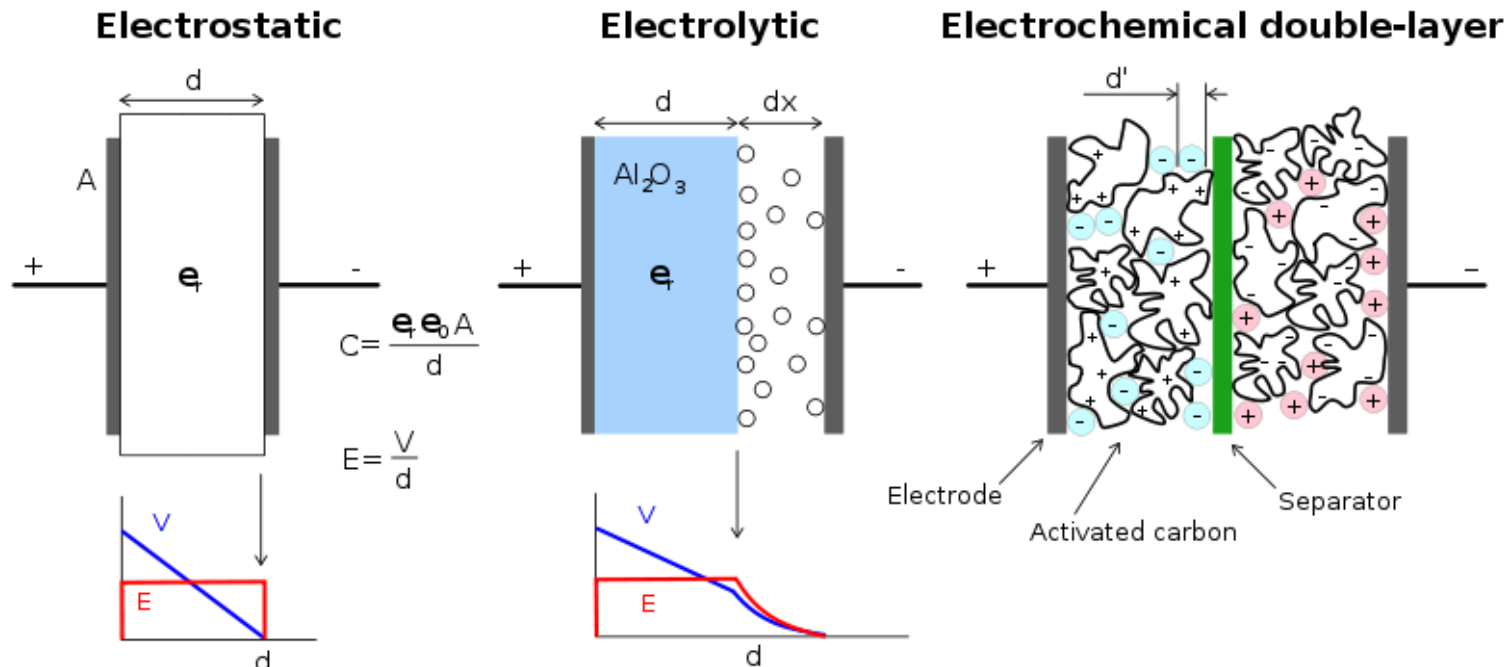


Supercapacitor vs Battery

- ❑ The **supercapacitor (electrochemical double-layer capacitor)** resembles a regular capacitor with the exception that it offers very high capacitance in a small package. Energy storage is by means of static charge rather than of an electrochemical process that is inherent to the battery.
- ❑ The concept is similar to an electrical charge that builds up when walking on a carpet. The supercapacitor concept has been around for a number of years. Newer designs allow higher capacities in a smaller size.
- ❑ RuO_x is a leading candidate of supercapacitor materials



Supercapacitors



Disadvantages

- The amount of energy stored per unit weight is considerably lower than that of an electrochemical battery (3-5 W·h/kg for an ultracapacitor compared to 30-40 W·h/kg for a lead acid battery). It is also only about 1/10,000th the volumetric energy density of gasoline.
- The voltage varies with the energy stored. To effectively store and recover energy requires sophisticated electronic control and switching equipment.

Advantages

- Very high rates of charge and discharge.
- Little degradation over hundreds of thousands of cycles.
- Good reversibility
- Low toxicity of materials used.
- High cycle efficiency (95% or more)
- Low cost per cycle compared to batteries

Electrochemical Currents

□ Faradaic current

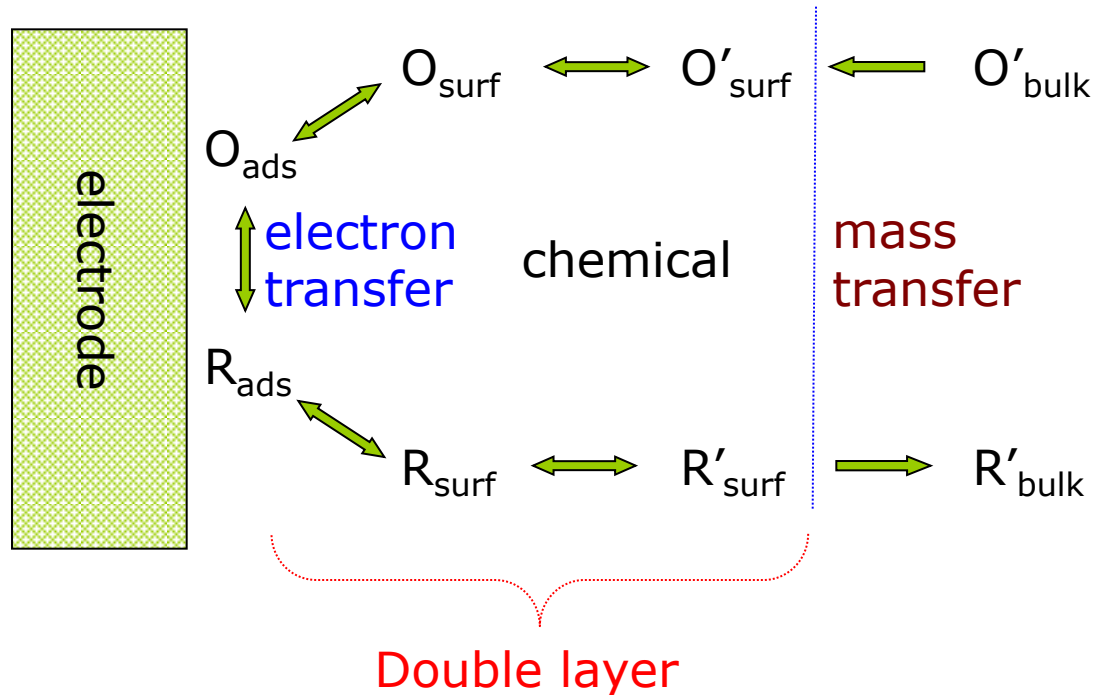
- Faraday's law $N = Q/nF$
- Rate = $dN/dt = i/nF$ (as electrochemical reactions are heterogeneous in nature, they are depending upon the electrode surface area, so typically, $\text{rate} = i/nFA$)

□ Double-layer Charging current

- Classic Physics $C = q/E$
- Double-layer charging current $i_{DL} = C_{DL}Av$

□ Total current $I = i_{DL} + i_F$

Electrode Reactions



- Mass-transfer control
- Kinetic control

Walther Nernst

- ❑ **Walther Hermann Nernst** (25 June 1864 – 18 November 1941) was a German physical chemist and physicist who is known for his theories behind the calculation of chemical affinity as embodied in the third law of thermodynamics, for which he won the 1920 Nobel Prize in chemistry.
- ❑ Nernst helped establish the modern field of physical chemistry and contributed to electrochemistry, thermodynamics, solid state chemistry and photochemistry. He is also known for developing the **Nernst equation**.

$$E = E^o + \frac{RT}{nF} \ln \frac{C_o(x=0)}{C_R(x=0)}$$



Mass-Transfer Control

- Nernstian reversible reaction (i.e., kinetically fast)

- Reaction rate = mt rate = i/nFA

- Nernst-Planck equation

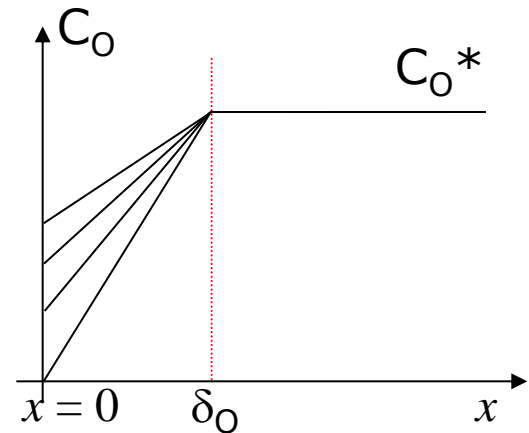
$$J_j(x) = -D_j \frac{\partial C_j(x)}{\partial x} - \frac{z_j F}{RT} D_j C_j \frac{\partial \phi(x)}{\partial x} + C_j v(x)$$

- Diffusion (concentration gradient)
 - Migration (field gradient)
 - Convection (physical motion)

Semiempirical Treatment of Steady-State Mass Transfer

$$v_{MT} = D_o \left(\frac{dC_o(x)}{dx} \right)_{x=0} = \frac{i}{nFA}$$

$$\left\{ \begin{array}{l} i = nFA \frac{D_o}{\delta_o} [C_o^* - C_o(x=0)] \\ i = nFA \frac{D_R}{\delta_R} [C_R(x=0) - C_R^*] \end{array} \right. \Rightarrow i_{LIM} = nFA \frac{D_o}{\delta_o} C_o^*$$

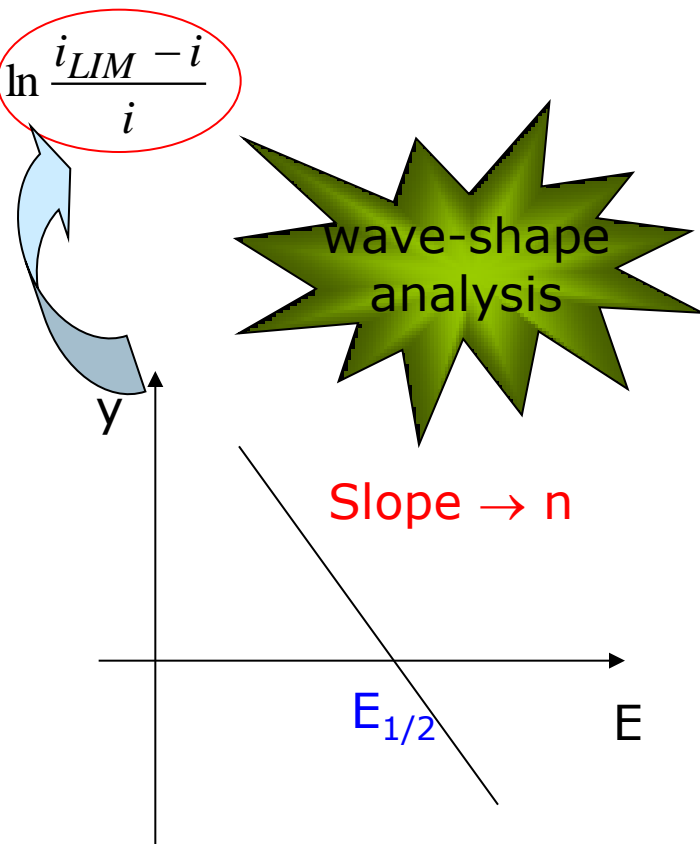
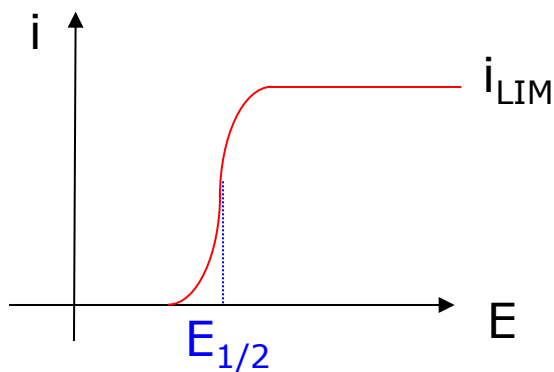


Experimental Condition (I)

□ R initially absent

$$E = E^o + \frac{RT}{nF} \ln \frac{C_o(x=0)}{C_R(x=0)} = E^o - \frac{RT}{nF} \ln \frac{m_o}{m_R} + \frac{RT}{nF} \ln \frac{i_{LIM} - i}{i}$$

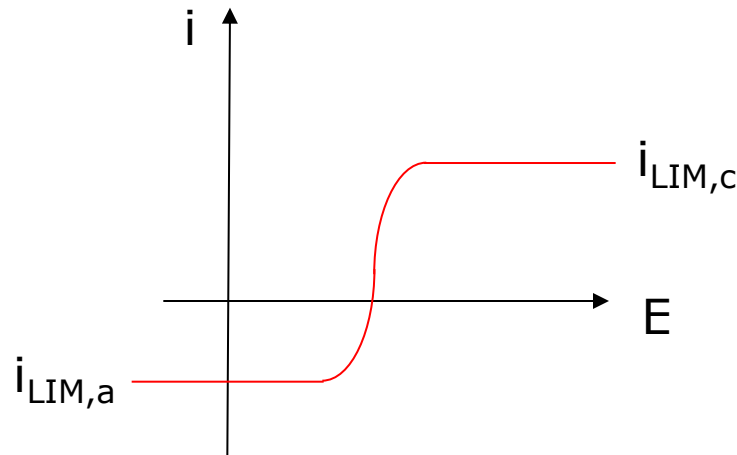
$E_{1/2}$
half-wave potential



Experimental Condition (II)

- Both O and R are initially present

$$E = E^o + \frac{RT}{nF} \ln \frac{C_o(x=0)}{C_R(x=0)} = E^o - \frac{RT}{nF} \ln \frac{m_o}{m_R} + \frac{RT}{nF} \ln \frac{i_{LIM,c} - i}{i - i_{LIM,a}}$$



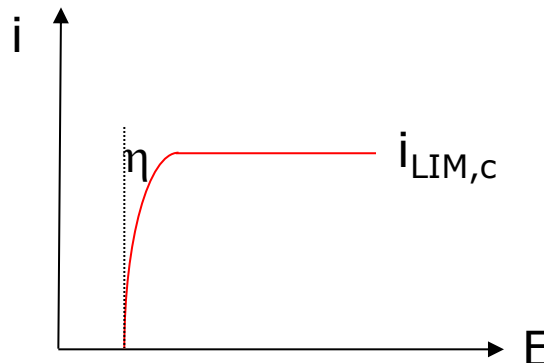
Experimental Condition (III)

□ R is insoluble

- $a_R = 1$

- At $\eta \rightarrow \infty$, $i \rightarrow i_{LIM}$

$$E = E^o + \frac{RT}{nF} \ln \frac{C_o(x=0)}{C_R(x=0)} = E^o + \frac{RT}{nF} \ln C_o^* + \frac{RT}{nF} \ln \frac{i_{LIM} - i}{i_{LIM}}$$



Experimental Condition (IV)

□ Transient response (potential ramp)

$$i = nFA \frac{D_o}{\delta_o(t)} [C_o^* - C_o(x=0)]$$

$$\frac{A\delta(t)}{2} [C_o^* - C_o(x=0)] = \int_0^t \frac{i}{nF} dt$$

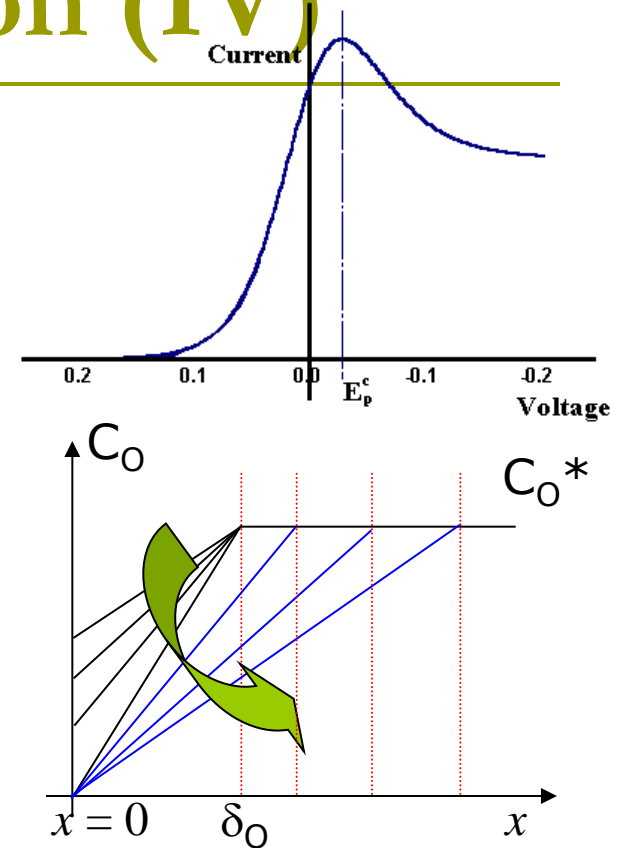
$$\frac{A}{2} [C_o^* - C_o(x=0)] \frac{d\delta(t)}{dt} = \frac{i}{nF} = \frac{D_o A}{\delta(t)} [C_o^* - C_o(x=0)]$$

$$\frac{d\delta(t)}{dt} = \frac{2D_o}{\delta(t)}$$

$$\delta(t) = 2\sqrt{D_o t}$$

Diffuse layer thickness

$$i = \frac{nFA}{2} \sqrt{\frac{D_o}{t}} [C_o^* - C_o(x=0)]$$



growth of depletion
layer with time

Kinetically Controlled Reactions

□ Overpotential (η)

- Deviation from the equilibrium potential (extra driving force) $\eta = E - E_{\text{eq}}$
- The reaction overpotential can be reduced or eliminated with the use of homogeneous or heterogeneous electrocatalysts. The electrochemical reaction rate and related current density is dictated by the kinetics of the electrocatalyst and substrate concentration (e.g., ORR)
 - $\text{O}_2 + 4\text{H}^+ + 4\text{e} \rightleftharpoons 2\text{H}_2\text{O}, +1.229 \text{ V}$

Chemical Reversibility

- ❑ Chemically reversible
 - $\text{Pt}|\text{H}_2|\text{H}^+, \text{Cl}^-|\text{AgCl}|\text{Ag}$, $E = 0.222 \text{ V}$
 - Overall reaction $\text{H}_2 + 2\text{AgCl} \rightleftharpoons 2\text{Ag} + 2\text{Cl}^- + 2\text{H}^+$ may reverse the reaction upon the application of an outside voltage of 0.222 V
- ❑ Chemically irreversible, e.g., $\text{Zn}|\text{H}^+, \text{Cl}^-|\text{Pt}$
 - Galvanic cell: $\text{Zn} + 2\text{H}^+ \rightleftharpoons \text{Zn}^{2+} + \text{H}_2$
 - Electrolytic cell: $2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2$
 - ❑ $2\text{H}^+ + 2\text{e} \rightleftharpoons \text{H}_2$ (Zn electrode)
 - ❑ $2\text{H}_2\text{O} \rightleftharpoons 4\text{H}^+ + 4\text{e} + \text{O}_2$ (Pt electrode)
- ❑ Important parameters
 - cell condition
 - time scale

Alkaline Battery

- Electrolyte: KOH, NH_4Cl , ZnCl_2 , etc
- A type of disposable battery dependent upon the reaction between zinc (anode) and manganese (IV) oxide (cathode)
 - $\text{Zn(s)} + 2\text{OH}^-(\text{aq}) \rightarrow \text{ZnO(s)} + \text{H}_2\text{O(l)} + 2\text{e}^-$
 - $2\text{MnO}_2(\text{s}) + \text{H}_2\text{O(l)} + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3(\text{s}) + 2\text{OH}^-(\text{aq})$
- Overall Reaction
 - $\text{Zn(s)} + 2\text{MnO}_2(\text{s}) \rightarrow \text{ZnO(s)} + \text{Mn}_2\text{O}_3(\text{s})$



Leaking of KOH

Lead Acid Battery

- Electrolyte is fairly concentrated sulfuric acid (H_2SO_4 , about 4M).

