Lecture Note #6

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

Reading: Bard, ch. 13

Thermodynamics of the double layer

Gibbs adsorption isotherm

Suppose an interface of surface area A separating two phases, α & β

$\rightarrow$ interfacial zone (~ 100 Å)

$\rightarrow$ *excesses* and *deficiencies*

in the concentration of components

Surface excess (in # of moles of any species)

$n_i^o = n_i^S - n_i^R$

n_i^o: 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 $\rightarrow$ 1st two terms can be dropped

$(\partial\overline{G}^R/\partial n_i^R) = \overline{\mu}_i$ (electrochemical potential) $\rightarrow$ 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*
$$d\bar{G}^o = d\bar{G}^S - d\bar{G}^R = \gamma dA + \sum \bar{\mu}_i d(n_i^S - n_i^R)$$
$$d\bar{G}^o = \gamma dA + \sum \bar{\mu}_i dn_i^o$$

Euler's theorem for variables, A and n_i (const T and P)
$$\bar{G}^o = (\partial \bar{G}^o / \partial A)A + \sum (\partial \bar{G}^o / \partial n_i^o) n_i^o$$
$$\bar{G}^o = \gamma A + \sum \bar{\mu}_i n_i^o$$

$\rightarrow$
$$d\bar{G}^o = \gamma dA + \sum \bar{\mu}_i dn_i^o + A d\gamma + \sum n_i^o d\bar{\mu}_i$$
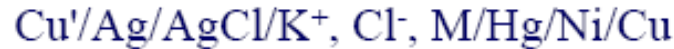
$$A d\gamma + \sum n_i^o d\bar{\mu}_i = 0$$

Surface excess concentration, $\Gamma_i = n_i^o / A$ (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 $(X_i/X_S)\Gamma_S$

Electrocapillary equation

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

→ 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

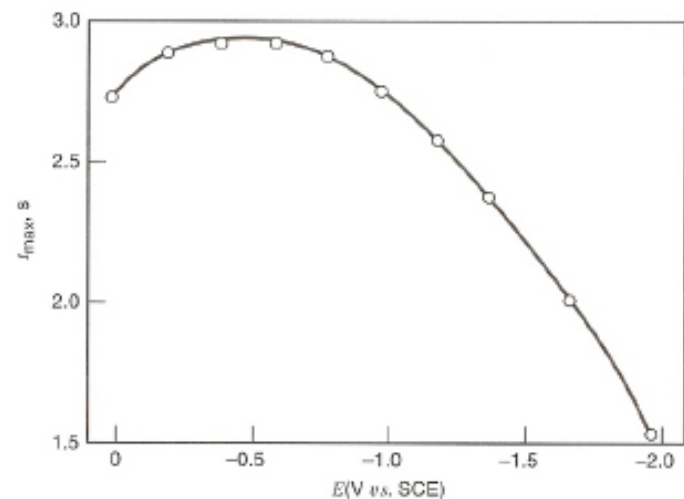$\rightarrow t_{max}$ vs. E has same shape as the electrocapillary curve

Excess charge and capacitance

From electrocapillary equation,

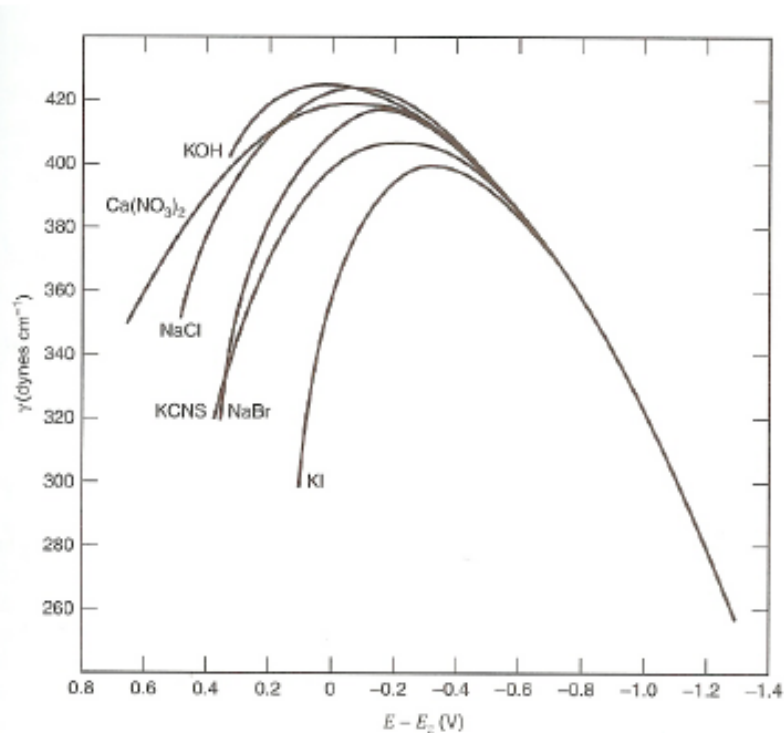$$\sigma^M = (\partial \gamma / \partial E_-)_{\mu KCl, \mu M}$$

the excess charge on the electrode
$\rightarrow$ 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 <u>maximum</u> in surface tension
→ potential at maximum: "<u>electrocapillary maximum (ECM)</u>"
→ 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
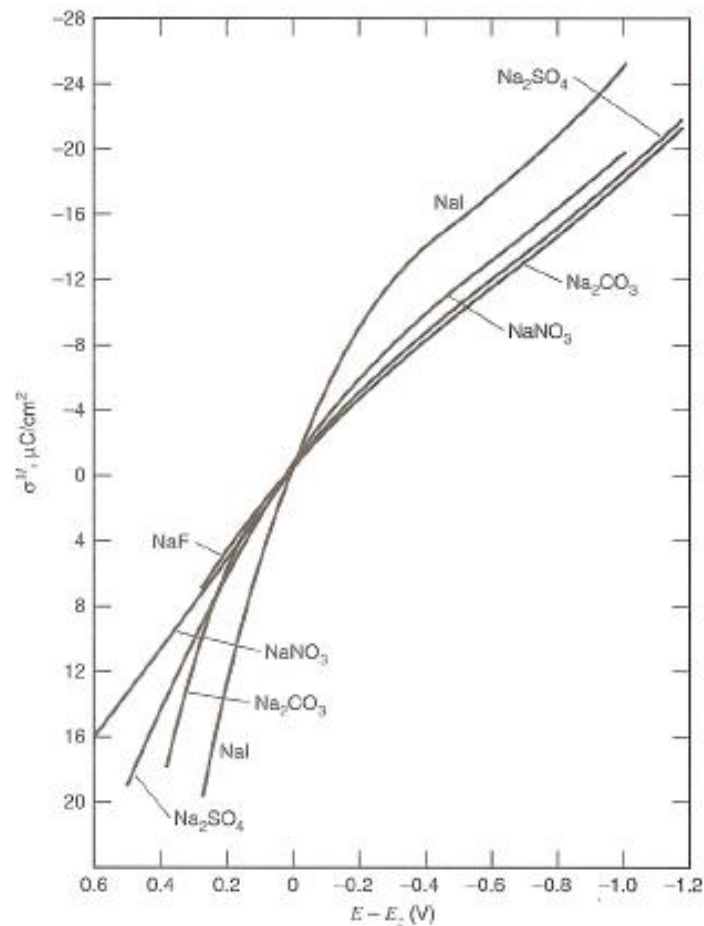
The capacitance of the interface → its ability to store charge in response to a
   perturbation in potential

