Lecture #6. Fall, 2012
Electrochemical Energy Engineering

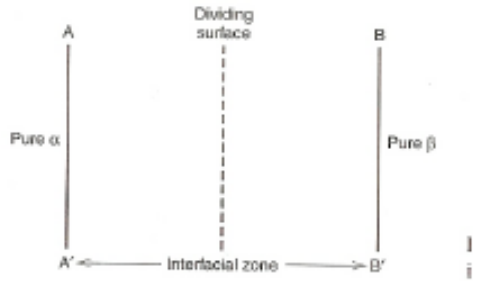
Double layer structure & adsorption (Ch. 13)

Thermodynamics of the double layer
Experimental evaluation of surface excesses & electrical parameters
Models for double layer structure
Helmholtz model
Gouy-Chapman theory
Stern's modification
Specific adsorption
Studies at solid electrodes
Double layer at solids
Single-crystal electrode surfaces
Solid metal-solution interface
Extent & rate of specific adsorption
Nature of specific adsorption
Adsorption isotherms
Rate of adsorption
Effect of adsorption of electroinactive species
Double layer effects on electrode reaction rates

Thermodynamics of the double layer

Gibbs adsorption isotherm

Suppose an interface of surface area A separating two phases, α & β
→ interfacial zone (~ 100 Å)
→ *excesses* and *deficiencies*
in the concentration of components



Surface excess (in # of moles of any species)
$n_i^{\sigma} = n_i^{S} - n_i^{R}$
n_i^{σ}: excess quantity (any extensive variable, e.g., electrochemical free energy),
n_i^{S} & n_i^{R}: # of moles of species i in interfacial region for actual & reference systems

Electrochemical free energy
For the reference system, $\overline{G}^{R} = \overline{G}^{R}(T, P, n_i^{R})$
For the actual system, $\overline{G}^{S} = \overline{G}^{S}(T, P, A, n_i^{S})$

$$d\overline{G}^{R} = (\partial\overline{G}^{R}/\partial T)dT + (\partial\overline{G}^{R}/\partial P) + \sum(\partial\overline{G}^{R}/\partial n_i^{R})dn_i^{R}$$

$$d\overline{G}^{S} = (\partial\overline{G}^{S}/\partial T)dT + (\partial\overline{G}^{S}/\partial P)dP + (\partial\overline{G}^{S}/\partial A)dA + \sum(\partial\overline{G}^{S}/\partial n_i^{S})dn_i^{S}$$

At const T & P → 1st two terms can be dropped
$(\partial\overline{G}^{R}/\partial n_i^{R}) = \overline{\mu}_i$ (electrochemical potential) → const at equilibrium

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

$(\partial \bar{G}^S/\partial A) = \gamma$ (surface tension): a measure of the energy required to produce a unit area of new surface

Differential *excess free energy*

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

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

Euler's theorem for variables, A and n_i (const T and P)

$$\bar{G}^\sigma = (\partial \bar{G}^\sigma/\partial A)A + \sum(\partial \bar{G}^\sigma/\partial n_i^\sigma)n_i^\sigma$$

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

$\rightarrow$

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

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

Surface excess concentration, $\Gamma_i = n_i^\sigma/A$ (excesses per unit area of surface)

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

Gibbs adsorption isotherm: importance of surface tension for interfacial structure

Electrocapillary equation

Consider

$$Cu'/Ag/AgCl/K^+, Cl^-, M/Hg/Ni/Cu$$

M: neutral species

Gibbs adsorption isotherm; components of Hg electrode, ions, neutral

$$-d\gamma = (\Gamma_{Hg} d\bar{\mu}_{Hg} + \Gamma_e d\bar{\mu}_e^{Hg}) + (\Gamma_{K+} d\bar{\mu}_{K+} + \Gamma_{Cl-} d\bar{\mu}_{Cl-}) + (\Gamma_M d\bar{\mu}^M + \Gamma_{H2O} d\bar{\mu}_{H2O})$$

$\bar{\mu}_e^{Hg}$: electrons in the mercury phase

Some linkages:

$\bar{\mu}_e^{Hg} = \bar{\mu}_e^{Cu}$

$\bar{\mu}_{KCl} = \mu_{KCl} = \bar{\mu}_{K+} + \bar{\mu}_{Cl-}$

$\bar{\mu}_{H2O} = \mu_{H2O}$

$\bar{\mu}_M = \mu_M$

$d\bar{\mu}_{Hg} = d\bar{\mu}_{Hg}^0 = 0$

$$-d\gamma = \Gamma_e d\bar{\mu}_e^{Cu} + (\Gamma_{K+} d\bar{\mu}_{KCl} - \Gamma_{K+} d\bar{\mu}_{Cl-} + \Gamma_{Cl-} d\bar{\mu}_{Cl-}) + (\Gamma_M d\mu_M + \Gamma_{H2O} d\mu_{H2O})$$

From the equilibrium at the reference interface

$\overline{\mu}_{AgCl} + \overline{\mu}_e^{Cu'} = \overline{\mu}_{Ag} + \overline{\mu}_{Cl^-}$

Since $d\overline{\mu}_{AgCl} = d\overline{\mu}_{Ag} = 0$, $d\mu_e^{Cu'} = d\mu_{Cl^-}$

$$-d\gamma = \Gamma_e d\overline{\mu}_e^{Cu} - (\Gamma_{K^+} - \Gamma_{Cl^-}) d\overline{\mu}_e^{Cu'} + \Gamma_{K^+} d\mu_{KCl} + \Gamma_M d\mu_M + \Gamma_{H2O} d\mu_{H2O}$$

Excess charge density on the metallic side of the interface

$$\sigma^M = -F\Gamma_e$$

Opposite charge density on the solution side

$$\sigma^S = -\sigma^M = F(\Gamma_{K^+} - \Gamma_{Cl^-})$$

$$d\overline{\mu}_e^{Cu} - d\overline{\mu}_e^{Cu'} = -Fd(\phi^{Cu} - \phi^{Cu'}) = -FdE_-$$

E_-: potential of the mercury electrode with respect to the reference

$$-d\gamma = \sigma^M dE_- + \Gamma_{K^+} d\mu_{KCl} + \Gamma_M d\mu_M + \Gamma_{H2O} d\mu_{H2O}$$

Gibbs-Duhem relation at const T and P

$$\sum X_i d\mu_i = 0$$

Xi: mole fraction

$$X_{H2O} d\mu_{H2O} + X_{KCl} d\mu_{KCl} + X_M d\mu_M = 0$$

Remove $d\mu_{H2O}$

$$-d\gamma = \sigma^M dE_- + [\Gamma_{K+} - (X_{KCl}/X_{H2O})\Gamma_{H2O}]d\mu_{KCl} + [\Gamma_M - (X_M/X_{H2O})\Gamma_{H2O}]d\mu_M$$

Relative surface excess: measurable parameters

$$\Gamma_{K+(H2O)} = \Gamma_{K+} - (X_{KCl}/X_{H2O})\Gamma_{H2O}$$

$$\Gamma_{M(H2O)} = \Gamma_M - (X_M/X_{H2O})\Gamma_{H2O}$$

Cannot measure absolute surface excess of K^+, but only excess relative to water
e.g., zero excess: same mole ratio of adsorption of K^+ and H_2O
positive excess: $K^+ > H_2O$
Water: reference component
Dilute solutions: negligible $(X_i/X_S)\Gamma_S$

<u>Electrocapillary equation</u>

$$-d\gamma = \sigma^M dE_- + \Gamma_{K+(H2O)}d\mu_{KCl} + \Gamma_{M(H2O)}d\mu_M$$