- **Anode**

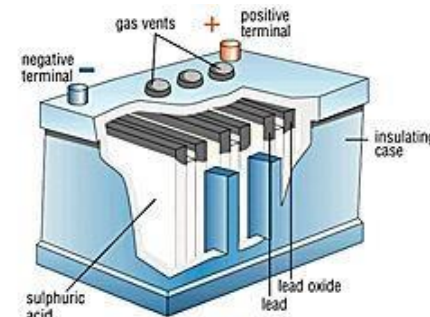
- a thick, porous plate of metallic lead (Pb)
- $\text{Pb} + \text{HSO}_4^- \rightarrow \text{PbSO}_4 + \text{H}^+ + 2\text{e}^-$

- **Cathode**

- a plate consisting mostly of porous lead dioxide (PbO_2) paste, supported on a thin metal grid
- $\text{PbO}_2 + 3\text{H}^+ + \text{HSO}_4^- + 2\text{e}^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$

- **Overall Reactions**

- $\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$



Lead Acid Battery



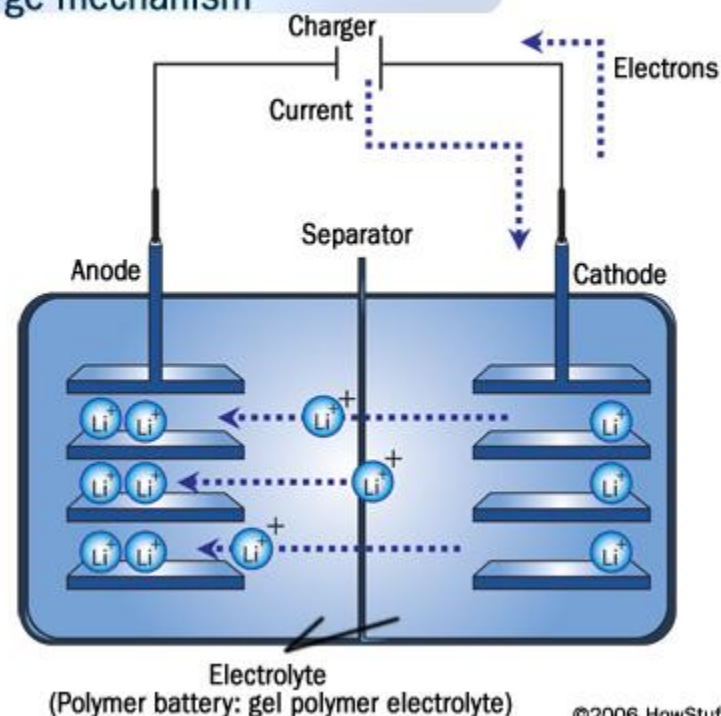
Lithium Ion Battery



- Electrolyte is a lithium salt in an organic solvent
- Cathode contains lithium
 - $\text{LiCoO}_2 \rightleftharpoons \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^-$
- The anode is generally made of a type of porous carbon
 - $x\text{Li}^+ + xe^- + 6\text{C} \rightleftharpoons \text{Li}_x\text{C}_6$
- Overall Reaction



Lithium-ion rechargeable battery
Charge mechanism



Thermodynamic Reversibility

- Reversible reactions (fast ET kinetics)
 - Achieve thermodynamic equilibrium
 - Can be readily reversed with an infinitesimal driving force
 - Concentration profiles follow Nernstian equation

$$E = E^o + \frac{RT}{nF} \ln \frac{C_O}{C_R}$$

- Thermodynamic parameters

- $\Delta G = -nFE$ $\Delta G^o = -nFE^o = -RT \ln K_{eq}$

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_P = nF\left(\frac{\partial E}{\partial T}\right)$$

$$\Delta H = nF\left[T\left(\frac{\partial E}{\partial T}\right) - E\right]$$

Reaction thermodynamics
determines the electromotive
force of the cell

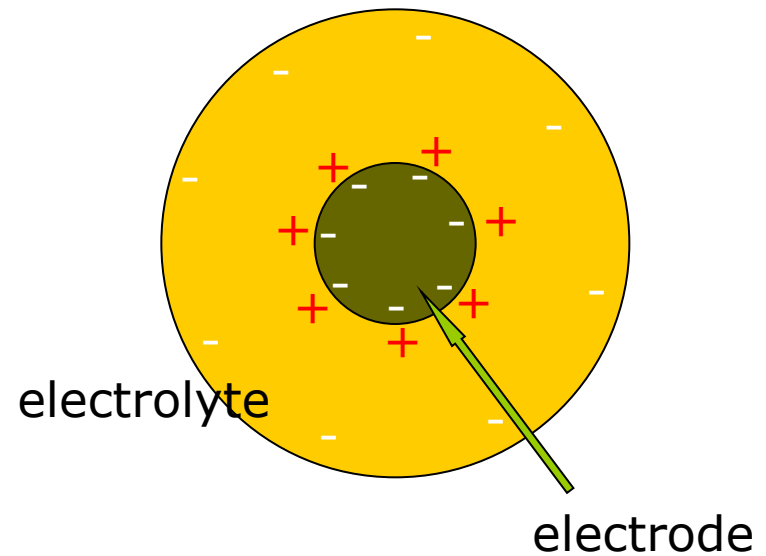
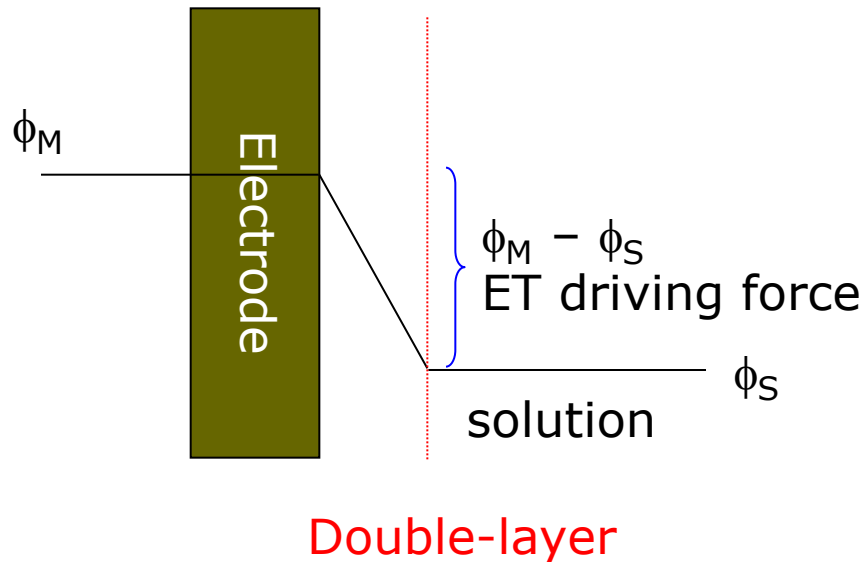
Potential Distribution in a Conducting Phase

- ❑ Changes in the potential can be effected by the charge
- ❑ If the phase undergoes a charge, its charge carriers the excess becomes who **entire boundary** of the phase
- ❑ The surface distribution is field strength **within the** current condition
- ❑ The interior of the phase **potential**



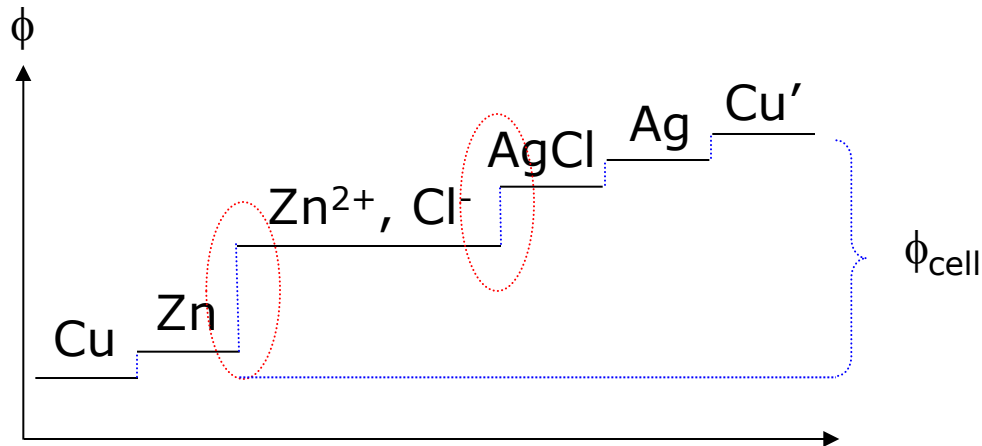
Interfacial Distribution of Potential

- At equilibrium (null current), all conducting phases exhibit an equi-potential surface; that means, the potential difference only occurs at the interface



Interfacial Distribution of Potential

- Overall cell potential = Σ (all interfacial potential drops)
- $\text{Cu} \mid \text{Zn} \mid \text{Zn}^{2+}, \text{Cl}^{-} \mid \text{AgCl} \mid \text{Ag} \mid \text{Cu}'$



Electrochemical Potential

$$\bar{\mu}_i^\alpha = \mu_i^\alpha + z_i F \phi^\alpha$$

- For uncharged species, $\bar{\mu}_i^\alpha = \mu_i^\alpha$
- For any substance, $\mu_i^\alpha = \mu_i^{\alpha,0} + RT \ln a_i^\alpha$
- For a pure substance of unit activity, $\bar{\mu}_i^\alpha = \mu_i^{\alpha,0}$
- For electrons in a metal, $\bar{\mu}_i^\alpha = \mu_i^{\alpha,0} - F \phi^\alpha$
- At equilibrium, $\bar{\mu}_i^\alpha = \bar{\mu}_i^\beta$

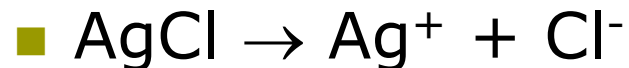
Electrochemical Potential

- Reactions in a single phase w/o charge transfer



$$\bar{\mu}_{\text{HAc}} = \bar{\mu}_{\text{H}^+} + \bar{\mu}_{\text{Ac}^-} \quad \Rightarrow \quad \mu_{\text{HAc}} = \mu_{\text{H}^+} + \mu_{\text{Ac}^-}$$

- Reactions involving two phases but no charge transfer



$$\bar{\mu}_{\text{AgCl}}^{\text{AgCl}} = \bar{\mu}_{\text{Ag}^+}^s + \bar{\mu}_{\text{Cl}^-}^s \quad \Rightarrow \quad \mu_{\text{AgCl}}^{\text{AgCl},o} = \mu_{\text{Ag}^+}^s + \mu_{\text{Cl}^-}^s$$

Chemical
Potential
(μ)

Formulation of Cell Potential



$$\bar{\mu}_{\text{Zn}}^{\text{Zn}} + 2\bar{\mu}_{\text{AgCl}}^{\text{AgCl}} + 2\bar{\mu}_e^{\text{Cu}} = \bar{\mu}_{\text{Zn}^{2+}}^s + 2\bar{\mu}_{\text{Ag}}^{\text{Ag}} + 2\bar{\mu}_{\text{Cl}^-}^s + 2\bar{\mu}_e^{\text{Cu}'}$$

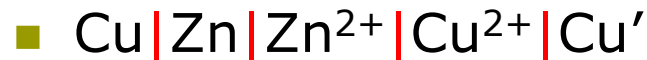


$$E = E^o - \frac{RT}{2F} \ln a_{\text{Zn}^{2+}} a_{\text{Cl}^-}^2$$

Nernst Equation

Liquid Junction Potential

- Potential differences at the electrolyte-electrolyte interface

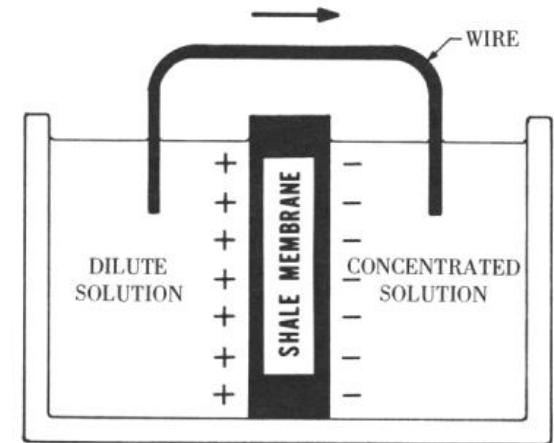


$$E = (\phi^{\text{Cu}'} - \phi^{\text{Cu}^{2+}}) - (\phi^{\text{Cu}} - \phi^{\text{Zn}^{2+}}) +$$

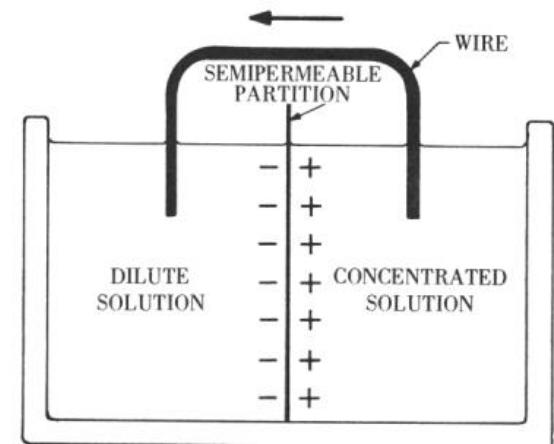
$$(\phi^{\text{Cu}^{2+}} - \phi^{\text{Zn}^{2+}})$$

- Three major cases

- Two solutions of the same electrolyte at different concentrations
 - Two solutions at the same concentration but of different electrolytes that share a common ion
 - Others



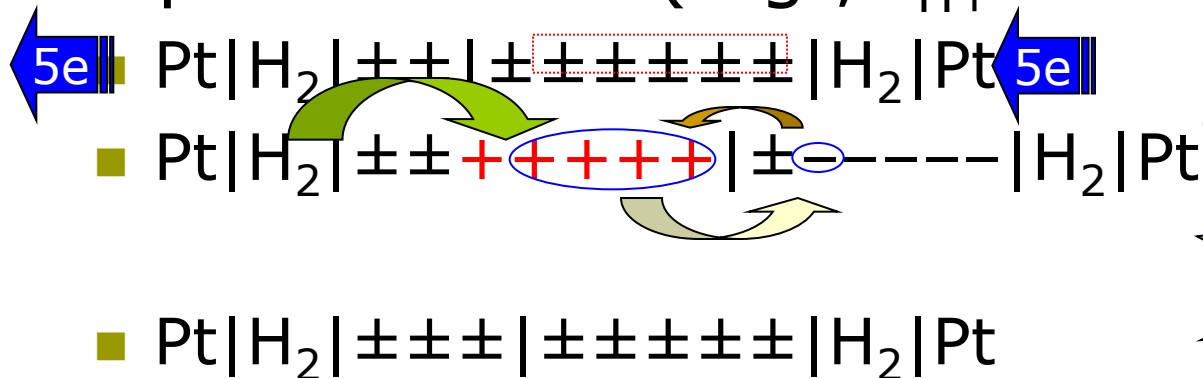
Shale Potential



Liquid-Junction Potential

Transference Numbers

- Transference or transport number (t)
 - In an electrolyte solution, the current is carried by the movement of ions, the fraction of which carried by the cation/anion is called transference number (t_+ and t_-)
 - $t_+ + t_- = 1$ or in general $\sum t_i = 1$
- Liquid Junction (e.g., $t_{H^+} = 0.8$, $t_{Cl^-} = 0.2$)



ionic movement
in electrolyte solution

Mobility

□ Definition (u_i , $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)

- Limiting velocity of the ion in an electric field of unit strength, when the dragging force ($6\pi\eta rv$) is in balance with the electric force ($|z|e\xi$).

$$u_i = \frac{v}{\xi} = \frac{|z_i|e}{6\pi\eta r}$$

$$r = \frac{kT}{6\pi D \eta}$$

Einstein-Stokes eq.

□ Einstein relation

$$D = \frac{u_i kT}{|z_i|e}$$

Fe^{3+} in water, $D = 5.2 \times 10^{-6} \text{ cm}^2/\text{s}$

$\eta = 0.01 \text{ g/cm.s}$, $r = 4.20 \text{ \AA}$

Cf. $r = 0.49 \sim 0.55 \text{ \AA}$ in ionic crystals

Transference Number

□ Solution Conductivity $\kappa = F \sum_i |z_i| u_i C_i$

□ Relationship to transference number

$$t_i = \frac{|z_i| u_i C_i}{\sum_j |z_j| u_j C_j}$$

Liquid Junction Potential

- $\text{Pt}|\text{H}_2|\text{H}^+(\alpha)|\text{H}^+(\beta)|\text{H}_2|\text{Pt}'$
 - Anode $\frac{1}{2}\text{H}_2 \rightarrow \text{H}^+(\alpha) + \text{e}(\text{Pt})$
 - Cathode $\text{H}^+(\beta) + \text{e}(\text{Pt}') \rightarrow \frac{1}{2}\text{H}_2$
 - Overall $\text{H}^+(\beta) + \text{e}(\text{Pt}') \rightarrow \text{H}^+(\alpha) + \text{e}(\text{Pt})$
- Electrochemical potential at null current

$$\bar{\mu}_{\text{H}^+}^{\beta} + \bar{\mu}_e^{\text{Pt}'} = \bar{\mu}_{\text{H}^+}^{\alpha} + \bar{\mu}_e^{\text{Pt}}$$

$$FE = F\left(\phi^{\text{Pt}'} - \phi^{\text{Pt}}\right) = \bar{\mu}_{\text{H}^+}^{\beta} - \bar{\mu}_{\text{H}^+}^{\alpha}$$

$$E = \frac{RT}{nF} \ln\left(\frac{a_{\beta}}{a_{\alpha}}\right) + \boxed{\left(\phi^{\beta} - \phi^{\alpha}\right)} \quad \text{Liquid-junction potential}$$

Nernstian component

Charge Transport Across Liquid Junction

□ Charge balance

$$t_+H^+(\alpha) + t_-Cl^-(\beta) = t_+H^+(\beta) + t_-Cl^-(\alpha)$$

$$t_+\bar{\mu}_{H^+}^\alpha + t_-\bar{\mu}_{Cl^-}^\beta = t_+\bar{\mu}_{H^+}^\beta + t_-\bar{\mu}_{Cl^-}^\alpha$$

$$t_+(\bar{\mu}_{H^+}^\alpha - \bar{\mu}_{H^+}^\beta) = t_-(\bar{\mu}_{Cl^-}^\alpha - \bar{\mu}_{Cl^-}^\beta)$$

