



OREGON CENTER FOR  
ELECTROCHEMISTRY

## Part I

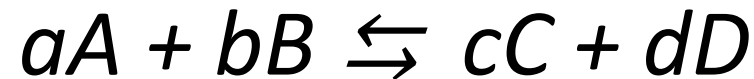
# Electrochemical Thermodynamics and Potentials: Equilibrium and the Driving Forces for Electrochemical Processes

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University of Oregon



# Chemical Thermodynamics

Consider a chemical reaction:



$$\Delta G_{rxn}^o = \Delta G_f^{o,products} - \Delta G_f^{o,reactants}$$

What criteria do we use to determine if the reaction goes forward or backwards?

- Gibbs free energy can be used to calculate the **maximum reversible work** that may be performed by system at a **constant temperature and pressure**.
- Gibbs energy is **minimized** when a system reaches **chemical equilibrium at constant pressure and temperature**.

# Chemical Thermodynamics

If not at standard state, then:

$$\Delta G_{rxn} = \Delta G_{rxn}^{\circ} + RT \ln Q$$

$$Q = \frac{\prod_p a_p^{v_p}}{\prod_r a_r^{v_r}} = \frac{\prod_p \left( \gamma_p \frac{c_p}{c_p^0} \right)^{v_p}}{\prod_r \left( \gamma_r \frac{c_r}{c_r^0} \right)^{v_r}}$$

$a_p$  is the activity of product  $p$

$a_r$  is the activity of reactant  $r$

$v_i$  is the stoichiometric number of  $i$

$\gamma_i$  is the activity coefficient of  $i$

$c_i$  is the concentration of  $i$

$c_i^0$  is the standard state concentration of  $i$

- Activity coefficients are “fudge” factors that allow for the use of ideal thermodynamic equations with non-ideal solutions.
- For dilute solutions,  $\gamma_i$  goes to 1

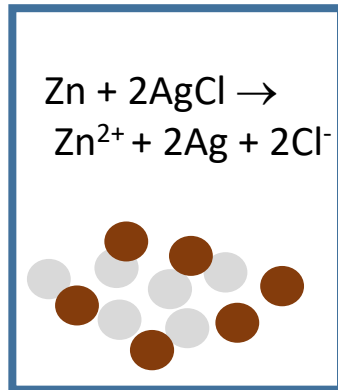


# Electrochemical Thermodynamics

Consider the following thought experiment

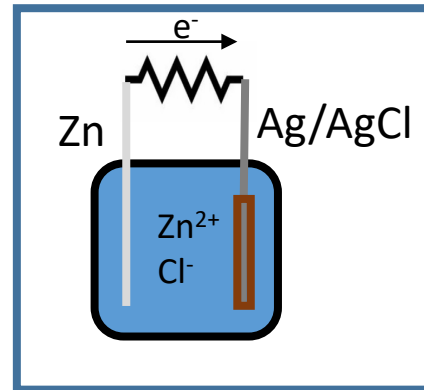


**A** do *chemical* reaction in calorimeter:



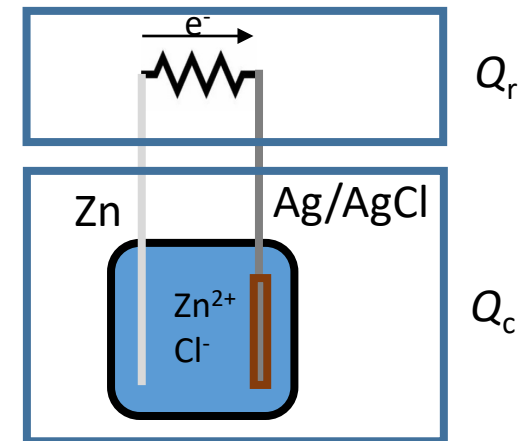
$$Q_c = \Delta H_{rxn} = -233 \text{ kJ/mol}$$

**B** do *electrochemical* reaction in calorimeter:



$$Q_c = \Delta H_{rxn} = -233 \text{ kJ/mol}$$

**C** do *electrochemical* reaction in calorimeter, resistor in *second* calorimeter



$$T\Delta S_{rxn} = \lim_{R \rightarrow \infty} Q_c = -43 \text{ kJ/mol}$$

$$\Delta G_{rxn} = \lim_{R \rightarrow \infty} Q_R = -190 \text{ kJ/mol}$$

$$Q_c + Q_r = \Delta H_{rxn} = -233 \text{ kJ/mol}$$

all species at standard state, extent of reaction small

# Electrochemical Thermodynamics

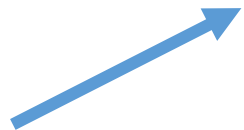
Gibbs energy change is the maximum reversible work the system can do.

$$\Delta G = -nFE_{cell}$$

$nF$  is the number of charges per mole of reaction,  
 $E_{cell}$  is the voltage... charge  $\times$  voltage = energy



$$\Delta G = \Delta G^0 + RT \ln Q$$



$$-nFE = -nFE^0 + RT \ln Q$$

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

$$E = E^0 - \frac{RT}{nF} \frac{\log Q}{\log e}$$

*Remember  $Q$  includes ALL species in the balanced reaction, including ions, solids, etc.*

$$E = E^0 - \frac{2.302 RT}{nF} \log Q$$

... and at 298.15 K,  $E = E^0 - \frac{0.0592 \text{ V}}{n} \log Q$

# Electrochemical Thermodynamics

Consider a electrochemical  
reaction:



$$E = E^0 - \frac{RT}{nF} \ln \frac{a_R}{a_O}$$

← activity of R  
← activity of O

$$E = E^0 - \frac{RT}{nF} \ln \frac{\gamma_R C_R}{\gamma_O C_O}$$

$$E = E^0 - \frac{RT}{nF} \ln \frac{\gamma_R}{\gamma_O} - \frac{RT}{nF} \ln \frac{C_R}{C_O}$$

# Electrochemical Thermodynamics

$$E = \boxed{E^0 - \frac{RT}{nF} \ln \frac{\gamma_R}{\gamma_O}} - \frac{RT}{nF} \ln \frac{C_R}{C_O}$$

$E^{0'}$



$$E = E^{0'} - \frac{RT}{nF} \ln \frac{C_R}{C_O}$$

**What happened to the  
“electrons” in our Nernst  
equation?**

the *formal potential*... this depends on the identity and concentration of all species present in solution

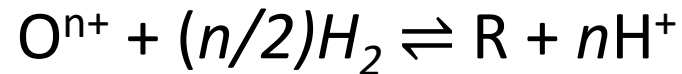


# Nernst Equation and Reference Electrodes

In this form we actually mean:

$$E(\text{vs. ref}) = E^{0'}(\text{vs. ref}) - \frac{RT}{nF} \ln \frac{C_R}{C_O}$$

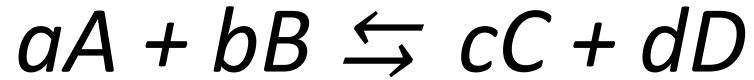
Which is (when the reference is the hydrogen electrode):



$$E_{rxn} = E_{rxn}^o - \frac{RT}{nF} \ln \frac{(a_{H^+})^n a_R}{(a_{H_2})^{n/2} a_O} \quad \text{at standard state, } a_{H^+} = a_{H_2} = 1.$$

**Key point:** anytime you write the Nernst equation for a “half” reaction you are in fact using a short hand to represent the full reaction including the reference electrode/reaction

# Equilibrium and the Chemical Potential

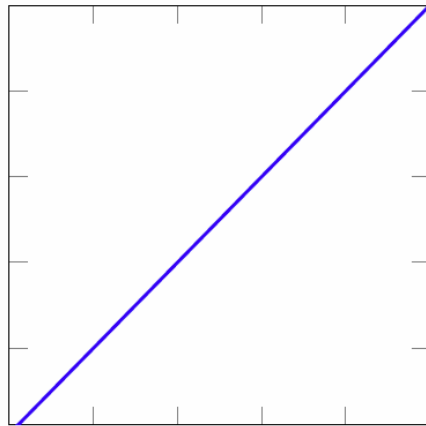


Gibbs energy is **minimized** when a system reaches **chemical equilibrium at constant pressure and temperature.**

How does the Gibbs energy change with amount of a substance?

pure  
substance

$G$

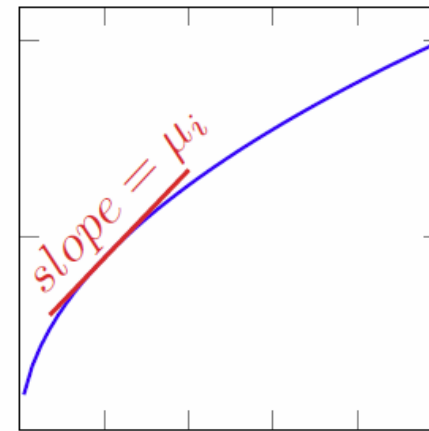


$n$  (amount in mol)

$$\mu = \frac{G}{n}$$

mixture or  
solution

$G_{mix}$



$n_i$  (amount in mol)

$$\mu_i = \frac{\partial G_{mix}}{\partial n}$$

figs. from  
Mark Lonergan

# Chemical potential

$$\mu_j^\alpha = \left( \partial G / \partial n_j \right)_{T, P, n_{i \neq j}}$$

$j$  is the species

$\alpha$  is the phase (e.g. metal, electrolyte, ionomer, etc.)

these are held constant

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

chemical potential increases with concentration...

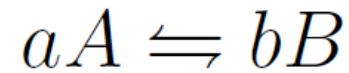
(arbitrary) standard  
state reference

activity term

although we call it a “potential” units are energy,  $J$

# Chemical Reactions and $\mu$

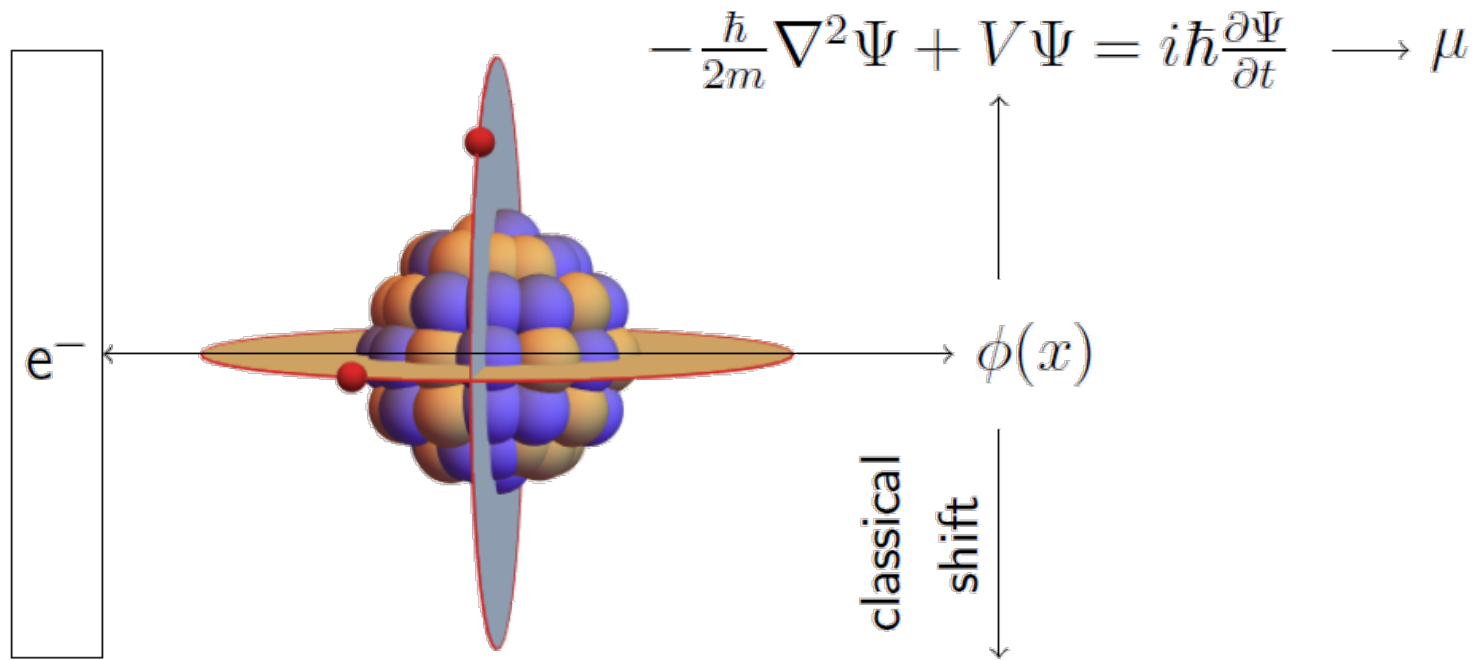
$$\Delta G_{rxn}(T, P, n_1, \dots, n_N) = \sum \nu_i \mu_i(T, P, n_1, \dots, n_N)$$



$$\begin{aligned}\Delta G &= \nu_B (\mu_B^\circ + RT \ln a_B) - \nu_A (\mu_A^\circ + RT \ln a_A) \\ &= \nu_B \mu_B^\circ - \nu_A \mu_A^\circ + RT \nu_B \ln a_B - RT \nu_A \ln a_A \\ &= \Delta G^\circ + RT \ln \frac{a_B^{\nu_B}}{a_A^{\nu_A}}\end{aligned}$$

