Lecture Note #6D (Fall, 2022)

Liquid Interfaces

1. Surface energy and surface tension (5.2.1)
2. Liquid surfaces (5.2.2-)
3. Liquid films (5.3, 5.4, 5.5, 5.6)
4. Thermodynamics of liquid Interfaces (5.7)
5. Electrified and charged Interfaces (5.1, 5.8)

Reading: Kolasinski, ch.5,
Somorjai, ch.3, Shaw, ch. 4
Pashley

Thermodynamics of liquid Interfaces (5.6)

Thermodynamics of surface (or interface)

- The surface tension γ of a pure solvent changes when a solute is added.
- $\Delta\gamma$ ($= \gamma - \gamma_0$) depends on the concentration c of the solute.
- Thermodynamics can tell the functional relation $\Delta\gamma(c)$.
- The thermodynamic equations for a bulk need to be modified when applied for a surface.

$dU = dq + dw = TdS - P\,dV$ for single-component bulk

$dU = dq + dw = TdS - P\,dV + \Sigma\, \mu_i dn_i$ for multi-component bulk

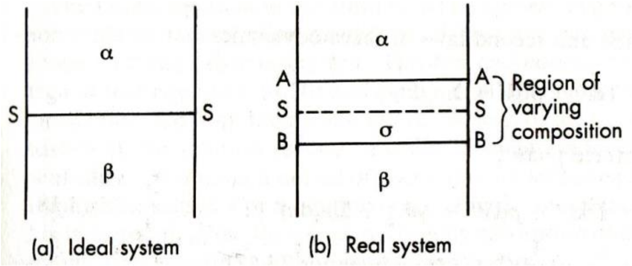
$U = TS - PV + \Sigma\, \mu_i n_i$ integration at constant T,P, and μ_i

$$\boxed{dU = SdT - VdP + \Sigma\, n_i d\mu_i = 0}$$

interface

Gibbs dividing surface (interface)

- The interface of a real system is blurred.
- The system is considered consisting of
  α phase + β phase + σ plane (ideal abrupt interface)
- The choice of the locus of the σ plane is arbitrarily.



(a) Ideal system (b) Real system

$dU^\sigma = dq + dw = TdS^\sigma - P\,dV^\sigma + \gamma\,dA + \Sigma\, \mu dn_i^\sigma$; surface, multi-component

$U^\sigma = q + w = TS^\sigma - P\,V^\sigma + \gamma\,A + \Sigma\, \mu n_i^\sigma$

$$\boxed{dU^\sigma = S^\sigma dT - V^\sigma dP + A\,d\gamma + \Sigma\, n_i^\sigma d\mu_i = 0}$$

Gibs-Duhem equation (extended to include the surface)

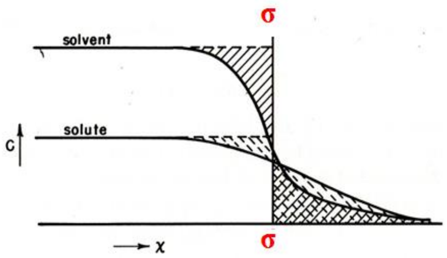
Gibbs adsorption equation

- In general, the concentration profile of solute is different from that of solvent.
- $dU^\sigma = S^\sigma\, dT - V^\sigma\, dP + A\, d\gamma + \Sigma\, n_i^\sigma d\mu_i = 0$
- $A\, d\gamma + \Sigma\, n_i^\sigma d\mu_i = 0$ at constant T and P
- $n_i^{total} = n_i^\alpha + n_i^\beta + n_i^\sigma$, where n is the number of molecules (solvent or solute).→ Material conservation

  $\Gamma_i \equiv n_i^\sigma / A$: surface excess A: interface area
- $A\, d\gamma + \Sigma\, n_i^\sigma d\mu_i = 0$ and $d\gamma = - \Sigma\, (n_i^\sigma / A) d\mu_i = - \Sigma\, \Gamma_i\, d\mu_i$ General form of Gibbs equation
- For a binary system, solvent (phase1) + solute (phase 2),

  $d\gamma = - (\Gamma_1\, d\mu_1 + \Gamma_2\, d\mu_2)$
- The position of the σ plane is conveniently taken so that $\Gamma_1 = 0$ for the solvent.
- Then, $d\gamma = - \Gamma_2\, d\mu_2$
- $\mu_2 = \mu_2^{\,0} + RT \ln a_2$ For a dilute solution, $a_2 \sim c_2$
- $d\mu_2 = RT\, (dc_2 / c_2)$

  $\boxed{\Gamma_2 = - c_2 / RT\, (d\gamma / dc_2)}$: Gibbs adsorption equation



concentration profile along the x direction (⊥σ)

- $\Gamma_2 > 0$ (+ adsorption): accumulation of solute at the surface (interface). Namely, the solute likes to be at the surface (interface).
- $\Gamma_2 < 0$ (- adsorption): depletion of solute at the surface (interface). The solute tends to avoid the surface (interface).
- If $\Gamma_2 > 0$, i.e., $d\gamma / dc_2 < 0$, γ decreases with increasing solute concentration.
- Surfactant molecules which causes a large $\Delta\gamma < 0$ strongly positively adsorbs at surface (interface)