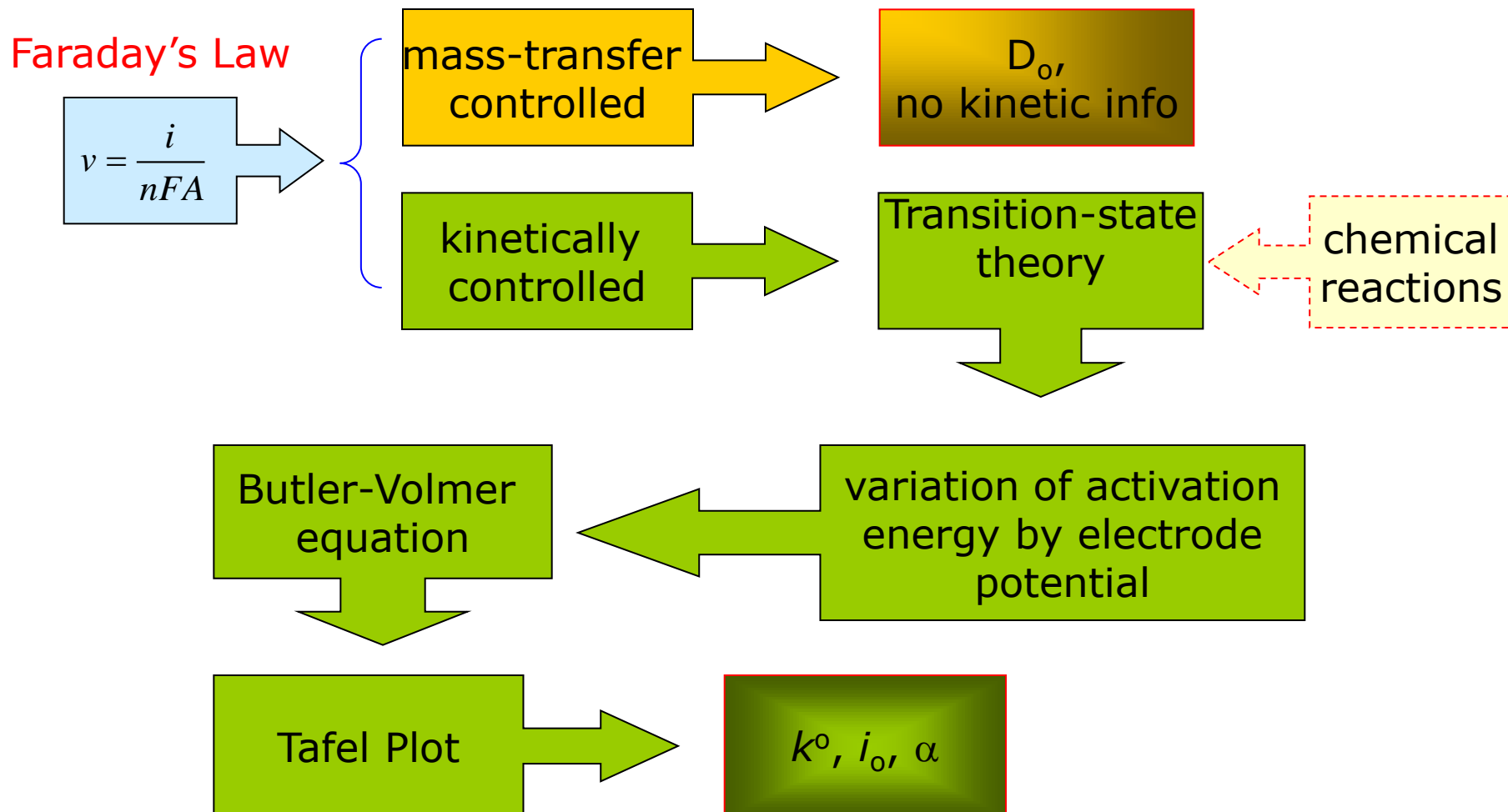
$$E_{LJ} = (\phi^\beta - \phi^\alpha) = (t_+ - t_-) \frac{RT}{F} \ln \left(\frac{a_\alpha}{a_\beta} \right)$$

□ Salt bridge: minimize LJ potential

- $t_+ \approx t_- \approx 0.5$ (KCl, KNO₃, etc)

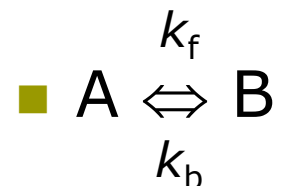


Quick Overview



Kinetics of Electrode Reactions

□ Overview of chemical reactions



■ $v_f = k_f C_A; v_b = k_b C_B$

■ $v_{\text{net}} = v_f - v_b = k_f C_A - k_b C_B$

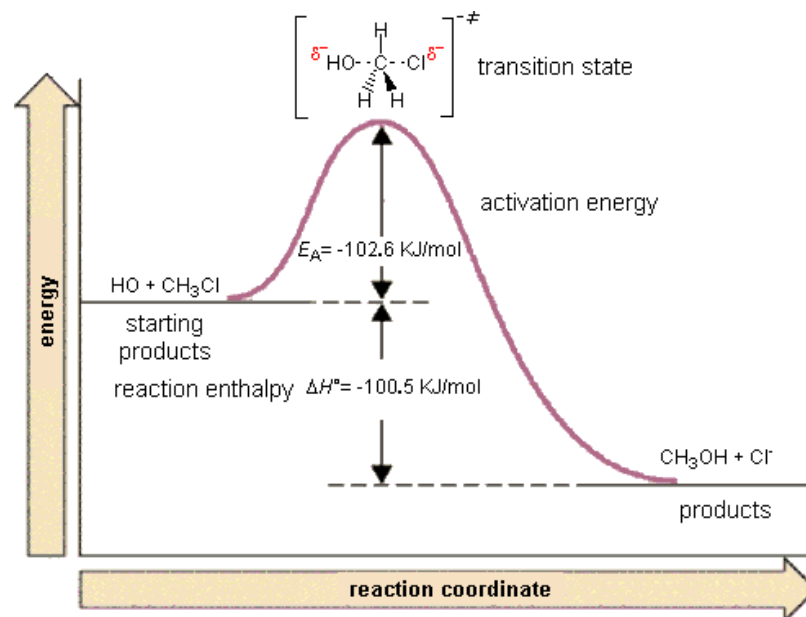
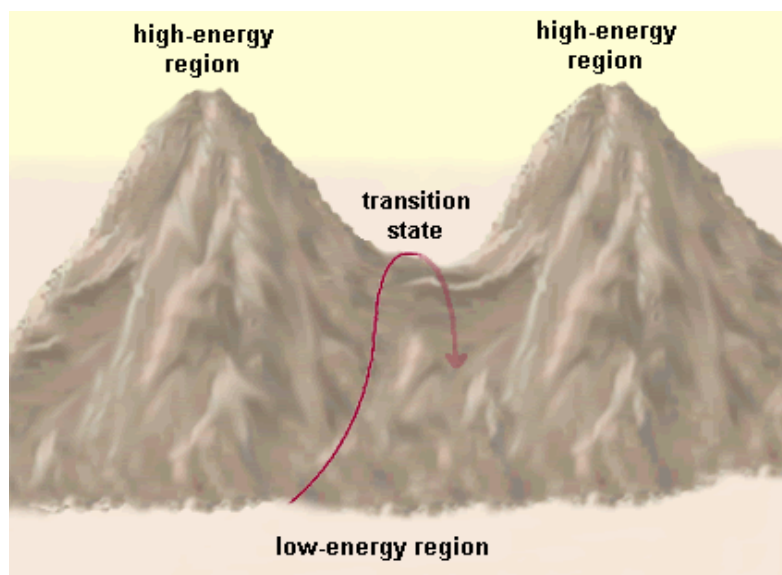
■ At equilibrium, $v_{\text{net}} = 0$, so $K_{EQ} = \frac{C_B}{C_A} = \frac{k_f}{k_b}$

Transition-State Theory

- ▣ The theory was first developed by R. Marcelin in 1915, then continued by Henry Eyring and Michael Polanyi (**Eyring equation**) in 1931, with their construction of a potential energy surface for a chemical reaction, and later, in 1935, by H. Pelzer and Eugene Wigner. Meredith Evans, working in coordination with Polanyi, also contributed significantly to this theory.

Transition-State Theory

- Transition state theory is also known as *activated-complex theory* or *theory of absolute reaction rates*.
- In chemistry, **transition state theory** is a conception of chemical reactions or other processes involving rearrangement of matter as proceeding through a continuous change or "transition state" in the relative positions and potential energies of the constituent atoms and molecules.



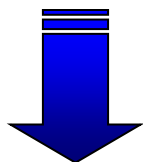
Svante August Arrhenius

- ❑ Svante August Arrhenius (19 February 1859 – 2 October 1927) was a Swedish scientist, originally a physicist, but often referred to as a chemist, and **one of the founders** of the science of physical chemistry.
- ❑ The Arrhenius equation, lunar crater Arrhenius and the Arrhenius Labs at Stockholm University are named after him.



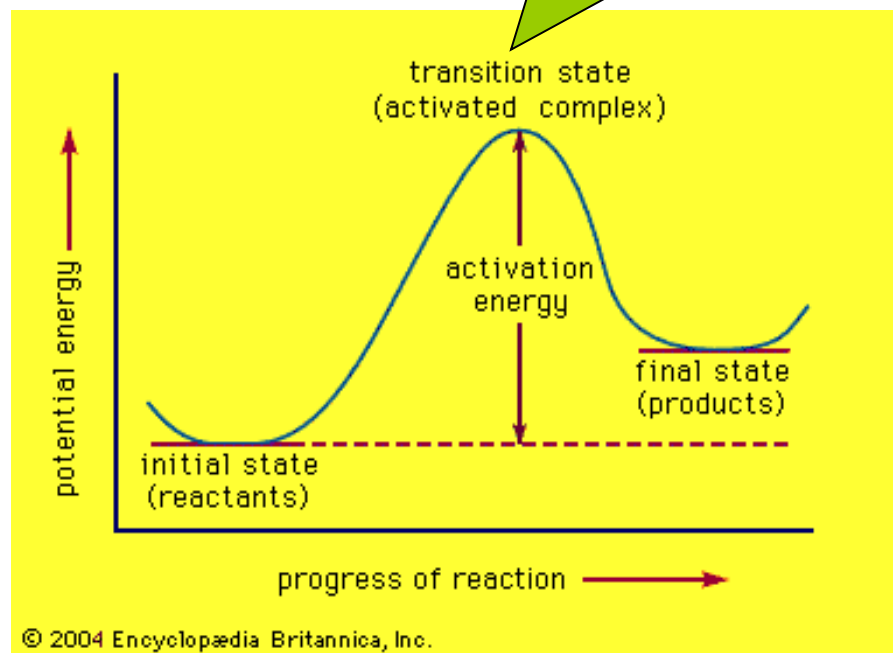
Arrhenius Equation

$$k = Ae^{-\left(E_A/RT\right)}$$



$$k = A'e^{-\left(\Delta G^\ddagger/RT\right)}$$

Wave function overlap



Transition-State Theory

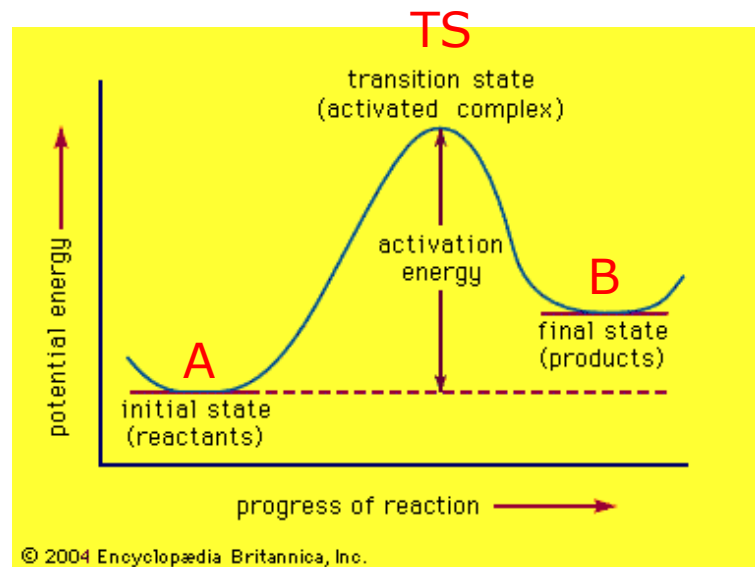
□ At equilibrium

- $k_f C_A = f_{AB} k' C_{TS}; k_b C_B = f_{BA} k' C_{TS}$

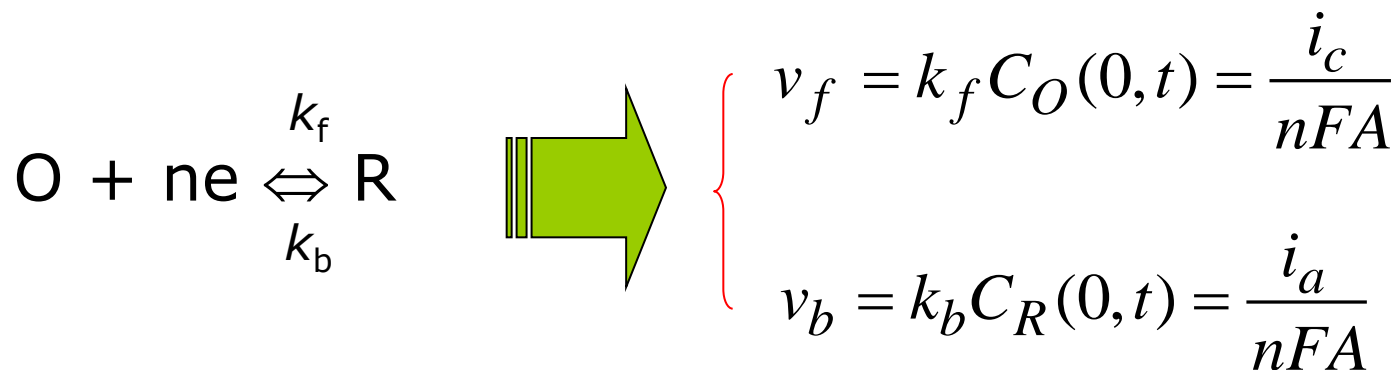
- $f_{AB} = f_{BA} = \kappa/2$



$$\left\{ \begin{array}{l} k_f = \frac{\kappa}{2} k' e^{-\left(\frac{\Delta G_f^\ddagger}{RT}\right)} \\ k_b = \frac{\kappa}{2} k' e^{-\left(\frac{\Delta G_b^\ddagger}{RT}\right)} \end{array} \right.$$



Electrode Reactions



$$v_{net} = v_f - v_b = k_f C_O(0,t) - k_b C_R(0,t) = \frac{i_c - i_a}{nFA}$$

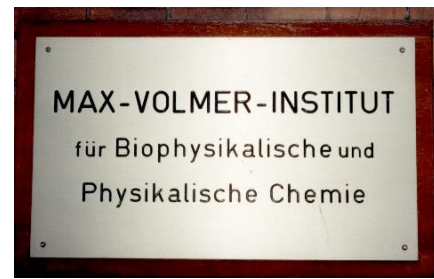
$$i = nFA \left[k_f C_O(0,t) - k_b C_R(0,t) \right]$$

Butler – Volmer Equation

John Alfred Valentine Butler

- John Alfred Valentine Butler (born 14 February, 1899) was the British physical chemist who was **the first to connect the kinetic electrochemistry** built up in the second half of the twentieth century **with the thermodynamic electrochemistry** that dominated the first half. He had to his credit, not only the first exponential relation between current and potential (1924), but also (along with R.W. Gurney) the introduction of energy-level thinking into electrochemistry (1951).
- However, Butler did not get all quite right and therefore it is necessary to give credit also to Max Volmer, a great German surface chemist of the 1930 and his student Erdey-Gruz. Butler's very early contribution in 1924 and the Erdey-Gruz and Volmer contribution in 1930 form the basis of phenomenological kinetic electrochemistry. The resulting famous **Butler-Volmer equation** is very important in electrochemistry.
- Butler was the **quintessential absent-minded** research scientist of legend, often lost to the world in thought. During such periods of contemplation he sometimes whistled softly to himself, though he was known on occasion to petulantly instruct nearby colleagues to be quiet.

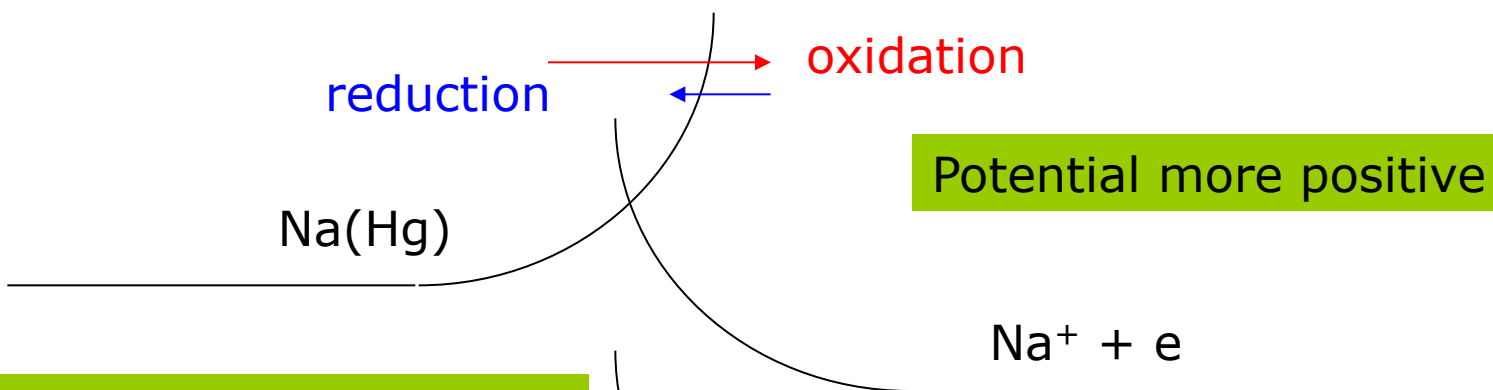
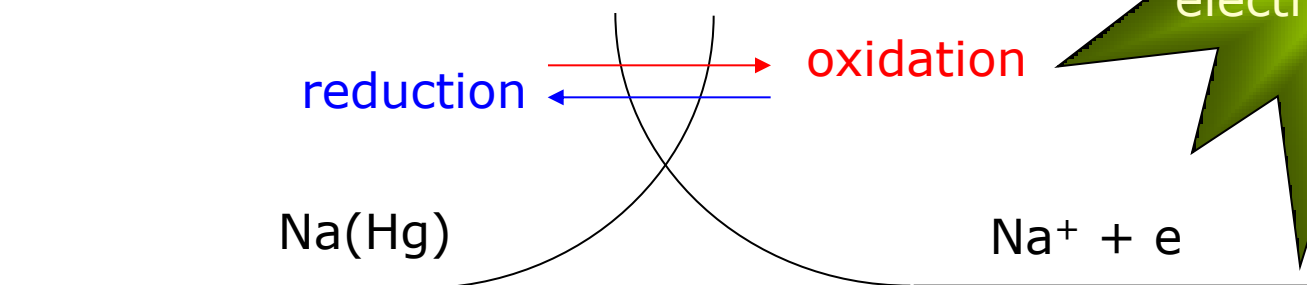
Max Volmer



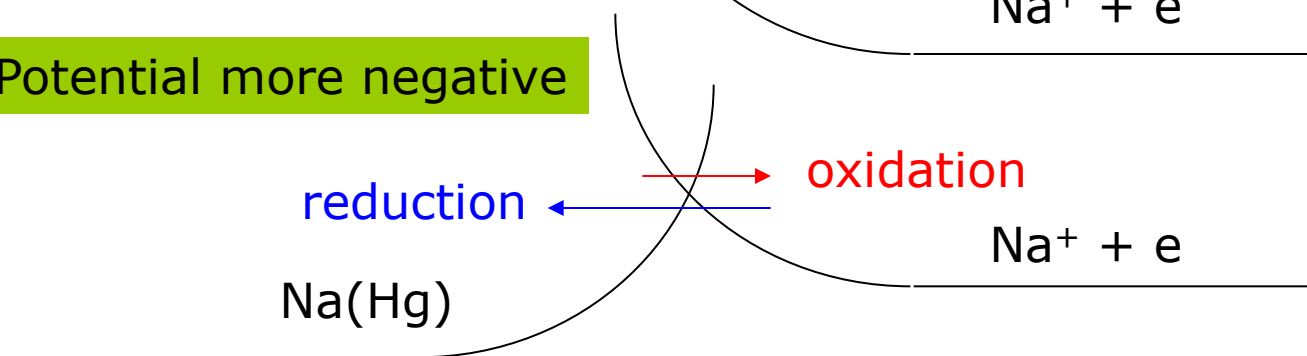
- ❑ Max Volmer (3 May 1885 in Hilden – 3 June 1965 in Potsdam) was a German physical chemist, who made important contributions in electrochemistry, in particular on electrode kinetics. He co-developed the Butler-Volmer equation.
- ❑ Volmer held the chair and directorship of the Physical Chemistry and Electrochemistry Institute of the Technische Hochschule Berlin, in Berlin-Charlottenburg. After World War II, he went to the Soviet Union, where he headed a design bureau for the production of heavy water. Upon his return to East Germany ten years later, he became a professor at the Humboldt University of Berlin and was president of the East German Academy of Sciences.