→ all measurable parameters

Experimental evaluation of surface excesses & electrical parameters

Electrocapillarity and the DME

For DME,

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

t_{max}: drop lifetime

→ t_{max} vs. E has same shape as the electrocapillary curve

Excess charge and capacitance

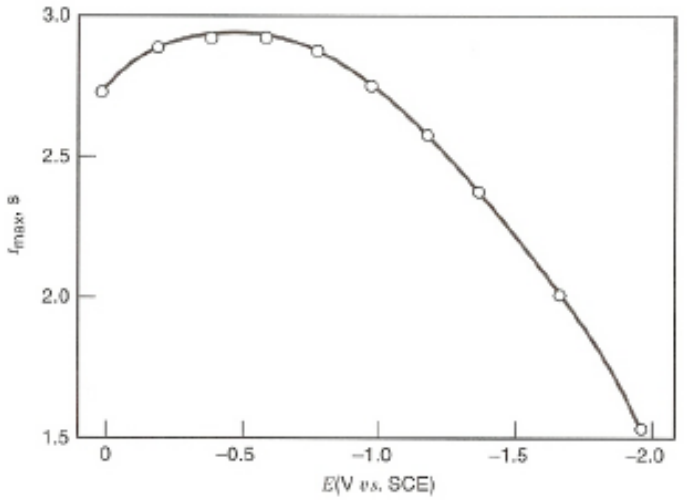
From electrocapillary equation,

$$\sigma^M = (\partial\gamma/\partial E_-)_{\mu KCl,\mu M}$$

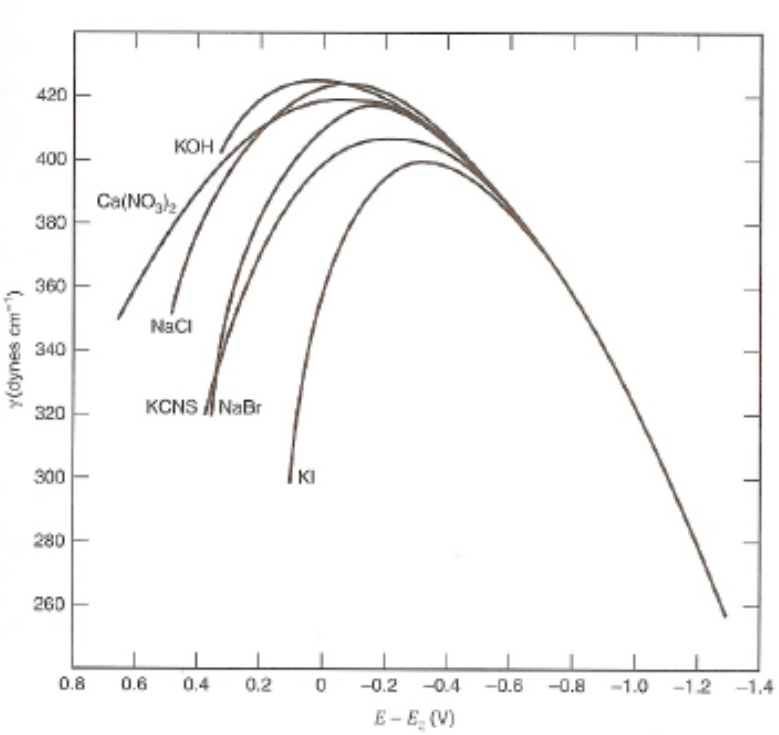
the excess charge on the electrode

→ slope of electrocapillary curve at any E

Drop time of a DME in 0.1 M KCl vs. E



Electrocapillary curve in different electrolyte



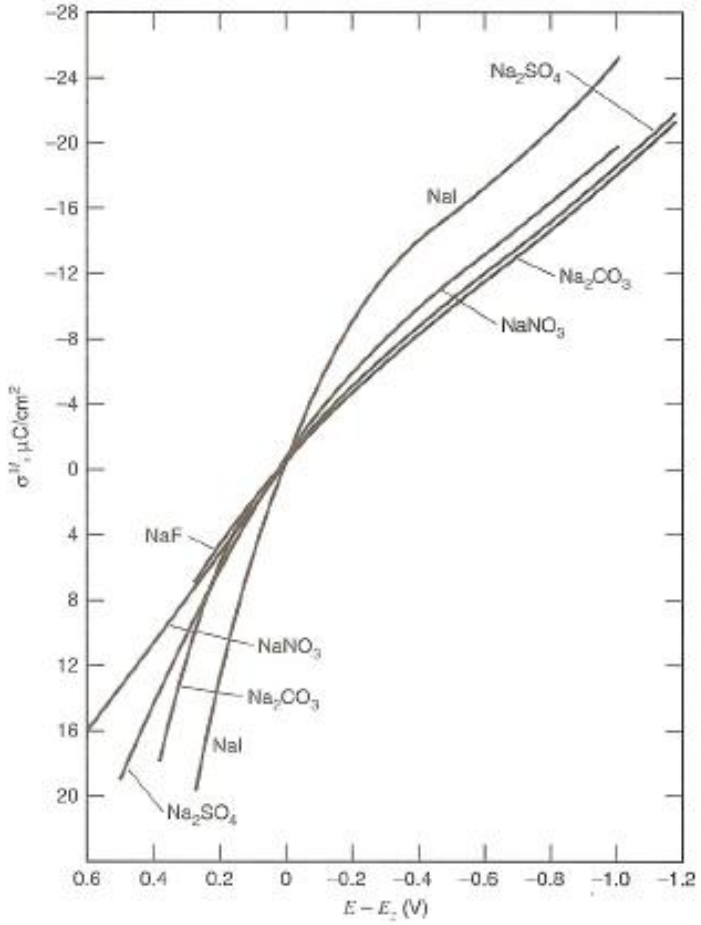
→ the existence of a maximum in surface tension

→ potential at maximum: "electrocapillary maximum (ECM)"

→ curve slope = 0 at ECM → "**potential of zero charge**" (PZC)

$$\sigma^M = \sigma^S = 0$$

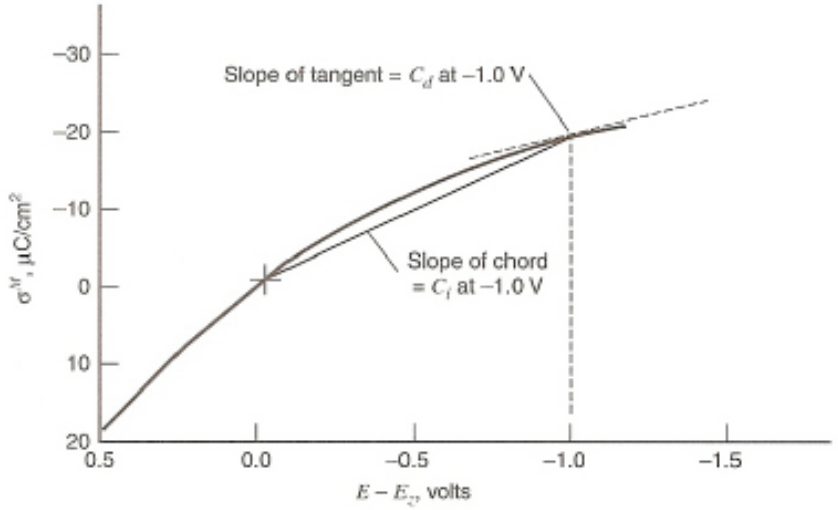
At more negative potentials → the electrode surface has a negative excess charge
At more positive potentials → positive surface charge
→ Plots of surface charge can be made by differentiating electrocapillary curves



The capacitance of the interface → its ability to store charge in response to a perturbation in potential

$$C_d = (\partial\sigma^M/\partial E)$$

Differential capacitance: the slope of the plot of σ^M vs. E



Integral capacitance, C_i (or K): ratio of total charge density (σ^M) at potential E to the total potential difference

$$C_i = \sigma^M/(E - E_Z)$$

E_Z: PZC

$$C_i = \int C_d dE / \int dE$$

Average of C_d over the potential range from E_Z to E

Differential capacitance is the more useful quantity, in part it is precisely measurable by impedance techniques

Capacitance can be obtained from the electrocapillary curves by double differentiation

$$\gamma = \int\int C_d dE$$

Relative surface excesses

From electrocapillary equation, relative surface excess of K^+ at the interface

$$\Gamma_{K+(H2O)} = -(\partial\gamma/\partial\mu_{KCl})_{E-,\mu}$$

Since $\mu_{KCl} = \mu^0_{KCl} + RT ln a_{KCl}$

$$\Gamma_{K+(H2O)} = -(1/RT)(\partial\gamma/\partial ln a_{KCl})_{E-,\mu M}$$

→ relative surface excess $\Gamma_{K+(H2O)}$ at any potential E- by measuring surface tension for several KCl activities (at const M)

Relative surface excess of Cl^-: from the charge balance ($\sigma^S = -\sigma^M = F(\Gamma_{K+} - \Gamma_{Cl-})$

Fig. 13.2.9: relative surface excess of 0.1 M KF in contact with mercury

At potentials positive of E_Z → surface excess of K^+: negative → K^+ conc in the interface is smaller than in the bulk (reverse for Cl^-)

At potentials negative of E_Z → opposite

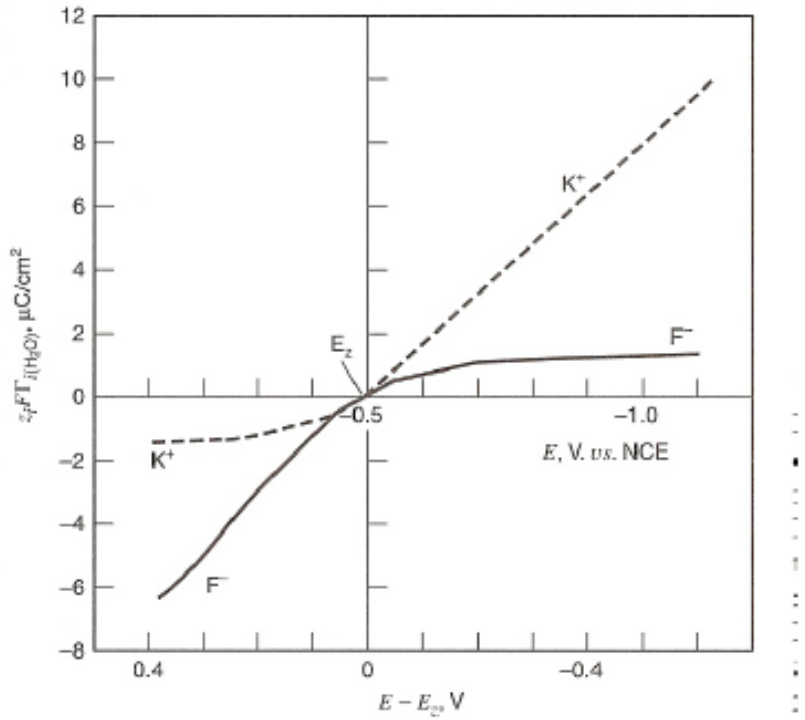
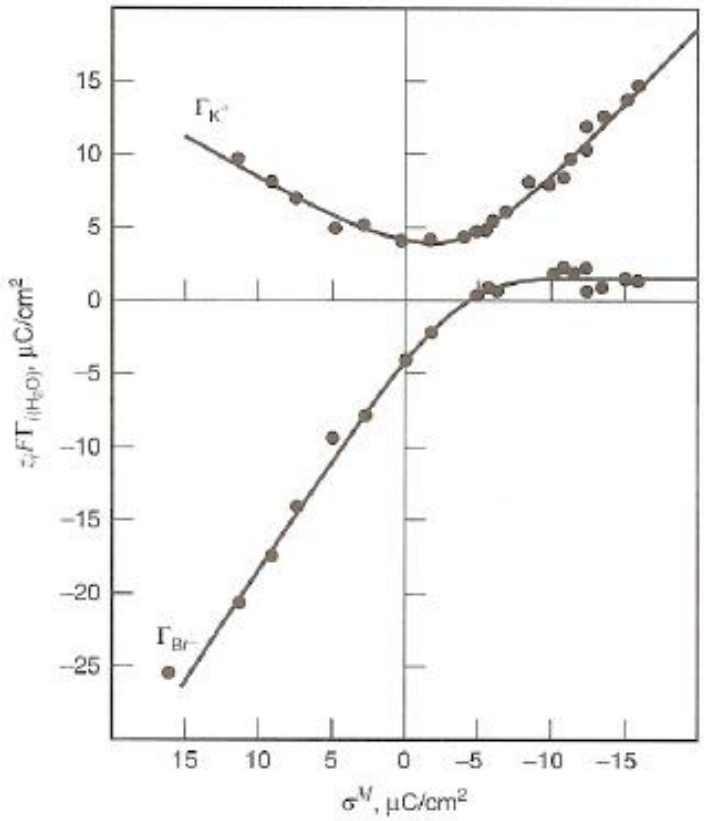