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

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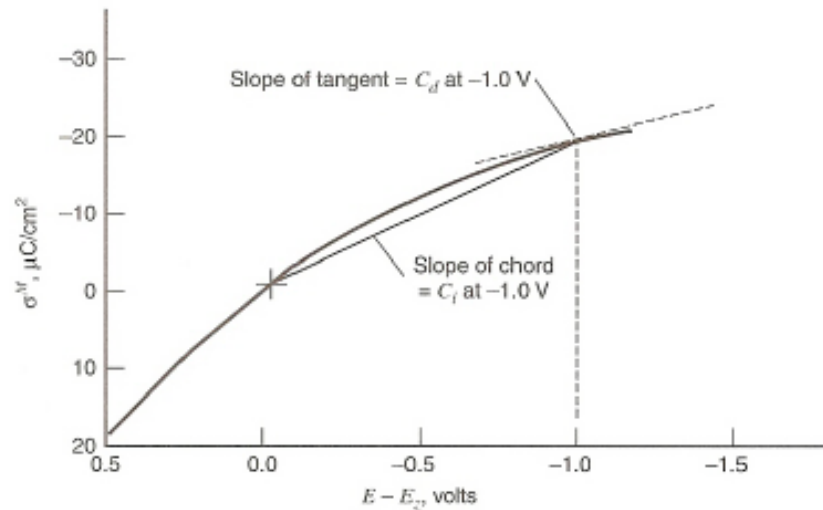
Integral capacitance, C_i (or K): ratio of total charge density (σ^M) at potential E to
   the total potential difference

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

E_Z: PZC

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

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

$$\gamma = \iint \quad C_d dE$$

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

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

$\rightarrow$ 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 $E_Z \rightarrow$ surface excess of K^+: negative $\rightarrow K^+$ conc in the
    interface is smaller than in the bulk (reverse for Cl⁻)
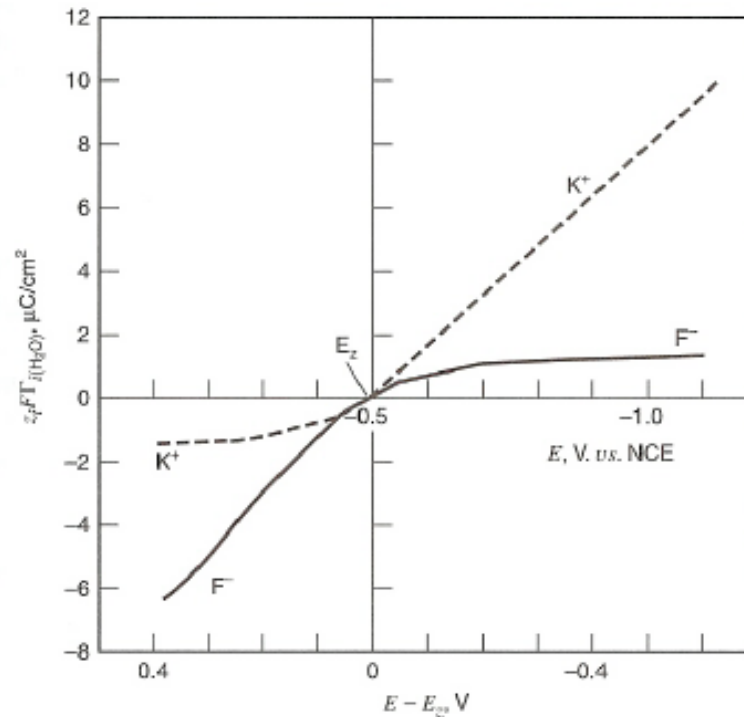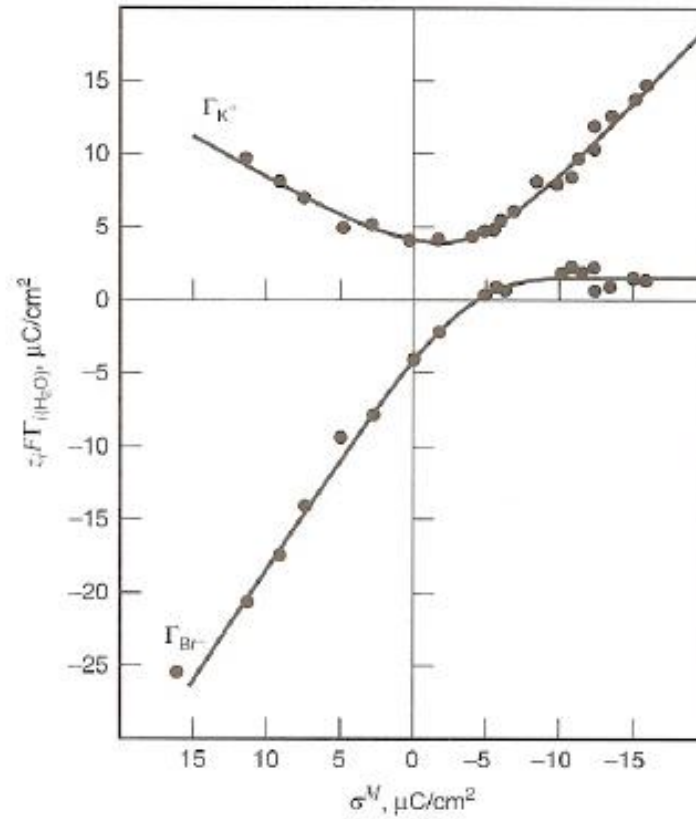At potentials negative of $E_Z \rightarrow$ opposite