Butler-Volmer Model

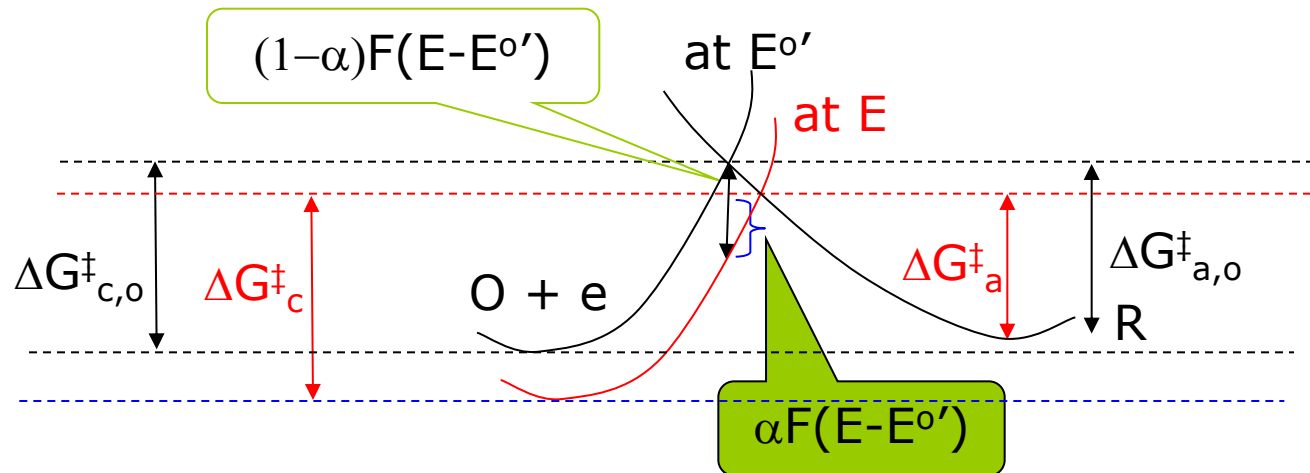
electrode potential
only changes the
electron energy



Potential more negative



Butler-Volmer Model

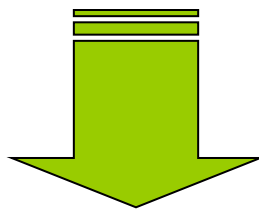


- ▣ $\Delta G_a^{\ddagger} = \Delta G_{a,0}^{\ddagger} - (1 - \alpha)F(E - E^{\circ'})$
- ▣ $\Delta G_c^{\ddagger} = \Delta G_{c,0}^{\ddagger} + \alpha F(E - E^{\circ'})$

α : transfer coefficient

Butler-Volmer Formulation

$$k_b = k^o e^{(1-\alpha)\frac{nF}{RT}(E-E^{o'})} \quad k_f = k^o e^{-\alpha\frac{nF}{RT}(E-E^{o'})}$$



$$i = nFAk^o \left[\underset{\text{Cathodic current}}{C_O(0,t)e^{-\alpha\frac{nF}{RT}(E-E^{o'})}} - \underset{\text{Anodic current}}{C_R(0,t)e^{(1-\alpha)\frac{nF}{RT}(E-E^{o'})}} \right]$$

applied to any electrochemical reactions under any conditions

Electrode Reaction Kinetics

$$k_b = A_b e^{-\left(\frac{\Delta G_a^\ddagger}{RT}\right)} = A_b e^{-\left(\frac{\Delta G_{b,o}^\ddagger}{RT}\right)} e^{\left(\frac{(1-\alpha)nF(E-E^{o'})}{RT}\right)} = k_{b,o} e^{\frac{(1-\alpha)nF}{RT}(E-E^{o'})}$$

$$k_f = A_f e^{-\left(\frac{\Delta G_c^\ddagger}{RT}\right)} = A_f e^{-\left(\frac{\Delta G_{c,o}^\ddagger}{RT}\right)} e^{\left(\frac{-\alpha nF(E-E^{o'})}{RT}\right)} = k_{f,o} e^{-\alpha \frac{nF}{RT}(E-E^{o'})}$$

□ At equilibrium ($i = 0$) where $C_O^* = C_R^*$, $E = E^{o'}$, thus $k_f = k_b = k^0$

Experimental Implications

□ At equilibrium $i_{\text{net}} = 0$

$$C_O(0,t)e^{-\alpha\frac{nF}{RT}(E_{eq}-E^{o'})} = C_R(0,t)e^{(1-\alpha)\frac{nF}{RT}(E_{eq}-E^{o'})} \quad \Rightarrow \quad \frac{C_O(0,t)}{C_R(0,t)} = e^{\frac{nF}{RT}(E_{eq}-E^{o'})}$$

$$E_{eq} = E^{o'} + \frac{RT}{nF} \ln \left[\frac{C_O(0,t)}{C_R(0,t)} \right] = E^{o'} + \frac{RT}{nF} \ln \left[\frac{C_O^*}{C_R^*} \right] \quad \text{Nernst equation}$$

□ Exchange current i_o

$$i_o = nFAk^o C_O^* e^{-\alpha\frac{nF}{RT}(E_{eq}-E^{o'})} = nFAk^o C_R^* e^{(1-\alpha)\frac{nF}{RT}(E_{eq}-E^{o'})} = nFAk^o C_O^{*(1-\alpha)} C_R^{*\alpha}$$

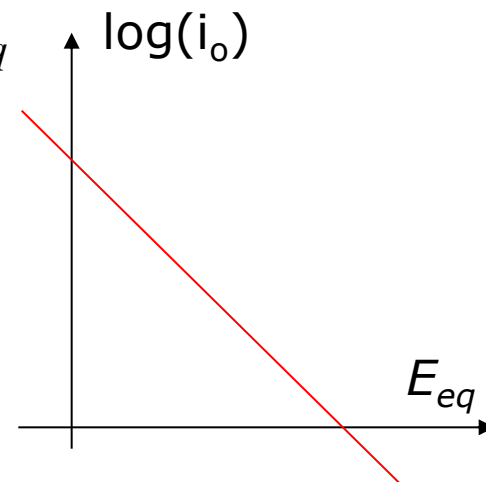
Exchange Current Plot

$$\log i_o = \log F A k^o + \log C_O^* + \left(\frac{\alpha F}{2.3RT} \right) E^{o'} - \left(\frac{\alpha F}{2.3RT} \right) E_{eq}$$

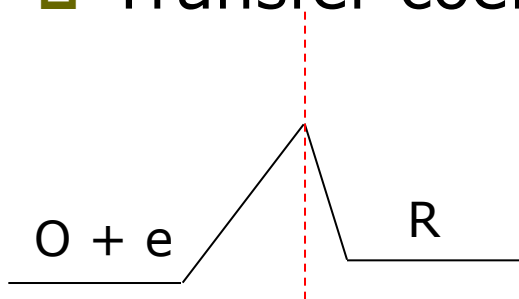
□ Plot of $\log(i_o)$ vs E_{eq}

■ Slope $\Rightarrow \alpha$

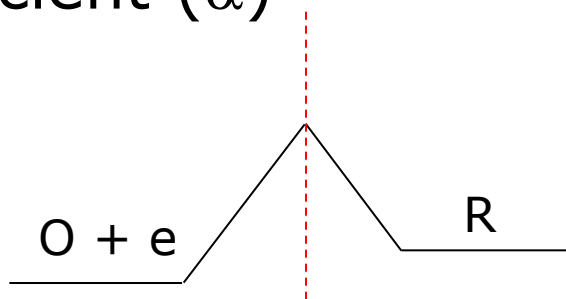
■ Intercept $\Rightarrow k^o$



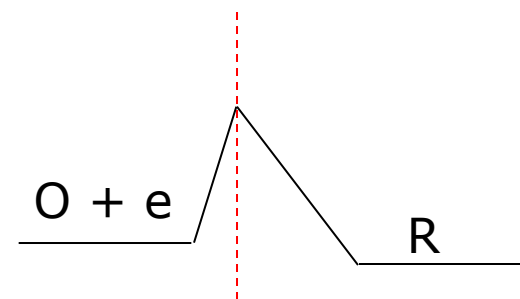
□ Transfer coefficient (α)



$\alpha < 0.5$



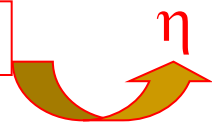
$\alpha = 0.5$



$\alpha > 0.5$

$i - \eta$ equation

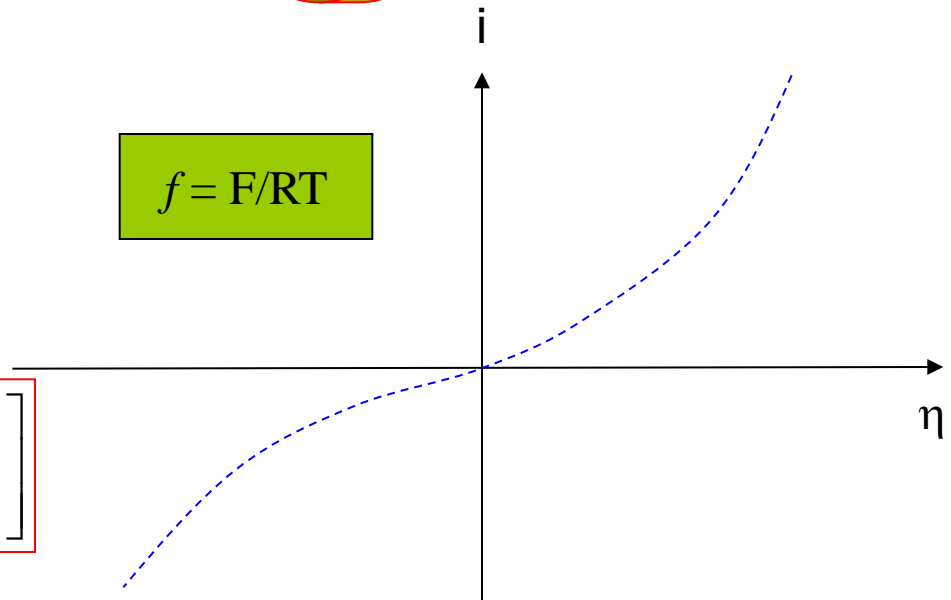
$$i = nFAk^o \left[C_O(0,t) e^{-\alpha \frac{nF}{RT} (E - E^{o'})} - C_R(0,t) e^{(1-\alpha) \frac{nF}{RT} (E - E^{o'})} \right]$$

$$\frac{i}{i_o} = \frac{C_O(0,t)}{C_O^*} e^{-\alpha \frac{nF}{RT} (E - E_{eq})} - \frac{C_R(0,t)}{C_R^*} e^{(1-\alpha) \frac{nF}{RT} (E - E_{eq})}$$


$$\frac{i}{i_o} = \frac{C_O(0,t)}{C_O^*} e^{-\alpha n f \eta} - \frac{C_R(0,t)}{C_R^*} e^{(1-\alpha) n f \eta}$$

$$f = F/RT$$

$$i = i_o \left[\frac{C_O(0,t)}{C_O^*} e^{-\alpha n f \eta} - \frac{C_R(0,t)}{C_R^*} e^{(1-\alpha) n f \eta} \right]$$

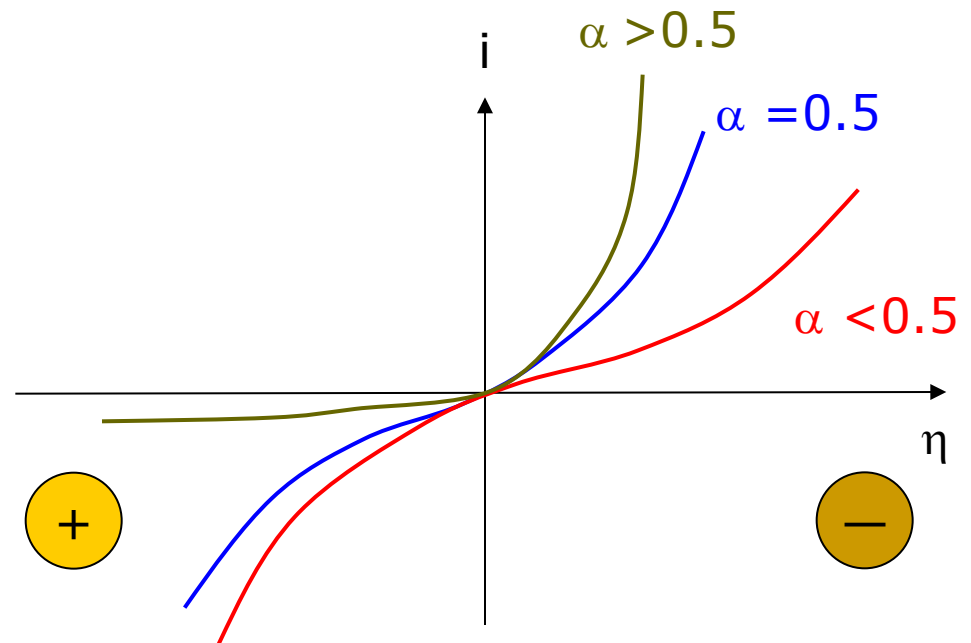


No Mass Transfer

- ▣ Solutions under vigorous stirring
- ▣ Very small current
- ▣ $C_O(0,t) = C_O^*$; $C_R(0,t) = C_R^*$

- ▣ $i = i_o [e^{-\alpha n f \eta} - e^{(1-\alpha) n f \eta}]$

Butler-Volmer Equation





Julius Tafel

The year 1898 marked a turning point in organic electrochemistry with Swiss chemist **Julius Tafel** (1862-1918) demonstrating the use of lead as an electrode for the reduction of organic compounds. Tafel, who was both an organic chemist and a physical chemist, made seminal contributions to organic electrochemistry and established the Tafel equation connecting the rates of electrochemical reactions and overpotential. The Tafel equation was unique in that it could be applied

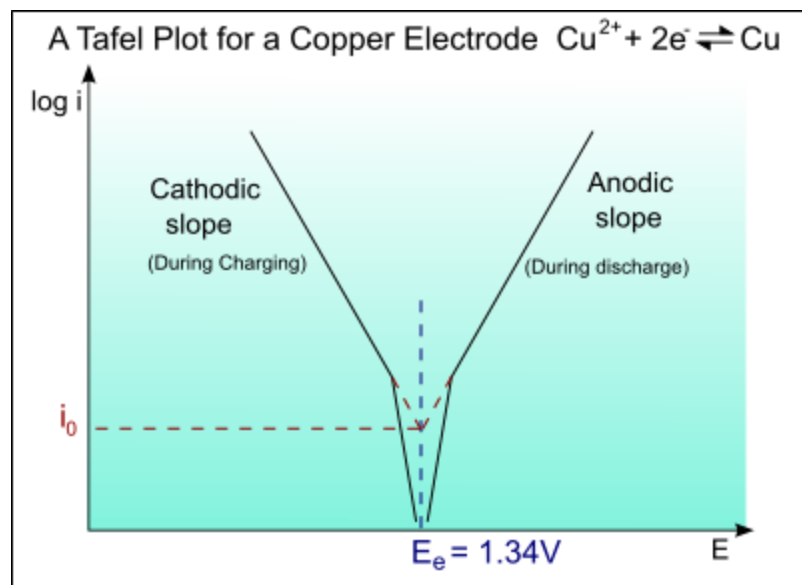
to irreversible electrochemical reactions that could not be described by thermodynamics. The several contributions he made in organic chemistry include reduction with amalgams and the Tafel rearrangement. Tafel is also known for introducing the hydrogen coulometer for measurement of electrochemical reaction rates and pre-electrolysis as a method for purifying solutions.