l-*l*, *l*-*v* interface: γ→ surface conc. *s*-*g* interface: surface conc → γ

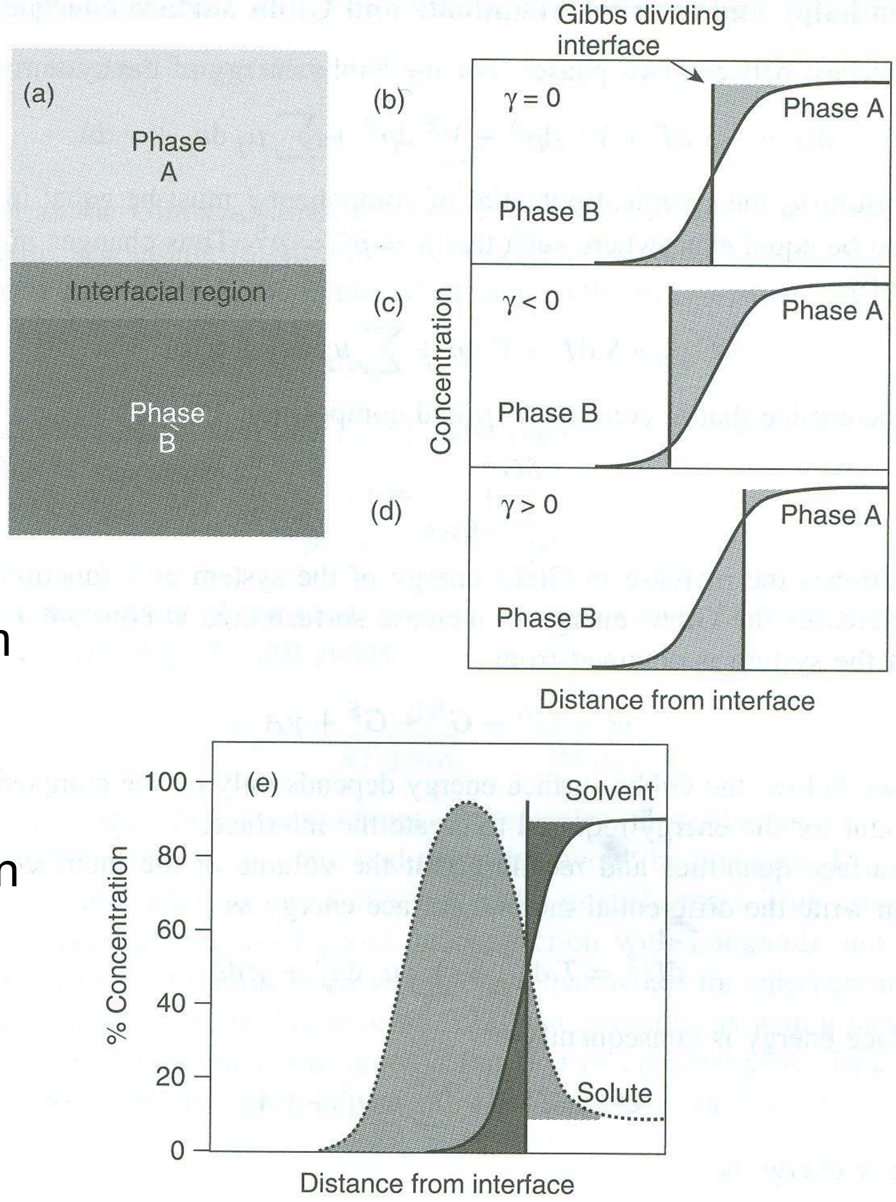


Figure 5.13 The definition of the Gibbs model of an interface. (a) The system is composed of two homogeneous phases separated by an interfacial region. (b)–(d) In the interfacial region, the composition varies. The Gibbs surface is drawn at an arbitrary plane in the interfacial region, conventionally such that the surface excess of one component vanishes as shown in (b). (e) In a solution, the composition of a solute near the interface is generally not the same as in the bulk and the Gibbs surface is drawn such that the surface excess of the solvent vanishes.

$\Gamma > 0$, $\gamma < 0$

+ adsorption

$\Gamma < 0$, $\gamma > 0$

- adsorption

General form of Gibbs equation

$$\boxed{d\gamma = -\Sigma\, \Gamma_i\, d\mu_i}$$

→ fundamental of all adsorption process

Γ_i: surface excess

Electrified and charged Interfaces (5.1, 5.8)

Structure of liquid/solid interface (5.1)