$Q$

# Electrochemical potential



When we quantify  $(\partial G / \partial n_j)$  for a charged particle, it is useful to define a new quantity,  $\bar{\mu}$ , that partitions the “quantum mechanical” internal free energy and the “classical” electrostatic energy

fig. from Mark Lonergan

$$\phi = - \int_{path} \vec{E} \cdot d\ell$$

$$+zq\phi \longrightarrow \bar{\mu} = \mu + zq\phi$$

electrochemical potential

in electrochemistry, **electrochemical potential determines equilibrium** (other sources of free energy could be included, e.g. gravitational, but these are not generally important)



# Properties of the electrochemical potential

For an uncharged species:  $\bar{\mu}_i^\alpha = \mu_i^\alpha$

For any substance:  $\mu_i^\alpha = \mu_i^{0\alpha} + RT \ln a_i^\alpha$

For any pure phase at unit activity  $\mu_i^\alpha = \mu_i^{0\alpha}$

For electrons in a metal ( $z = -1$ ):  $\bar{\mu}_e^\alpha = \mu_e^{0\alpha} - F\phi^\alpha$

For equilibrium of species  $i$  between phases  $\alpha$  and  $\beta$ :  $\bar{\mu}_i^\alpha = \bar{\mu}_i^\beta$

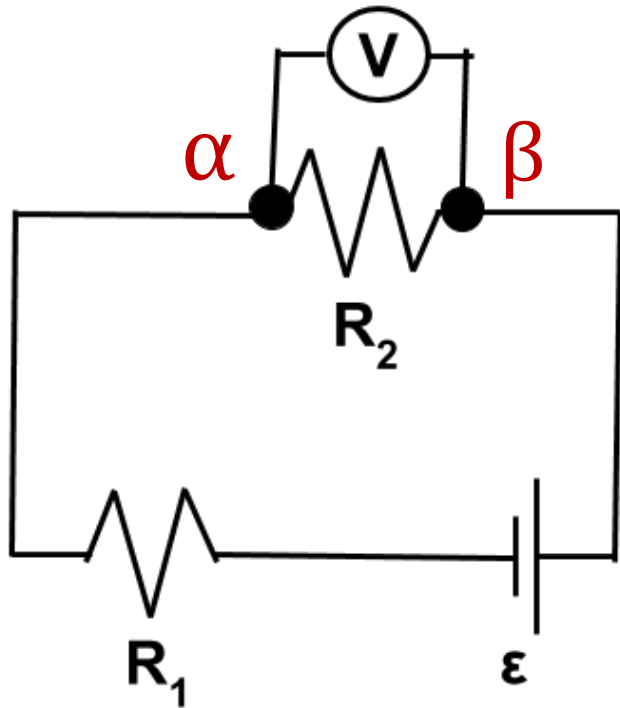


# Other Potentials in Electrochemistry

term	symbol	unit	brief definition	significance / example of use
electrochemical potential	$\bar{\mu}_j^\alpha$	J/mol	partial molar Gibbs free energy of a given species j in phase $\alpha$	defines criteria for equilibrium; differences in $\bar{\mu}_j^\alpha$ drive the transport, transfer, and reactivity of both charged and uncharged species
chemical potential	$\mu_j^\alpha$	J/mol	partial molar free energy of a given species j in phase $\alpha$ neglecting electrostatic contributions <sup>a</sup>	differences in $\mu_j^\alpha$ describe driving force for reactions between uncharged species and the direction of diffusive transport
electric potential	$\phi$	V	electric work needed to move a test charge to a specific point in space from a reference point (often at infinite distance) divided by the value of the charge	defines direction of electron transport in metals; gradient gives electric field; used to calculate electric potential energy
electrode potential	$E_{we}$	V	free-energy change divided by the electron charge associated with moving an electron (and any associated ions/solvent movement/rearrangement) from a reference state (often a reference electrode) to the working electrode	indicates oxidizing or reducing power of an electrode; related to the Fermi level of electrons in electrode
solution potential	$E_{sol}$	V	free-energy change divided by the electron charge associated with moving an electron (and any associated ions/solvent movement/rearrangement) from a reference state (often a reference electrode) into the bulk of a solution via a redox reaction	indicates oxidizing or reducing power of electrons involved in electrochemical redox equilibria; related to "Fermi level" of the electrons in solution and equivalent to the solution reduction potential
overpotential	$\eta$	V	generally, the difference between the applied electrode potential and the electrode potential when in equilibrium with the target electrochemical reaction	$\eta \cdot F$ gives the heat released, above that required by thermodynamics, per mole of electrons to drive an electrochemical process at a given rate; $F = 96485 \text{ C}\cdot\text{mol}^{-1}$

<sup>a</sup> that is, no 'long-range' electrostatic interactions due to uncompensated charge, as would be described by the Poisson equation in classical electrostatics. The electrostatic terms that describe electron-nucleus and electron-electron interactions and dictate Coulombic potentials in the Schrödinger equation are included.

# What does a voltmeter measure?



Voltage, but what is voltage?

$$\phi = - \int_{path} \vec{E} \cdot d\ell \quad ? \quad \text{Not in this case}$$

If the resistor/wire is the same material, then:

$$\begin{aligned} \Delta \bar{\mu}_e &= \bar{\mu}_e^\alpha - \bar{\mu}_e^\beta \\ &= \mu_e^\alpha - F\phi^\alpha - \mu_e^\beta + F\phi^\beta = -F\Delta\phi \end{aligned}$$



# Changes in total free energy drive transport

$$\mathbf{J}_j = - \left( \frac{C_j D_j}{RT} \right) \nabla \bar{\mu}_j$$

flux (mol cm<sup>-2</sup> s<sup>-1</sup>)

gradient in electrochemical potential

$$\bar{\mu}_j^\alpha = \mu_j^\alpha + z_j F \phi^\alpha$$

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

The electrochemical potential is usually the proper measure of free energy in electrochemical systems, though other terms might be added in special cases

$$u_i = D_i \left( \frac{|z_i| F}{RT} \right)$$

$u_i$  is mobility

# Changes in total free energy drive transport

In one dimension, the gradient of  $\bar{\mu}_j$  leads to the drift diffusion equation.

$$J_i = \underbrace{-D_i \frac{dc_i}{dx}}_{\text{diffusion}} + \underbrace{\frac{z_i}{|z_i|} u_i c_i \mathcal{E}}_{\text{drift}} = -D_i \frac{dc_i}{dx} - \frac{z_i}{|z_i|} u_i c_i \frac{d\phi}{dx}$$

$u_i$  is mobility

$$\mathcal{E} = -\frac{d\phi}{dx}$$

$D_i$  – diffusion coefficient (  $\text{cm}^2 \text{s}^{-1}$  )

$u_i$  – mobility (  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$  )

$\mathcal{E}$  – electric field (  $\text{V m}^{-1}$  )

$\phi$  – electrostatic potential

$$u_i = D_i \left( \frac{|z_i| F}{RT} \right)$$



# Consider the electrode potential

- units of  $V$
- given by the difference in  $\bar{\mu}_e$ , per charge, in the working electrode, relative to  $\bar{\mu}_e$  in a second electrode
- second electrode is usually reversible electrochemical half reaction (i.e. a reference electrode):

$$E_{\text{we}} \text{ (vs. } E_{\text{re}}) = \frac{-(\bar{\mu}_e^{\text{we}} - \bar{\mu}_e^{\text{re}})}{F}$$

- $E_{\text{we}}$  and  $E_{\text{re}}$  are each themselves defined relative to an arbitrary reference (that cancel in the difference). The cell voltage is usually written  $E_{\text{cell}} = E_{\text{we}} - E_{\text{re}}$  or  $(E_{\text{cathode}} - E_{\text{anode}})$



# Summary of Key Points

- Measurements of “potential differences” are necessarily of the total free-energy difference. Decomposing into differences in activity, electric potential, and other terms requires a model and assumptions.
- Transport of any species is governed by the spatial gradient in the electrochemical potential.
- At equilibrium, the electrochemical potential of any given species must be the same throughout the system
- For any chemical reaction, the sum of the electrochemical potentials of the reactants must equal those of the products. Processes with very slow kinetics are typically ignored.
- The use of the word ‘potential’ alone should be avoided; the type of should be clear.



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## Part II

# Electrochemical Thermodynamics and Potentials: Applications

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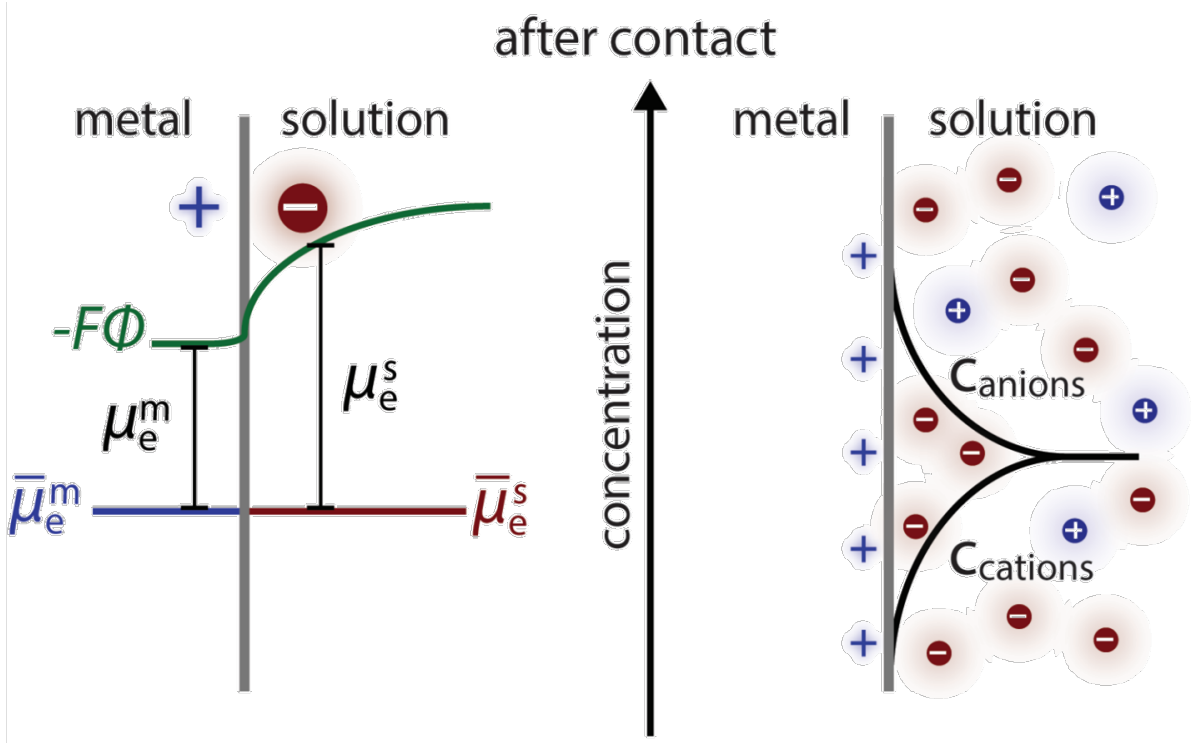
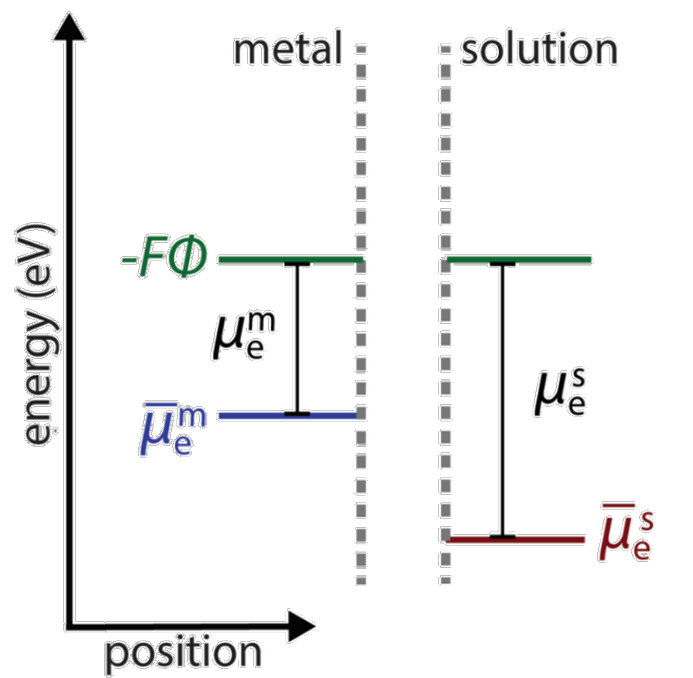


# Review of Key Points

- Measurements of “potential differences” are necessarily of the total free-energy difference. Decomposing into differences in activity, electric potential, and other terms requires a model and assumptions.
- Transport of any species is governed by the spatial gradient in the electrochemical potential.
- At equilibrium, the electrochemical potential of any given species must be the same throughout the system
- For any chemical reaction, the sum of the electrochemical potentials of the reactants must equal those of the products. Processes with very slow kinetics are typically ignored.
- The use of the word ‘potential’ alone should be avoided; the type of should be clear.