Tafel Plots

Slope: α
Intercept: i_0

- Very small η
 - $i = -i_0 F \eta / RT$ and $R_{CT} = |\eta / i| = RT / n F i_0$
- Very large η
 - Negative η , $i = i_0 e^{-\alpha n f \eta}$
 - Positive η , $i = i_0 e^{(1-\alpha) n f \eta}$
- From the plot, i_0 (k°) and α can be determined.

experimentally sometimes nonlinear profiles appear, suggesting multiple reactions



Very Facile Reactions

$$i_o \rightarrow \infty \gg \frac{i}{i_o} \rightarrow 0$$

$$C_O(0,t)e^{-\alpha n f(E_{eq} - E^{o'})} = C_R(0,t)e^{(1-\alpha)n f(E_{eq} - E^{o'})}$$

$$E_{eq} = E^{o'} + \frac{RT}{nF} \ln \left(\frac{C_O(0,t)}{C_R(0,t)} \right)$$

$$E_{eq} = E^{o'} + \frac{RT}{nF} \ln \left(\frac{C_O^*}{C_R^*} \right)$$

Nernstian process: kinetically facile reactions

Effects of Mass Transfer

$$\left. \begin{aligned} \frac{C_O(0,t)}{C_O^*} &= 1 - \frac{i}{i_{l,c}} \\ \frac{C_R(0,t)}{C_R^*} &= 1 - \frac{i}{i_{l,a}} \end{aligned} \right\} \frac{i}{i_o} = \left(1 - \frac{i}{i_{l,c}}\right) e^{-\alpha n f \eta} - \left(1 - \frac{i}{i_{l,a}}\right) e^{(1-\alpha) n f \eta}$$



$$\frac{i}{i_o} = \frac{C_O(0,t)}{C_O^*} - \frac{C_R(0,t)}{C_R^*} - \frac{nF\eta}{RT} \quad \Rightarrow \quad \eta = -i \left(\frac{RT}{nF} \right) \left(\frac{1}{i_o} + \frac{1}{i_{l,c}} - \frac{1}{i_{l,a}} \right)$$

$$\eta = -i \left(R_{ct} + R_{mt,c} + R_{mt,a} \right)$$

$R_{ct} \ll R_{mt}$: mt controlled

$R_{ct} \gg R_{mt}$: ct controlled

Electrochemical and Chemical Reactions

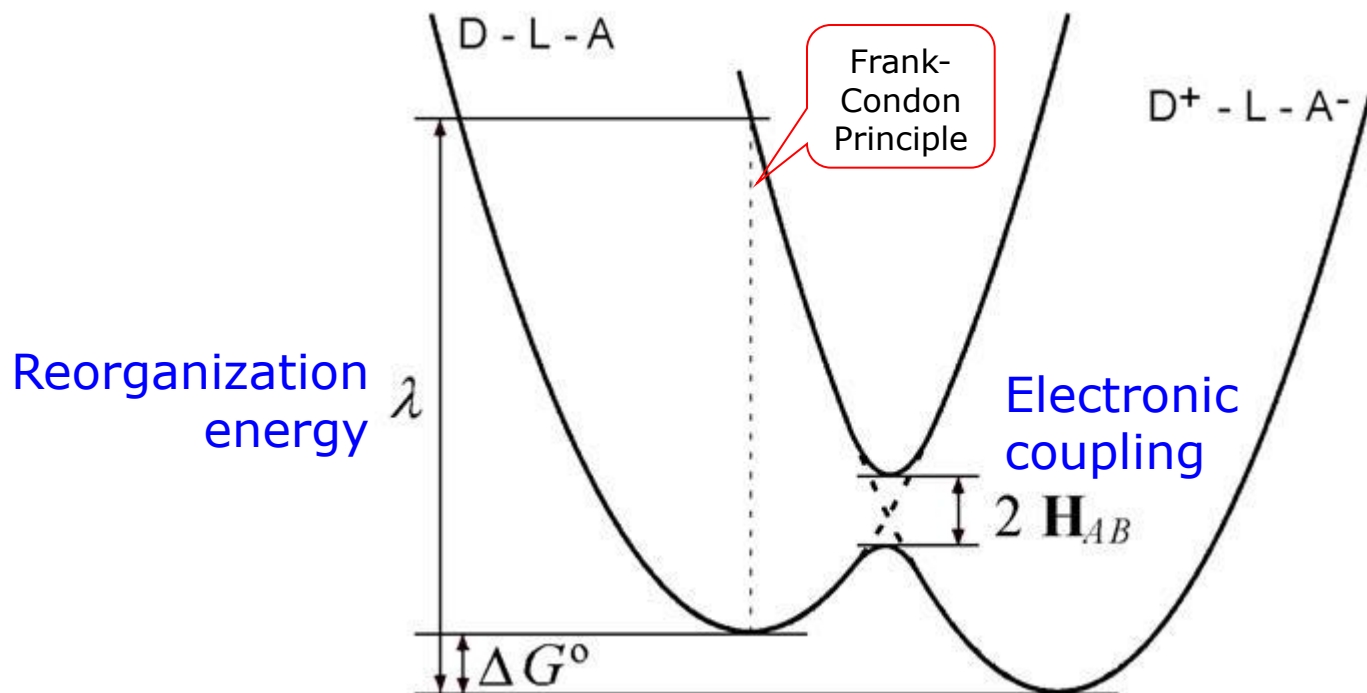
- | | |
|---|---|
| <ul style="list-style-type: none">□ Net Reaction Rate = difference between forward and backward reactions□ Transition State Theory<ul style="list-style-type: none">■ Arrhenius equation | <ul style="list-style-type: none">□ Net Reaction Rate = difference between forward and backward reactions□ Transition State Theory<ul style="list-style-type: none">■ Arrhenius equation |
| <ul style="list-style-type: none">□ Effects of Electrode Potential on Reaction Activation Energy<ul style="list-style-type: none">■ Extent of influence varies between the cathodic and anodic processes (α)■ Butler-Volmer equation | <ul style="list-style-type: none">□ Independence of Potential |

Markus Theory



- ❑ A theory originally developed by Rudolph A. Marcus, starting in 1956, to explain the rates of electron transfer reactions – the rate at which an electron can move or hop from one chemical species (called the electron donor) to another (called the electron acceptor).
- ❑ It was originally formulated to address **outer sphere** electron transfer reactions, in which the two chemical species aren't directly bonded to each other, but it was also extended to **inner sphere** electron transfer reactions, in which the two chemical species are attached by a chemical bridge, by Noel S. Hush (Hush's formulation is known as Marcus-Hush theory).
- ❑ Marcus received the **Nobel Prize in Chemistry** in 1992 for this theory.

Markus Theory



$$k_{et} = \frac{2\pi}{\hbar} |H_{AB}|^2 \frac{1}{\sqrt{4\pi\lambda k_b T}} \exp\left(-\frac{(\lambda + \Delta G^\circ)^2}{4\lambda k_b T}\right)$$

Electron-Transfer Kinetics in Organized Thiol Monolayers with Attached Pentaammine(pyridine)ruthenium Redox Centers

Harry O. Finklea* and Dwight D. Hanshew

Contribution from the Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506. Received August 26, 1991.

Revised Manuscript Received November 14, 1991

Abstract: Thiols with pendant redox centers ($\text{HS}(\text{CH}_2)_n\text{CONHCH}_2\text{pyRu}(\text{NH}_3)_5^{2+}$, $n = 10, 11, 15$) adsorb from acetonitrile solutions onto gold electrodes to form electroactive monolayers. Mixed monolayers can be formed when the electroactive thiols are co-adsorbed with alkanethiols ($\text{HS}(\text{CH}_2)_n\text{CH}_3$, $n = 11, 15$) and ω -mercaptoalkanecarboxylic acids ($\text{HS}(\text{CH}_2)_n\text{COOH}$, $n = 10, 11, 15$); the diluent thiol in each case is slightly shorter than the electroactive thiol. The $\text{pyRu}(\text{NH}_3)_5^{2+/3+}$ redox centers are stable in pH 4 aqueous Na_2SO_4 electrolyte and have a formal potential near 0.0 V vs SCE. At sufficiently slow scan rates, cyclic voltammograms of the electroactive monolayers are nearly ideal (peak splitting = 0 mV and peak half-width = 90–100 mV) for all combinations of electroactive thiol and diluent thiol and at all coverages of the electroactive thiols. The kinetics of electron transfer in the electroactive monolayers are examined by cyclic voltammetry and chronoamperometry. Evidence is given for the existence of a population of “fast” redox centers which can mediate charge transfer to the monolayer; however, rates of direct electron transfer between the electrode and the redox centers can be obtained. Experimental Tafel plots exhibit symmetric slopes in the cathodic and anodic branches, in contradiction to the prediction of through-space tunneling. The Tafel plots are fitted to Marcus theory to obtain the solvent reorganization parameter for the redox centers. The solvent reorganization parameter varies from 0.45 to 0.7 eV, with the parameter increasing with increasing chain length. Standard rate constants obtained from intercepts of the Tafel plots are primarily determined by the chain length and are independent of the terminal group in the diluent thiol. The standard rate constants tend to be larger for the anodic branch than for the cathodic branch, which implies slight differences in monolayer conformation for the two oxidation states of the redox centers. The standard rate constants for the mixed monolayers decay exponentially with increasing chain length. The slope of the $\ln k^0$ vs n plot is $-1.06 (\pm 0.04)$ per CH_2 . Through-bond tunneling is proposed as the mechanism of electron transfer.

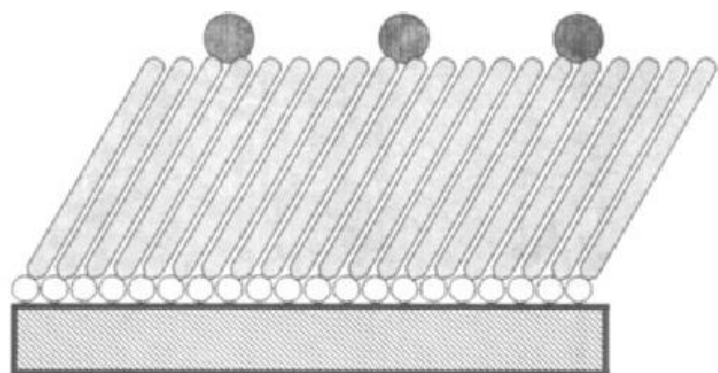


Figure 1. Mixed monolayer with electroactive and diluent thiols.

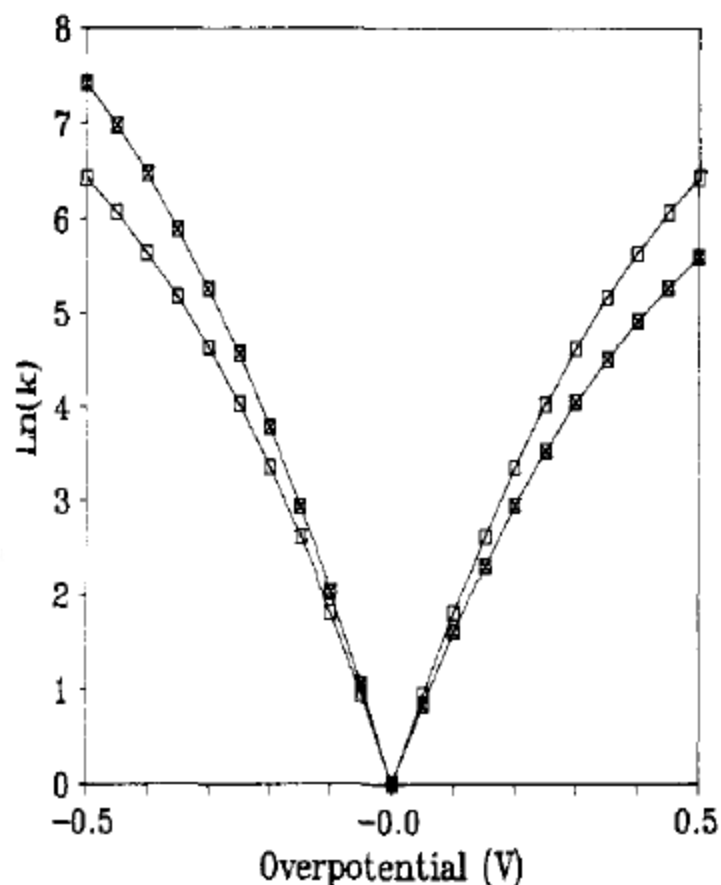
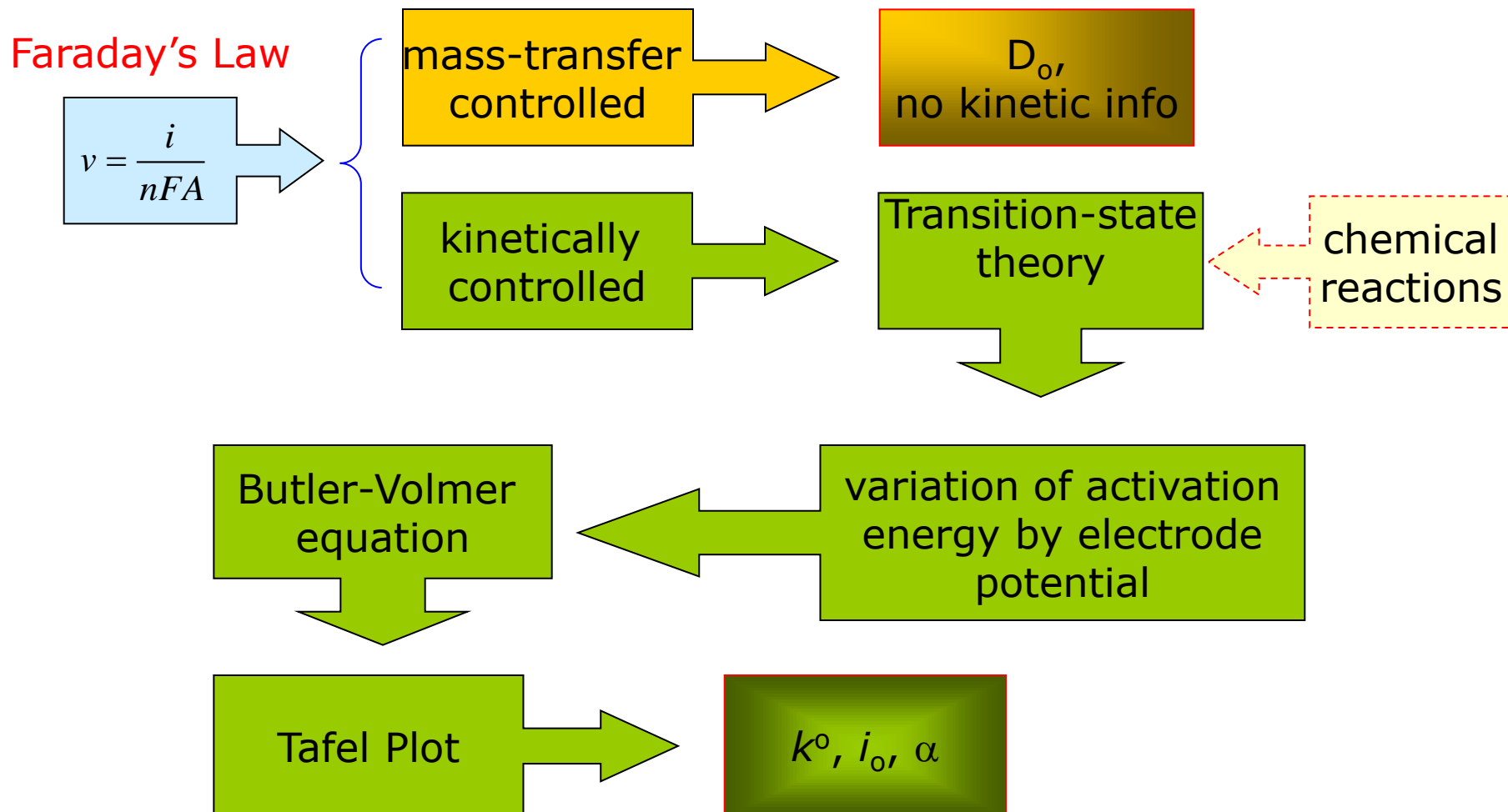


Figure 2. Simulated Tafel plots. The anodic rate constants are plotted for positive overpotential and the cathodic rate constants for negative overpotential; both are plotted relative to the standard rate constant. The open squares mark the Tafel plot for electron transfer without through-space tunneling, while the squares with crosses mark the Tafel plot which includes through-space tunneling with a barrier height of 2.4 eV and a barrier thickness of 20 Å (see the Appendix). The solvent reorganization energy is 0.6 eV in both plots.

Quick Overview



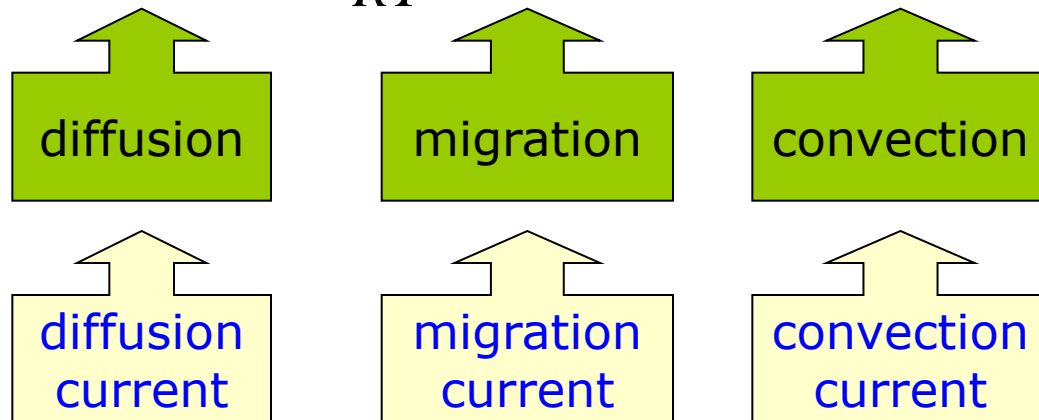
Mass Transfer Issues

► In a one-dimension system,

$$J_j(x) = -D_j \frac{\partial C_j(x)}{\partial x} - \frac{z_j F}{RT} D_j C_j \frac{\partial \phi(x)}{\partial x} + C_j v(x)$$

► In a three-dimension system,

$$\vec{J}_j(\vec{r}) = -D_j \vec{\nabla} C_j(\vec{r}) - \frac{z_j F}{RT} D_j C_j \vec{\nabla} \phi(\vec{r}) + C_j \vec{v}(\vec{r})$$



Migration

- In bulk solution, the concentration gradient is small, so the current is dominated by migration contribution

$$i_j = z_j F A J_j(x) = - \frac{z_j^2 F^2 A}{RT} D_j C_j \frac{\partial \phi(x)}{\partial x}$$

$$i_j = |z_j| F A u_j C_j \frac{\partial \phi(x)}{\partial x}$$

$$u_i = \frac{v}{\xi} = \frac{|z_i| e}{6\pi\eta r}$$

$$t_i = \frac{|z_i| u_i C_i}{\sum_j |z_j| u_j C_j}$$

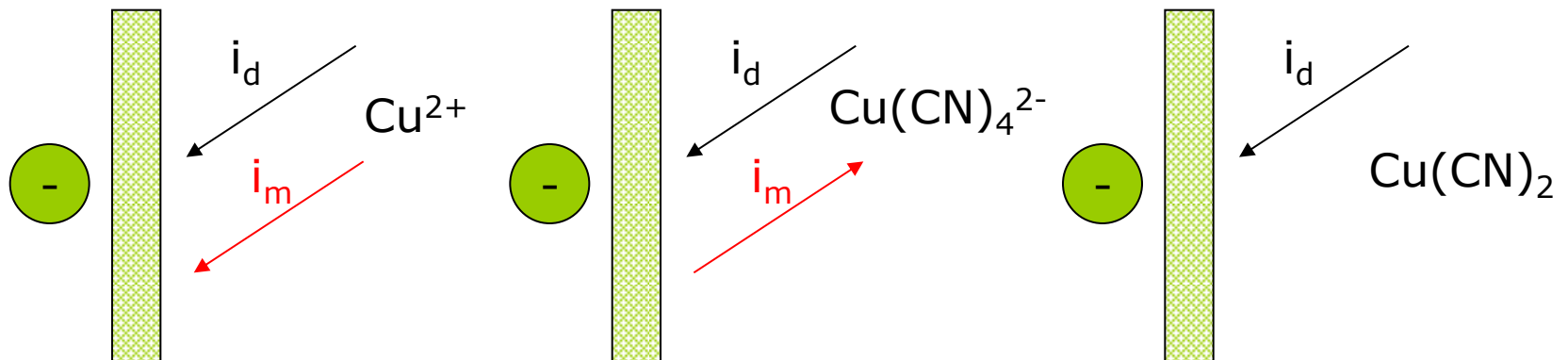
In a linear electric field, $\frac{\partial \phi(x)}{\partial x} = \frac{\Delta E}{l}$ $i = \sum_j i_j = F A \frac{\Delta E}{l} \sum_j |z_j| u_j C_j$

Solution conductance $L = \frac{1}{R} = \frac{i}{\Delta E} = \frac{F A}{l} \sum_j |z_j| u_j C_j = \kappa \frac{A}{l}$

conductivity

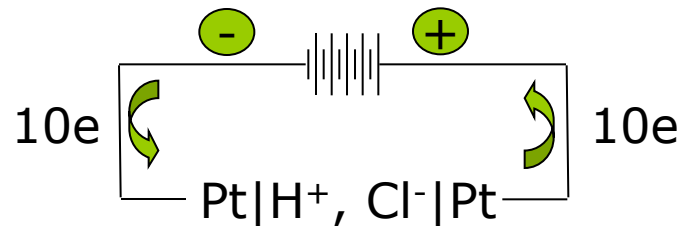
Migration

- Direction of migration current is dependent upon the ion charge
- Diffusion current always dictated by the direction of concentration gradient