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

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

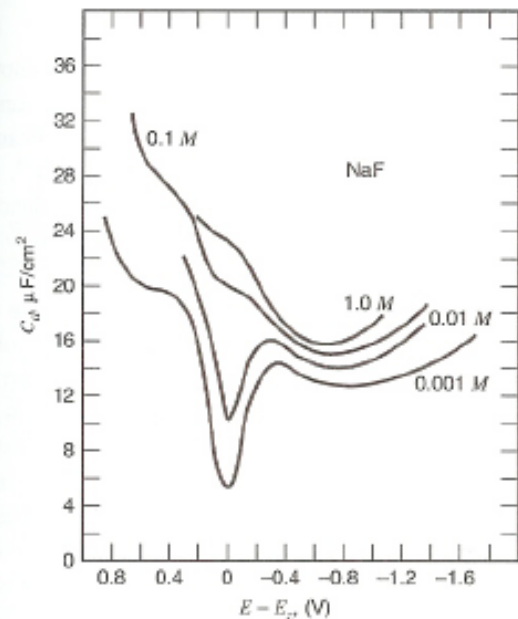Weakness of this model: predict C_d is const
e.g., Fig. 13.3.1
Differential capacitance vs. E
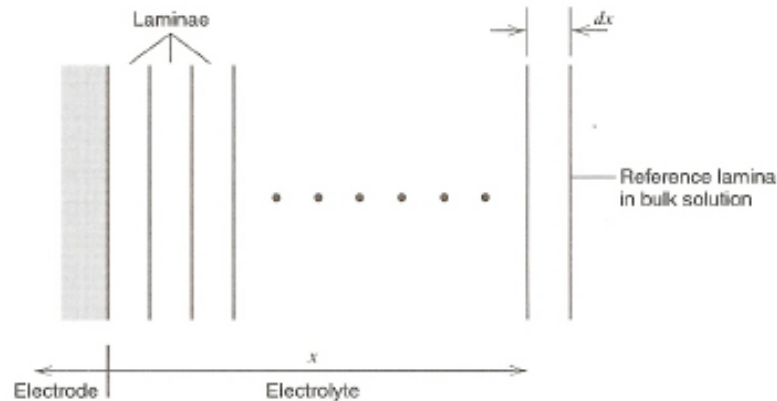in Hg/NaF interface
→ potential dependence
→ more sophisticated model needed

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

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

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

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

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

(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 $\qquad\qquad \kappa = (2n^0 z^2 e^2/\varepsilon\varepsilon_0 kT)^{1/2}$

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}

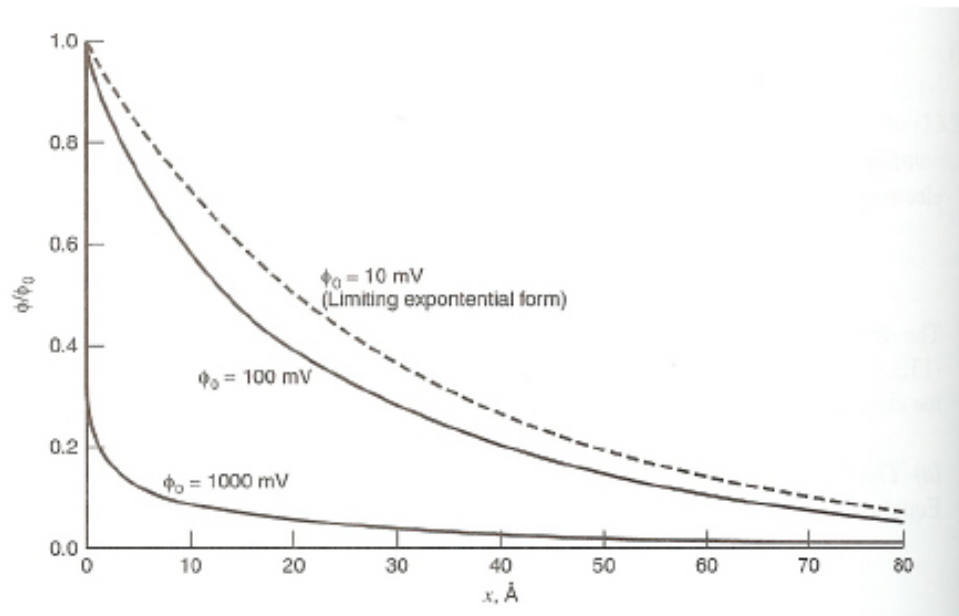Potential profile for several different ϕ_0: potential decay away from the surface

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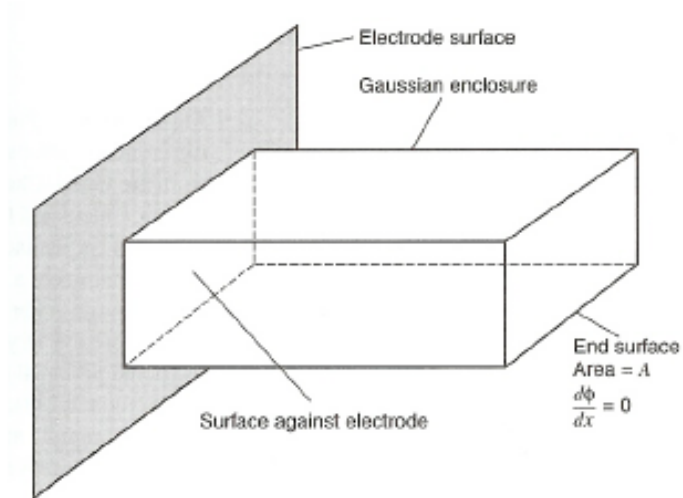If ϕ_0 is sufficiently low $(\tanh(ze\phi/kT) \sim ze\phi/kT)$

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

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

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

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

Electrode surface
Gaussian enclosure
End surface
Area = A
$\frac{d\phi}{dx} = 0$
Surface against electrode

Gauss law, charge

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

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 $\mu C/cm^2$

(c) Differential capacitance

$$C_d = d\sigma^M/d\phi_0 = (2z^2e^2\varepsilon\varepsilon_0 n^0/kT)^{1/2}\cosh(ze\phi_0/2kT)$$