# Equilibration at a metal/redox-electrolyte solution interface

consider  $O + ne_m \rightleftharpoons R$



How do these equilibrate?

$$\bar{\mu}_e^m = \frac{\bar{\mu}_R^s - \bar{\mu}_O^s}{n} \equiv \bar{\mu}_e^s$$

We define  $\bar{\mu}_e^s$  even though there are "practically" no electrons in the solution

shows no surface charge initially, in reality  $E_{\sigma=0}$  is the applied potential where this surface charge is balanced by electronic charge such that the net charge is zero.

# The solution potential

expand via definition of electrochemical potential

$$\frac{-\bar{\mu}_e^S}{F} = -\left(\frac{\bar{\mu}_R^S - \bar{\mu}_O^S}{nF}\right) = -\left(\frac{\mu_R^O}{nF} + \frac{RT}{nF} \ln a_R^S + \frac{z_R}{n} \phi^S - \frac{\mu_O^O}{nF} - \frac{RT}{nF} \ln a_O^S - \frac{z_O}{n} \phi^S\right)$$

$$= E_{O/R}^O - \frac{RT}{nF} \ln \frac{a_R^S}{a_O^S} - \phi^S = E_{sol}$$

Nernst equation

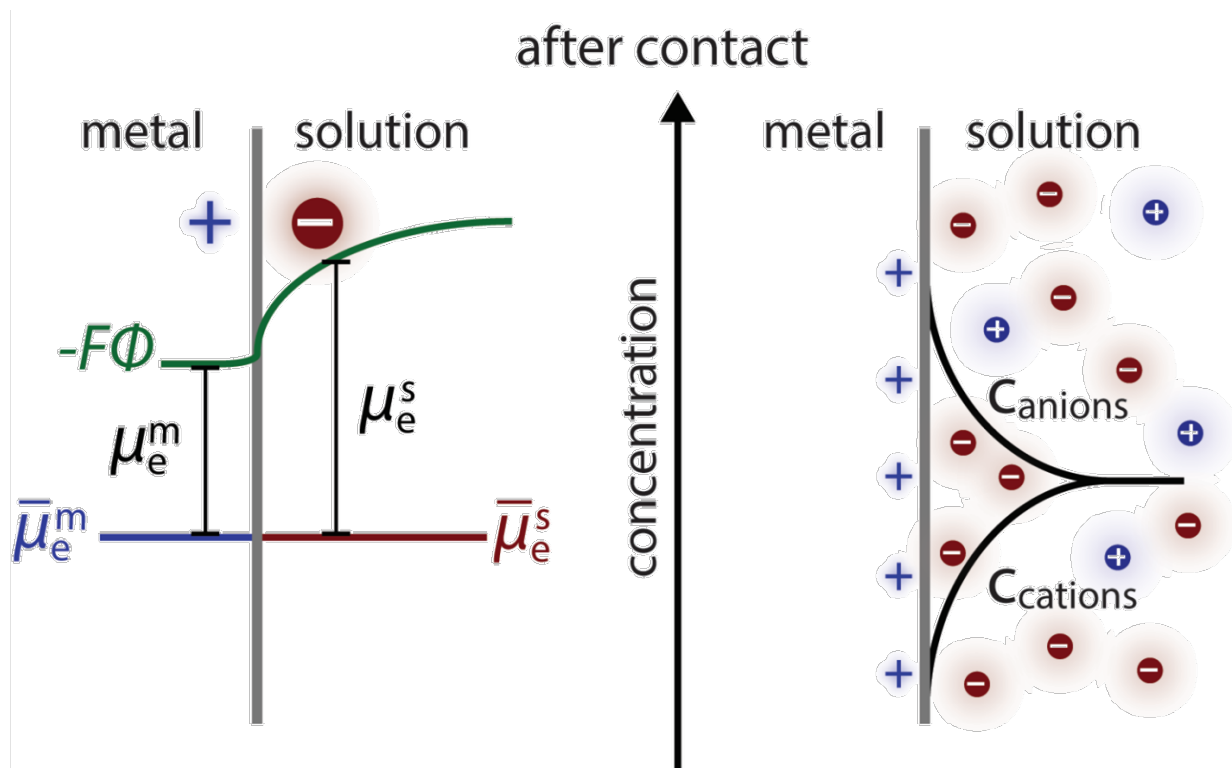
need to account for different electrostatic potentials!

the addition of the  $-\phi^S$  term that depends on the electric potential reference state and cancels when measured versus a reference electrode at the same  $\phi^S$





# Equilibration at a metal/redox-electrolyte solution interface

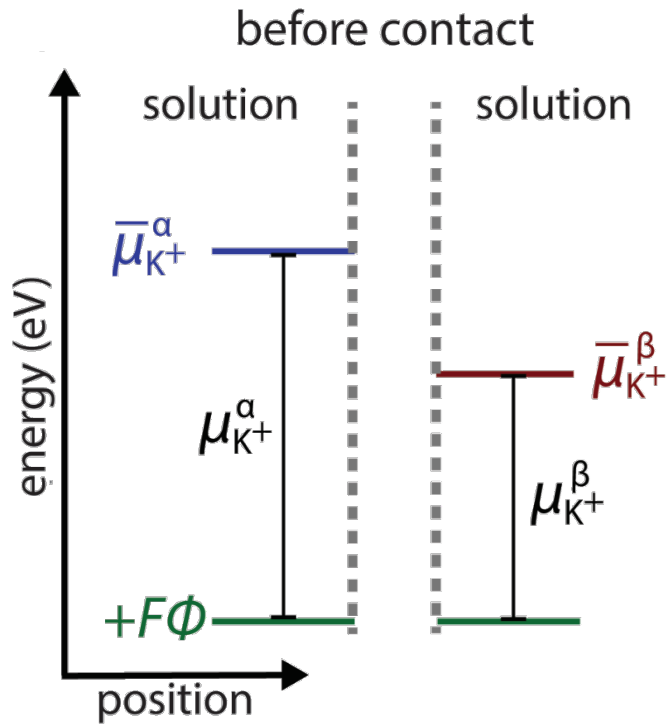


- initial difference in  $\bar{\mu}_e$  drives charge transfer across the interface, leading to an interfacial *electric* potential drop that affects  $\bar{\mu}_e^m$  until it equals  $\bar{\mu}_e^s$
- amount of charge transferred depends on the *capacitance* of the electrode
  - small compared to the number of electrons in the metal and redox species in the electrolyte (so that the bulk activity and thus  $\mu$  for all the species is practically unchanged)
- concentration of the compensating ions given by the Poisson-Boltzmann distribution
- $\bar{\mu}_j$  for all species are constant with position

# Membrane (Donnan) potentials

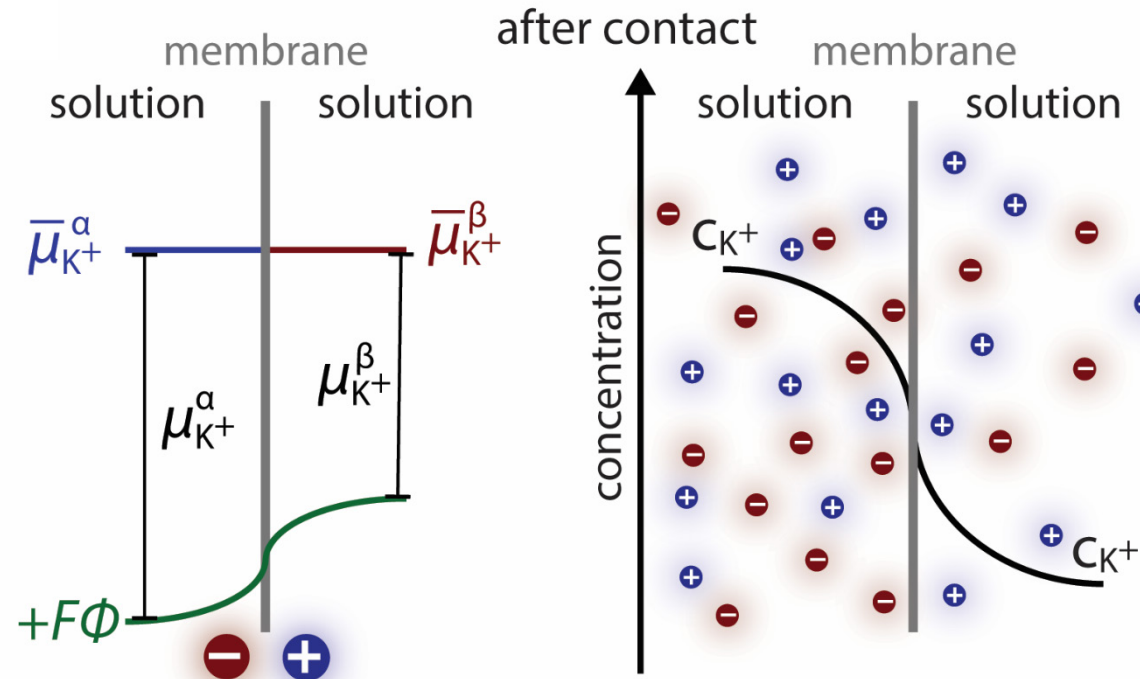
consider two solutions with different concentrations of KCl

What happens if we connect them with a cation-selective membrane like Nafion?



$$\bar{\mu}_{K^+}^{\alpha} = \mu_{K^+}^{\alpha} + RT \ln a_{K^+}^{\alpha} + F\phi^{\alpha} = \mu_{K^+}^{\beta} + RT \ln a_{K^+}^{\beta} + F\phi^{\beta} = \bar{\mu}_{K^+}^{\beta}$$

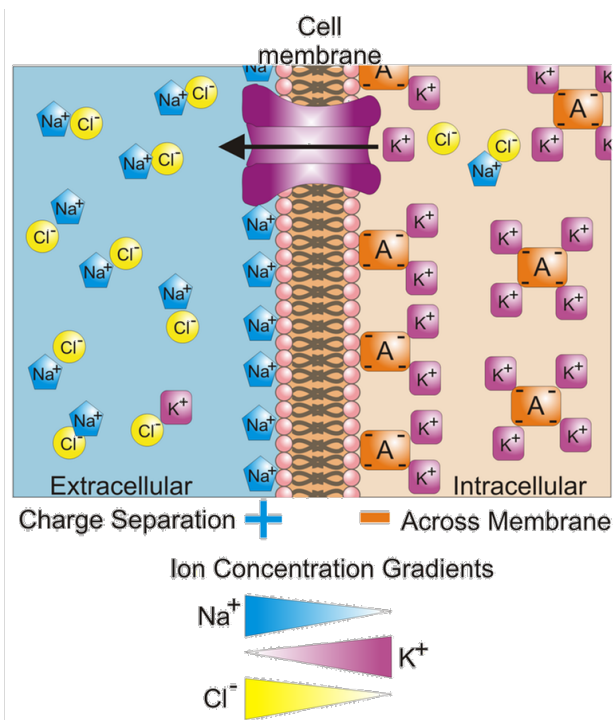
$$\phi^{\alpha} - \phi^{\beta} = \frac{RT}{F} \ln \frac{a_{K^+}^{\beta}}{a_{K^+}^{\alpha}}$$



membrane block  $\text{Cl}^-$  transport  $\bar{\mu}_{\text{Cl}^-}^{\alpha} \neq \bar{\mu}_{\text{Cl}^-}^{\beta}$ .



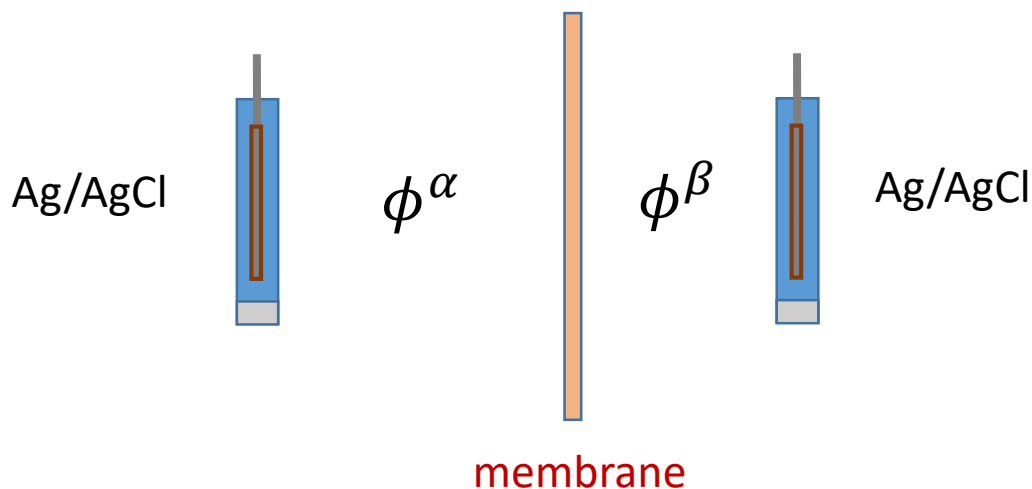
# Measuring membrane potentials



How do we measure electrostatic potential changes in electrochemical cells?