Fig. 13.2.6: 0.1 M KBr

At potentials positive of E_Z (i.e., for $\sigma^M > 0$) → surface excess of K^+: positive → specific adsorption of Br^- on mercury



Models for double layer structure

The Helmholtz model

Two sheets of charge, having opposite polarity, separated by a distance of molecular order → equivalent to a parallel-plate capacitor

Relation of stored charge density, σ, and voltage drop V between the plate

$$\sigma = (\varepsilon\varepsilon_0/d)V$$

ε: dielectric const of the medium, ε_0: permittivity of free space, d: spacing

Differential capacitance

$$\partial\sigma/\partial V = C_d = \varepsilon\varepsilon_0/d$$

Weakness of this model: predict C_d is const

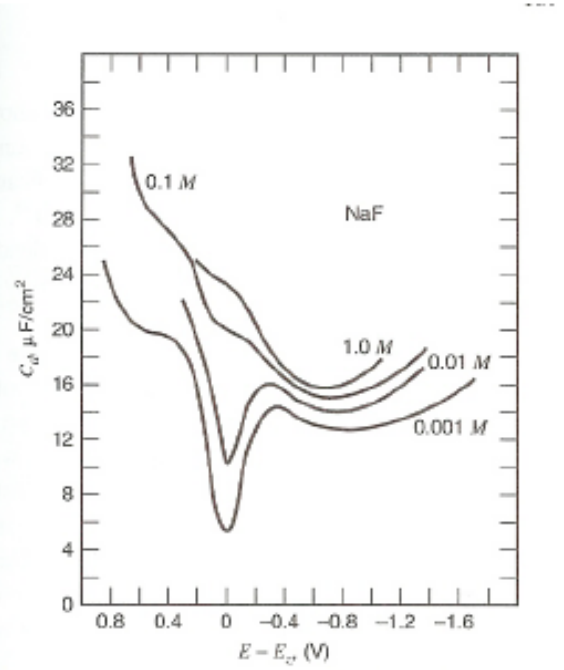
e.g., Fig. 13.3.1

Differential capacitance vs. E

in Hg/NaF interface

→ potential dependence

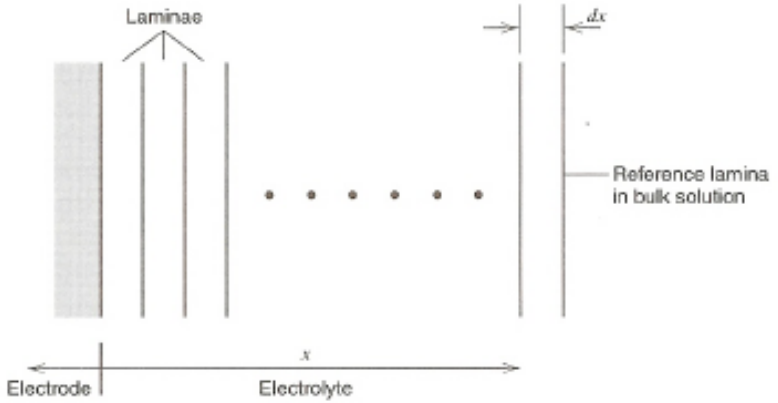
→ more sophisticated model needed



The Gouy-Chapman theory

Charge on the electrode is confined to the surface

Charge in the solution: *diffusion layer*



Population in any lamina (number concentration of species)

$$n_i = n_i^0 \exp(-z_i e\phi/kT)$$

n_i^0: bulk concentration, ϕ: electrostatic potential (ϕ measured with respect to the bulk)

Total charge per unit volume in any lamina

$$\rho(x) = \sum n_i z_i e = \sum n_i^0 z_i e \exp(-z_i e\phi/kT)$$

$\rho(x)$ is related to the potential at distance x by the Poisson equation

$$\rho(x) = -\varepsilon\varepsilon_0(d^2\phi/dx^2)$$

Poisson-Boltzmann equation

$$d^2\phi/dx^2 = -(e/\varepsilon\varepsilon_0)\sum n_i^0 z_i \exp(-z_i e\phi/kT)$$

$$d^2\phi/dx^2 = (1/2)(d/d\phi)(d\phi/dx)^2$$

$\rightarrow$

$$(d\phi/dx)^2 = (2kT/\varepsilon\varepsilon_0)\sum n_i^0[\exp(-z_i e\phi/kT) - 1]$$

For z:z electrolyte $d\phi/dx = -(8kTn^0/\varepsilon\varepsilon_0)^{1/2}\sinh(ze\phi/2kT)$

(a) Potential profile in the diffusion layer

ϕ_0: potential at x = 0 relative to the bulk solution
= potential drop across the diffusion layer

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

Where

$$\kappa = (2n^0z^2e^2/\varepsilon\varepsilon_0kT)^{1/2}$$

For dilute aqueous solution ($\varepsilon = 78.49$) at 25°C

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

C^*: bulk z:z electrolyte conc in mol/L, κ: cm^{-1}

Potential profile for several different ϕ_0: potential decay away from the surface

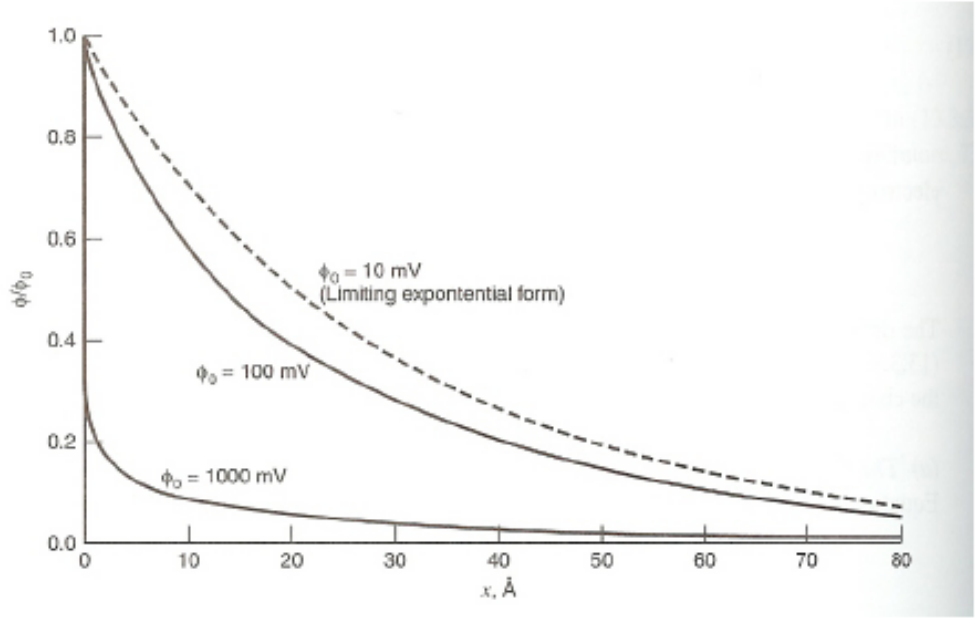
At large ϕ_0 (a highly charged electrode), the drop is precipitous because the diffusion layer is relatively compact

As ϕ_0 smaller, the decline is more gradual

If ϕ_0 is sufficiently low ($\tanh(ze\phi/kT) \sim ze\phi/kT$)