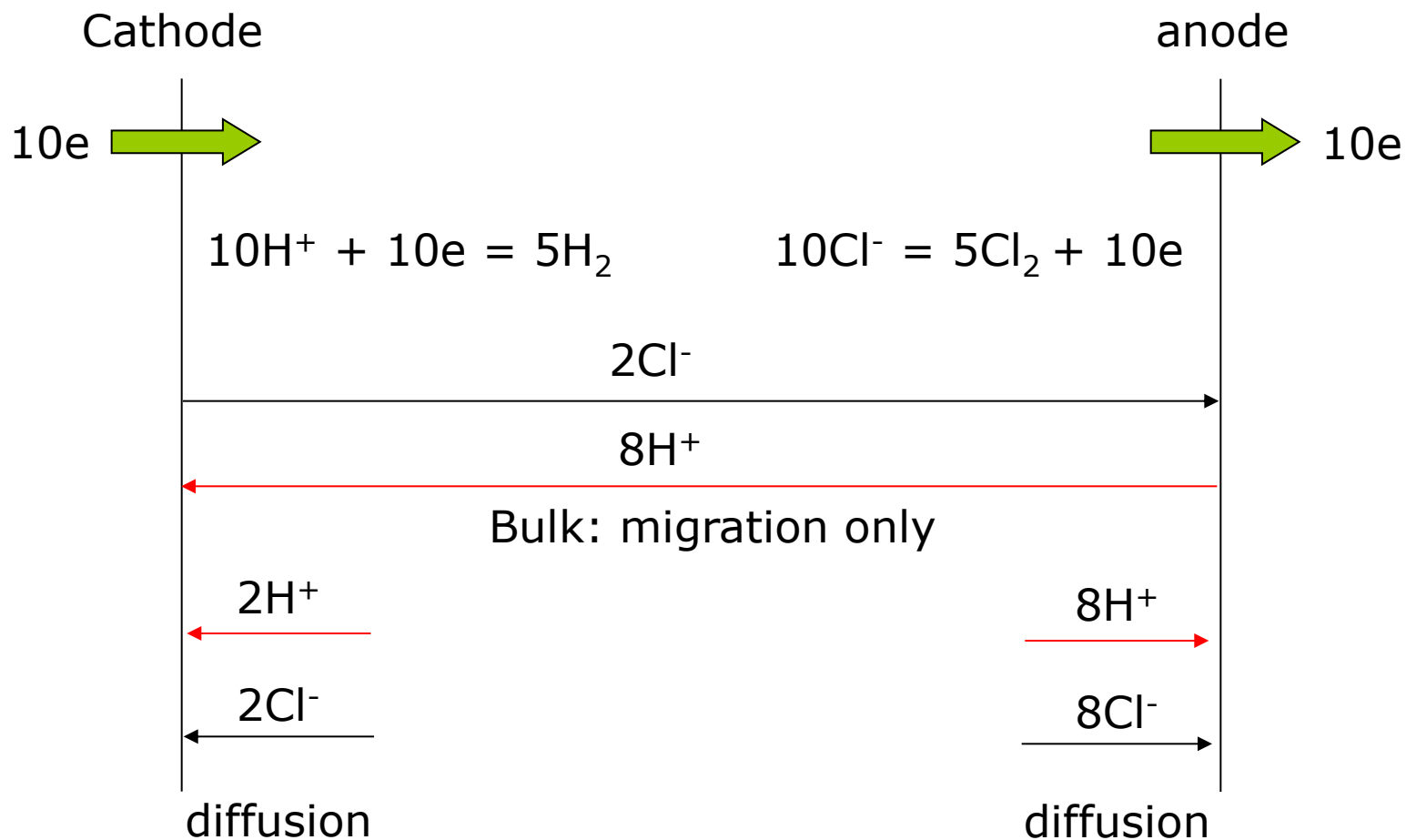
Mixed Migration and Diffusion

- Balance sheet for mass transfer during electrolysis
 - Bulk: migration, no diffusion
 - Interface: migration + diffusion



$$t_+ = 0.8, \text{ and } t_- = 0.2, \text{ so } \lambda_+ = 4\lambda_-$$

Mass Balance Sheet



Another Example

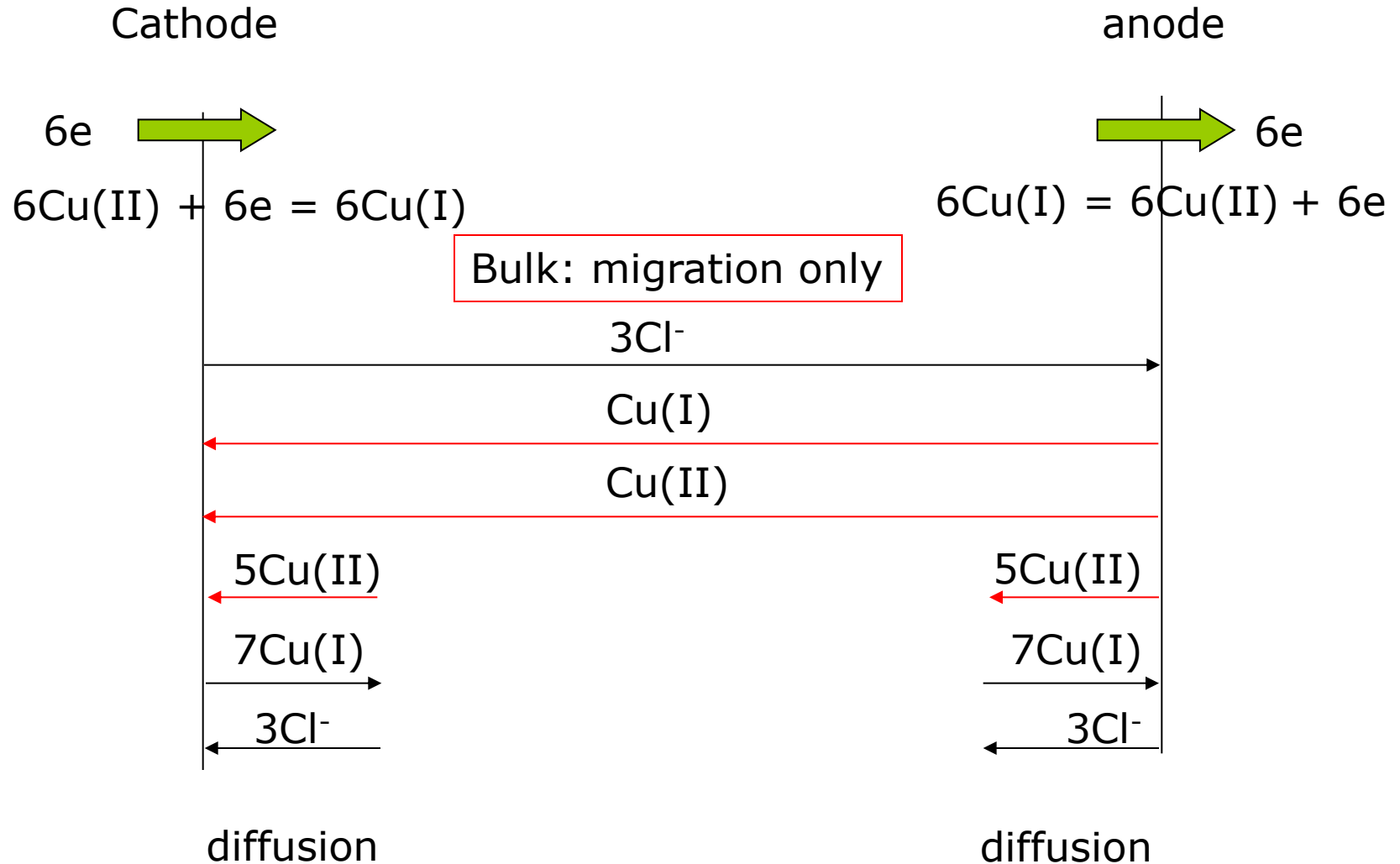


Assuming $\lambda_{\text{Cu(II)}} = \lambda_{\text{Cu(I)}} = \lambda_{\text{Cl}^-} = \lambda$

$[\text{Cu(II)}] = 1 \text{ mM}; [\text{Cu(I)}] = 1 \text{ mM}, [\text{Cl}^-] = 3 \text{ mM}$

So $t_{\text{Cu(II)}} = 1/3; t_{\text{Cu(I)}} = 1/6; t_{\text{Cl}^-} = 1/2$

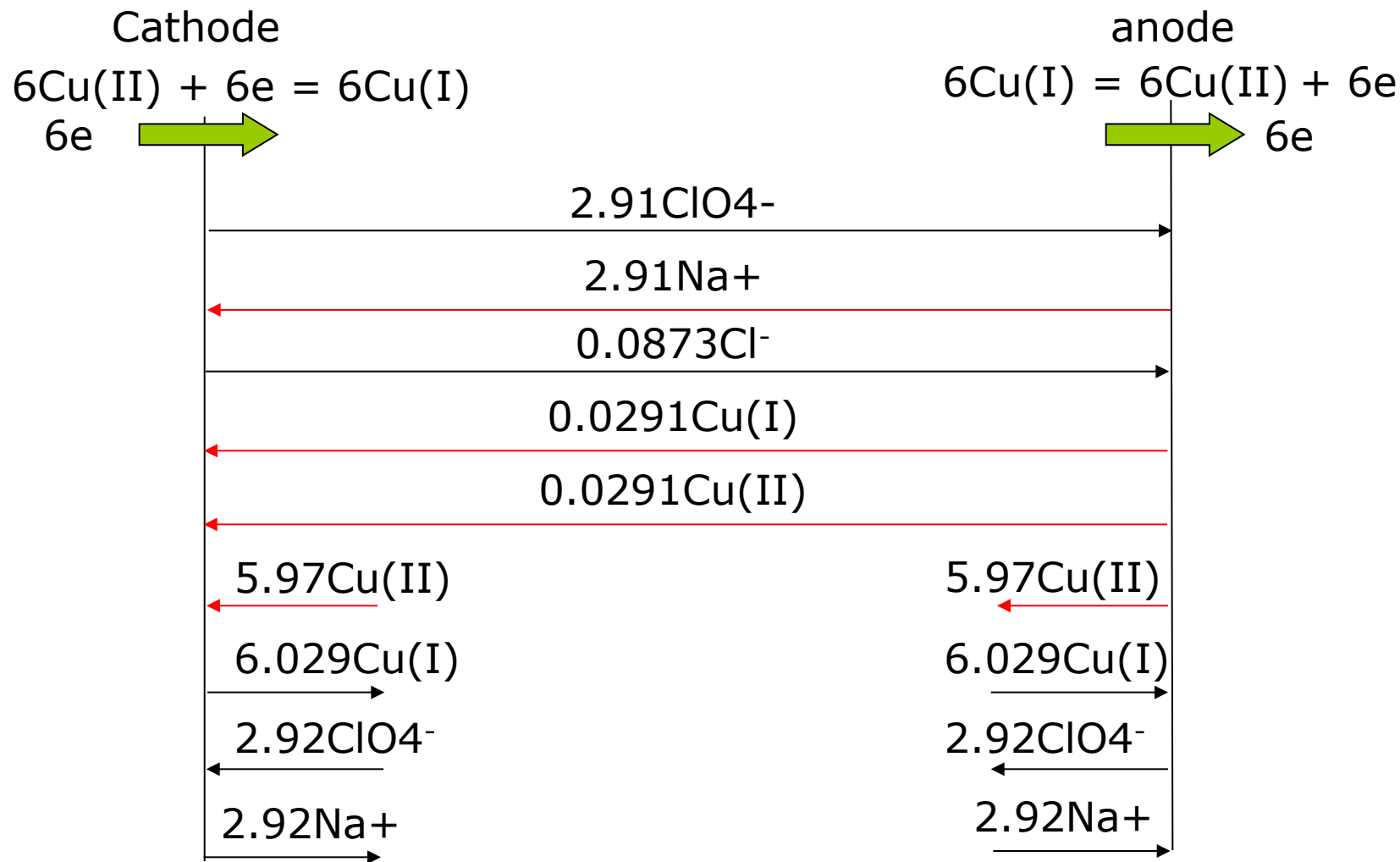
Mass Balance



Effect of Supporting Electrolyte

- Add 0.1 M NaClO_4
- Again, assuming all ions have the same conductance (λ)
- The transference numbers (t) for all ionic species
 - $t_{\text{Na}^+} = t_{\text{ClO}_4^-} = 0.485$
 - $t_{\text{Cu(II)}} = 0.0097$; $t_{\text{Cu(I)}} = 0.00485$; $t_{\text{Cl}^-} = 0.0146$
 - Apparently, most of the migration current will be carried by the added electrolyte NaClO_4

Mass Balance Sheet



Double-Layer Structure


□ Gibbs adsorption isotherm

- Discrepancy of concentration at the interface vs in the bulk

- Surface excess

- Concentration $n_i^\sigma = n_i^S - n_i^R$
- Electrochemical potential ($\bar{\mu}$)
- ...

Reference
(e.g., bulk)


$$\bar{G}^R = G^R(T, P, n_i^R)$$

$$\bar{G}^S = G^S(T, P, A, n_i^S)$$

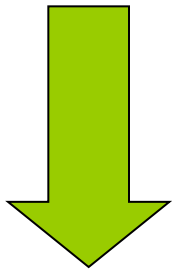
PURE α

PURE β

Gibbs Adsorption Isotherm

$$d\bar{G}^R = \left(\frac{\partial \bar{G}^R}{\partial T} \right) dT + \left(\frac{\partial \bar{G}^R}{\partial P} \right) dP + \sum \left(\frac{\partial \bar{G}^R}{\partial n_i^R} \right) dn_i^R$$

$$d\bar{G}^S = \left(\frac{\partial \bar{G}^S}{\partial T} \right) dT + \left(\frac{\partial \bar{G}^S}{\partial P} \right) dP + \left(\frac{\partial \bar{G}^S}{\partial A} \right) dA + \sum \left(\frac{\partial \bar{G}^S}{\partial n_i^S} \right) dn_i^S$$



Const T and P
at equilibrium

$$\bar{\mu}_i = \left(\frac{\partial \bar{G}^R}{\partial n_i^R} \right) = \left(\frac{\partial \bar{G}^S}{\partial n_i^S} \right)$$

$$\gamma = \left(\frac{\partial \bar{G}^S}{\partial A} \right) \text{ Surface tension}$$

$$d\bar{G}^\sigma = d\bar{G}^S - d\bar{G}^R = \gamma dA + \sum \bar{\mu}_i dn_i^\sigma$$

Gibbs Adsorption Isotherm

$$\bar{G}^{\sigma} = \gamma A + \sum \bar{\mu}_i n_i^{\sigma}$$

Euler's theorem

$$\bar{G}^{\sigma} = \left(\frac{\partial \bar{G}^{\sigma}}{\partial A} \right) A + \sum_i \left(\frac{\partial \bar{G}^{\sigma}}{\partial n_i^{\sigma}} \right) n_i^{\sigma}$$

$$d\bar{G}^{\sigma} = \gamma dA + A d\gamma + \sum \bar{\mu}_i dn_i^{\sigma} + \sum n_i^{\sigma} d\bar{\mu}_i$$

$$A d\gamma + \sum n_i^{\sigma} d\bar{\mu}_i = 0$$

$$d\gamma = -\sum \frac{n_i^{\sigma}}{A} d\bar{\mu}_i = -\sum \Gamma_i d\bar{\mu}_i$$

Surface excess or surface coverage

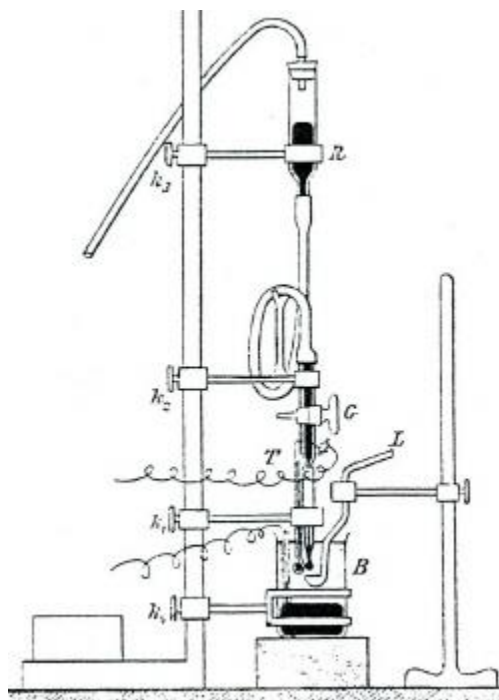
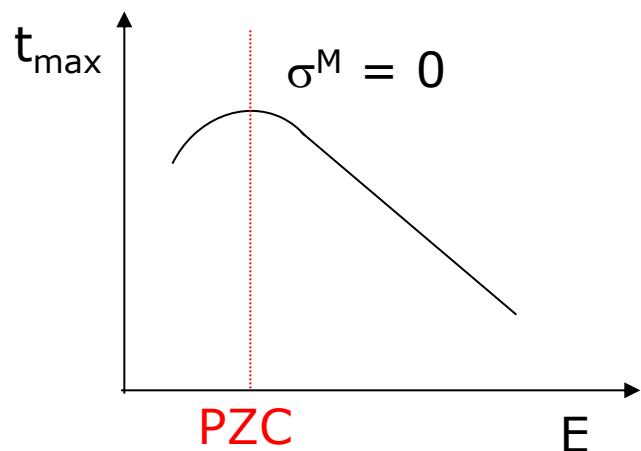
Electrocapillary Equation

$$-d\gamma = \sigma^M dE + \sum \Gamma_i d\mu_i$$

□ Dropping mercury electrode

- $gmt_{\max} = 2\pi r_c \gamma$

- $t_{\max} = 2\pi r_c \gamma / gm$

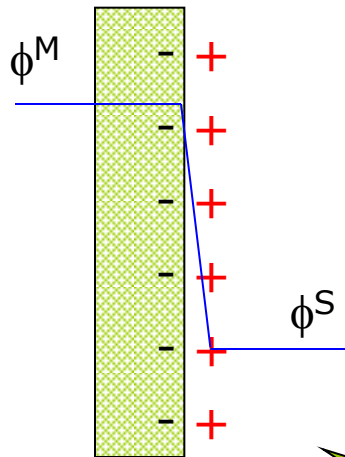


Electrical Double Layer

- The concept and model of the double layer arose in the work of [von Helmholtz](#) (1853) on the interfaces of colloidal suspensions and was subsequently extended to surfaces of metal electrodes by [Gouy, Chapman, and Stern](#), and later in the notable work of [Grahame](#) around 1947.
- Helmholtz envisaged a [capacitor-like](#) separation of anionic and cationic charges across the interface of colloidal particles with an electrolyte. For electrode interfaces with an electrolyte solution, this concept was extended to model the separation of "electronic" charges residing at the metal electrode surfaces (manifested as an excess of negative charge densities under negative polarization with respect to the electrolyte solution or as a deficiency of electron charge density under positive polarization), depending in each case, on the corresponding potential difference between the electrode and the solution boundary at the electrode. For zero net charge, the corresponding potential is referred to as the "[potential of zero charge \(PZC\)](#)".