For dilute aqueous solutions at 25°C

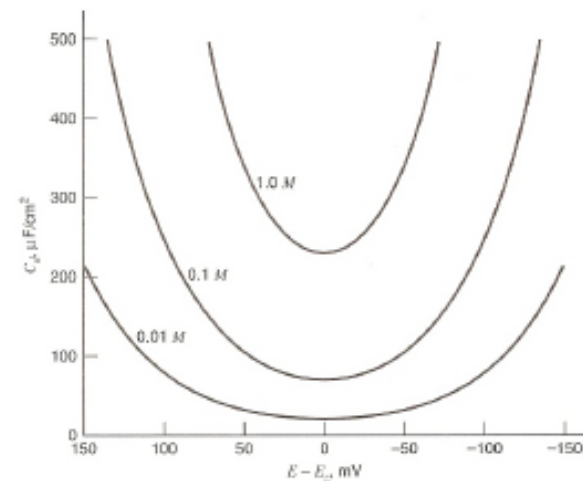$$C_d = 228zC^{*1/2}\cosh(19.5z\phi_0)$$

where C_d is in $\mu F/cm^2$

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

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

$\rightarrow$ 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
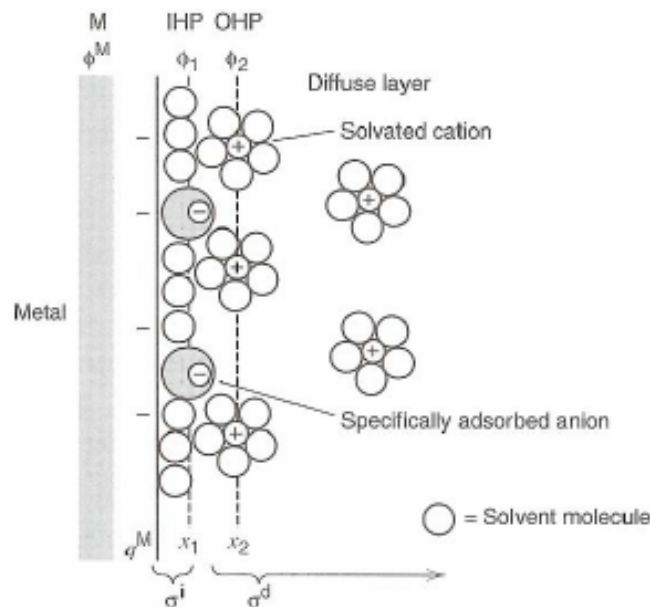
X_2: outer Helmholtz plane (OHP)

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

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

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

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

Two components

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

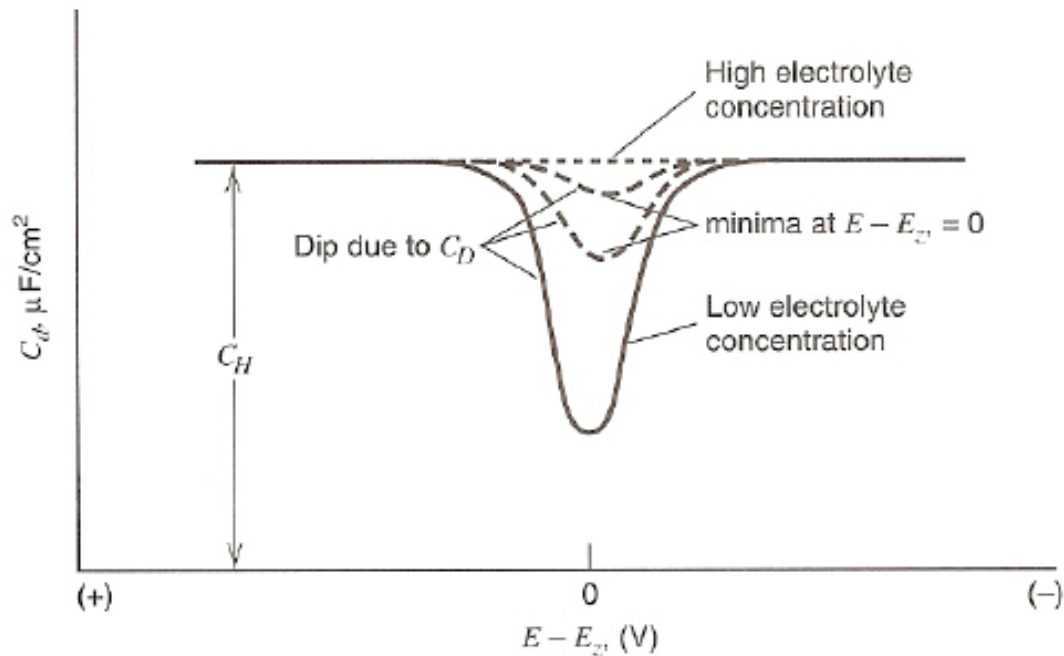C_D: capacitance of the charge at OHP, C_D: truly diffuse charge

Gouy-Chapman-Stern model
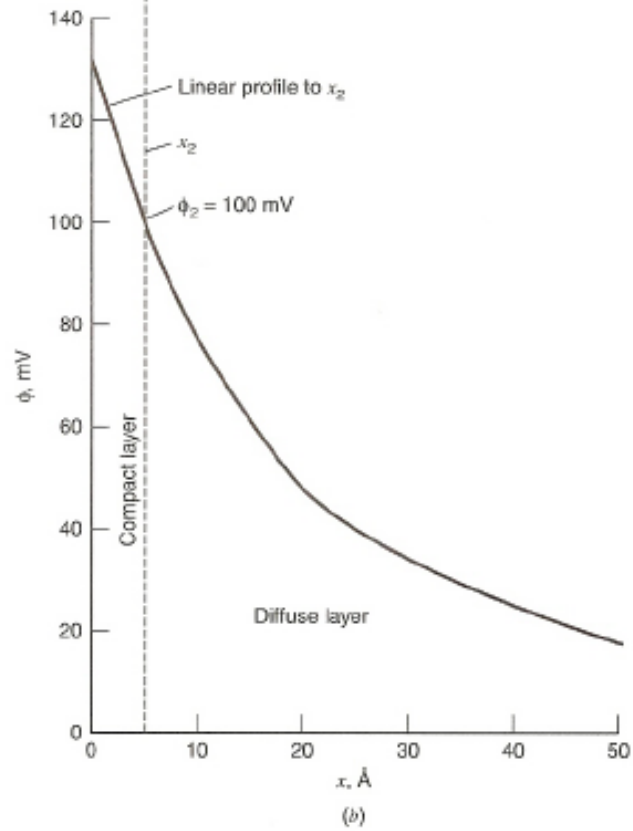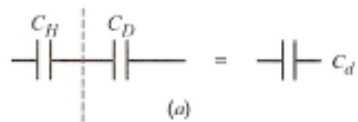
C_H: independent of potential

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 $\rightarrow C_D$ is so large $\rightarrow C_H$