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

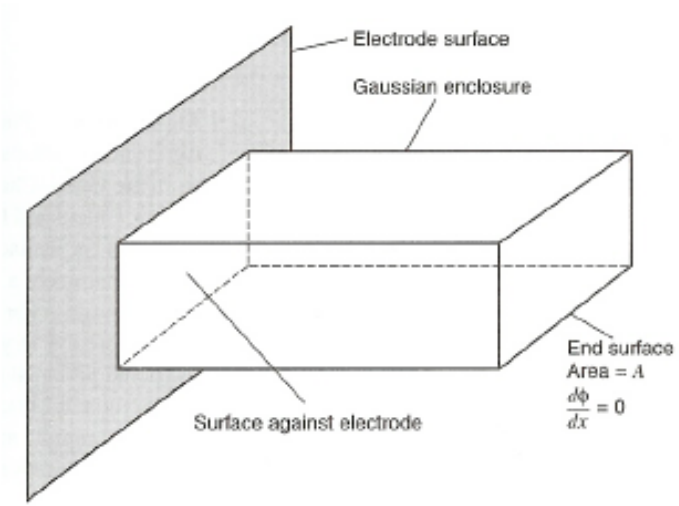
Good approximation for $\phi_0 \leq 50/z$ mV at 25°C



Reciprocal of κ: unit of distance and characterizes the spatial decay of potential
→ kind of characteristic thickness of the diffusion layer
→ thicker as conc of electrolyte falls

$C^*(M)^b$	$1/\kappa$(Å)
1	3.0
10^{-1}	9.6
10^{-2}	30.4
10^{-3}	96.2
10^{-4}	304

(b) Relation between σ^M and ϕ
Suppose Gaussian surface



Gauss law, charge

$$q = \varepsilon\varepsilon_0 \int_{surface} \boldsymbol{E}\cdot d\mathbf{S}$$
$$= \varepsilon\varepsilon_0 A(d\phi/dx)_{x=0}$$

Using $q/A = \sigma^S$ and $d\phi/dx = -(8kTn^0/\varepsilon\varepsilon_0)^{1/2}\sinh(ze\phi/2kT)$

$$\sigma^S = -\sigma^M = (8kTn^0\varepsilon\varepsilon_0)^{1/2}\sinh(ze\phi_0/2kT)$$

For dilute solution at 25°C

$$\sigma^M = 11.7C^{*1/2}\sinh(19.5z\phi_0)$$

Where C^* is in mol/L for σ^M in μC/cm^2

(c) Differential capacitance

$$C_d = d\sigma^M/d\phi_0 = (2z^2e^2\varepsilon\varepsilon_0n^0/kT)^{1/2}\cosh(ze\phi_0/2kT)$$

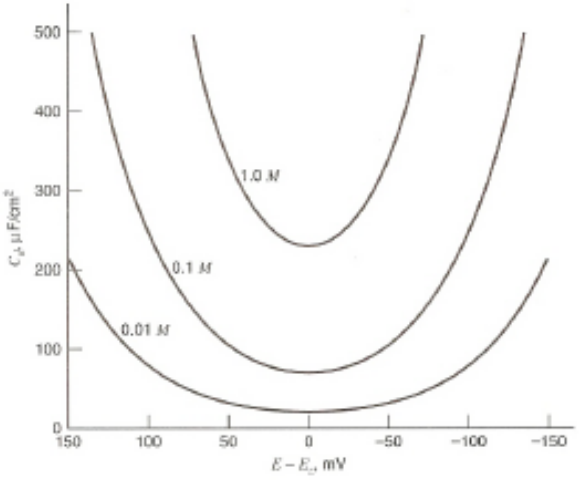
For dilute aqueous solutions at 25°C

$$C_d = 228zC^{*1/2}\cosh(19.5z\phi_0)$$

where C_d is in μF/cm^2

Predicted plot (V-shape) vs. observed one
i) low conc & near PZC에서만 유사
ii) 실험치가 예측치보다 훨씬 작음
→ need better theory!

Smaller in experiment than in prediction



Stern's modification

Gouy-Chapman model: unlimited rise in differential capacitance with ϕ_0

→ ions are not restricted with respect to location in solution phase
(point charge can approach the surface arbitrarily closely)

→ not realistic: ions have a finite size & cannot approach the surface any closer than the ionic radius. If solvated, larger radius. Solvent layer should be considered

X_2: outer Helmholtz plane (OHP)

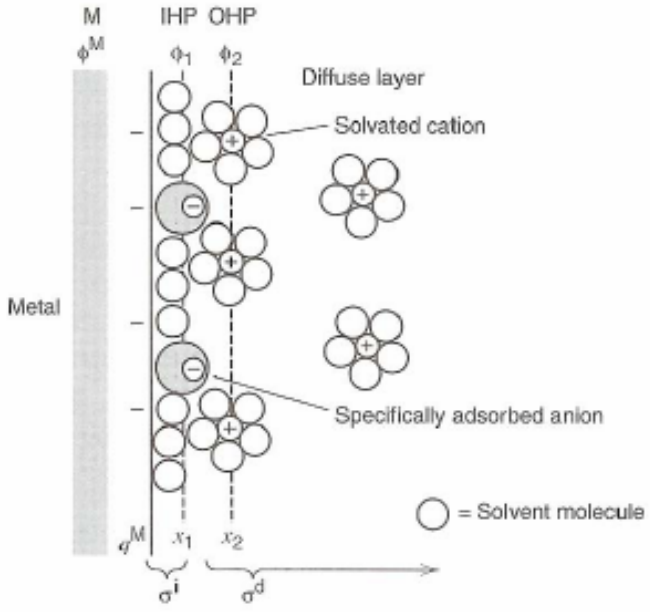


Figure 1.2.3 Proposed model of the double-layer region under conditions where anions are specifically adsorbed.

Poisson-Boltzmann equation for $x \geq x_2$

$$\tanh(ze\phi/4kT)/\tanh(ze\phi_2/4kT) = e^{-\kappa(x-x2)}$$

Where ϕ_2 is the potential at x_2

Field strength at x_2, $\quad (d\phi/dx)_{x=x2} = -(8kTn^0/\varepsilon\varepsilon_0)^{1/2}\sinh(ze\phi_2/2kT)$

Total potential drop across the double layer

$$\phi_0 = \phi_2 - (d\phi/dx)_{x=x2}x_2$$

$$\sigma^M = -\sigma^S = -\varepsilon\varepsilon_0(d\phi/dx)_{x=x2} = (8kTn^0\varepsilon\varepsilon_0)^{1/2}\sinh(ze\phi_2/2kT)$$

$$\sigma^M = (8kTn^0\varepsilon\varepsilon_0)^{1/2}\sinh[ze/2kT(\phi_0 - \sigma^M x_2/\varepsilon\varepsilon_0)]$$

Differential capacitance

$$C_d = d\sigma^M/d\phi_0 = (2z^2e^2\varepsilon\varepsilon_0n^0/kT)^{1/2}\cosh(ze\phi_2/2kT)/[1 + (x_2/\varepsilon\varepsilon_0)(2\varepsilon\varepsilon_0z^2e^2n^0/kT)^{1/2}\cosh(ze\phi_2/2kT)]$$

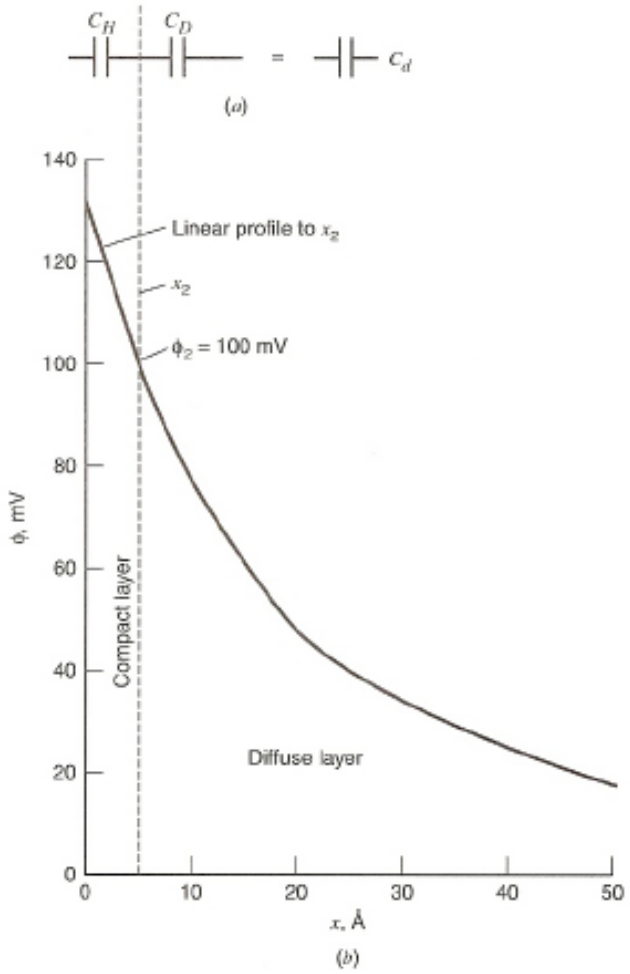
$$1/C_d = x_2/\varepsilon\varepsilon_0 + 1/[(2\varepsilon\varepsilon_0z^2e^2n^0/kT)^{1/2}\cosh(ze\phi_2/2kT)]$$