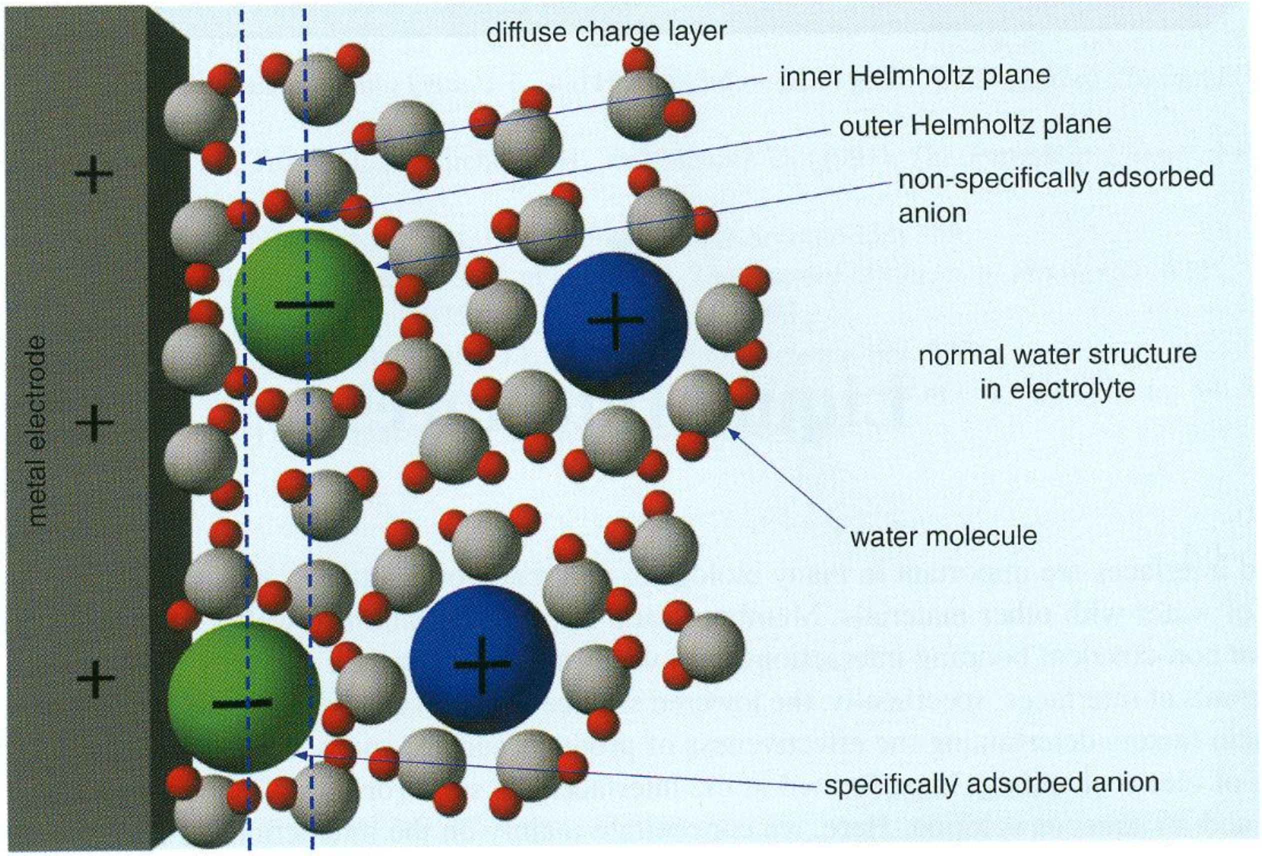


Figure 5.1 *A model of the liquid/solid interface with examples of specific and non-specific adsorption. (a) The structure of the Helmholtz layers and a pure solvent is also shown. (b) The potential drop across the interface in case of non-specific (—) and specific (- - -) ion adsorption. Source: Adapted from K.W. Kolasinski,* Physical Chemistry: How Chemistry Works *with permission from Wiley.*

Structure of water/solid interface

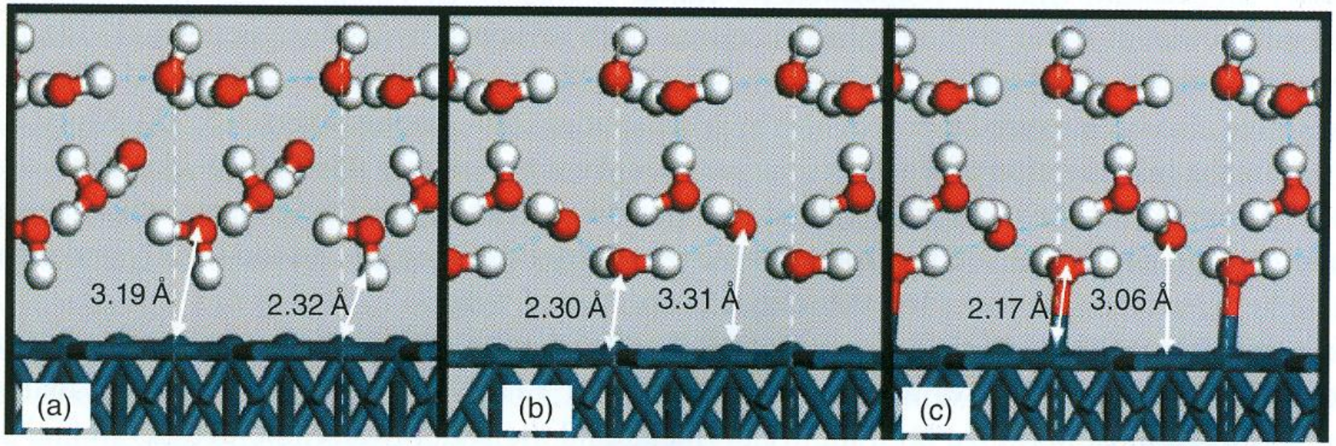
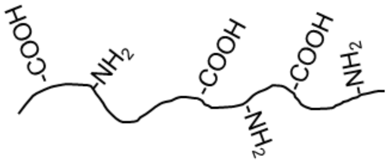


Figure 5.2 *Water bilayer structure for adsorption on close-packed metal surfaces. The optimized structure of water changes in response to an applied electric field flipping from H atom down in panel (a) at −3.0 V to flat in panel (b) at −0.02 V to O atom down in panel (c) at +1.6 V. Source: Reproduced from J.-S. Filhol [20]. © 2006 with permission from Wiley.*

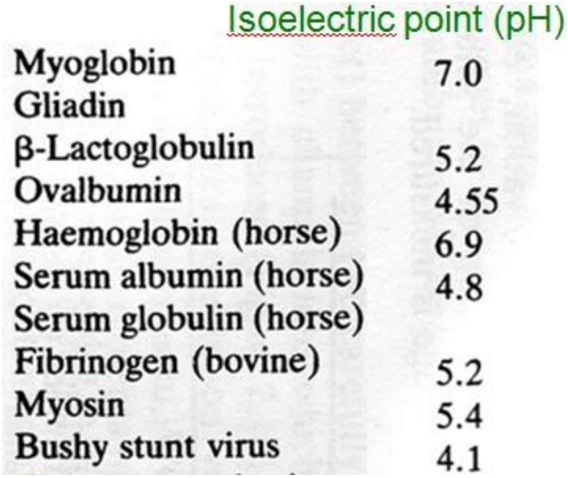
Origin of the charge at colloidal surfaces