With a voltmeter? But a voltmeter doesn't measure electrostatic potential!?

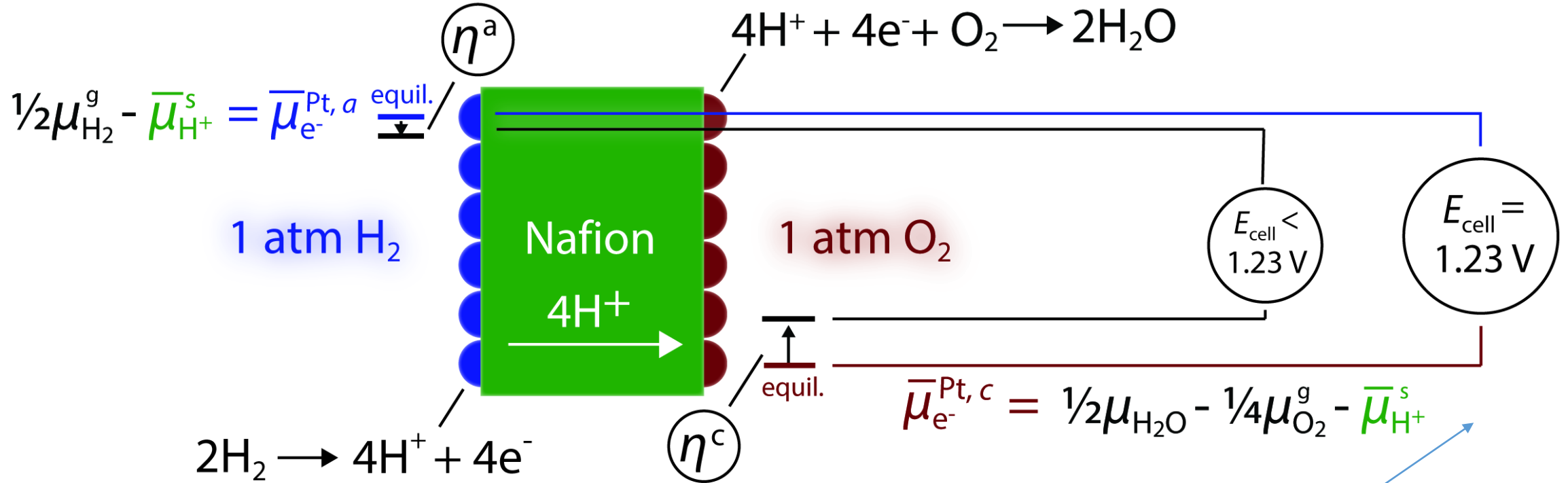
Consider what you measure with two reference electrodes:



$$\bar{\mu}_{e^-}^{\text{Ag}} = \bar{\mu}_{\text{Ag}}^{\text{Ag}} + \bar{\mu}_{\text{Cl}^-}^{\text{s}} - \bar{\mu}_{\text{AgCl}}^{\text{AgCl}} \quad \rightarrow \quad \bar{\mu}_{\text{Cl}^-}^{\text{s, re1}} \neq \bar{\mu}_{\text{Cl}^-}^{\text{s, re2}} \quad \text{and} \quad \bar{\mu}_{e^-}^{\text{s, re1}} \neq \bar{\mu}_{e^-}^{\text{s, re2}}$$

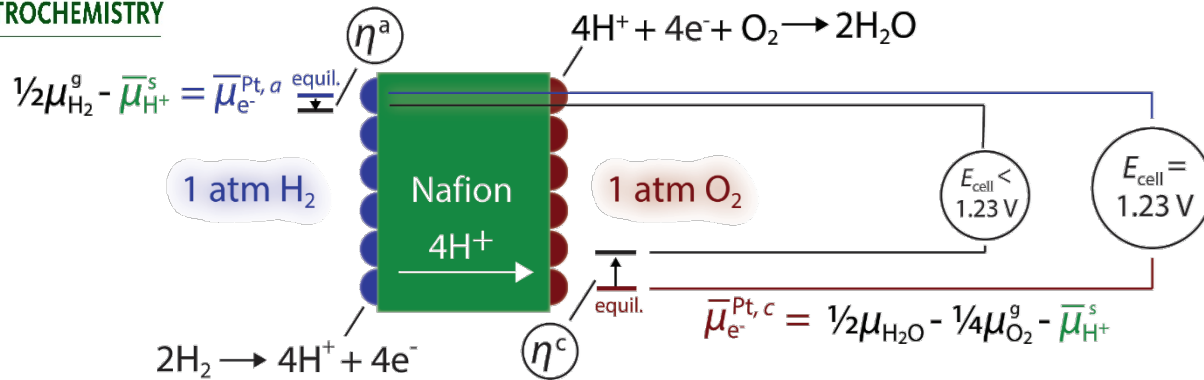
The two reference electrodes make a "battery" and are not a equilibrium.

# Fuel cells and batteries

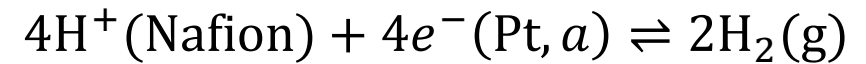


first consider "open circuit"  
 negligible net current is flowing through the external circuit  
 (e.g. during measurement with a high-impedance voltmeter)

# Fuel cells and batteries: open circuit



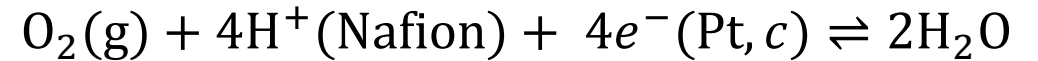
No.



$$\bar{\mu}_{\text{e}^-}^{\text{Pt},a} = \frac{1}{2} \bar{\mu}_{\text{H}_2}^{\text{g}} - \bar{\mu}_{\text{H}^+}^{\text{s}} \approx 0 \text{ kJ/mol} \quad \text{Why?}$$

Anode:

**Open circuit:** If zero net current is flowing does that mean  $\bar{\mu}_{\text{e}^-}$  at the Pt anode and cathode are the same?



Cathode:

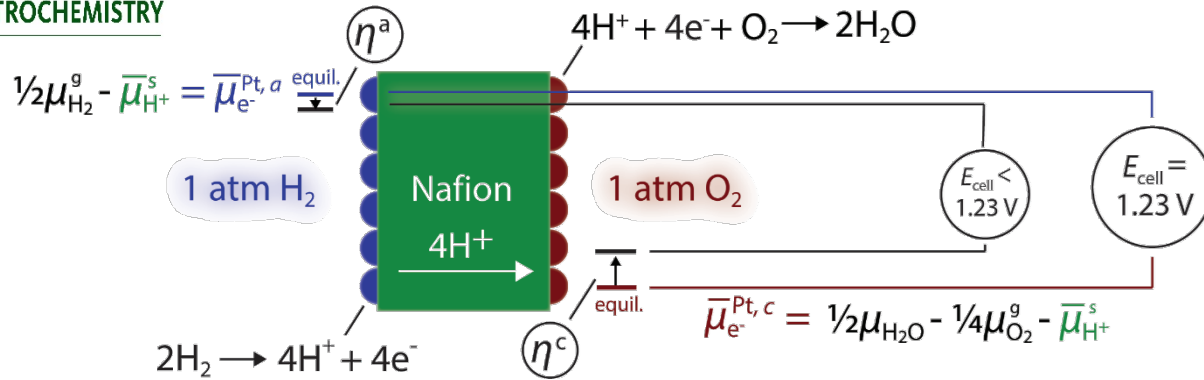
$$\bar{\mu}_{\text{e}^-}^{\text{Pt},c} = \frac{1}{2} \mu_{\text{H}_2\text{O}}^{\text{l}} - \frac{1}{4} \bar{\mu}_{\text{O}_2}^{\text{g}} - \bar{\mu}_{\text{H}^+}^{\text{s}} \approx -119 \text{ kJ/mol}$$

out of equilibrium -  $\text{O}_2$  and  $\text{H}_2$  cannot mix across the membrane and react; electrons cannot exchange

$$\bar{\mu}_{\text{e}^-}^{\text{Pt},c} - \bar{\mu}_{\text{e}^-}^{\text{Pt},a} = \frac{\Delta G_{\text{rxn}}}{n} = -F E_{\text{cell,oc}}$$

$$E_{\text{cell,oc}} = 1.23 \text{ V}$$

# Fuel cells and batteries: during operation



$$\bar{\mu}_{\text{H}^+}^{\text{Nafion}} = \mu_{\text{K}^+}^{\circ} + RT \ln a_{\text{H}^+}^{\text{Nafion}} + F\phi^{\text{Nafion}}$$

under current flow there must be gradients in  $\bar{\mu}$  of all species that transport – electrons, ions, water.

What drives the flow of H<sup>+</sup>?

$$\nabla \bar{\mu}_{\text{H}^+}^{\text{Nafion}} \approx F \nabla \phi^{\text{Nafion}}$$

What drives the interfacial electrochemical reactions for ORR and HOR?

$$\eta = E_{\text{app}} - E_{\text{rev}} \text{ (for a given reaction)}$$

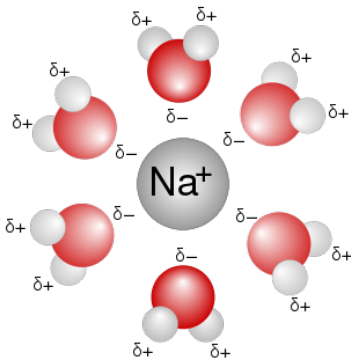
in terms of electrostatic potentials:

$$\eta = \Delta\phi - \Delta\phi_{\text{eq}}$$

# Electroosmotic effects and concentrated electrolytes

Transport of solvent and electrolyte ions are coupled.  
Electric potential leads to solvent movement too.

- $\kappa$ : ionic conductivity (S/m)
- $\xi$ : electroosmotic drag coefficient (unitless)
- $\phi_2$ : electric potential in electrolyte (V)
- $\alpha$ : dimensionless diffusion coefficient (unitless)
- $\mu_0$ : chemical potential of water (J/mol)



ion flux carrying  
water

diffusion of water

$$\text{Flux of water:} = -\frac{\kappa\xi}{F} \nabla\phi_2 - \left( \alpha + \frac{\kappa\xi^2}{F^2} \right) \nabla\mu_0$$

$$\text{Proton current:} = -\kappa \nabla\phi_2 - \frac{\kappa\xi}{F} \nabla\mu_0$$

Ohm's Law

Gradient in water chemical  
potential can drive ion transport



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## Part III

# Electrochemical Thermodynamics and Potentials: Double Layer Structure and Adsorption

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# Double Layer Structure - Basics

- The **inner Helmholtz plane (IHP)** passes through the center of the *specifically adsorbed* ions.
  - typically anions, that can shed hydration sphere e.g. sulfate.
- The **outer Helmholtz plane (OHP)** passes through the center of solvated ions at the distance of their closest approach.
- A layer of orientated “low-entropy” water covers the surface.
  - if  $C_i = \epsilon_{r,i} \epsilon_0 / d_i$ , where  $C_i$  and  $d_i$  are the capacitance and thickness of layer  $i$ , respectively, then  $\epsilon_{r,i} \sim 6$  at metals.
- Double layer structure is critical in influencing electrode kinetics, as we will see later.