Two components

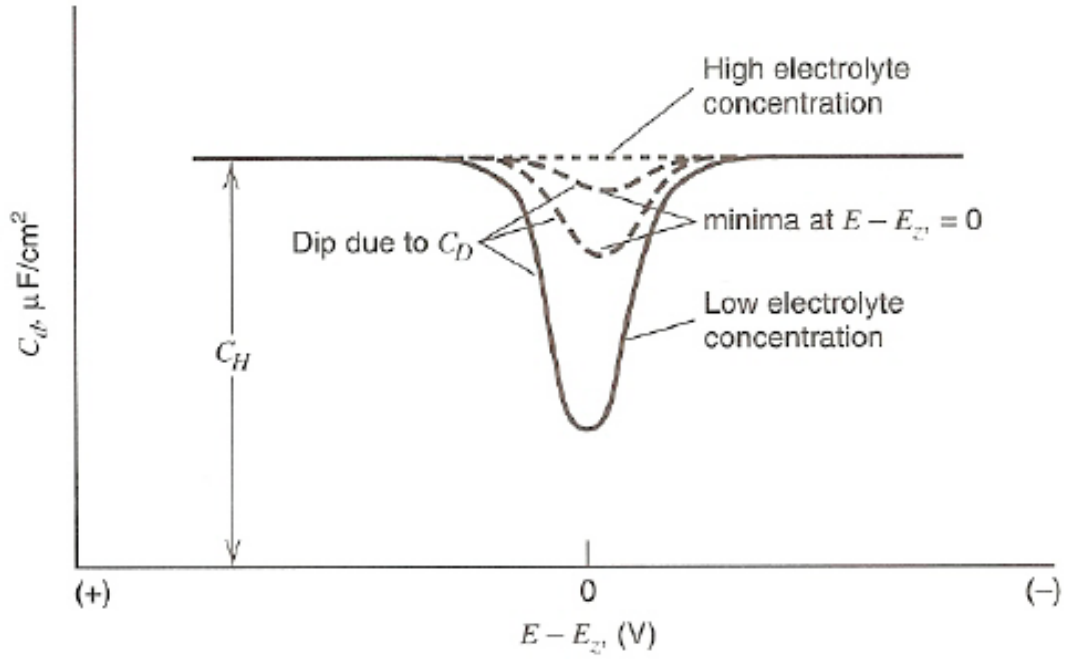
$$1/C_d = 1/C_H + 1/C_D$$

C_D: capacitance of the charge at OHP, C_D: truly diffuse charge

Gouy-Chapman-Stern model



C_H: independent of potential
C_D: varies in V-shaped depending potential
C_d: V-shaped near PZC with low electrolyte conc (characteristic of C_D)
At large electrolyte conc or large polarization → C_D is so large → C_H
→ Gouy-Chapman-Stern (GCS) model



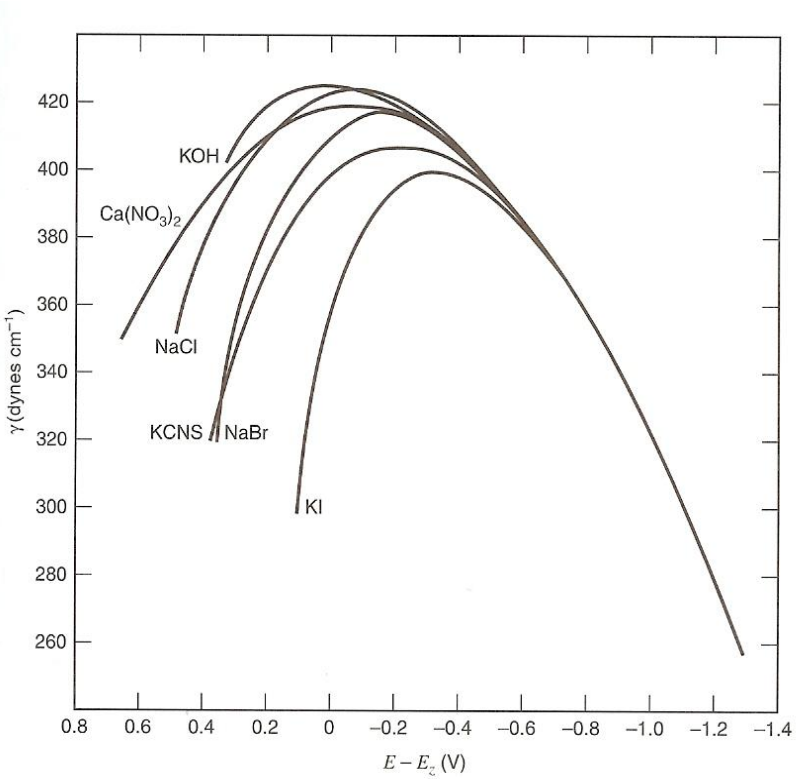
Specific adsorption

Fig.13.2.2

Potential more negative than PZC: decline & same regardless composition (GCS model)

Potential more positive than PZC: depend specifically on the composition

→ *specific adsorption* of anions: their center: *inner Helmholtz plane* (IHP), x_1



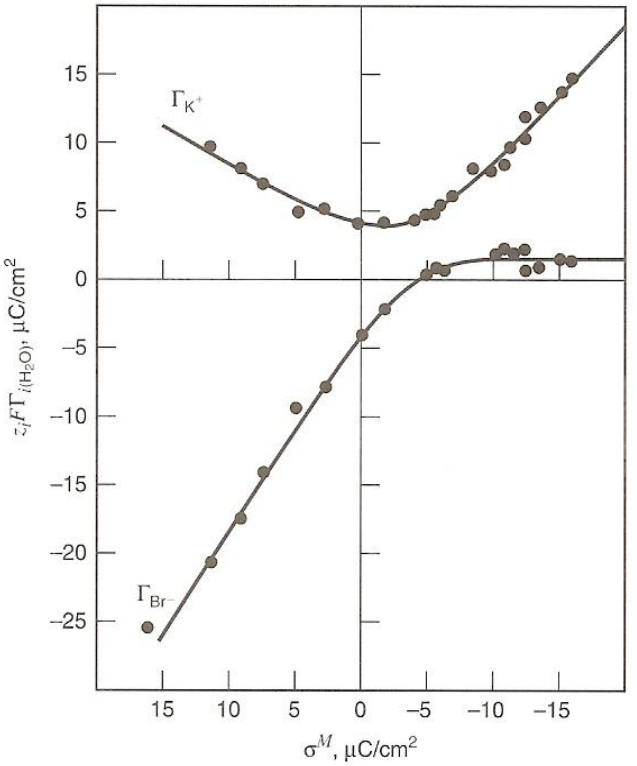


Fig.13.2.6 Br^-

(i) Specifically adsorbed ion → considering the slopes of $z_i F\Gamma_{i(H2O)}$ vs. σ^M

$$\sigma^M = -[F\Gamma_{K+(H2O)} - F\Gamma_{Br-(H2O)}]$$

In the absence of specific adsorption: charge on the electrode is counterbalanced by the excess of one ion and a deficiency of the other (Fig.13.2.5)

→ Fig. 13.2.6: more positive than PZC → superequivalent adsorption of bromide (considering slopes & compare with Fig. 13.2.5)

(ii) Esin-Markov effect: shift in PZC with change in electrolyte conc

Table by "Grahame"

→ shift : linear with *ln*[activity]

→ slope: Esin-Markov coefficient at $\sigma^M = 0$

(non-specific adsorption: EM coeff = 0

$$(1/RT)(\partial E_{\pm}/\partial \ln a_{salt})_{\sigma M} = (\partial E_{\pm}/\partial \mu_{salt})_{\sigma M}$$

Electrolyte	Concentration, *M*	E_z, V *vs.* NCE[b]
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

Studies at solid electrodes

Double layer at solids

Most measurements on mercury

→ solid electrode: difficulty to reproduce same & clean surface, not atomically smooth…

Well-defined single crystal electrode surfaces

Different crystal faces exhibit different properties (e.g., PZC, work function..)

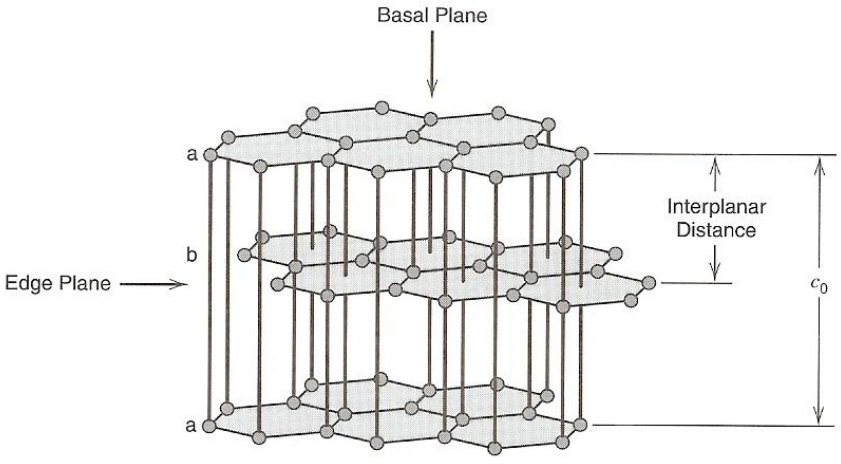
Pt, Pd, Ag, Ni, Cu: FCC crystal structures

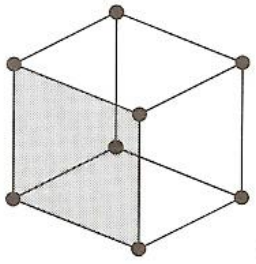
→ low-index crystal faces: stable, polishable

→ higher-index planes: more edges, step & kink sites

Reconstruction: minimize surface energy

Carbon: highly oriented pyrolytic graphite (HOPG)