$\rightarrow$ 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
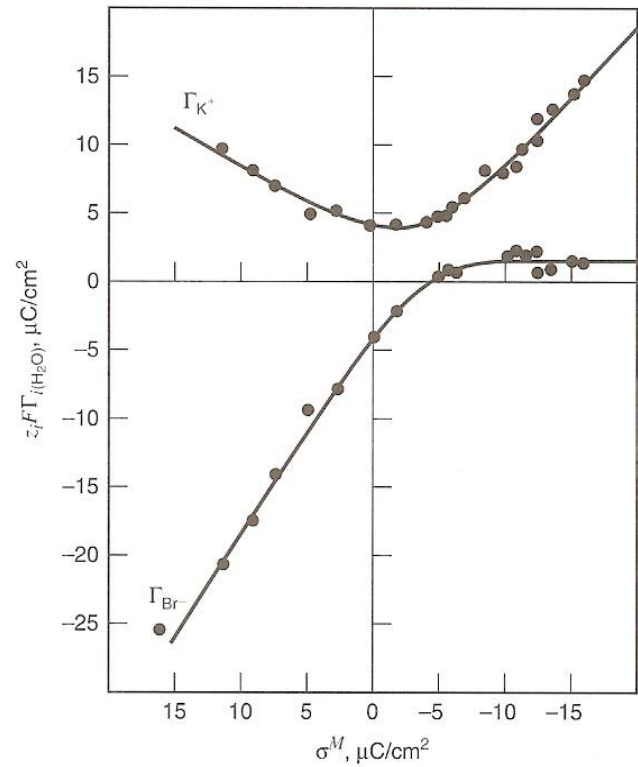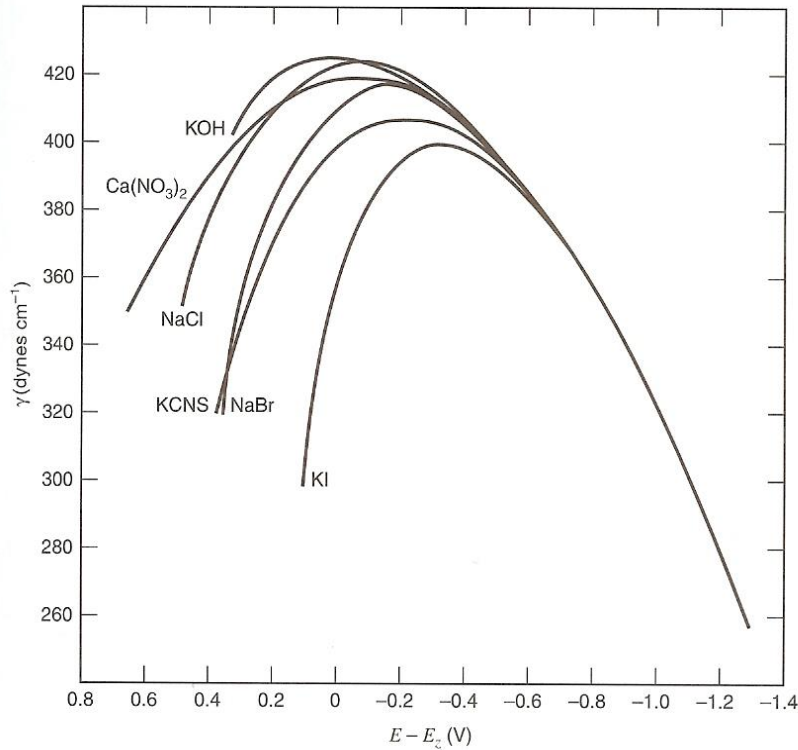
Fig.13.2.6 Br

(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
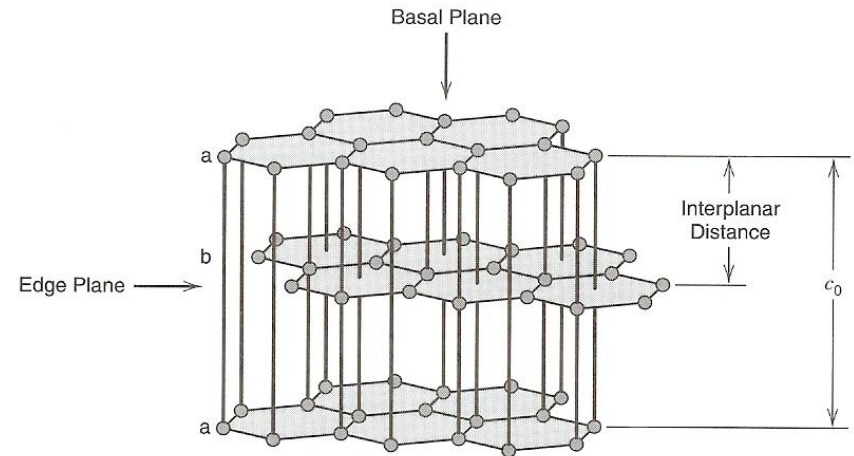Different crystal faces exhibit different properties (e.g., PZC, work function..)
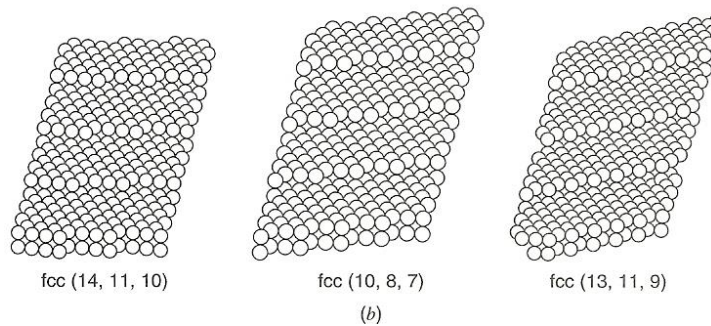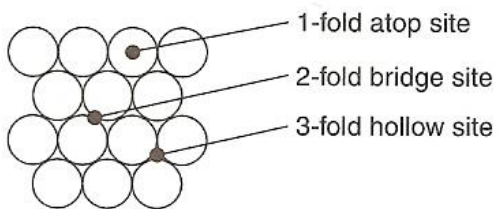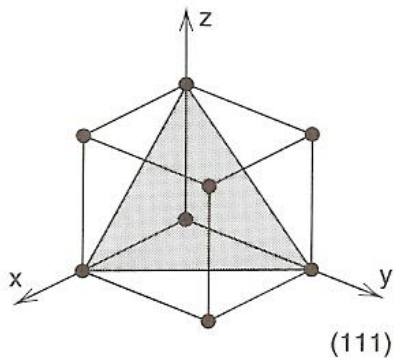Pt, Pd, Ag, Ni, Cu: FCC crystal structures
→ low-index crystal faces: stable, polishable
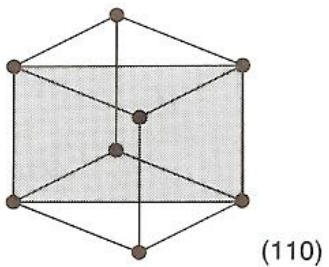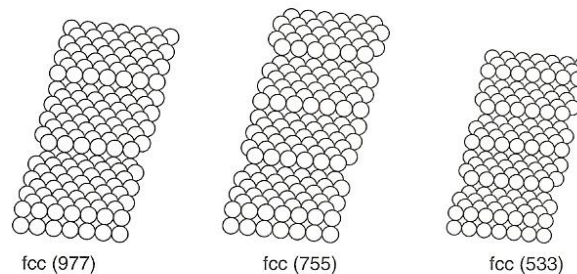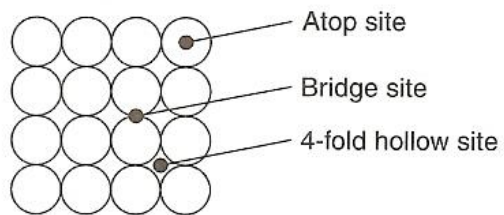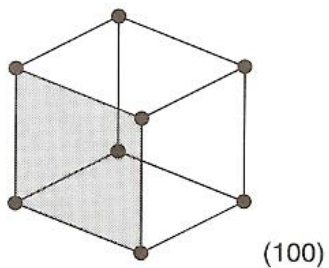→ higher-index planes: more edges, step & kink sites