1. Ionization

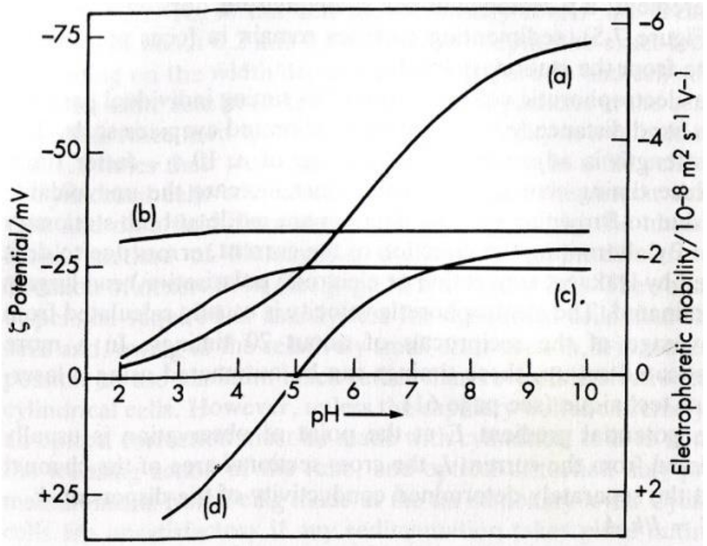
- Proteins acquire their charge by ionization of –COOH and NH_2 group.
- The degree of ionization, hence the charge, is pH-dependent.
- Isoelectric point (pH) : the pH at which the net charge is zero
- Experimentally measured electrophoretic mobility can provide information on the sign and magnitude of the surface charge



proteins



	Isoelectric point (pH)
Myoglobin	7.0
Gliadin	
β-Lactoglobulin	5.2
Ovalbumin	4.55
Haemoglobin (horse)	6.9
Serum albumin (horse)	4.8
Serum globulin (horse)	
Fibrinogen (bovine)	5.2
Myosin	5.4
Bushy stunt virus	4.1



High pH -COOH → $-COO^- + H^+$ -charge

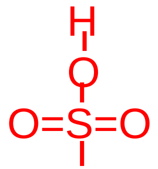
Low pH $-NH_2 + H^+ \rightarrow -NH_3^+$ +charge

a) HC oil droplet, b) Sulfonated PS

c) Arabic acid (carboxylated polymer),

d) Serum albumin adsorbed on to oil droplets

2. Ion adsorption



$$\overset{\overset{\displaystyle H}{|}}{\underset{|}{\overset{\displaystyle O}{|}}}\quad O{=}S{=}O$$

Sulfonic acid

- Unequal adsorption of (+) and (-) ions at colloid surfaces from the bulk solution.
- Ions may be electrolytes, the ubiquitous H^+ and OH^- present in the solution.
  *(+) ions are usually small and so more hydrated than (-) ions.
  * (-) ions are less hydrated and easily polarized.
- Larger hydrated (+) ions have a smaller adsorption tendency: weaker electrostatic interaction with the surface.
- Surfaces in contact with aqueous media are more often (-)ly charged than (+)ly charged.

- Hydrocarbon oil droplets and even air bubbles in aqueous media are (-)ly charged, which can be explained in terms of Gibbs adsorption at the interface:
  * The smaller (+) ions usually have a more negative adsorption at the interface than (-) ions.
  * (-) ions like to be at the interface than (+) ions do.
  * $\gamma\uparrow$ by addition of NaCl in water has the same origin.

ex: μ (oil droplet) = $- 6 \times 10^{-8}\ m^2/V\cdot s$ vs. μ (Cl^- ion) = $- 7.8 \times 10^{-8}\ m^2/V\cdot s$

Electrophoresis: $F = F_{elec} - F_{fric} = 0$ at equilibrium $\rightarrow qE = fv_d = 6\pi\eta a v_d$
mobility $\mu \equiv v_d / E = q/6\pi\eta a$

* Similar μ values mean that the oil droplet has a very large surface charge.

3. Ion dissolution

- Ionic substances can acquire a surface charge by unequal dissolution of (+) and (-) ions.

  Ex: AgI(s) $\leftrightarrow$ $Ag^+(aq) + I^-(aq)$: $K_{sp} = [Ag^+][I^-] \sim 10^{-16}$ at RT.

  * Zero point of charge is achieved at pAg = 5.5 → $[Ag^+] = 3.16 \times 10^{-6}$ M

  * The smaller Ag^+ ion is less strongly bound than I^- ion in AgI(s) and so it is mobile.
- The smaller ion has a stronger tendency of solvation (hydration) than a larger ion.

  $Ag^+(s) \rightarrow Ag^+(aq)$; ΔG_{Ag} and $I^-(s) \rightarrow I^-(aq)$; $\Delta G_I > \Delta G_{Ag}$ (more negative).

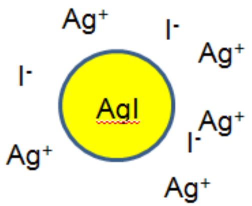
- Additionally added Ag^+ or I^- ions can modify the surface charge by via adsorption.

  * Thus, Ag^+ or I^- is called the potential-determining ion.

- H+ and OH- ions are the potential-determining ions for hydrous metal oxide sols.

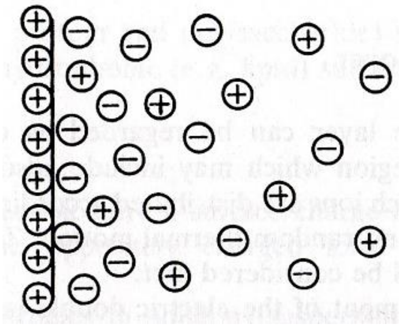
  * $\text{-M-OH} + H^+ \rightarrow \text{-M-OH}_2^+$

  * $\text{-M-OH} + OH^- \rightarrow \text{-M-O}^- + H_2O$



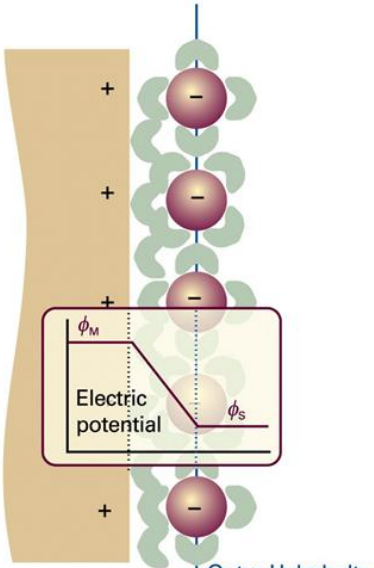
Diffuse (electrical) double layer

- Electrolytes present in the solution.
- Electrical neutrality.
- Coions and counter ions
- Coions are repelled and counter-ions are attracted by the surface charges.
- How are these ions distributed near the charged surface ?