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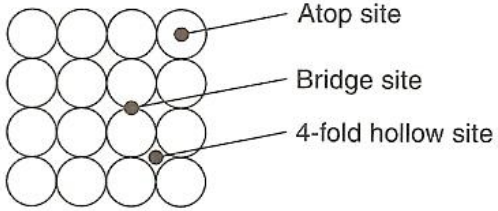
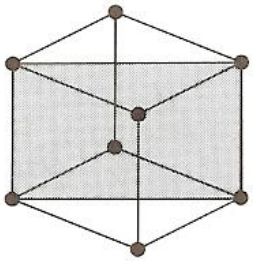
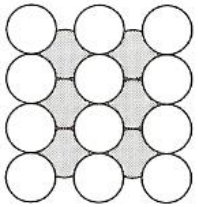
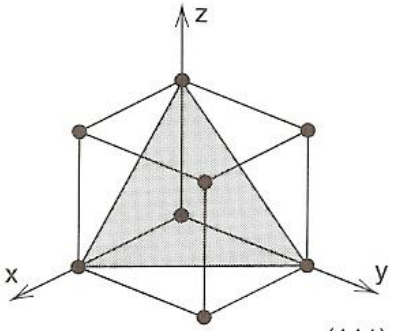


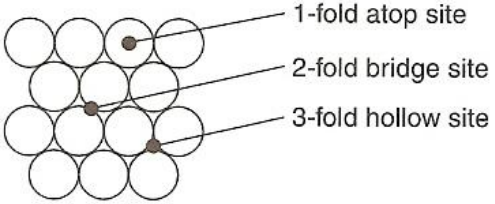


(110)

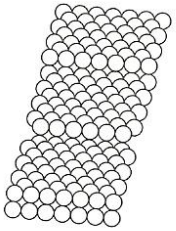




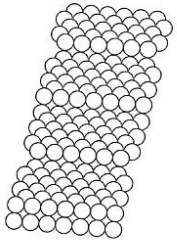
(111)



Face-centered cubic (FCC) structure



fcc (977)



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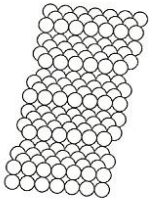
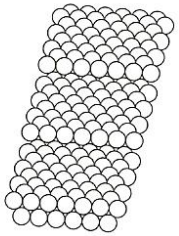
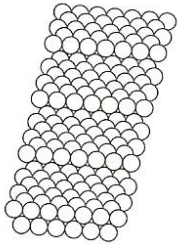


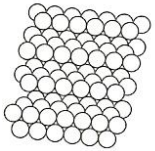
fcc (533)



fcc (443)

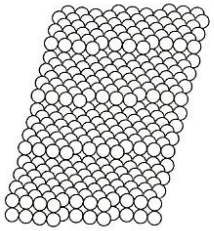


fcc (332)

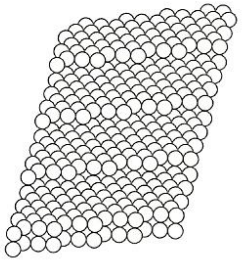


fcc (331)

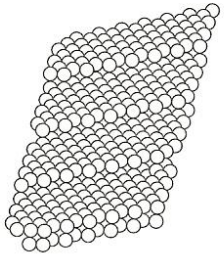
(*a*)



fcc (14, 11, 10)



fcc (10, 8, 7)



fcc (13, 11, 9)

(*b*)

Potential of zero charge

Table 1. Potentials of zero charge of sp metals, $E_{\sigma=0}$ (V) vs. the standard hydrogen electrode (SHE).[a]

Hg	Sb	Bi	Bi(111)	Sn	Pb	In	In(Ga)	Tl	Tl(Ga)	Ga	Cd	Zn
-0.19	−0.17	−0.38	−0.41	−0.39	−0.60	−0.65	−0.67	−0.71	−0.69	−0.69	−0.75	−0.91

[a]The uncertainty varies mostly between 0.01 and 0.02 V, but it is higher for d metals and lower (0.001 V) for Hg. (Reproduced from Trasatti and Lust (1999)[16] by permission of Plenum.)

Table 2. Potentials of zero charge of sd metals, $E_{\sigma=0}$ (V) vs. SHE.[a]

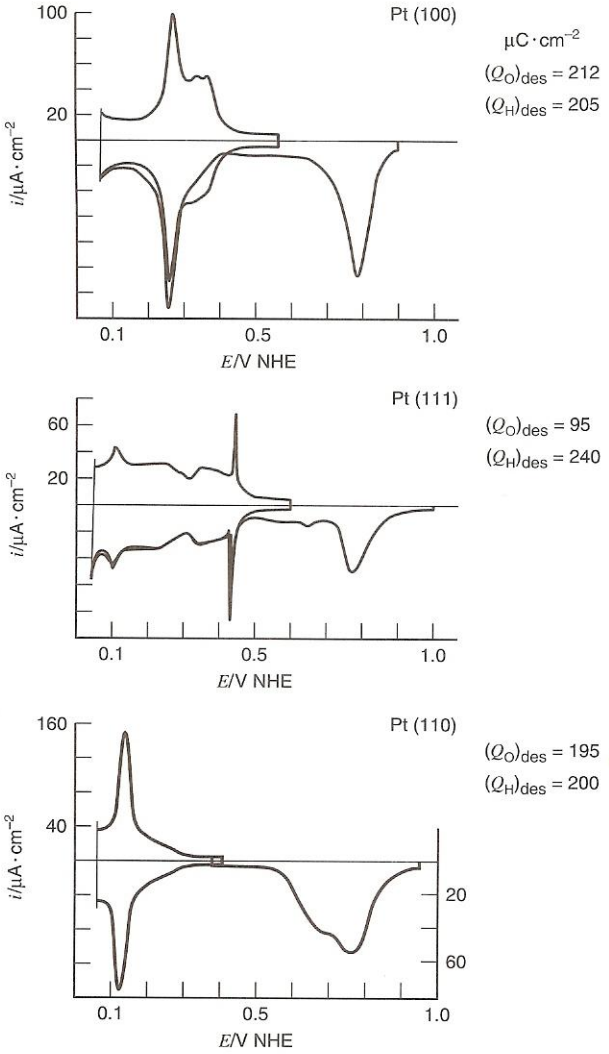
Ag	Ag(111)	Ag(100)	Ag(110)	Au	Au(111)	Au(100)	Au(110)	Cu	Cu(110)
−0.70	−0.45	−0.62	−0.74	0.20	0.56	0.32	0.20	−0.64	−0.69

[a]As per Table 1.

cf. Pt: 0.18 V, Ni: -0.33 V

Different crystal faces exhibit different properties (e.g., PZC, work function..)
e.g., PZC on Ag(111) (-0.69 V vs. SCE), Ag(110) (-0.98 V),
→ -0.8 V: carry negative charge in (111), positive charge in (110)

Different catalytic & adsorption properties
e.g., different CV in Pt (0.5 M H_2SO_4)



Solid metal-solution interface

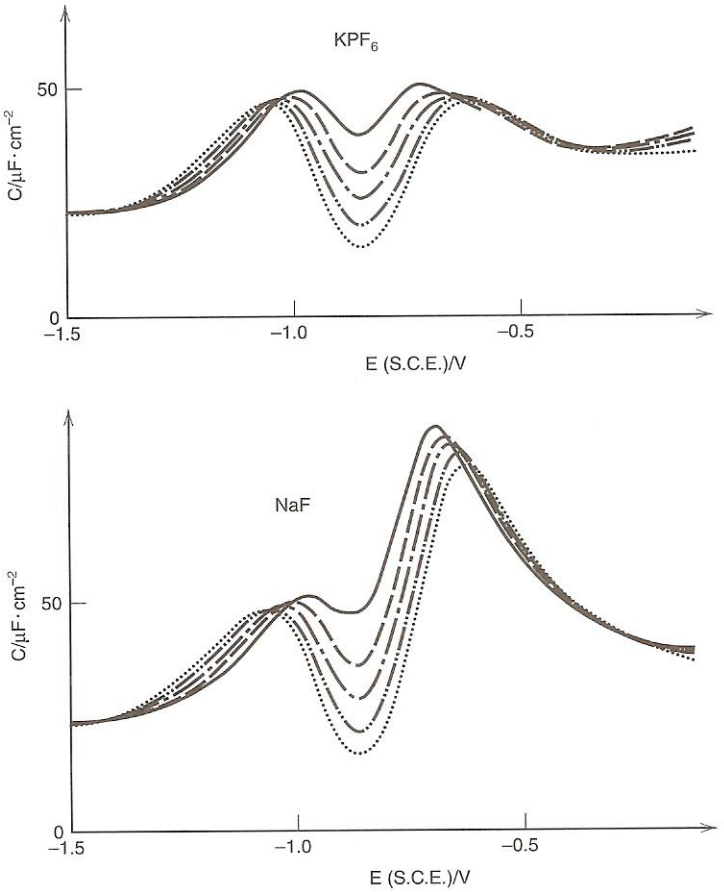
Information on PZC & interface from capacitance measurements

Capacitance curves for Ag(100) at different conc of KPF_6 and NaF

(top to bottom 100, 40, 20, 10, and 5 mM)