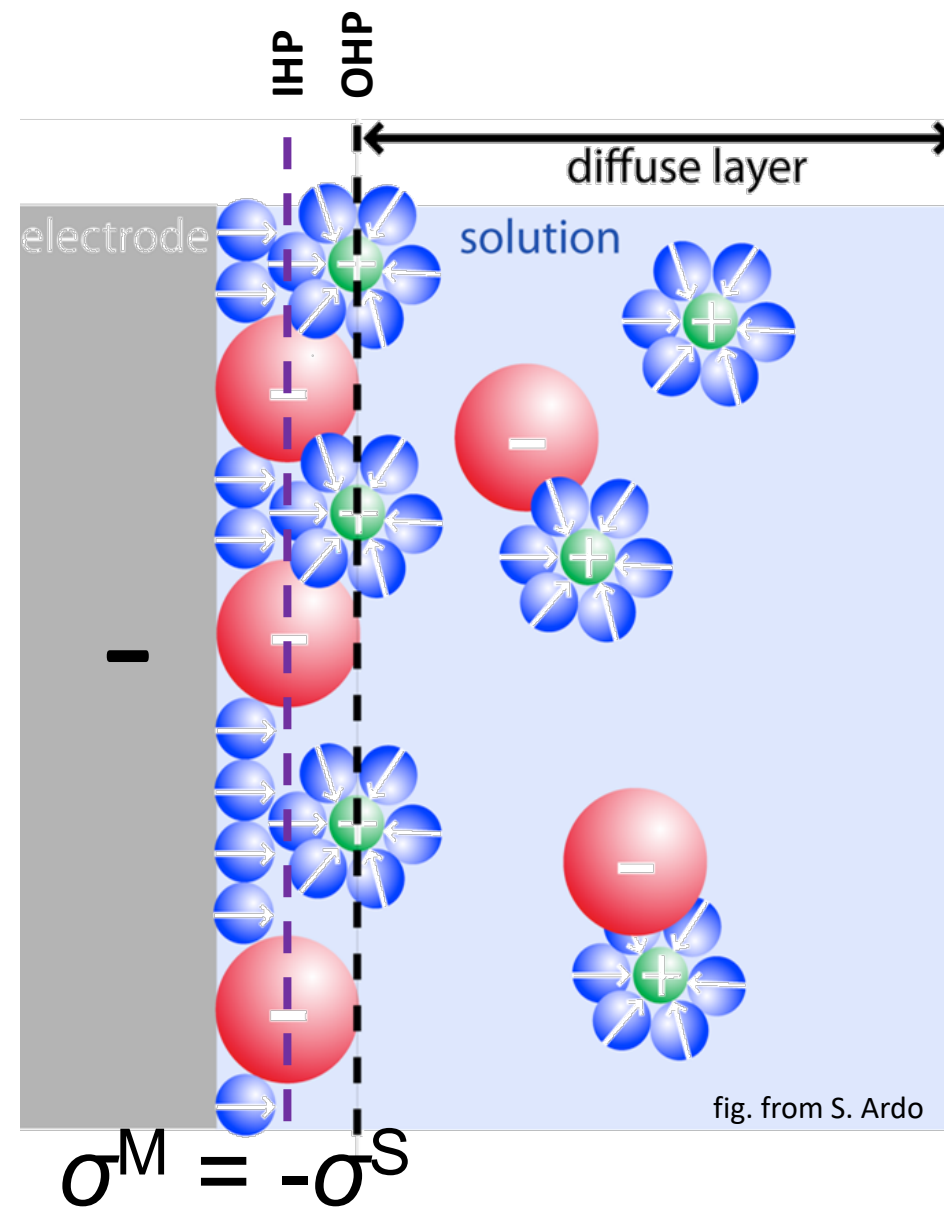


fig. from S. Ardo

# Interface Thermodynamics

Consider a ideally polarizable electrode (no faradaic charge transfer)

The interface is a “phase” with finite thickness where concentrations differ from bulk values.

$$n_i^\sigma = n_i^S - n_i^R \quad \text{define excess concentrations}$$

$$d\bar{G}^R = \left(\frac{\partial \bar{G}^R}{\partial T}\right) dT + \left(\frac{\partial \bar{G}^R}{\partial P}\right) dP + \sum_i \left(\frac{\partial \bar{G}^R}{\partial n_i^R}\right) dn_i^R \quad \text{total differential of electrochemical Gibbs energy of reference phases (no interface)}$$

$$d\bar{G}^S = \left(\frac{\partial \bar{G}^S}{\partial T}\right) dT + \left(\frac{\partial \bar{G}^S}{\partial P}\right) dP + \left(\frac{\partial \bar{G}^S}{\partial A}\right) dA + \sum_i \left(\frac{\partial \bar{G}^S}{\partial n_i^S}\right) dn_i^S \quad \text{total differential of Gibbs energy of interface region}$$

change in G with interface area A

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

$$\bar{\mu}_i = \left(\frac{\partial \bar{G}^R}{\partial n_i^R}\right) = \left(\frac{\partial \bar{G}^S}{\partial n_i^S}\right) \quad \text{at equilibrium } \bar{\mu} \text{ must be the same everywhere for any species}$$

how much free energy it takes to create new interface

# Gibbs adsorption isotherm

$$d\bar{G}^\sigma = d\bar{G}^S - d\bar{G}^R = \gamma dA + \sum_i \bar{\mu}_i d(n_i^S - n_i^R) = \gamma dA + \sum_i \bar{\mu}_i dn_i^\sigma$$

differential "excess" free energy of interface

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

The Euler theorem allows one to define linear homogenous function in terms of derivatives and variables.

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



$$d\bar{G}^\sigma = \gamma dA + \sum_i \bar{\mu}_i dn_i^\sigma + A d\gamma + \sum_i n_i^\sigma d\bar{\mu}_i \quad \longrightarrow \quad A d\gamma + \sum_i n_i^\sigma d\bar{\mu}_i = 0$$

total differential

compare to above, then

Gibbs adsorption isotherm

$$-d\gamma = \sum_i \Gamma_i d\bar{\mu}_i$$

$$\Gamma_i = n_i^\sigma / A$$

surface excess concentration

# Gibbs adsorption isotherm

Now following Schmickler and Santos for a more general form:

$$d\gamma = - \sum_i \Gamma_i^* d\tilde{\mu}_i^\sigma$$

Gibbs absorption isotherm

absolute surface excess of species

$$\sum N_i d\tilde{\mu}_i = 0$$

in solution bulk, Gibbs-Duhem eqn. (at constant  $T$  and  $P$ ) holds  
[http://staff.um.edu.mt/jgr1/teaching/che2372/notes/05/02/01/gibbs\\_duhem.html](http://staff.um.edu.mt/jgr1/teaching/che2372/notes/05/02/01/gibbs_duhem.html)

places a compositional constraint upon any changes in the electrochemical potential in a mixture

Define a reference phase, usually the solvent, and remove from sum in Gibbs-Duhem eqn

$$d\tilde{\mu}_0^s = - \sum_i^{sol} \frac{N_i^s}{N_0^s} d\tilde{\mu}_i^s$$

Define “relative surface excess” with respect to the bulk reference phase (i.e. solvent, 0):

$$\Gamma_i = \Gamma_i^* - \frac{N_i^s}{N_0^s} \Gamma_0^*$$

we cannot measure absolute surface excess, only relative to the solvent reference



# Gibbs adsorption isotherm

rewrite Gibbs adsorption isotherm

$$d\gamma = - \sum_i^{sol} \Gamma_i d\tilde{\mu}_i^s \quad \boxed{- \Gamma_{M^{z+}} d\tilde{\mu}_{M^{z+}}^\sigma - \Gamma_e d\tilde{\mu}_e^\sigma - \Gamma_M d\mu_M^\sigma}$$

positive charge in electrode
neutral metal

everything in the solution
negative charge in electrode

Expand electrochemical potentials:

$$\begin{aligned}
 & - \Gamma_{M^{z+}} d\tilde{\mu}_{M^{z+}}^\sigma - \Gamma_e d\tilde{\mu}_e^\sigma - \Gamma_M d\mu_M^\sigma \\
 & = - \Gamma_{M^{z+}} d\mu_{M^{z+}}^m - \Gamma_e d\mu_e^m - d\phi^m (ze_0\Gamma_{M^{z+}} - e_0\Gamma_e) - \Gamma_M d\mu_M^m \\
 \text{(A)} \quad & = \boxed{- \Gamma_{M^{z+}} d\mu_{M^{z+}}^m - \Gamma_e d\mu_e^m - \sigma d\phi^m - \Gamma_M d\mu_M^m}
 \end{aligned}$$

$$\sigma = ze_0\Gamma_{M^{z+}} - e_0\Gamma_e = - \sum_j z_j e_0 \Gamma_j \quad \text{balanced by excess charge in the electrolyte}$$

surface charge density;  $e_0$  here is fundamental charge



# Gibbs adsorption isotherm



in eq. with constant  $\phi$  in metal

decompose electrochemical potential of solution species

(B)  $\mu_M = \mu_{M^{z+}} + z\mu_e$

(C)  $\tilde{\mu}_j^s = \mu_j^s + z_j\phi^s$

use (A), (B) and (C) to simplify expression for differential surface tension:

$$d\gamma = -\sigma d\phi - \sum_i \Gamma_i d\mu_i^s$$

from the electrostatic energy terms

uncharged solution species except solvent

This is the *electrocapillary equation*.

# Gibbs adsorption isotherm

$$d\gamma = -\sigma d\phi - \sum_i \Gamma_i d\mu_i^s$$

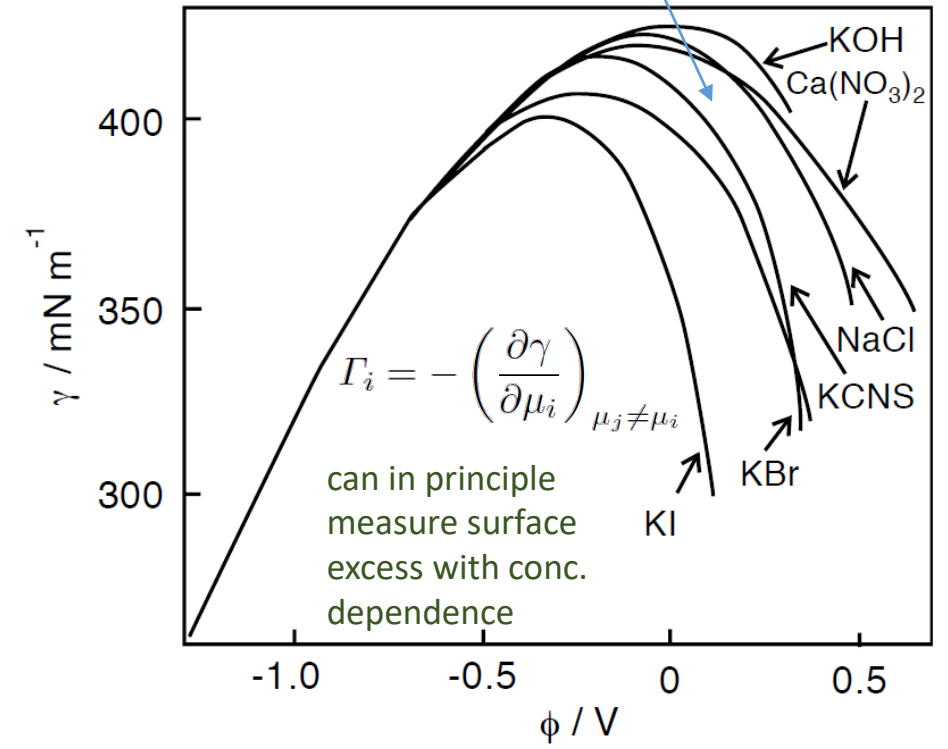
$$\sigma = - \left( \frac{\partial \gamma}{\partial \phi} \right)_{\mu_i}$$

Lippmann Equation

- At the potential of zero charge (PZC),  $\sigma = 0$  and there is no net charge on the metal.
- Moving from the PZC, charge accumulates and tends to repel, counteracting surface tension

Notice there is a maximum in surface energy with potential. Why?

Divergence due to increase of the work function by anion adsorption.



Interfacial tension of a mercury electrode at 0.1 M electrolyte.