Helmholtz model

- Simplest model but it does not accurately represent the actual double layer.
- **Inner** Helmholtz plane: charged surface
- **Outer** Helmholtz plane: fixed distance from the surface equal to the **radius of a solvated counter-ion**.
- Inner region: only solvent molecules present.
- Outside OHP: random distribution of both ions.
- Electrical potential variation as show in the right figure.



Outer Helmholtz plane

Charge density σ, voltage drop V (or ΔΦ)

$$\boxed{\sigma = \varepsilon_r \varepsilon_0 \Delta\Phi / d}$$

ε_r: dielectric constant of the medium ($\varepsilon_r = \varepsilon/\varepsilon_0$),
ε_0: permittivity of free space (vacuum)
d: spacing

$d\sigma/d\Phi = C_d = \varepsilon_r\varepsilon_0/d$, Capacitance (C/V)cm^{-2} = Fcm^{-2}

electric potential (ϕ or ψ), electric field E

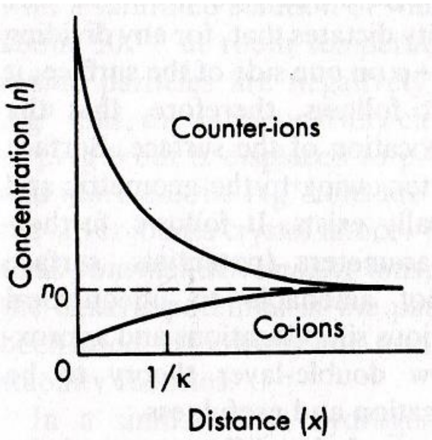
$$\nabla\phi = -E$$

1-D $\frac{d\phi}{dx} = -E$

Poisson equation $\nabla E = -\nabla^2\phi = \frac{+\rho}{\epsilon}$

ρ : charge density, ε: permittivity

Gouy-Chapman model



Assumptions

1. Uniformly charged flat surface of infinite extent.
2. Ions in the diffuse layer are point charges: Boltzmann distribution
3. Symmetrical ions of z^+z^- type.

Boltzmann distribution law

$$n_+ = n_0 \exp\left[\frac{-ze\psi}{kT}\right] \qquad n_- = n_0 \exp\left[\frac{+ze\psi}{kT}\right]$$

$$\rho = ze(n_+ - n_-) = zen_0\left(\exp\left[\frac{-ze\psi}{kT}\right] - \exp\left[\frac{+ze\psi}{kT}\right]\right) = -2zen_0 \sinh\frac{ze\psi}{kT}$$

$$\frac{d^2\psi}{dx^2} = -\frac{\rho}{\epsilon} \qquad \frac{d^2\psi}{dx^2} = \frac{2zen_0}{\epsilon}\sinh\frac{ze\psi}{kT}$$

Poisson-Boltzmann equation

Boundary conditions: $\psi(0) = \psi_0$ at the flat surface and $d\psi/dx = 0$ at $x = \infty$.

$$\psi = \frac{2kT}{ze}\ln\left(\frac{1+\gamma\exp[-\kappa x]}{1-\gamma\exp[-\kappa x]}\right) \qquad \gamma = \frac{\exp[ze\psi_0/2kT]-1}{\exp[ze\psi_0/2kT]+1}$$

$$\kappa = \left(\frac{2e^2 n_0 z^2}{\epsilon kT}\right)^{1/2} = \left(\frac{2e^2 N_A c z^2}{\epsilon kT}\right)^{1/2} = \left(\frac{2F^2 c z^2}{\epsilon RT}\right)^{1/2}$$

1/ κ = Debye screening = avg. EDL
(shielding) length thickness

Debye-Hückel approximation

If $ze\psi_0/2kT \ll 1$ $(kT/e = 25.6 \text{ mV at } 25°\text{C})$

$$n_+ = n_0 \exp\left[\frac{-ze\psi}{kT}\right] = n_0(1 - ze\psi/kT)$$

$$n_- = n_0 \exp\left[\frac{+ze\psi}{kT}\right] = n_0(1 + ze\psi/kT)$$

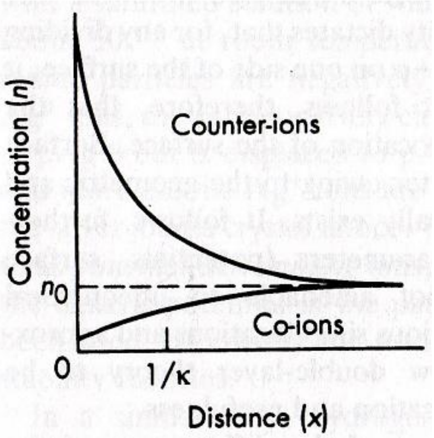
$$\rho = ze(n_+ - n_-) = -2zen_0\frac{ze\psi}{kT}$$

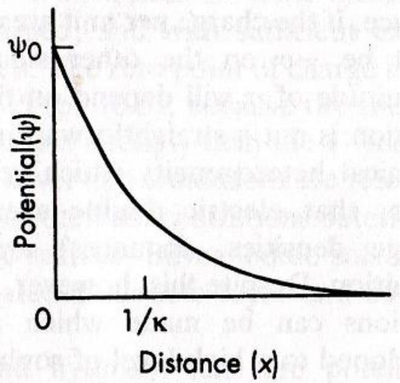
$$\frac{d^2\psi}{dx^2} = -\frac{\rho}{\epsilon} = (2n_0z^2e^2/\varepsilon kT)\psi = \kappa^2\psi$$

$$\frac{d^2\psi}{dx^2} - \kappa^2\psi = 0 \rightarrow \boxed{\psi = \psi_0\exp[-\kappa x]}$$