Models for Double-Layer Structure

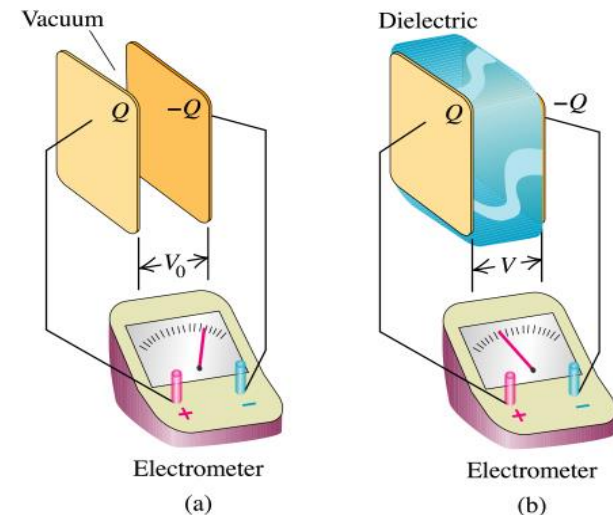
- Helmholtz model
 - Rigid layers of ions at the interface
 - Constant double-layer capacitance



$$\sigma = \frac{\epsilon\epsilon_0}{d} V$$

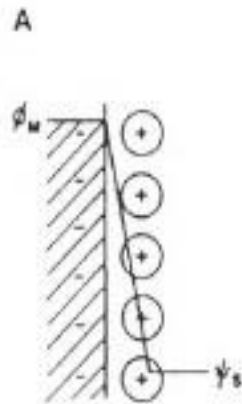
$$C = \frac{\epsilon\epsilon_0}{d}$$

A crude model

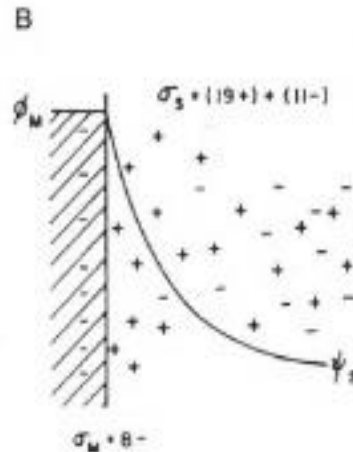


Guoy-Chapman Model

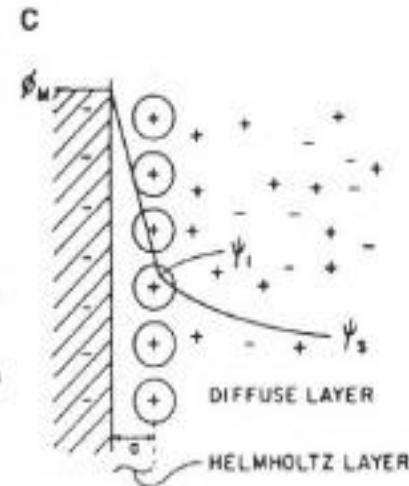
Helmholtz Model



Guoy-Chapman Model



Guoy-Chapman-Stern Model



The layer of solution ions is diffusive rather than rigid

Guoy-Chapman Model

- Distribution of ions follows Boltzmann's law

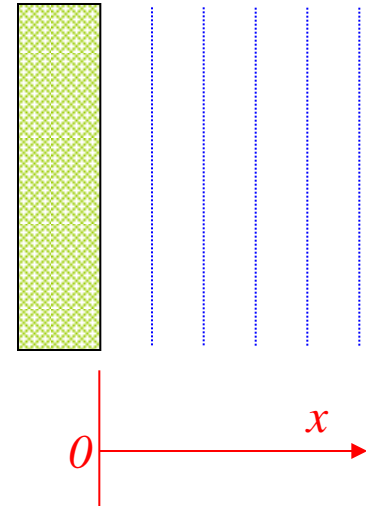
$$n_i = n_i^o \exp\left(-\frac{z_i e \phi}{kT}\right)$$

- The total charge per unit volume in any lamina

$$\rho(x) = \sum n_i z_i e = \sum z_i e n_i^o \exp\left(-\frac{z_i e \phi}{kT}\right)$$

- Poisson's equation

$$\rho(x) = -\epsilon \epsilon_o \left(\frac{d^2 \phi}{dx^2} \right)$$



Guoy-Chapman Model

□ Poisson-Boltzmann equation

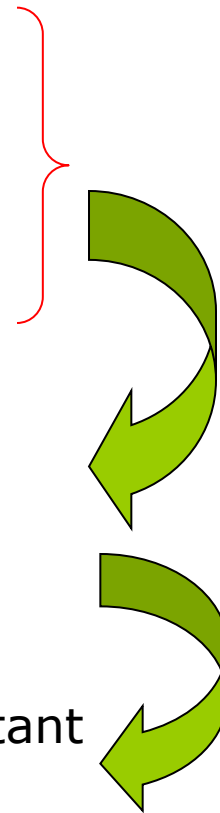
$$\left(\frac{d^2\phi}{dx^2}\right) = -\frac{e}{\epsilon\epsilon_o} \sum z_i n_i^o \exp\left(-\frac{z_i e \phi}{kT}\right)$$

$$\left(\frac{d^2\phi}{dx^2}\right) = \frac{1}{2} \frac{d}{d\phi} \left(\frac{d\phi}{dx}\right)^2$$

$$d\left(\frac{d\phi}{dx}\right)^2 = -\frac{2e}{\epsilon\epsilon_o} \sum z_i n_i^o \exp\left(-\frac{z_i e \phi}{kT}\right) d\phi$$

$$\left(\frac{d\phi}{dx}\right)^2 = \frac{2kT}{\epsilon\epsilon_o} \sum n_i^o \exp\left(-\frac{z_i e \phi}{kT}\right) + \text{constant}$$

integration

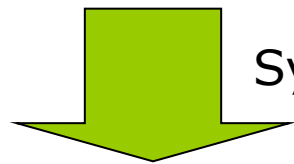


Guoy-Chapman Model

- Take the bulk solution as the reference point of potential

- $\phi = 0, d\phi/dx = 0$

$$\left(\frac{d\phi}{dx}\right)^2 = \frac{2kT}{\epsilon\epsilon_o} \sum n_i^o \left[\exp\left(-\frac{z_i e \phi}{kT}\right) - 1 \right]$$



Symmetrical electrolyte ($z_+ = z_- = z$)

$$\left(\frac{d\phi}{dx}\right) = -\sqrt{\frac{8kTn^o}{\epsilon\epsilon_o}} \sinh\left(\frac{ze\phi}{2kT}\right)$$

Guoy-Chapman Model

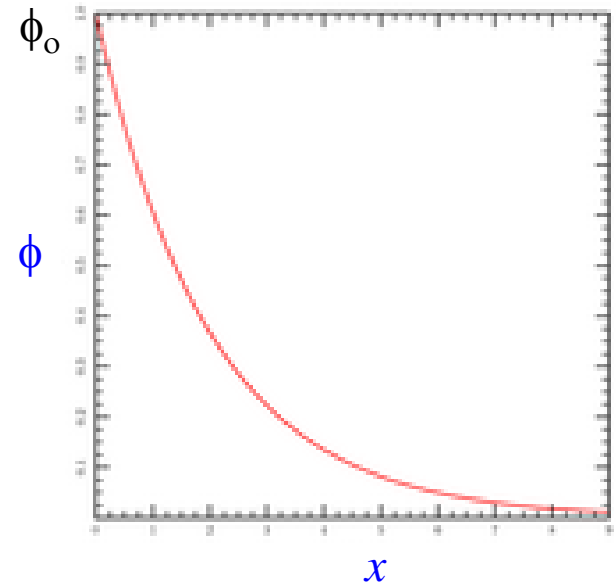
$$\int_{\phi_o}^{\phi} \frac{d\phi}{\sinh\left(\frac{ze\phi}{2kT}\right)} = -\sqrt{\frac{8kTn^o}{\epsilon\epsilon_o}} \int_0^x dx = -\sqrt{\frac{8kTn^o}{\epsilon\epsilon_o}} x$$

$$\frac{2kT}{ze} \ln \left[\frac{\tanh(ze\phi/4kT)}{\tanh(ze\phi_o/4kT)} \right] = -\left(\frac{8kTn^o}{\epsilon\epsilon_o} \right) x$$

□ at small ϕ , $\phi \sim \phi_o e^{-\kappa x}$

□ **diffuse layer thickness** = κ^{-1}

$$\text{with } \kappa = \sqrt{\frac{2n^o z^2 e^2}{\epsilon\epsilon_o kT}} = (3.29 \times 10^7) z C^{*1/2}$$



C* (M)	1	10 ⁻¹	10 ⁻²	10 ⁻³	10 ⁻⁴
κ ⁻¹ (Å)	3.0	9.6	30.4	96.2	304

A Reversibly Switching Surface

Joerg Lahann,¹ Samir Mitragotri,² Thanh-Nga Tran,¹
Hiroki Kaido,¹ Jagannathan Sundaram,² Insung S. Choi,^{1*}
Saskia Hoffer,³ Gabor A. Somorjai,³ Robert Langer^{1†}

Science **2003**, 299, 371

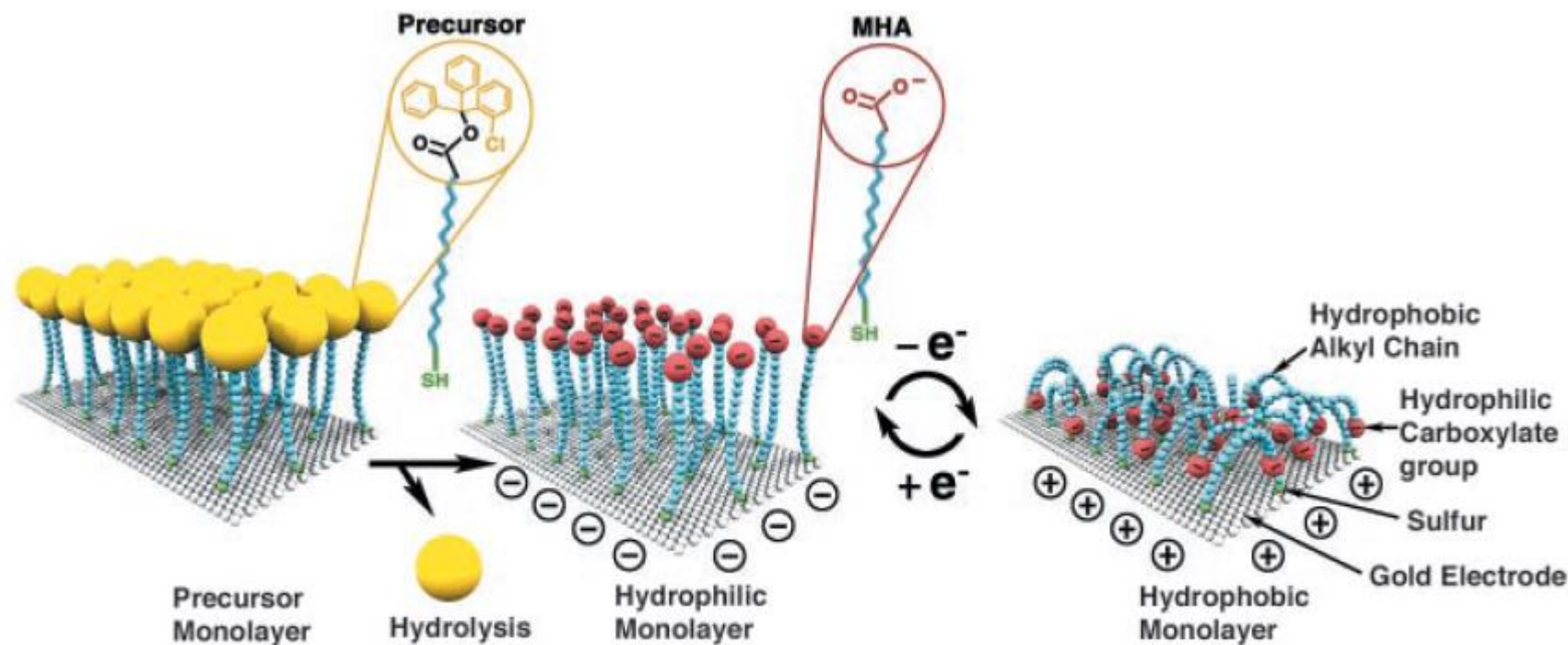


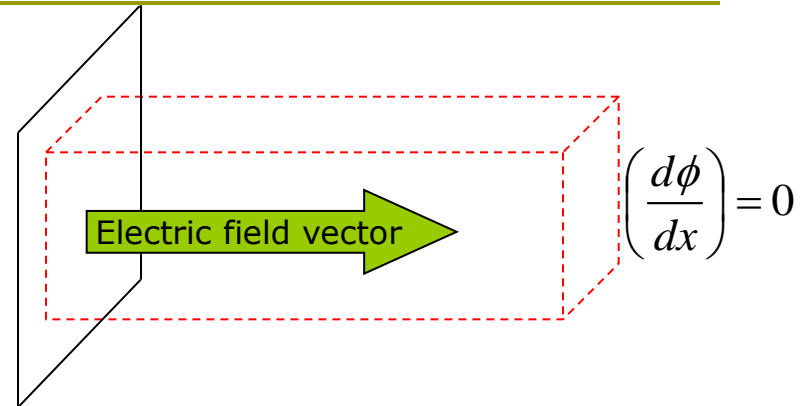
Fig. 1. Idealized representation of the transition between straight (hydrophilic) and bent (hydrophobic) molecular conformations (ions and solvent molecules are not shown). The precursor molecule MHA, characterized by a bulky end group and a thiol head group, was synthesized from MHA by introducing the (2-chlorophenyl)diphenylmethyl ester group.

Guoy-Chapman Model

$$q = \oint \epsilon \epsilon_o \vec{\xi} d\vec{S}$$

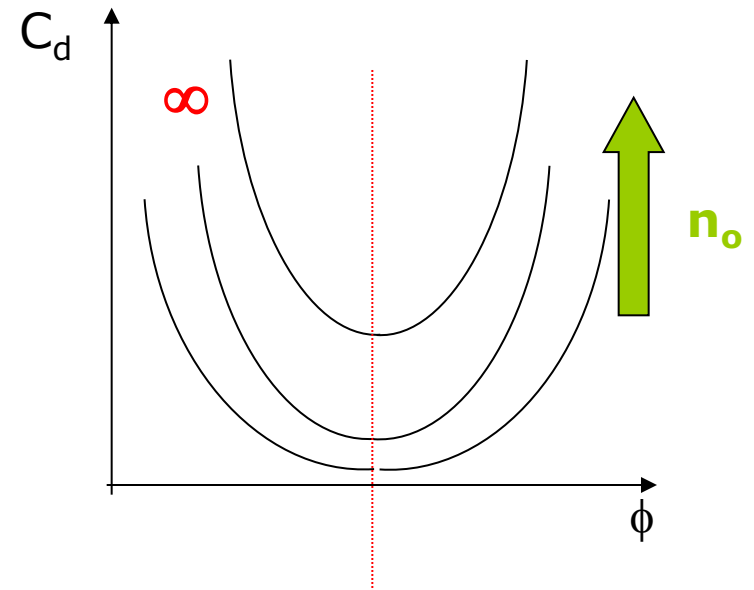
$$q = \epsilon \epsilon_o \left(\frac{d\phi}{dx} \right)_{x=0} A$$

Electrode
Surface



$$\sigma^M = -\sigma^S = \sqrt{8kT\epsilon\epsilon_o n_o} \sinh\left(\frac{ze\phi_o}{2kT}\right)$$

$$C_d = \frac{d\sigma^M}{d\phi_o} = ze \sqrt{\frac{2\epsilon\epsilon_o n_o}{kT}} \cosh\left(\frac{ze\phi_o}{2kT}\right)$$



Stern Modification

- GC Model: all ions are point charge (no size)
- Stern Modification: in reality, the closest distance an ion can get to the electrode surface is nonzero (x_2), defined as **Outer Helmholtz Plane (OHP)**

$$\int_{\phi_2}^{\phi} \frac{d\phi}{\sinh\left(\frac{ze\phi}{2kT}\right)} = -\sqrt{\frac{8kTn^o}{\epsilon\epsilon_o}} \int_{x_2}^x dx = -\sqrt{\frac{8kTn^o}{\epsilon\epsilon_o}} (x - x_2)$$

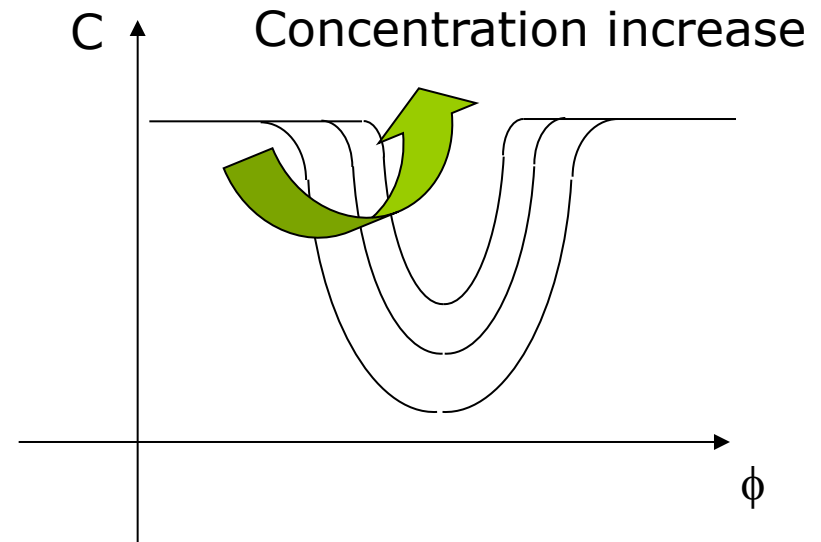
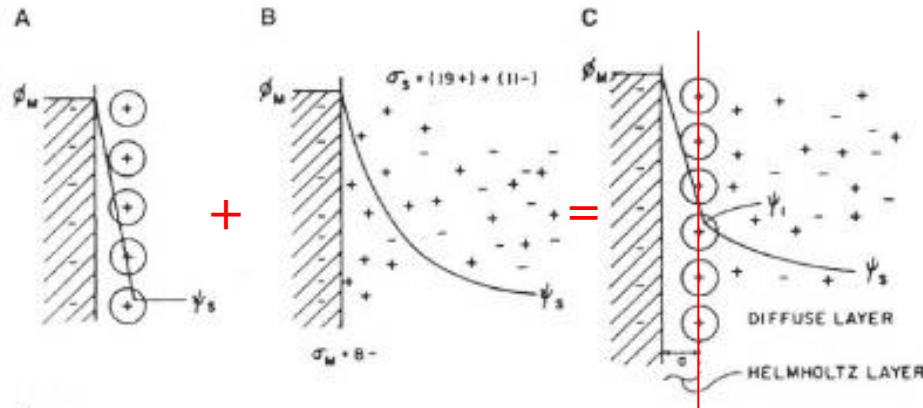
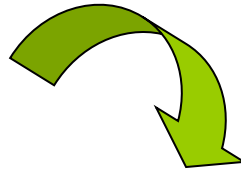
$$\frac{\tanh\left(\frac{ze\phi}{4kT}\right)}{\tanh\left(\frac{ze\phi_2}{4kT}\right)} = -\sqrt{\frac{8kTn^o}{\epsilon\epsilon_o}} (x - x_2) \quad \phi_2 = \phi_o + \left(\frac{d\phi}{dx}\right)_{x_2} x_2$$