D.C. Grahame, *Chem. Revs.* **41** (1947) 441



# Interfacial differential capacitance

$$\left( \frac{\partial^2 \gamma}{\partial \phi^2} \right)_{\mu_i} = -C$$

The differential capacitance of an interface is given by the second derivative of the interface tension, because:

$$\frac{d\sigma}{dE} = C$$

i.e. the capacitance measures how much charge is stored as the electrode potential is changed by modulating  $\Delta\phi$

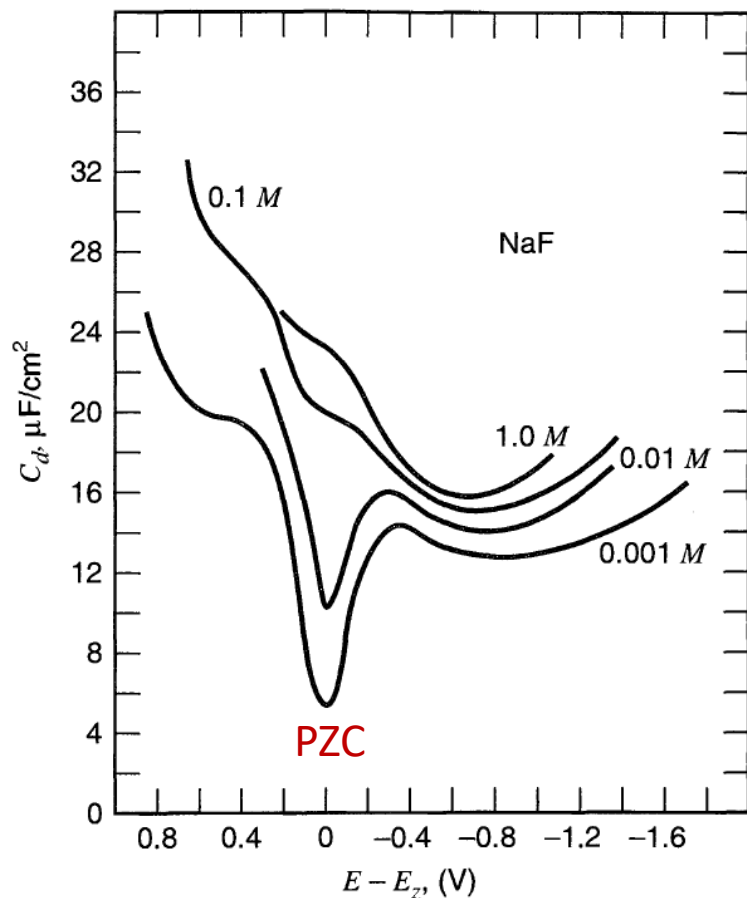
This is extremely useful, because we can measure interfacial capacitance directly using impedance spectroscopy



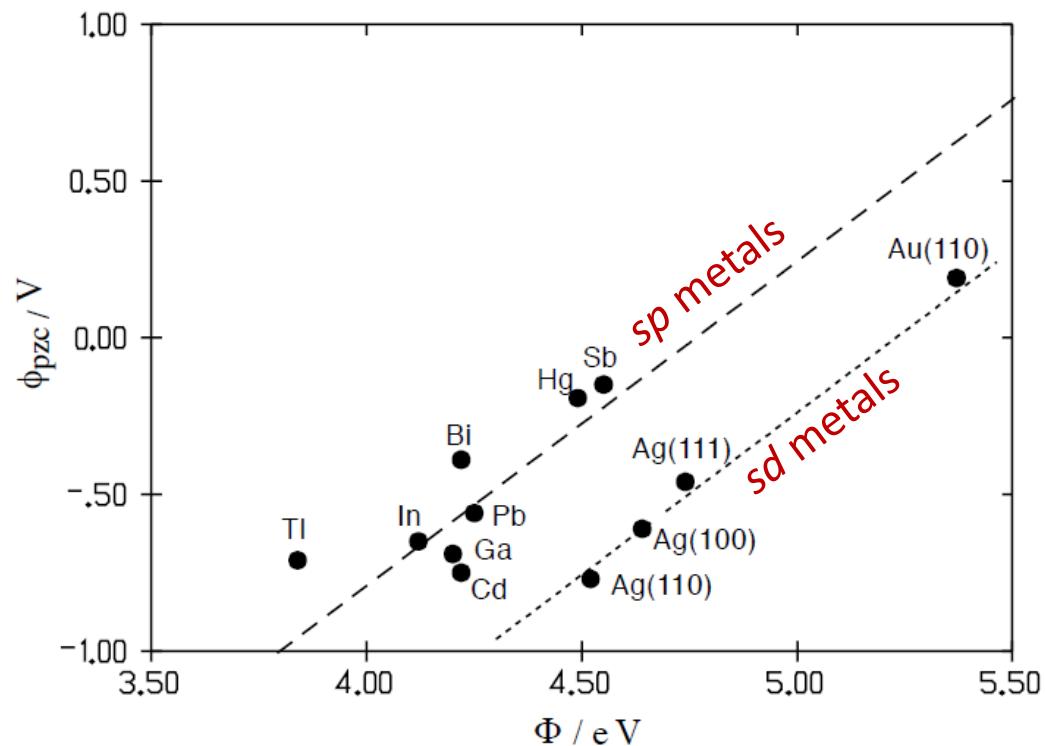


# Interfacial differential capacitance

higher work function = more electronegative = more positive PZC



D. C. Grahame, *Chem. Rev.*, **41**, 441 (1947)



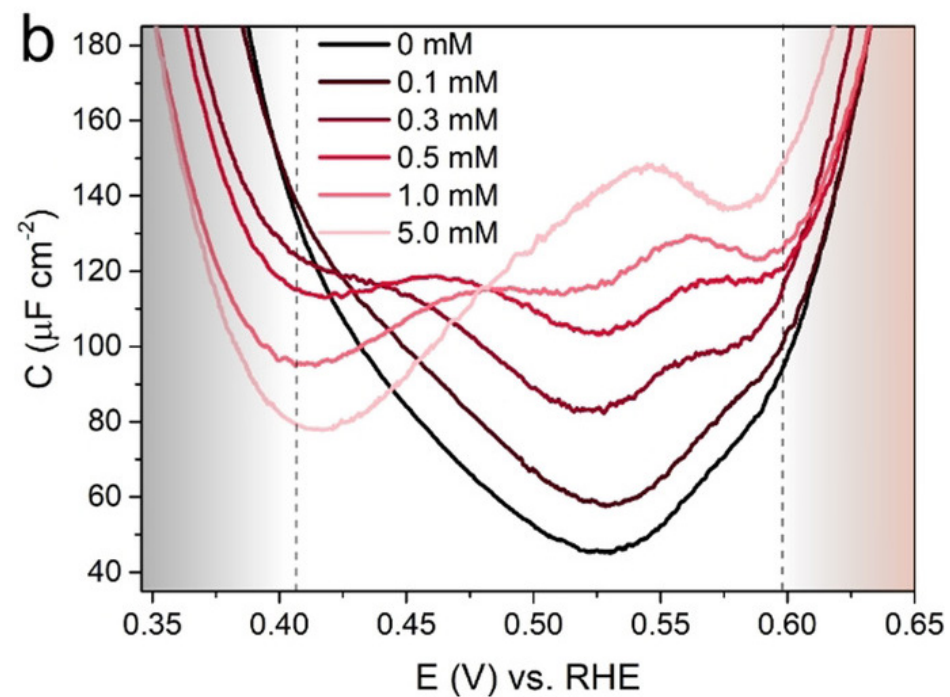
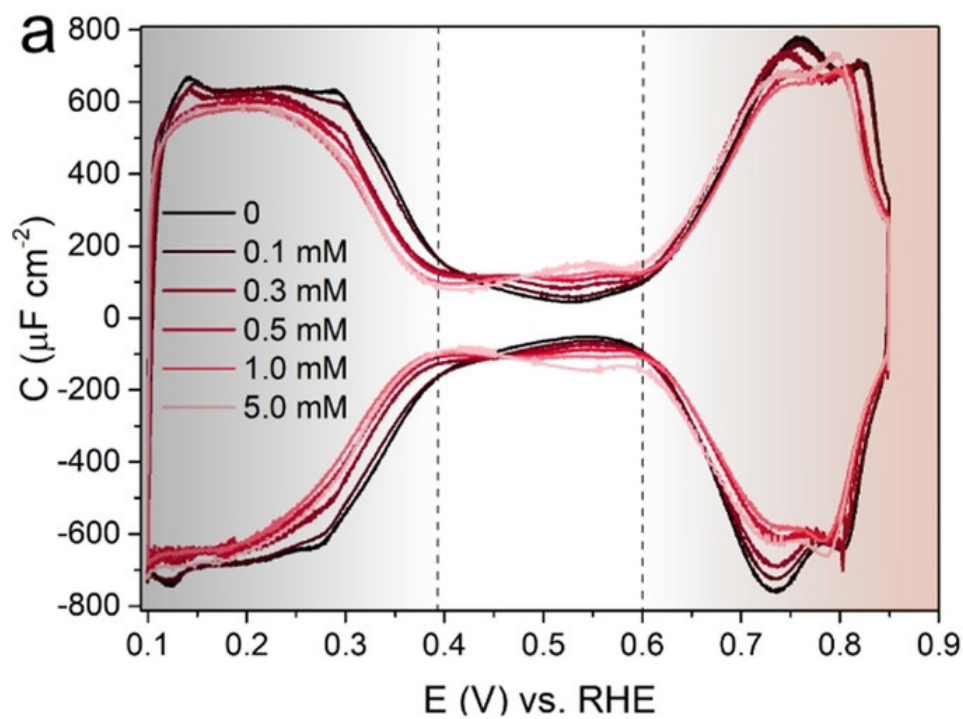
S. Trasatti, *Advances in Electrochemistry and Electrochemical Engineering*

- A minimum in  $C_d$  exists at the pzc.
- $C_d$  increases with salt concentration at all potentials, and the "dip" near the pzc disappears.



## Double Layer at the Pt(111)–Aqueous Electrolyte Interface: Potential of Zero Charge and Anomalous Gouy–Chapman Screening

*Kasinath Ojha, Nakkiran Arulmozhi, Diana Aranzales, and Marc T. M. Koper\**



# Models of the Electrical Double Layer

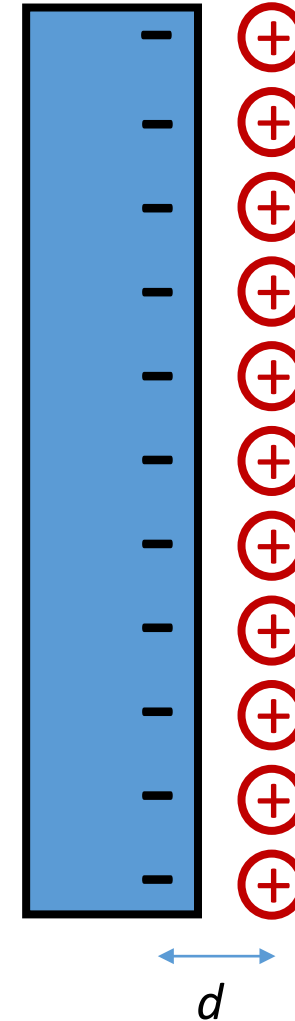
- Helmholtz

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

surface charge on a parallel plate capacitor

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

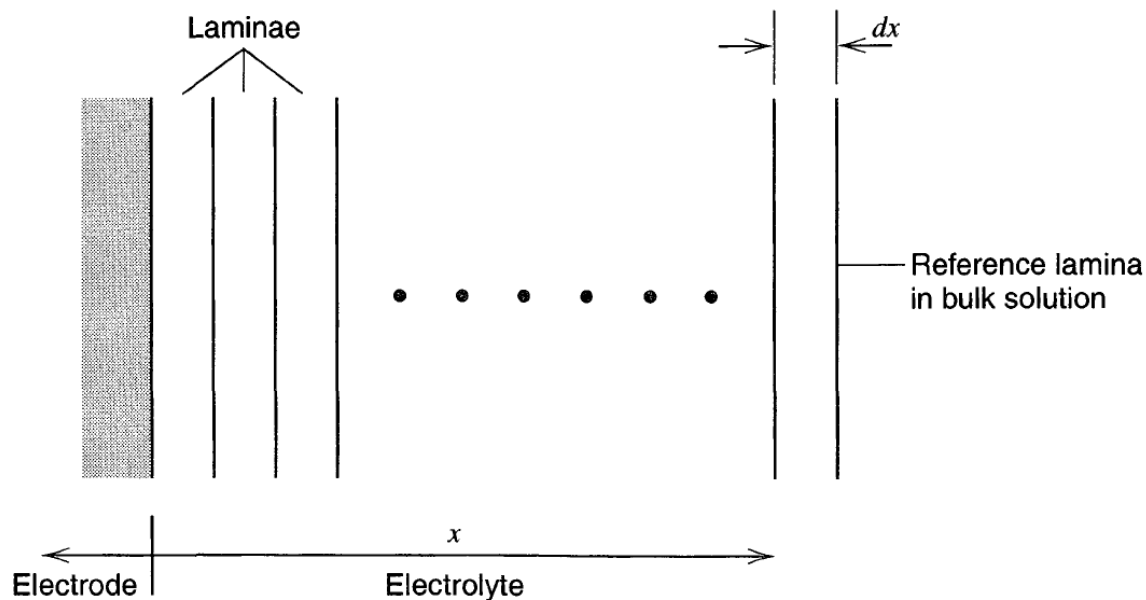
predicts constant  $C_d$ , which is not what is observed experimentally.