- $\psi = \psi_0 \exp(\kappa x)$ was discarded because of $d\psi/dx = 0$ at $x = \infty$.

$$\sigma_0 = -\int_0^\infty \rho\,dx \rightarrow \boxed{\sigma_0 = \epsilon\kappa\psi_0}$$





Surface charge vs. surface potential

$$\sigma_0 = \epsilon\kappa\psi_0$$

For a symmetrical electrolyte at 25 ^{o}C

$$\kappa = 0.329\times10^{10}\left(\frac{cz^2}{\mathrm{mol\,dm^{-3}}}\right)^{\frac{1}{2}}\mathrm{m^{-1}}$$

- Meaning of $1/\kappa$: thick of diffuse double layer.
- ψ_0 determined by σ_0 and κ or
  σ_0 determined by ψ_0 and κ

$1/\kappa$ ~ 1 nm for c = 0.1 M and
$1/\kappa$ ~ 10 nm for $c = 10^{-3}$ M
of 1:1 electrolyte

Two cases

1) ψ_0 fixed and σ_0 adjusted:

- When the surface charge is due to adsorption of potential-determining ion. ex: AgI sol.
  → ψ_0 is determined by the concentration of Ag^+ (and I^-) ions in solution.
- Addition of inert electrolyte increases κ and results in more adsorption of ion to keep ψ_0 approximately constant.

2) σ_0 fixed and ψ_0 adjusted:

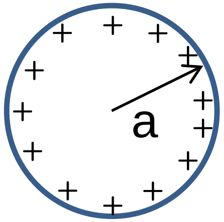
- The charge density at an ionogenic surface remains constant upon adding an inert electrolyte and ψ_0 decreases.
  ex: protein solution

Gouy-Chapman model for spherical interface

$$\nabla^2 \psi = \frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{r^2 \mathrm{d}\psi}{\mathrm{d}r}\right) = \frac{2zen_0}{\epsilon}\sinh\frac{ze\psi}{kT} \qquad (7.11)$$

within Debye-Hückel approximation

$$\nabla^2\psi = \kappa^2\psi$$



Boundary conditions

$$\psi = 0,\ \mathrm{d}\psi/\mathrm{d}r = 0 \text{ at } r = \infty$$

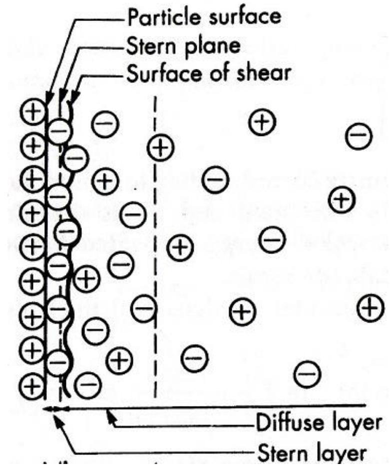
$$\psi = \psi_0\,\frac{a}{r}\,\exp[-\kappa(r - a)]$$

- Debye-Hückel approximation (zeψ << ~ 25 meV) is often not a good one for colloid and surface phenomena. Unapproximated, numerical solution to eq.(7.11) can be computed.

Stern model

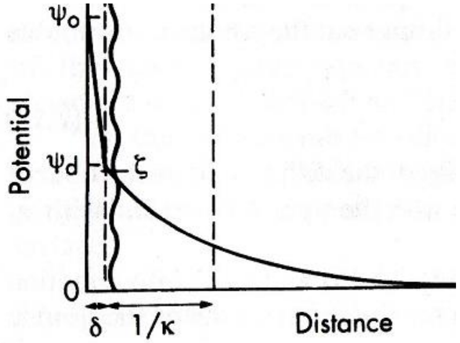
Modification of the Gouy-Chapman model by considering

1. Finite size of ion: ions cannot approach the surface (Stern plane) within the radius of hydrated ion.
2. Specific ion adsorption in the Stern layer is included.
3. EDL is divided into two parts: inner part + diffuse DL, the boundary of which is the Stern plane.
4. Surface of shear is located outside of the Stern plane because of the hydrated ions
5. The potential at the shear plane is called electrokinetic or zeta (ζ) potential, which can be measured experimentally.

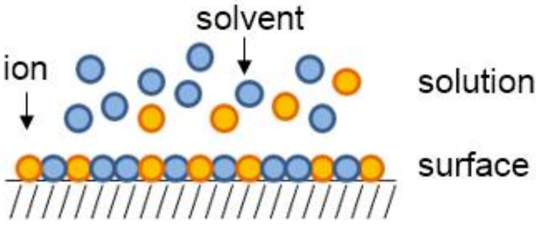


Inner part of EDL(Stern layer)

- Thickness of $\delta \sim 5$ Å
- Specifically adsorbed ions may be present.
- Oriented solvent molecules in the Stern layer has a smaller $\varepsilon'(\sim 5 - 10) < \varepsilon(= 78.5$ for $H_2O)$ due to mutual depolarization.



Specific ion adsorption



- Counter-ion adsorption in Stern plane
- I(bulk) + S(surf) ↔ I(surf) + S(bulk); solvent =1, ion = 2

  $K' = a_2^s\, a_1^b / a_1^s\, a_2^b$

- Assuming a 2D ideal solution for the adsorbed layer
- $a_i \sim c_i = n\, x_i$; n = total moles/unit surface area, x_i = mole fraction
- $a_2^s / a_1^s = x_2^s / x_1^s = x_2^s / (1 - x_2^s)$
- $K'\, a_2^b / a_1^b = a_2^s / a_1^s = x_2^s / (1 - x_2^s)$
- Solving for x_2^s, $\mathbf{x_2^s = K'(a_2^b / a_1^b) / \{(1 + K'(a_2^b / a_1^b)\} = 1/\{1 + (a_1^b / K' a_2^b)\}}$
- Since $\mathbf{x_2^s + x_1^s} = 1$, $\mathbf{x_2^s = \theta}$ (coverage).
- Letting $\mathbf{K' / a_1^b}$ = K (a new constant), $\mathbf{\theta = K\, a_2^b / (1 + K a_2^b)}$.
- This is one form of the Langmuir adsorption isotherm.