Guoy-Chapman-Stern Model

$$\sigma^M = -\sigma^S = \sqrt{8kT\varepsilon\varepsilon_o n_o} \sinh\left(\frac{ze}{2kT}\left(\phi_o - \frac{\sigma^M x_2}{\varepsilon\varepsilon_o}\right)\right)$$

$$C_d = \frac{d\sigma^M}{d\phi_o} = \frac{ze\sqrt{\frac{2\varepsilon\varepsilon_o n_o}{kT}} \cosh\left(\frac{ze\phi_2}{2kT}\right)}{1 + \left(\frac{x_2}{\varepsilon\varepsilon_o}\right) ze\sqrt{\frac{2\varepsilon\varepsilon_o n_o}{kT}} \cosh\left(\frac{ze\phi_2}{2kT}\right)}$$

$$\frac{1}{C_d} = \frac{1}{C_H} + \frac{1}{C_D}$$



Surface Adsorption

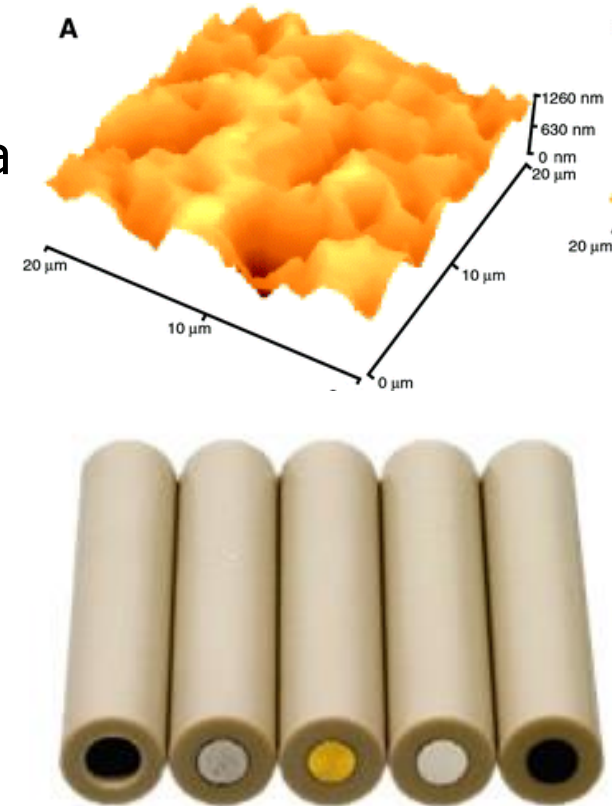
- Roughness factor
 - Ratio of actual area vs geometric area
 - Typically 1.5 ~ 2.0 or more
- Adsorption isotherm
 - concentration dependent adsorption
 - At equilibrium $\bar{\mu}_i^A = \bar{\mu}_i^b$

$$\bar{\mu}_i^{o,A} + RT \ln a_i^A = \bar{\mu}_i^{o,b} + RT \ln a_i^b$$

$$\Delta \bar{G}_i^o = \bar{\mu}_i^{o,A} - \bar{\mu}_i^{o,b} = RT \ln \left(\frac{a_i^b}{a_i^A} \right)$$

$$a_i^A = \beta_i a_i^b$$

$$\beta_i = \exp \left(- \frac{\Delta \bar{G}_i^o}{RT} \right)$$



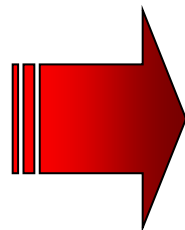
Langmuir Isotherm



- No interaction between adsorbates
- No heterogeneity of the substrate surface (all sites are equal)
- At high bulk concentrations, surface coverage becomes saturated (Γ_s)

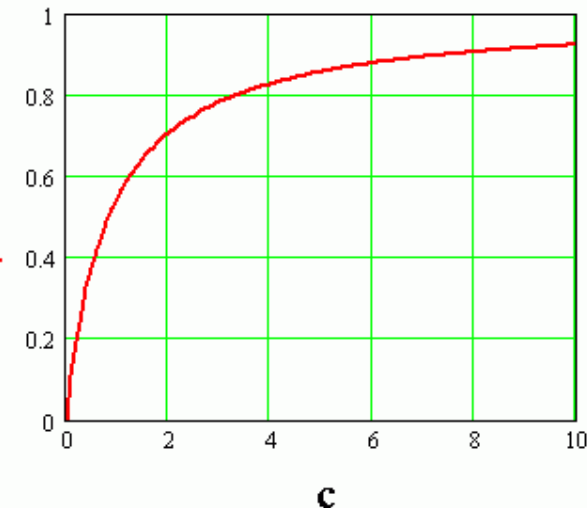
$$\frac{\Gamma_i}{\Gamma_s - \Gamma_i} = \beta_i a_i^b$$

$$\frac{\theta_i}{1 - \theta_i} = \beta_i a_i^b$$



$$\Gamma_i = \frac{\beta_i a_i^b}{1 + \beta_i a_i^b} \Gamma_s$$

θ



Other Isotherms

□ Logarithmic Temkin isotherm

$$\Gamma_i = \frac{RT}{2g} \ln(\beta_i a_i^b) \quad (0.2 < \theta < 0.8)$$

□ Frumkin isotherm

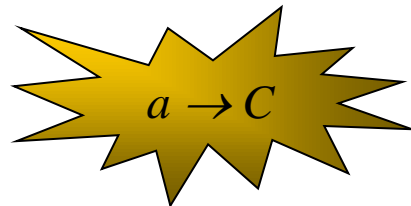
$$\beta_i a_i^b = \frac{\Gamma_i}{\Gamma_s - \Gamma_i} \exp\left(-\frac{2g\Gamma_i}{RT}\right)$$

$$\beta_i a_i^b = \frac{\theta_i}{1 - \theta_i} \exp(-2g' \theta_i)$$

$$g' = \frac{g\Gamma_s}{RT}$$



- $g \rightarrow 0$, Frumkin \rightarrow Langmuir
- Repulsive, $g < 0$
- Attractive, $g > 0$





Radiometric and voltammetric study of benzoic acid adsorption on a polycrystalline silver electrode

P. Waszczuk, P. Zelenay and J. Sobkowski

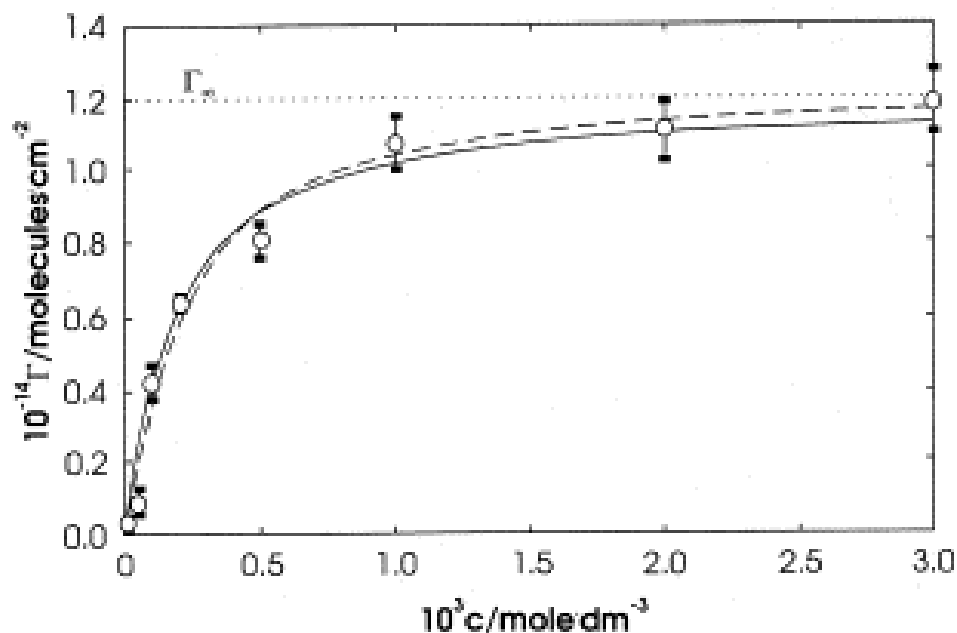


Fig. 5. Adsorption isotherm for benzoic acid on polycrystalline silver electrode in the range of solution concentration from 10^{-5} to 3×10^{-3} M. Circles represent experimental data points whereas **solid and dashed lines correspond to the Langmuir and Frumkin isotherms**, respectively (see text for isotherm parameters). The error bars correspond to the random errors of radiometric measurements. $E_{\text{ads}} = 0.50$ V. Supporting electrolyte: 0.1 M HClO_4

Redox-Active Ferrocenyl Dendrimers: Thermodynamics and Kinetics of Adsorption, In-Situ Electrochemical Quartz Crystal Microbalance Study of the Redox Process and Tapping Mode AFM Imaging

Kazutake Takada, Diego J. Díaz, Héctor D. Abruña,* Isabel Cuadrado,*
Carmen Casado, Beatriz Alonso, Moisés Morán,* and José Losada

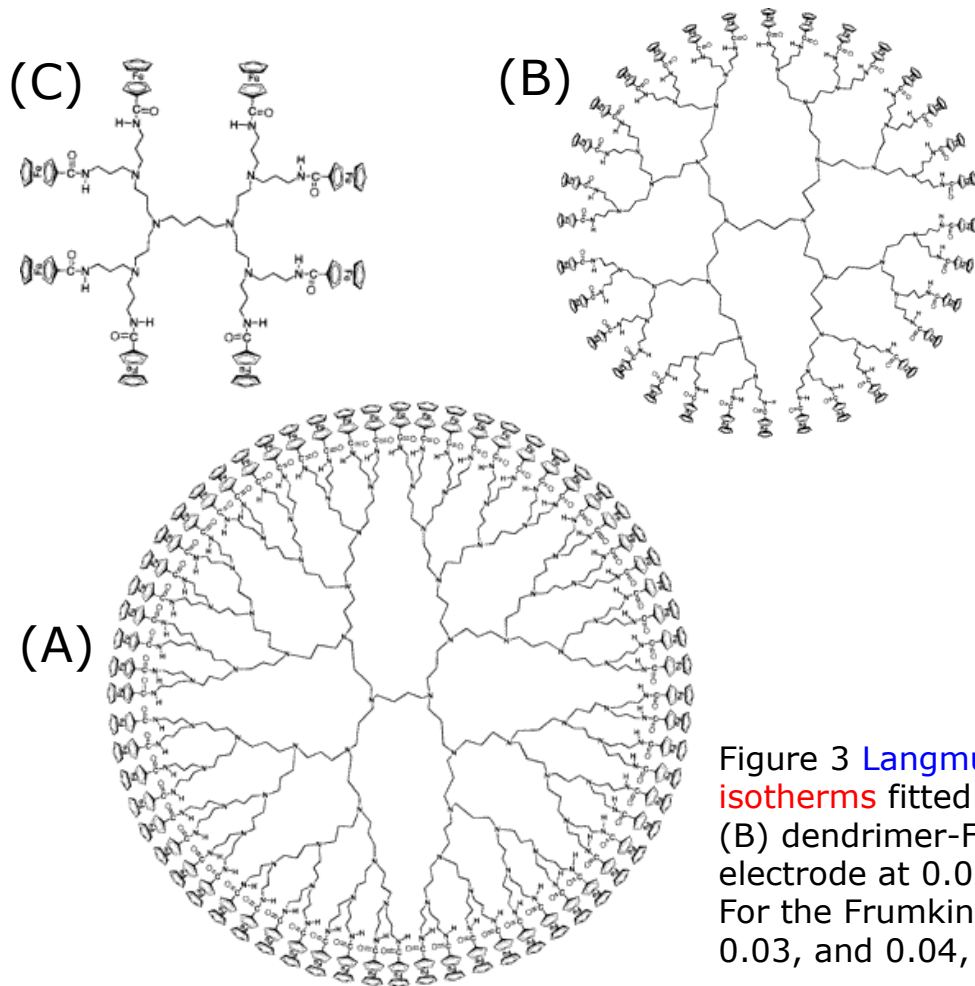
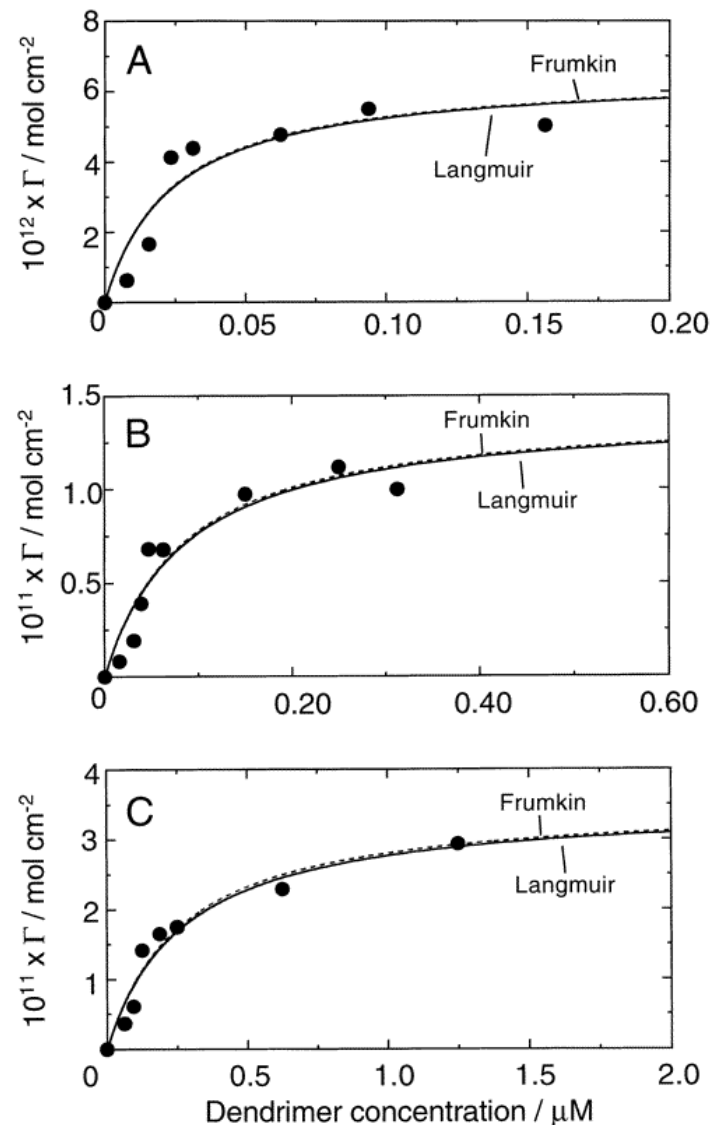
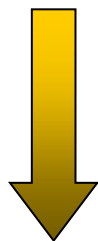


Figure 3 **Langmuir** (solid line) and **Frumkin** (broken line) isotherms fitted to experimental points for (A) dendrimer-Fc₆₄, (B) dendrimer-Fc₃₂, and (C) dendrimer-Fc₈ adsorbed to a Pt electrode at 0.0 V vs SSCE in a 0.10 M TBAP CH₂Cl₂ solution. For the Frumkin isotherms, values of g' employed were 0.02, 0.03, and 0.04, respectively.

Adsorption Free Energy

- From the adsorption coefficient β , the adsorption free energy (-53 ± 2 KJ/mol) was determined, using

- Fc_{64} , -53 ± 2 KJ/mol
- Fc_{32} , -50 ± 1 KJ/mol
- Fc_8 , -47 ± 1 KJ/mol



$$\beta_i = \exp\left(-\frac{\Delta\bar{G}_i^o}{RT}\right)$$

- The adsorption free energy of $[\text{Os}(\text{bpy})_2\text{CIL}]^+$ (ca. -49 kJ/mol), where bpy = 2,2'-bipyridine and L are various dipyridyl groups including 4,4'-bipyridine, *trans*-1,2-bis(4-pyridyl)ethylene, 1,3-bis(4-pyridyl)propane, or 1,2-bis(4-pyridyl)ethane, all of which have a pendant pyridyl group through which adsorption takes place.

Freundlich Isotherm

- The **Freundlich Adsorption Isotherm** is a curve relating the concentration of a solute on the surface of an adsorbent, to the concentration of the solute in the liquid with which it is in contact.
- The Freundlich Adsorption Isotherm is mathematically expressed as

$$\frac{x}{m} = Kp^{\frac{1}{n}} \quad \frac{x}{m} = KC^{\frac{1}{n}}$$

where

x = mass of adsorbate

m = mass of adsorbent

p = Equilibrium pressure of adsorbate

C = Equilibrium concentration of adsorbate in solution.

K and $1/n$ are constants for a given adsorbate and adsorbent at a particular temperature.

Sorption of Cd in Soils: Pedotransfer Functions for the Parameters of the **Freundlich Sorption Isotherm**

A. L. Horn, R.-A. Düring and S. Gäth

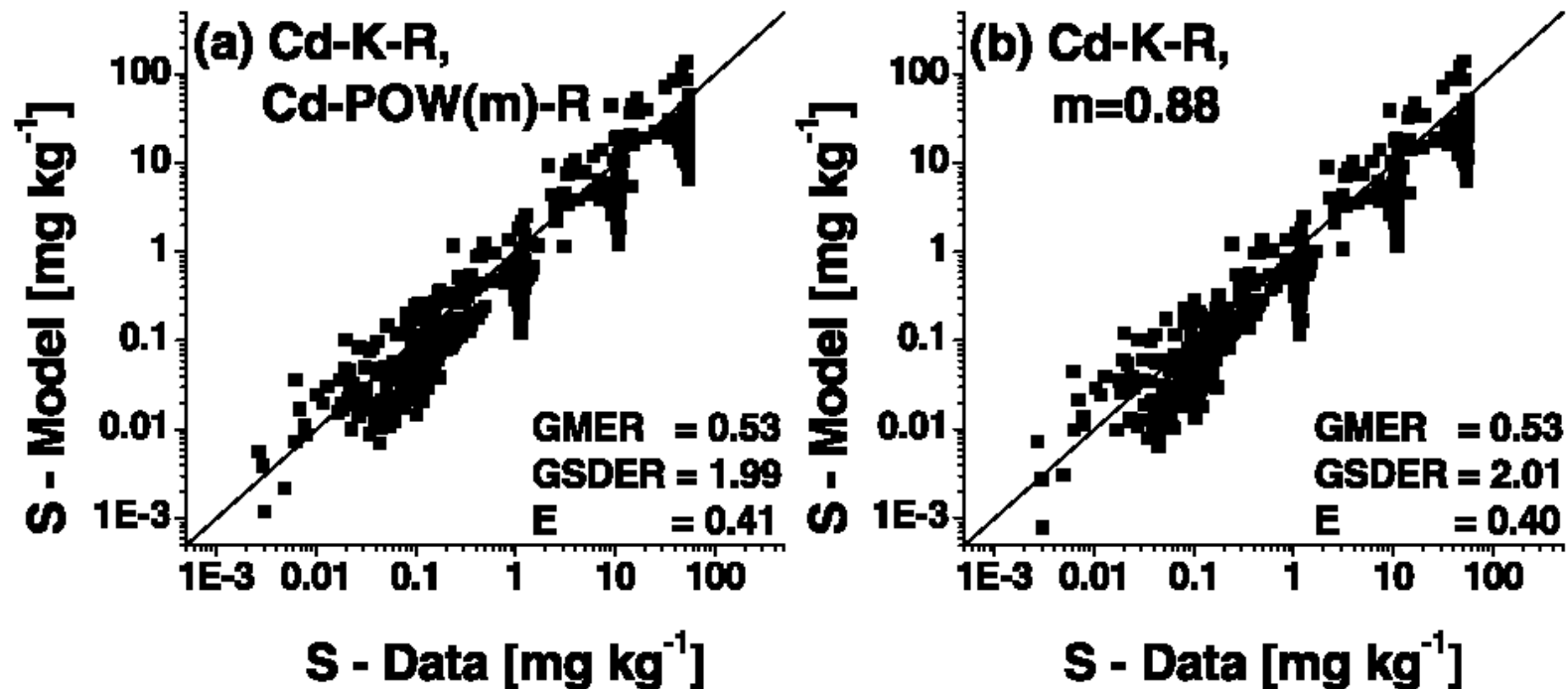


Figure 2. Comparison of measured and predicted concentrations of sorbed Cd in soil (S); predictions by (a) a pedotransfer function of the Freundlich sorption isotherm combined of Cd-K-R and Cd-POW(m)-R, and (b) a Freundlich isotherm approach implementing Cd-K-R and a constant value of the Freundlich exponent (mean of data used for parameterisation, $m = 0.88$).