# Gouy-Chapman theory and Boltzmann factors

lamina can be regarded as energy states with equivalent degeneracies – concentrations related by Boltzmann factor



bulk ion concentration

"bulk" electrostatic potential

$$n_i = n_i^0 \exp\left(\frac{-z_i e \phi}{kT}\right)$$

charge density

$$\rho(x) = \sum_i n_i z_i e \quad e \text{ is fundamental charge}$$

$$= \sum_i n_i^0 z_i e \exp\left(\frac{-z_i e \phi}{kT}\right)$$



# Poisson-Boltzmann Equation

$$\rho(x) = -\epsilon\epsilon_0 \frac{d^2\phi}{dx^2}$$

Poisson equation: integral of charge density is electric field,  
integral of electric field is electric potential

$$\frac{d^2\phi}{dx^2} = -\frac{e}{\epsilon\epsilon_0} \sum_i n_i^0 z_i \exp\left(\frac{-z_i e\phi}{kT}\right)$$

$$\frac{d\phi}{dx} = -\left(\frac{8kTn^0}{\epsilon\epsilon_0}\right)^{1/2} \sinh\left(\frac{ze\phi}{2kT}\right)$$

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

apply for 1:1  
electrolyte;  
e.g. NaCl or  
CaSO<sub>4</sub>

thus:  $d\left(\frac{d\phi}{dx}\right)^2 = -\frac{2e}{\epsilon\epsilon_0} \sum_i n_i^0 z_i \exp\left(\frac{-z_i e\phi}{kT}\right) d\phi$   $\xrightarrow{\text{integrate}}$   $\left(\frac{d\phi}{dx}\right)^2 = \frac{2kT}{\epsilon\epsilon_0} \sum_i n_i^0 \left[ \exp\left(\frac{-z_i e\phi}{kT}\right) - 1 \right]$

# Gouy-Chapman potential distribution

if:  $(ze\phi_0/4kT) < 0.5$

separate and integrate

$$\int_{\phi_0}^{\phi} \frac{d\phi}{\sinh(ze\phi/2kT)} = -\left(\frac{8kTn^0}{\epsilon\epsilon_0}\right)^{1/2} \int_0^x dx$$

then:  $\tanh(ze\phi/4kT) \approx ze\phi/4kT$

resulting in

$$\frac{\tanh(ze\phi/4kT)}{\tanh(ze\phi_0/4kT)} = e^{-\kappa x}$$

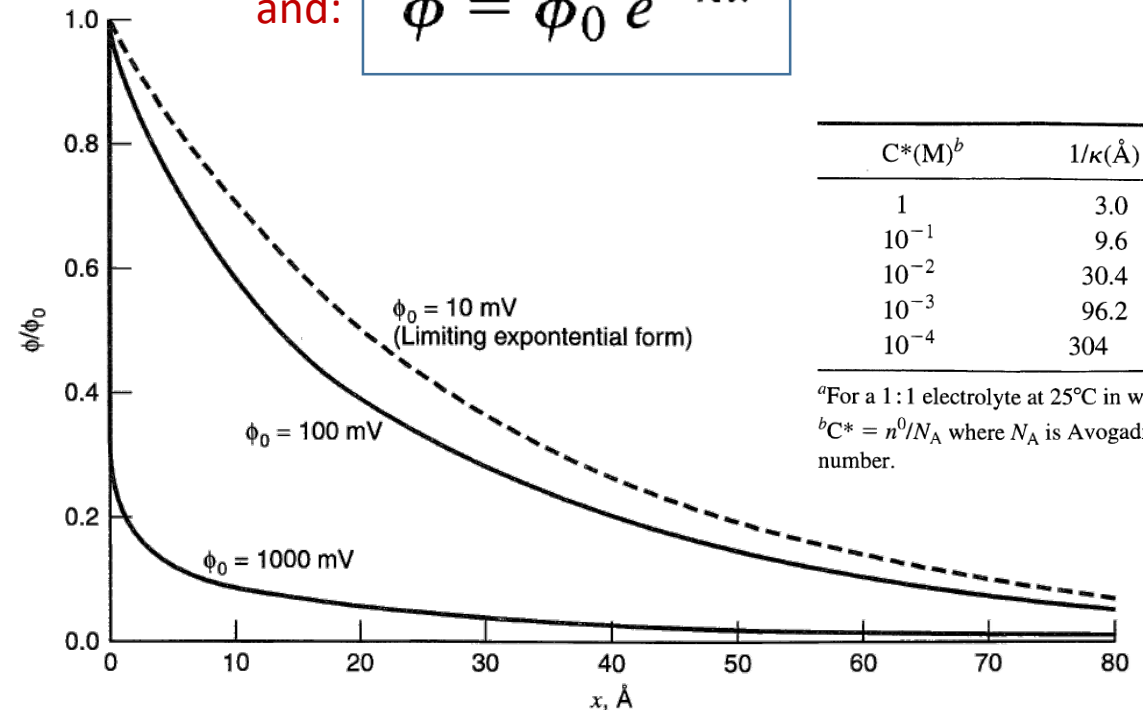
$$\kappa = \left(\frac{2n^0 z^2 e^2}{\epsilon\epsilon_0 kT}\right)^{1/2}$$

$$\kappa = (3.29 \times 10^7) z C^{*1/2}$$

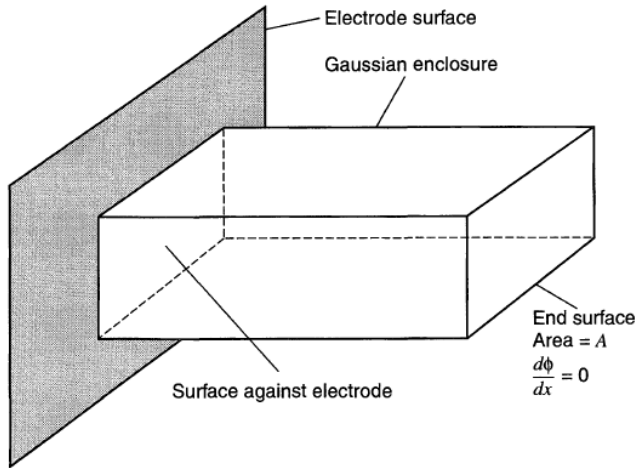
$$\kappa = 1/L_d$$

$L_d$  = Debye screening length

and:  $\phi = \phi_0 e^{-\kappa x}$



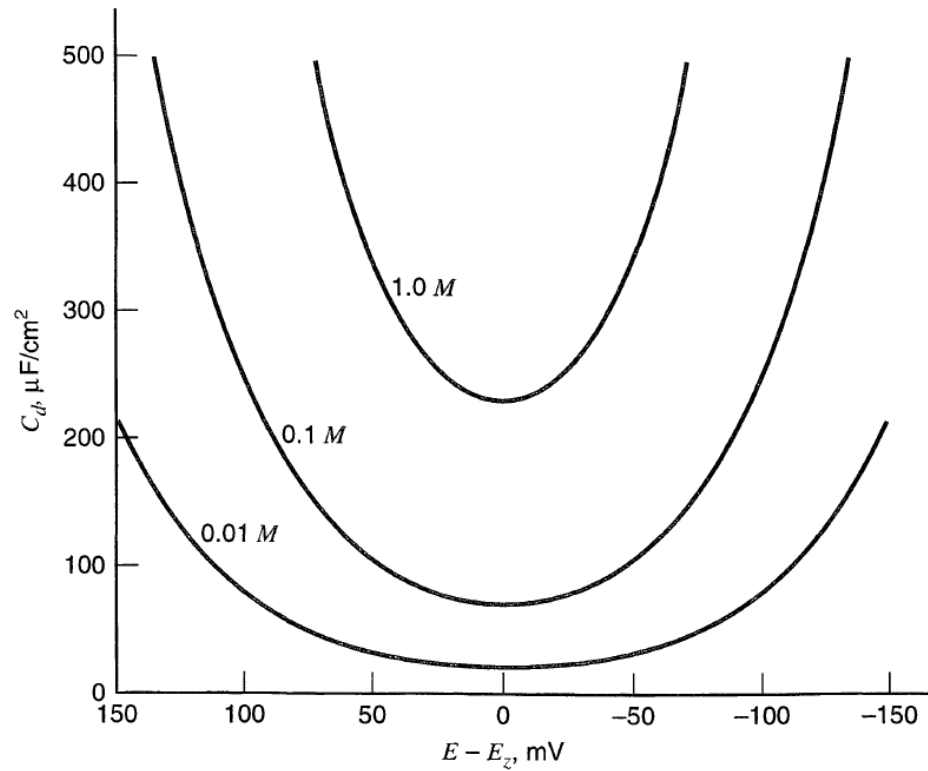
# Capacitance from Gouy-Chapman



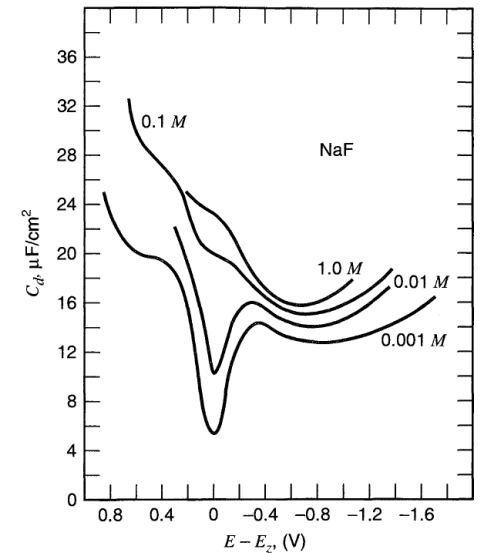
$$C_d = \frac{d\sigma^M}{d\phi_0} = \left( \frac{2z^2 e^2 \epsilon \epsilon_0 n^0}{kT} \right)^{1/2} \cosh\left( \frac{ze\phi_0}{2kT} \right)$$

$$q = \epsilon \epsilon_0 \left( \frac{d\phi}{dx} \right)_{x=0} \int_{\text{end surface}} dS$$

$$\sigma^M = -\sigma^S = (8kT\epsilon\epsilon_0 n^0)^{1/2} \sinh\left( \frac{ze\phi_0}{2kT} \right)$$



Any problems with this?



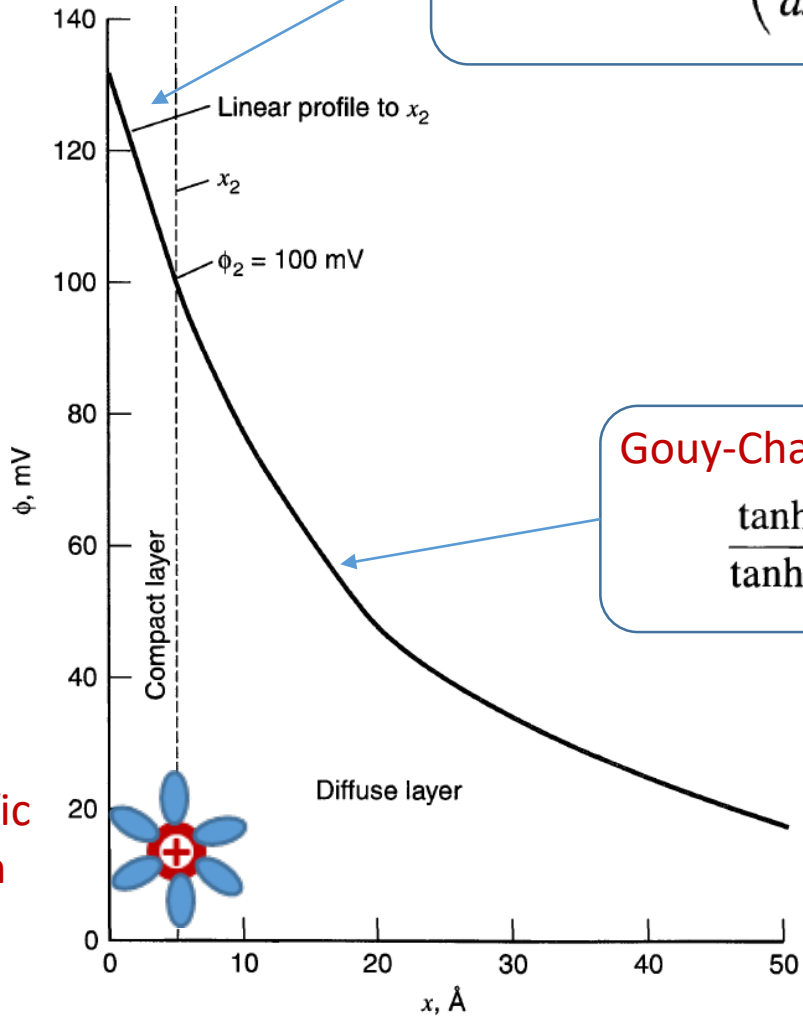
How is this different than experiment?