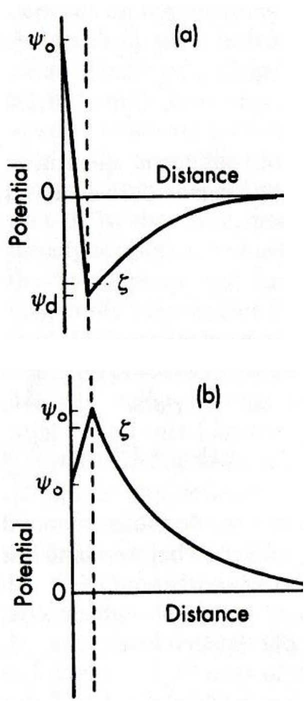
  cf: for gas adsorption **$\theta = Kp / (1 + Kp)$**

- $\Delta G^0 = -RT \ln K$
- $\Delta G^0 = \Delta H^0 - T\Delta S^0 \sim \Delta H^0 = \Delta E^0$ (no PV term involved)

  $= N_A (ze\,\psi_d + \Phi) \rightarrow K = \exp\{-N_A(ze\,\psi_d + \Phi)/RT\}$

  (Φ = van der Waals term)
- The electrical interaction is the dominant term at RT.
- Let σ_1 is the surface charge density due to specifically adsorbed ions.
- $x_2^s = \sigma_1 / \sigma_m = 1/\{1 + (a_1^b / K' a_2^b)\} \sim 1/\{1 + (c_1^b / K' c_2^b)\}$
- $c_1^b / c_2^b = (1/V_m) / (n_0/N_A)$, where V_m is the molar volume of solvent.

- **$\sigma_1 = \sigma_m / [1 + (N_A / V_m n_0) \exp\{(ze\psi_d + \Phi)/kT\}]$**



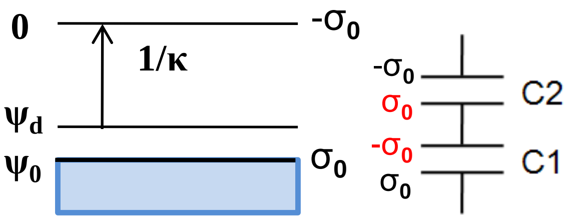
a) Reversal of charge due to the adsorption of surface-active or polyvalent counter-ions.
b) Adsorption of surface-active co-ions.

Capacitance of EDL

- Usually counter-ion adsorption is dominant.
- Adsorption of polyvalent ions can result is charge reversal.

I. If there is no specifically adsorbed ions

$$C_1 = \frac{\sigma_0}{\psi_0 - \psi_d} \quad \text{and} \quad C_2 = \frac{\sigma_0}{\psi_d} \rightarrow \boxed{\psi_d = \frac{C_1 \psi_0}{C_1 + C_2}}$$



II. If specifically adsorbed ions are present

$$\sigma_0 + \sigma_1 + \sigma_2 = 0$$; electrical neutrality

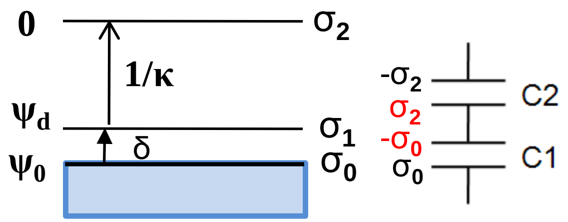
$$\sigma_0 = \frac{\epsilon'}{\delta}(\psi_0 - \psi_d), \quad \sigma_1 = \frac{\sigma_m}{1 + \frac{N_A}{n_0 v_m} \exp\left[\frac{ze\psi_d + \phi}{kT}\right]}$$

$$\sigma_0 + \sigma_1 + \sigma_2 =$$

$$\frac{\epsilon'}{\delta}(\psi_0 - \psi_d) + \frac{\sigma_m}{1 + \frac{N_A}{n_0 V_m} \exp\left[\frac{ze\psi_d + \phi}{kT}\right]} - (8 n_0 \epsilon kT)^{1/2} \sinh \frac{ze\psi_d}{2kT} = 0$$

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2},$$

$$C_2 = \frac{\sigma_2}{\psi_d} = \epsilon\kappa = 2.28 \left(\frac{cz^2}{\text{mol dm}^{-3}} \right)^{1/2} \text{F m}^{-2} \text{ for aqueous electrolyte at } 25^\circ\text{C} \qquad (1)$$



- For Hg- aqueous electrolyte interfaces C can be measured from electrocapillary measurements and
- for AgI- aqueous electrolyte interfaces from potentiometric measurements.
- C_2 can be calculated from the eq.(1) above.
- Then, from $C_1 = \epsilon'/\delta$ (Stern layer capacitance) can be obtained.
- For the AgI- aqueous electrolyte interface C1 ~ 0.1- 0.2 Fm^{-2}.
- Taking δ = 5 Å, one gets **ε'** = 5-10 (<< ε = 78.5 for H_2O at RT) → ordering of H_2O in the Stern layer.

Electrokinetic Phenomena

Relative motion between charged surface and diffuse double layer

1. Electrophoresis: $\mathscr{E} \rightarrow$ charge particle movement.
2. Electro-osmosis: $\mathscr{E} \rightarrow$ DL layer movement against fixed surface charge.
3. Streaming potential: DL layer movement $\rightarrow \mathscr{E}$ generation.
4. Sedimentation potential: charge particle movement $\rightarrow \mathscr{E}$ generation.