Reconstruction: minimize surface energy

Carbon: highly oriented pyrolytic graphite
        (HOPG)

(100)

Atop site

Bridge site

4-fold hollow site

fcc (977)   fcc (755)   fcc (533)

(110)

fcc (443)   fcc (332)   fcc (331)

(a)

1-fold atop site

2-fold bridge site

3-fold hollow site

fcc (14, 11, 10)   fcc (10, 8, 7)   fcc (13, 11, 9)

(b)

(111)
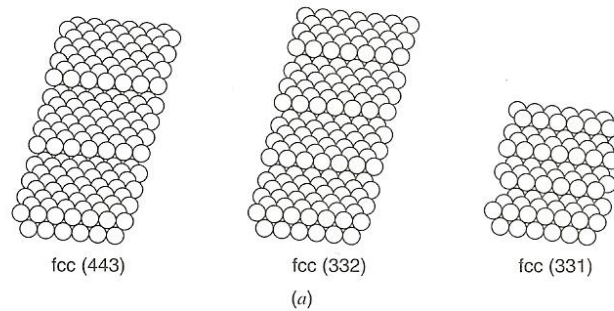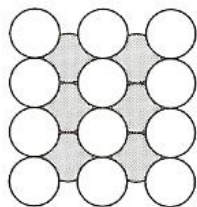
Face-centered cubic (FCC) structure

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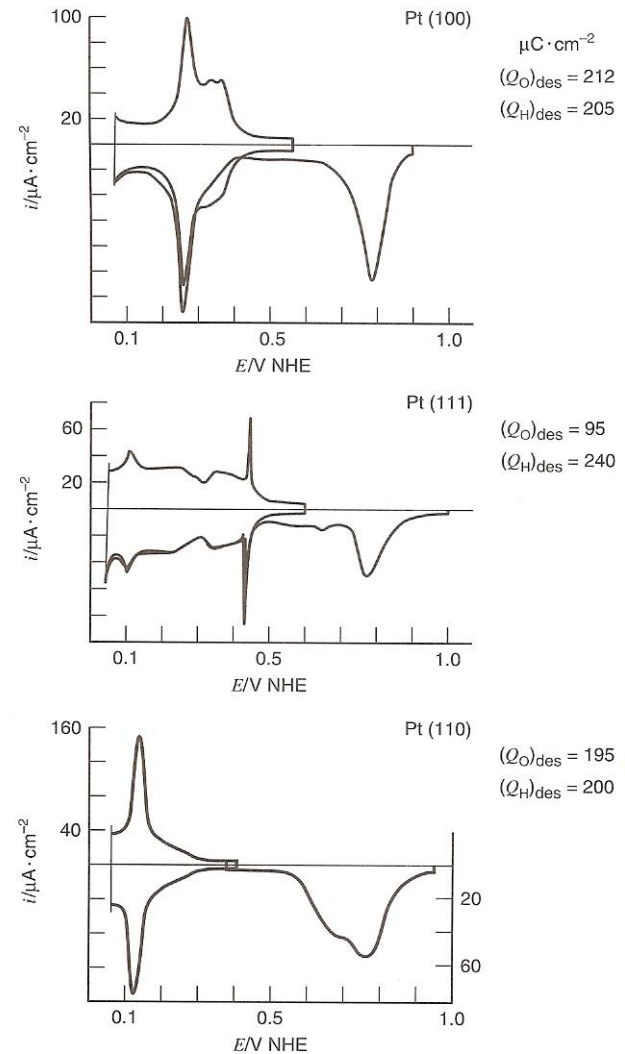
Ag	Ag(111)	Ag(100)	Ag(110)	Au	Au(111)	Au(100)	Au(110)	Cu	Cu(110)
-0.70	-0.45	-0.62	-0.74	0.20	0.56	0.32	0.20	-0.64	-0.69

[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
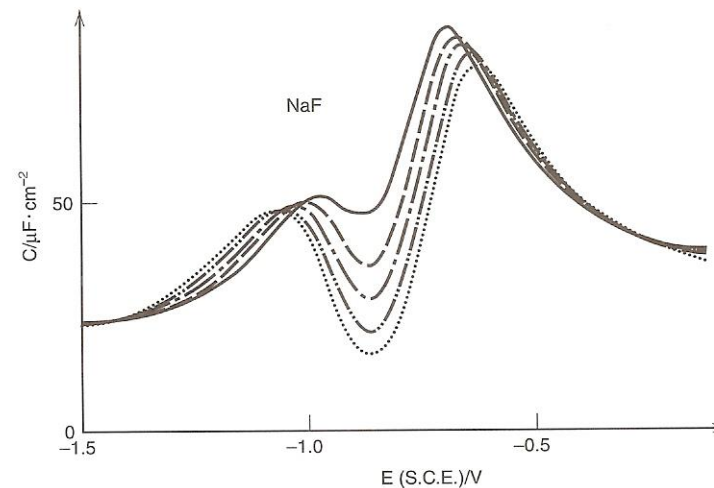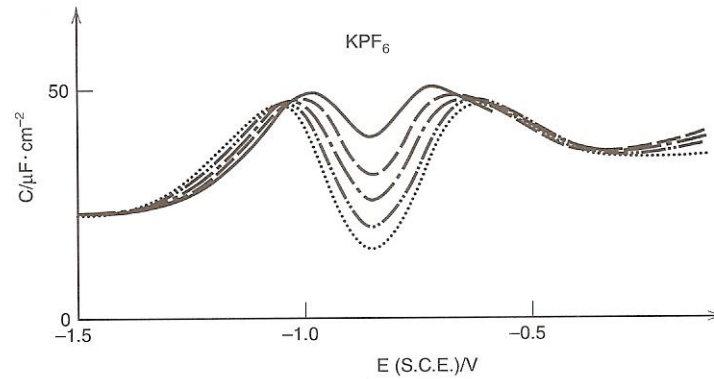e.g., different CV in Pt (0.5 M H_2SO_4)