# Stern's Modification

- Ions in Gouy-Chapman are point charges with no restriction on concentration
  - unrealistic at high ion density
- With no physical size, no distance of closest ion approach
- no limit to rise in differential capacitance



non-specific adsorption



Helmholtz parallel plate capacitor

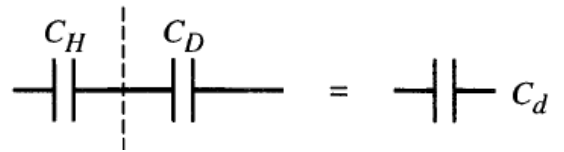
$$\phi_0 = \phi_2 - \left( \frac{d\phi}{dx} \right)_{x=x_2} x_2$$

Gouy-Chapman / Poisson Boltzmann

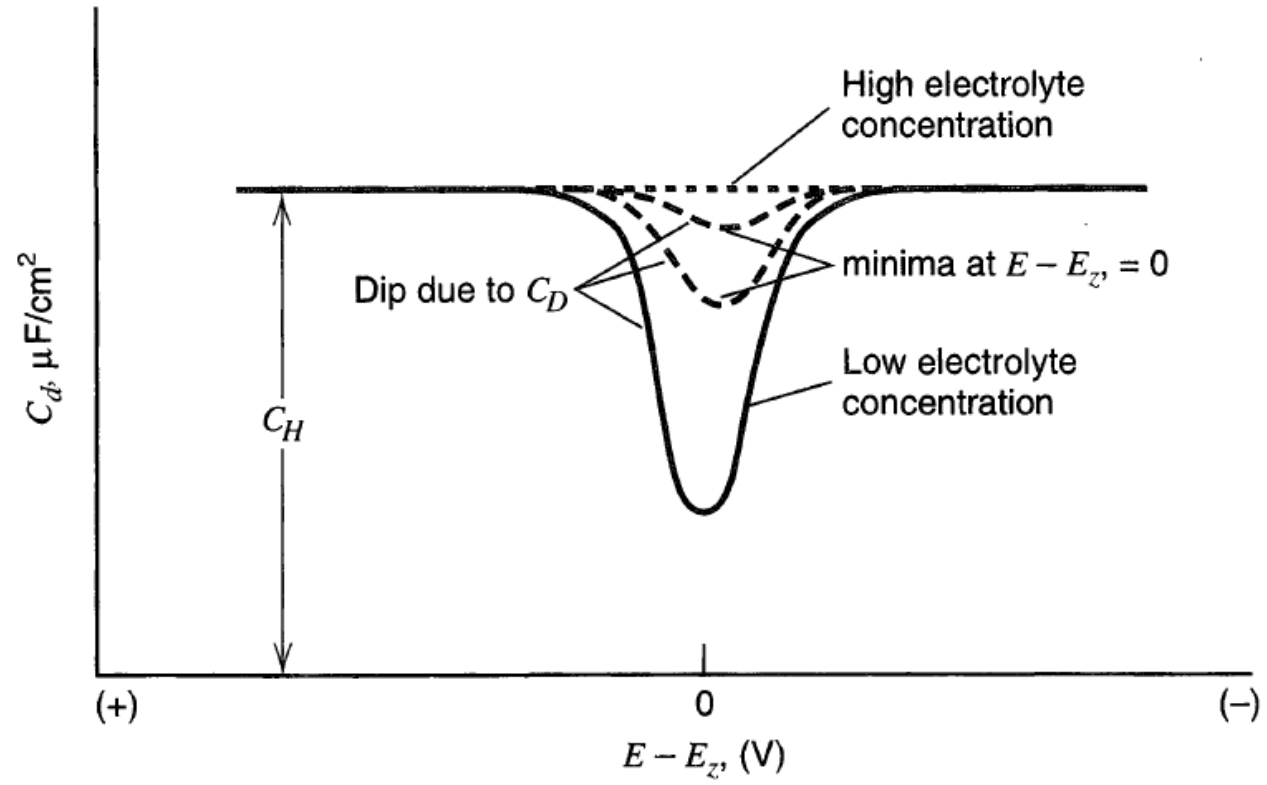
$$\frac{\tanh(ze\phi/4\epsilon T)}{\tanh(ze\phi_2/4\epsilon T)} = e^{-\kappa(x-x_2)}$$



# Capacitance in the *Gouy-Chapman-Stern* (GCS) model



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



Closer to experimental data. What else could be happening?

# Specific adsorption and the PZC

## PZC depends on concentration

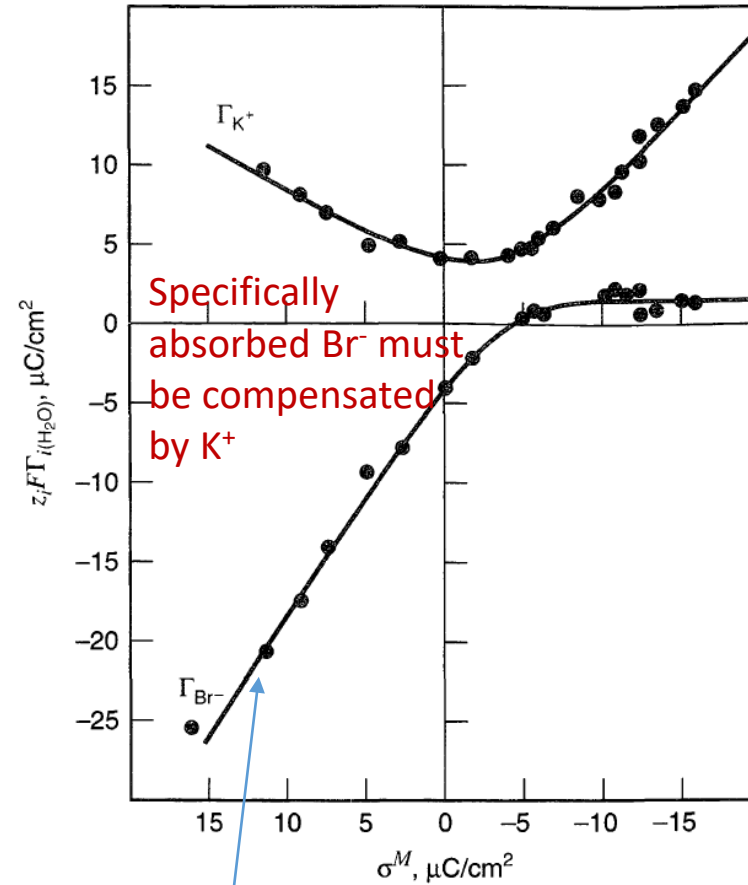
Electrolyte	Concentration, $M$	$E_z$ , V vs. NCE <sup>b</sup>
NaF	1.0	-0.472
	0.1	-0.472
	0.01	-0.480
	0.001	-0.482
NaCl	1.0	-0.556
	0.3	-0.524
	0.1	-0.505
KBr	1.0	-0.65
	0.1	-0.58
	0.01	-0.54
KI	1.0	-0.82
	0.1	-0.72
	0.01	-0.66
	0.001	-0.59

no specific adsorption

specific adsorption

<sup>a</sup>From D. C. Grahame, *Chem. Rev.*, **41**, 441 (1947).

<sup>b</sup>NCE = normal calomel electrode.



$$d(-F\Gamma_{Br^-(H_2O)})/d\sigma^M > 1$$

# Adsorption phenomena and isotherms

## Langmuir Isotherm

$S = k \ln W$   $W$  is number of ways of selecting  $M$  out of  $N$  sites

$$F = M\epsilon_{\text{ad}} - kT \ln \frac{N!}{M!(N-M)!}$$

Helmholtz free energy (constant V)      adsorption energy      entropy

$$\mu_{\text{ad}} = \frac{\partial F}{\partial M} = \epsilon_{\text{ad}} + kT \ln \frac{\theta}{1-\theta}$$

$\theta = M/N$  is the coverage

$$\mu_{\text{sol}} = \mu_0 + kT \ln \frac{c}{c_0} \quad \text{ideal solution}$$

$\ln n! \approx n \ln n - n$  for large  $n$

$$F = M\epsilon_{\text{ad}} + \left[ M \ln \frac{M}{N} + (N-M) \ln \frac{N-M}{N} \right]$$

$M$  are the filled sites  
 $N$  are the total sites

at equilibrium (electro)chemical potentials in adsorbed layer and electrolyte must be the same

$$\frac{\theta}{1-\theta} = \frac{c}{c_0} \exp \left( \frac{\mu_{\text{sol}} - \mu_{\text{ad}}}{kT} \right)$$

# Adsorption phenomena and isotherms

Langmuir adsorption ignores interactions between adsorbates.

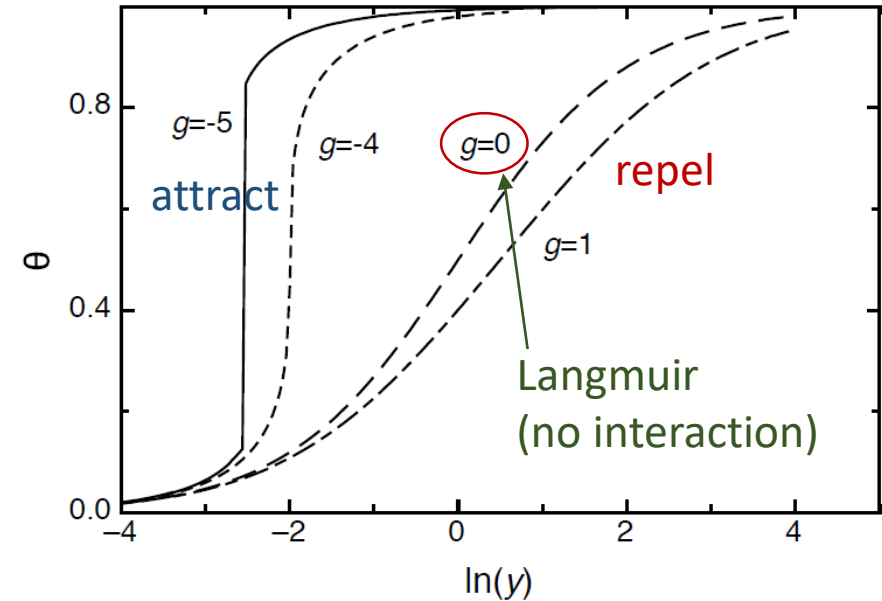
Frumpkin:  $\mu_{\text{ad}} = \mu_{\text{ad}}^0 + \gamma\theta$

positive if repel, negative if attract

$$\frac{\theta}{1 - \theta} = \frac{c}{c_0} \exp\left(\frac{\mu_{\text{sol}} - \mu_{\text{ad}}}{kT}\right) e^{-g\theta}$$

$$g = \gamma/RT$$

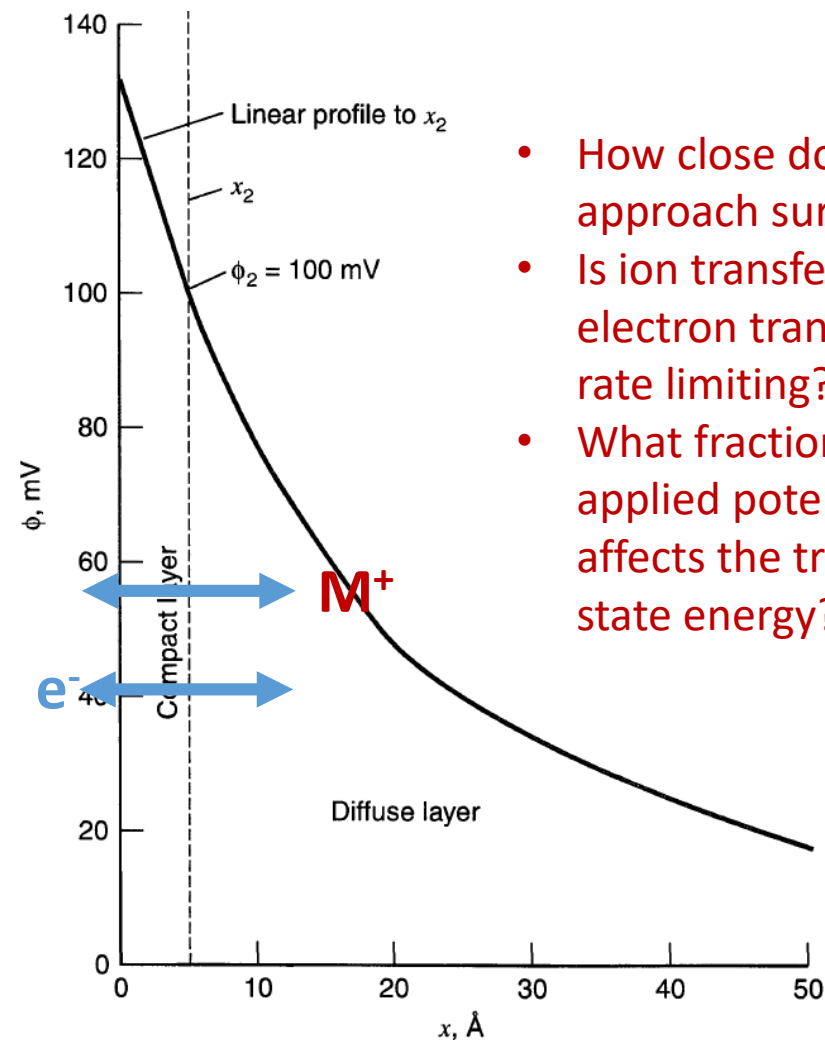
Frumpkin isotherms





# Why are these concepts important?

- Changes in  $\nabla\phi$  from equilibrium are responsible for affecting electrochemical reaction thermodynamics that drive ion and electron transfer
- In a mean field picture, the location of electroactive species in the double affects the driving force for charge transfer
- New ideas in electrocatalysis involve situations where mean-field approach breaks down



- How close do ions approach surface?
- Is ion transfer or electron transfer rate limiting?
- What fraction of the applied potential affects the transition state energy?