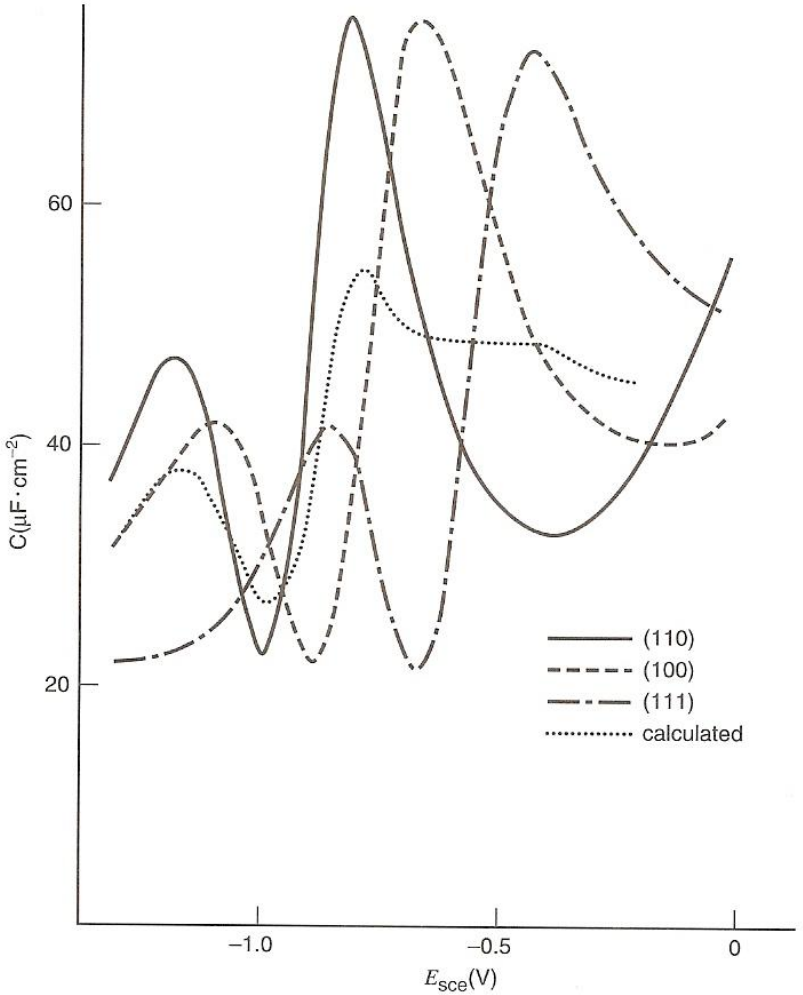
Independence of min in capacitance → weakly specificallyadsorbed on Ag

PZC from capacitance minimum

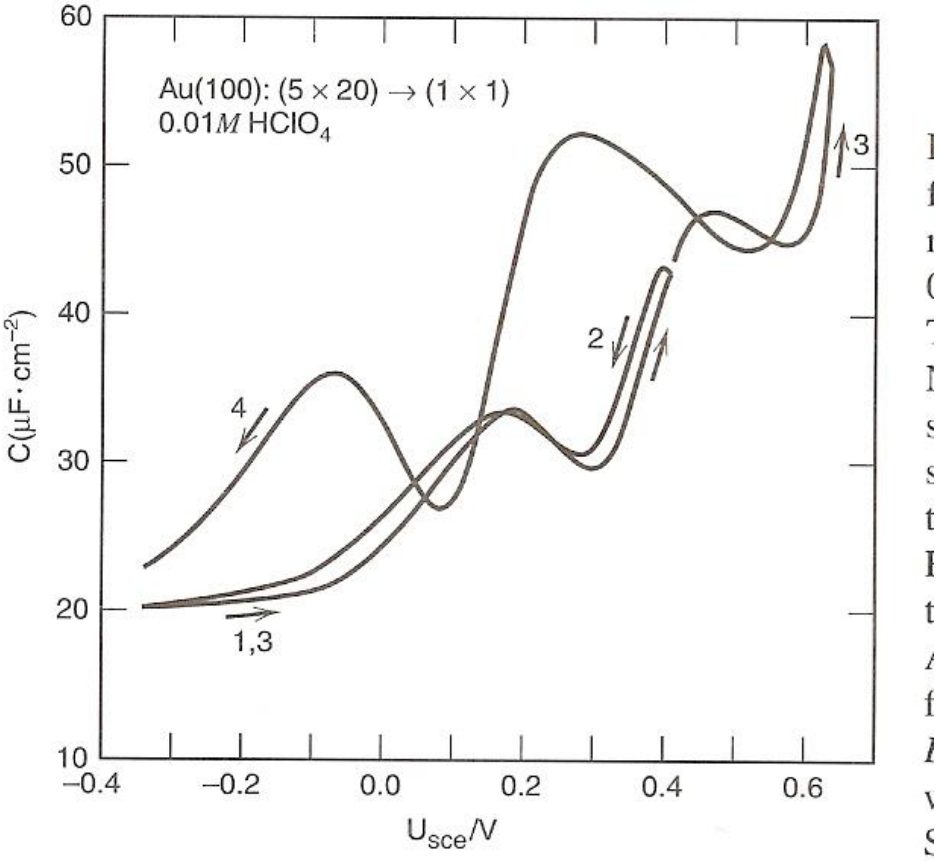


PZC depends upon crystal faces (e.g., Ag)

calculated: polycrystalline (46% (110), 23% (100), 31% (111))



Another complication: surface reconstruction
Au(100): reconstructed (5 x 20) during flame heating
< +0.5 V: maintained (5 x 20)
~+0.7 V: converted to original (100)

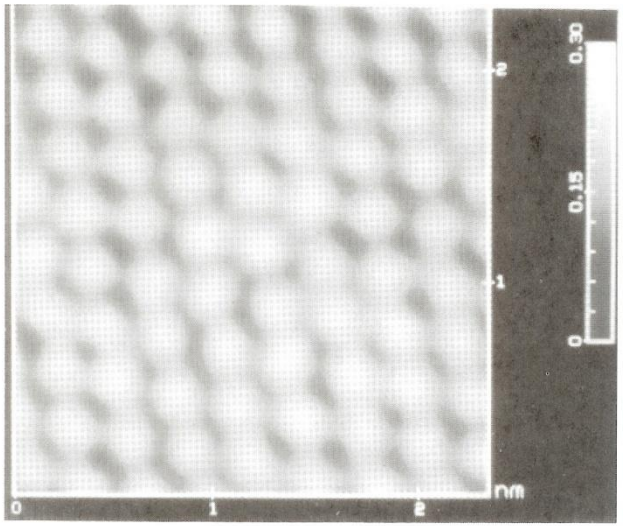


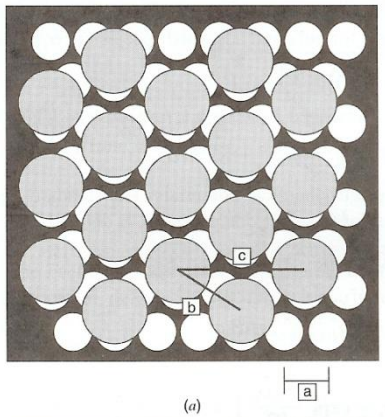
Extent and rate of specific adsorption

Nature and extent of specific adsorption

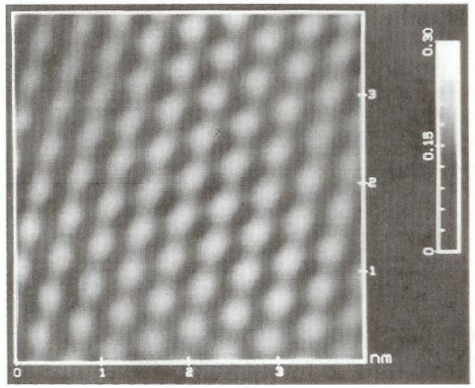
Commensurate: molecules adsorb in exact corresponding pattern with surface atoms
e.g., 1.5 x 10^{15} Au atoms/cm^2 on Au(111), spacing 2.9 Å
→ if adsorbate atoms on atop sites: (1 x 1) superlattice (2.5 x 10^{-9} mol/cm^2)

Iodine or 4-aminothiophenol: ($\sqrt{30}$ x $\sqrt{30}$)R30° → 1/3 Au (8.3 x 10^{-10} mol/cm^2)
Lower coverage for larger molecules





(*a*)



(*b*)

Roughness factor: actual area/projected area (~1.5 – 2 for smooth electrode)

Adsorption isotherms

Equal electrochemical potentials for bulk & adsorbed species i at equilibrium

$$\mu_i^A = \mu_i^b$$

$$\mu_i^{0,A} + RT\ ln\ a_i^A = \mu_i^{0,b} + RT\ ln\ a_i^b$$

Standard free energy of adsorption

$$\Delta G_i^0 = \mu_i^{0,A} - \mu_i^{0,b}$$

$$a_i^A = a_i^b\ e^{-\Delta Gi0/RT} = \beta_i a_i^b$$

Where $\beta_i = \exp(-\Delta G_i^0/RT)$

Langmuir isotherm

Assumption:

(a) No interactions between the adsorbed species on the electrode surface

(b) No heterogeneity of the surface

(c) At high bulk activities, saturation coverage of the electrode by adsorbate (e.g., to form a monolayer) of amount of Γ_s

$$\Gamma_i/(\Gamma_s - \Gamma_i) = \beta_i a_i^b$$

Fractional coverage, $\theta = \Gamma_i/\Gamma_s$

$$\theta/(1 - \theta) = \beta_i a_i^b$$

$$\Gamma_i = \Gamma_s \beta_i C_i / (1 + \beta_i C_i)$$

If two species i & j are adsorbed competitively,

$$\Gamma_i = \Gamma_{i,s} \beta_i C_i / (1 + \beta_i + \beta_j)$$
$$\Gamma_j = \Gamma_{j,s} \beta_j C_j / (1 + \beta_i + \beta_j)$$