Solid metal-solution interface
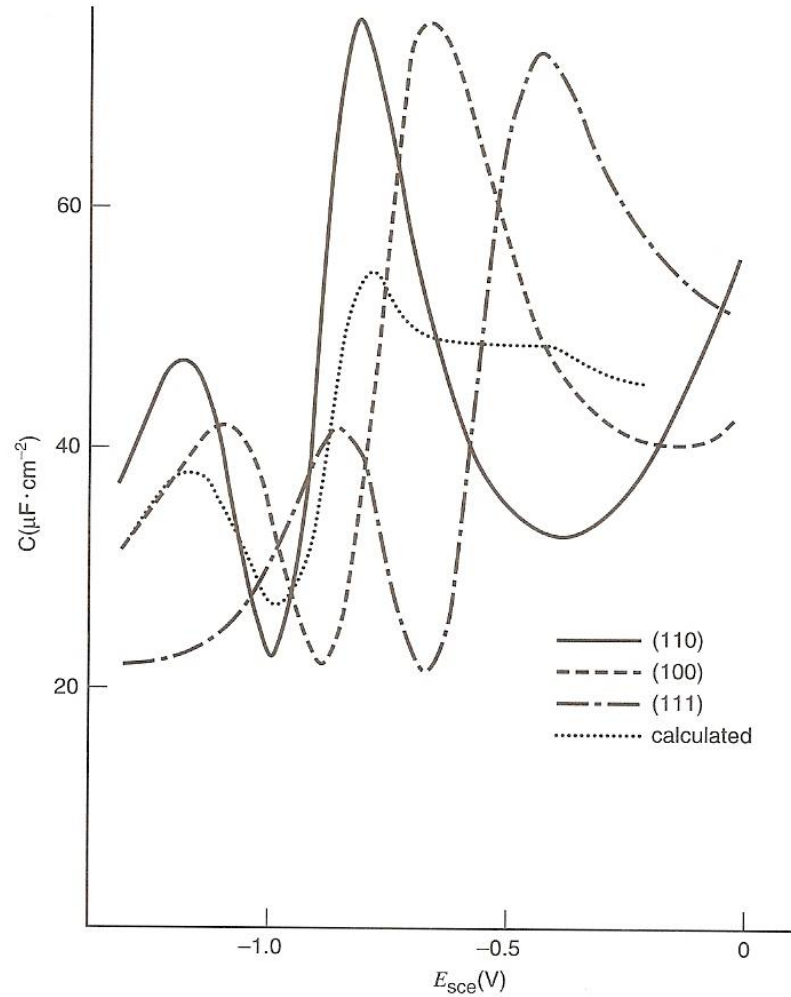Information on PZC & interface from capacitance measurements
Capacitance curves for Ag(100) at different conc of KPF_6 and NaF
(top to bottom 100, 40, 20, 10, and 5 mM)
Independence of min in capacitance → weakly specificallyadsorbed on Ag
PZC from capacitance minimum

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)

Au(100): (5 × 20) → (1 × 1)
0.01M HClO₄

**<u>Extent and rate of specific adsorption</u>**
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: (√30 x √30)R30° → 1/3 Au (8.3 x 10^{-10} mol/cm^2)
Lower coverage for larger molecules

(a)

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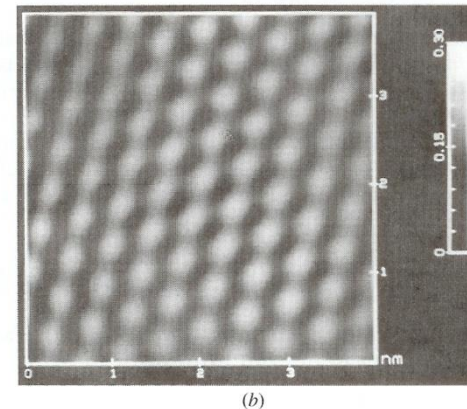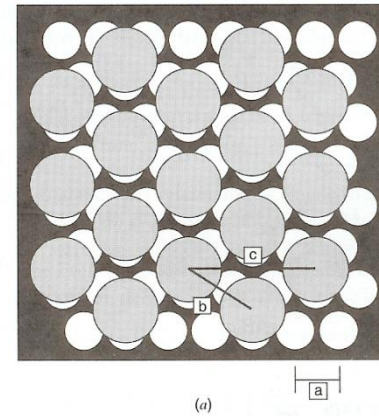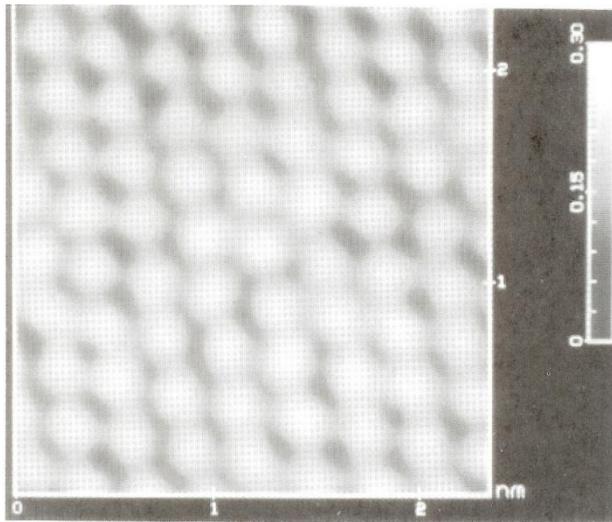
Roughness factor: actual area/projected area (~1.5 – 2 for smooth electrode)

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 $\rightarrow$ increased coverage changes the adsorption E of i
Positive g: interactions between adsorbed molecules are attractive
Negative g: repulsive interactions
As g $\rightarrow$ 0, Frumkin isotherm approaches the Langmuir isotherm