Logarithmic Temkin isotherm

Interactions between adsorbed species

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

Frumkin isotherm

Electrochemical free energy of adsorption is linearly related to Γ_i

$$\Delta G_i^0(\text{Frumkin}) = \Delta G_i^0 i\,(\text{Langmuir}) - 2g\Gamma_i$$

$$\beta_i a_i^b = [\Gamma_i/(\Gamma_s - \Gamma_i)]\exp(-2g\Gamma_i/RT)$$

g: J/mol per mol/cm^2 → increased coverage changes the adsorption E of i

Positive g: interactions between adsorbed molecules are attractive

Negative g: repulsive interactions

As g → 0, Frumkin isotherm approaches the Langmuir isotherm

Rate of adsorption

When $\beta_i C_i << 1$, $\Gamma_i = \Gamma_s \beta_i C_i = b_i C_i$

Where $b_i = \beta_i \Gamma_s$

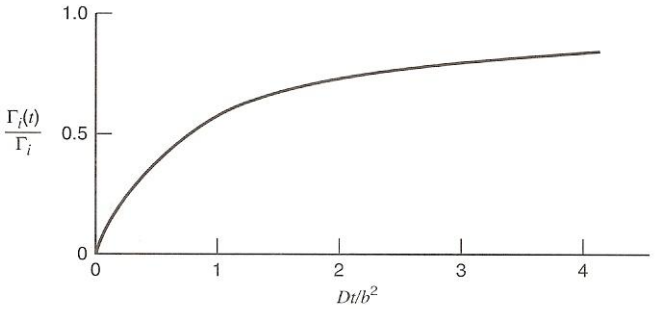
$$\Gamma_i(t) = b_i C_i(0,t)$$

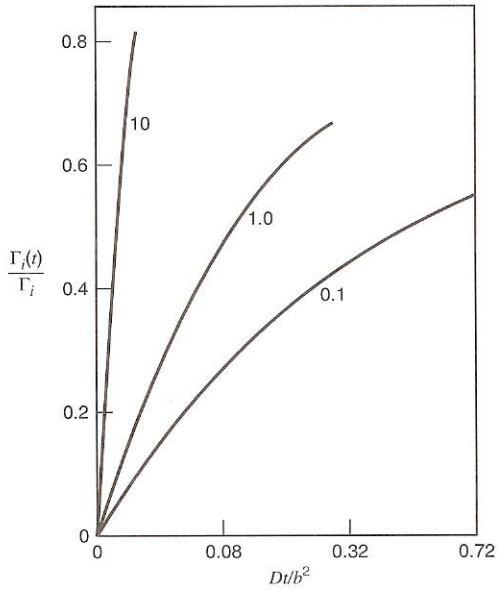
$C_i(x,0) = C_i^*$, $\lim C_i(x,t) = Ci^*$

$$\Gamma_i(t) = \int D_i [\partial C_i(x,t)/\partial x]_{x=0} \, dt$$

$\rightarrow$ $$\Gamma_i(t)/\Gamma_i = 1 - \exp(D_i t/b_i^2)\mathrm{erfc}[(D_i t)^{1/2}/b_i]$$

$\Gamma_i(t)/\Gamma_i$ is independent of C_i^*, but actually depend on.





bC^*/Γ_s

Effect of adsorption of electroinactive species

→ such adsorption inhibit (or poison) an electrode reaction or accelerate the electrode reaction (e.g., hydrogen or oxygen)

$$k^0 = k_{\theta=0}{}^0(1 - \theta) + k_c{}^0\theta$$

Where $k_{\theta=0}{}^0$ is the standard rate const at the bare surface & $k_c{}^0$ that at the filmed portions

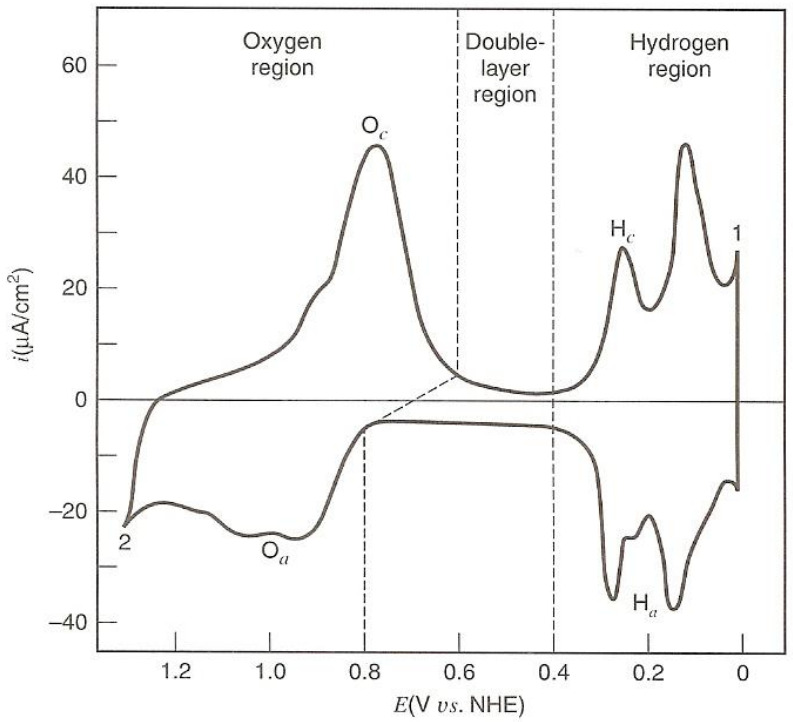
For completer blockage by the film, $k_c{}^0 = 0$

For catalysis by the filmed area, $k_c{}^0 > k_{\theta=0}{}^0$

Effect of adsorbed substances

Hydrogen & oxygen

CO & organics



Summary

Electrochemical potential (μ_i) = ($\partial G/\partial n_i$): const at equilibrium

Surface tension (γ) = ($\partial G/\partial A$): a measure of the energy required to produce a unit area of new surface

Surface excess concentration (Γ_i) = n_i/A: excess per unit area of surface

Gibbs adsorption isotherm: $-d\gamma = \Sigma\gamma_i d\mu_i$ **for general interface**

Electrocapillary equation: $-d\gamma = \sigma^M dE + \Sigma\Gamma_i d\mu_i$

for electrochemical interface

The excess charge density on the metallic side of interface: $\sigma^M = -\sigma^S$

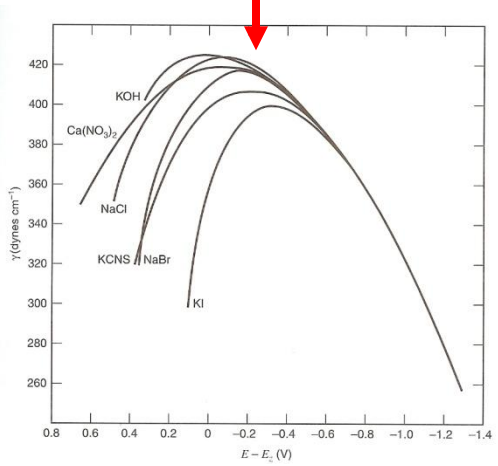
→ surface tension (γ) vs. charge density: $\sigma^M = -(\partial\gamma/\partial E)_\mu$

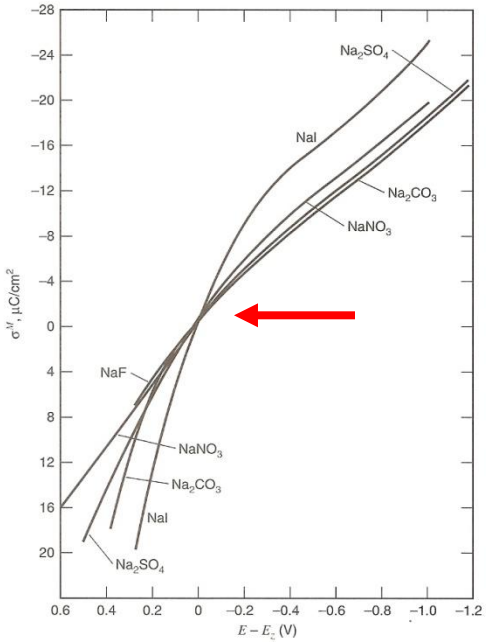
Surface tension (γ) vs. charge density: $\sigma^M = (\partial\gamma/\partial E)_\mu$

Curve slope = 0: "potential of zero charge"(pzc)

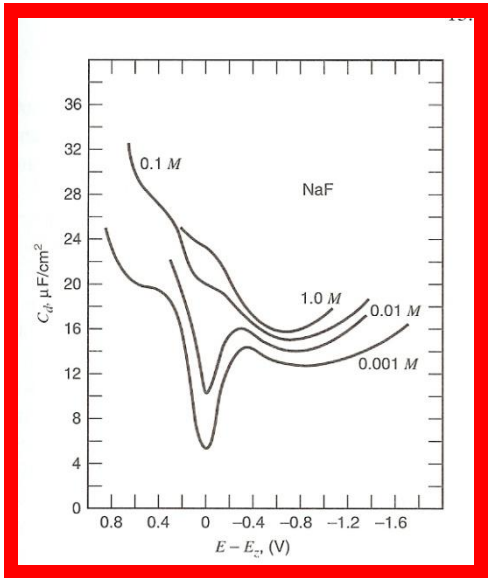
$\sigma^M = \sigma^S = 0$

- excess charge





Exp.



$C_d = (\partial\sigma^M/\partial E)$