Rate of adsorption

When $\beta_i C_i \ll 1$, $\qquad\qquad \Gamma_i = \Gamma_s \beta_i C_i = b_i C_i$
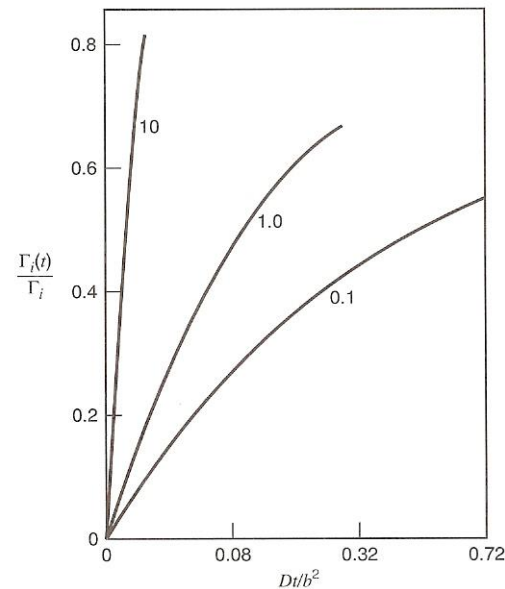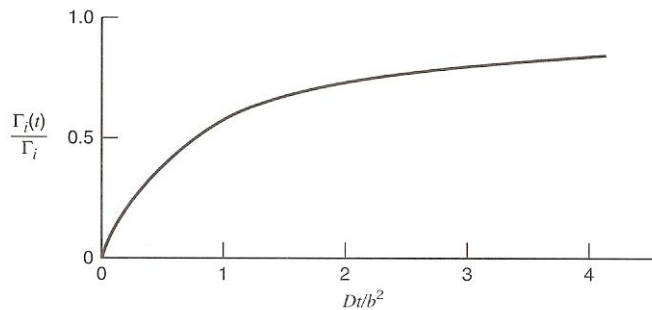
Where $b_i = \beta_i \Gamma_s$

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

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

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

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

$\Gamma_i(t)/\Gamma_i$ 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
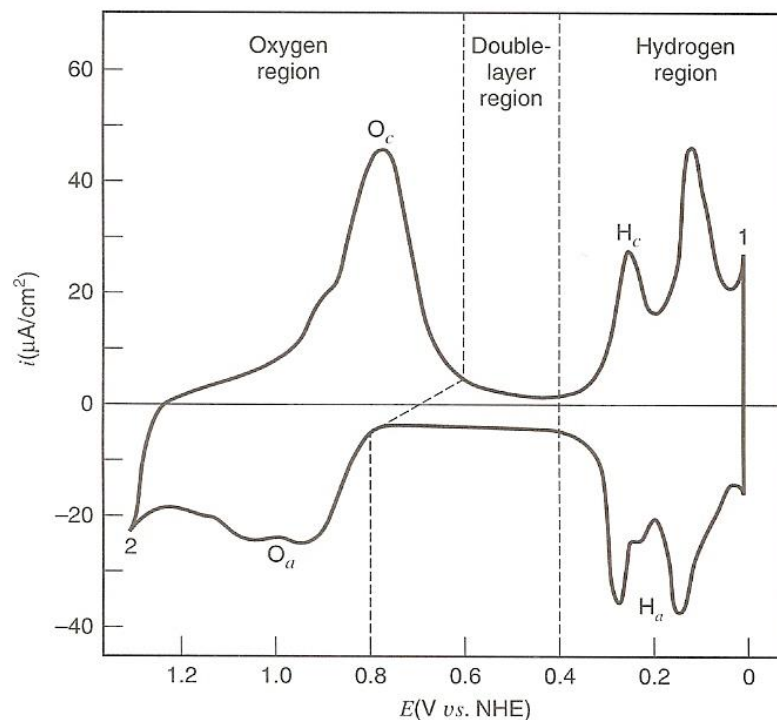
For completer blockage by the film, $k_c^0 = 0$

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__

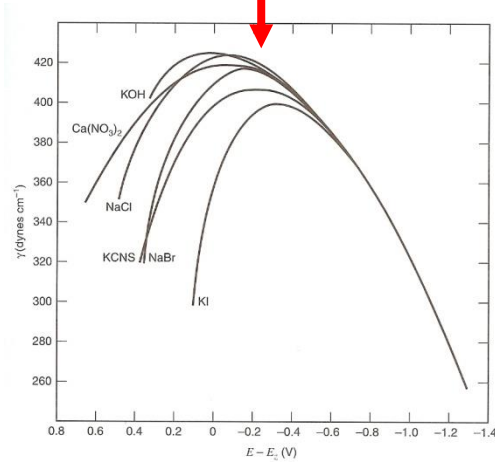**Electrocapillary equation: $-d\gamma = \sigma^M dE + \Sigma \Gamma_i d\mu_i$**

__for electrochemical interface__

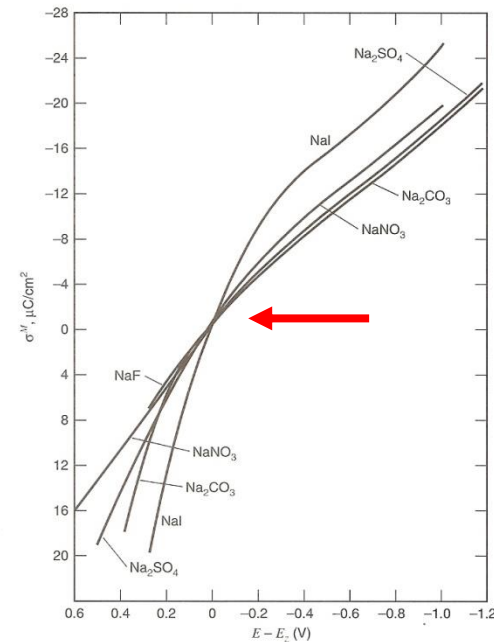**The excess charge density on the metallic side of interface: $\sigma^M = -\sigma^S$**

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

Surface tension (γ) vs. charge density: $\sigma^M = (\partial\gamma/\partial E)_\mu$
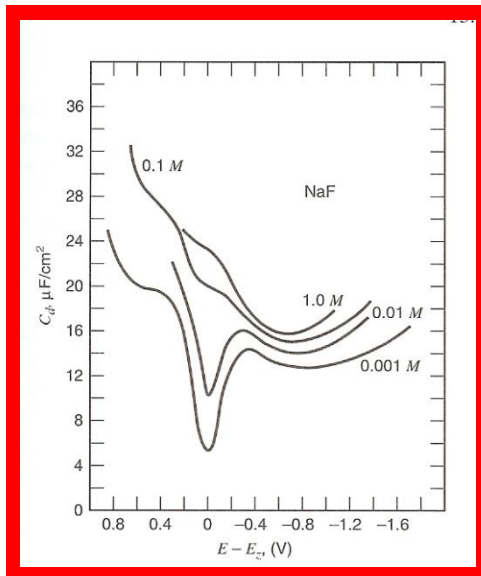
Curve slope = 0: "potential of zero charge"(pzc)
$$\sigma^M = \sigma^S = 0$$

- excess charge

Exp.

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