- All arising from the relative movement of particle with respect to the liquid.
- $\mathscr{E}$ field → relative motion: Electrophoresis, electro-osmosis
- relative motion → $\mathscr{E}$ field: Streaming potential,
sedimentation potential

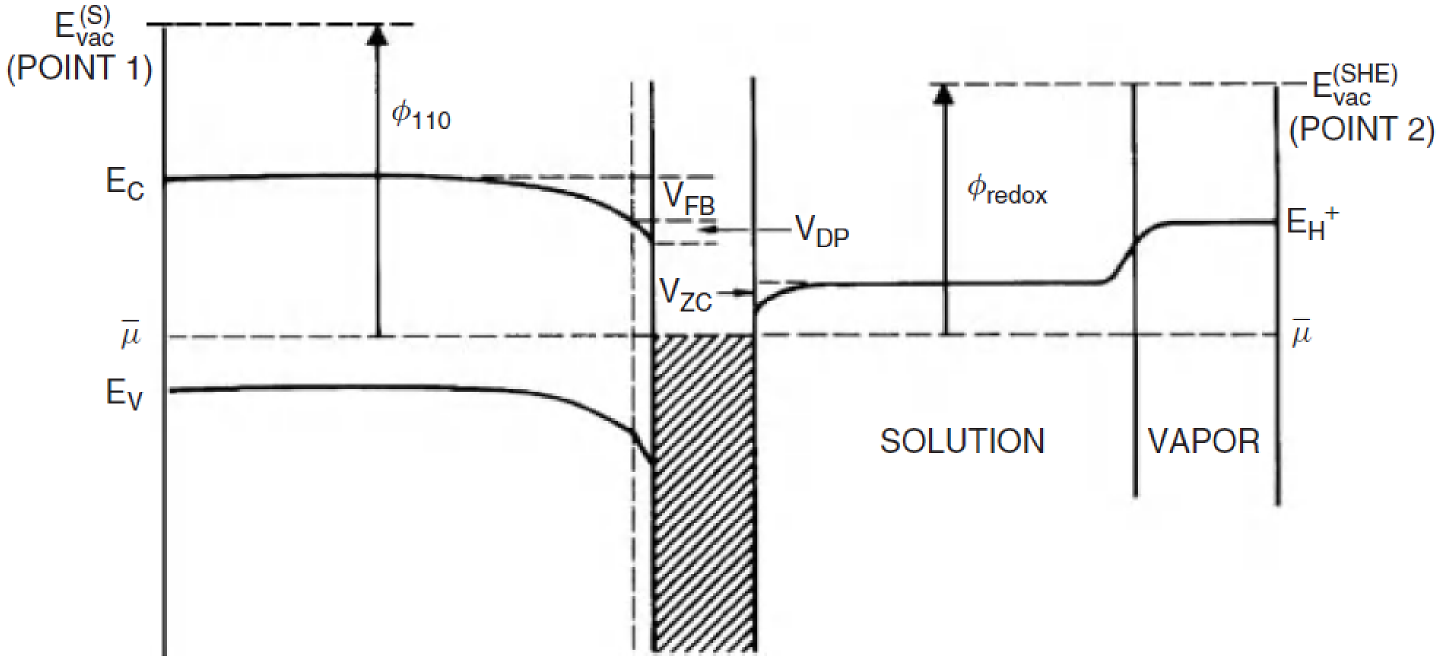


Figure 5.14 *An energy level diagram depicting the levels associated with the connection of a semiconductor electrode to a standard hydrogen electrode. Reproduced from H. Reiss, A. Heller,* J. Phys. Chem., *89, 4207. ©1985 with permission from the American Chemical Society.*

Summary

- At the liquid/solid interface we need to consider not only the structure of the adsorbed layer but also that the near-surface region of the liquid has a structure and composition that can differ markedly from that of the bulk.
- Strongly solvated solution species do not lose their solvation shell and can become non-specifically adsorbed. A solvated species that loses at least part of its solvation shell and chemisorbs to the solid is specifically adsorbed.
- The structure of water near the surface depends on the substrate, the presence of specifically adsorbed ions and the presence of an electric field. Field effects and direct ion-water dipole interactions influence the orientation of the water molecules. Water dissociates on some metal surfaces to form mixed H + OH layers.
- By adjusting the potential and the pH, the net charge on the surface can be tuned from positive to neutral to negative.
- Surface energy and surface tension are synonymous for liquids.
- Surface energy can be thought of as being analogous to a 2D pressure, compare Eq. (5.2.1) and (5.2.2), or else as the surface Gibbs energy per unit area of a pure liquid, Eq. (5.2.6).
- Curved interfaces act differently than planar interfaces. One consequence is that the vapour pressure changes, which leads to the instability of small droplets and capillary condensation within small pores and between small particles.
- Langmuir films are monomolecular films on the surface of a liquid.
- When these films are transferred onto a solid substrate, they are called Langmuir-Blodgett films.
- Self-assembled monolayers are ordered monolayer films that form spontaneously on a solid substrate. It is the chemical potential that provides the thermodynamic driving force for self-assembly.
- Whereas the chemisorption interaction between the head group and the surface accounts for the bulk of binding interaction in SAMs, it is the weak, predominantly noncovalent interactions between the chains and endgroups that lead to the order in the SAM.
- The Gibbs model of adsorption allows us to define the surface excess and calculate fundamental thermodynamic quantities at liquid interfaces.
- The Gibbs surface energy is always positive and creating additional surface area is always energetically unfavourable.
- The Stern-Guoy model describes the interface between an electrode and a solution in terms of a charged adsorbed layer, a layer of solvated ions above this (which together form the electric bilayer), followed by a diffuse and mobile continuous medium that extends into the remainder of the solution.
- The electrochemical potential and chemical potential are related by Eq. (5.8.2). The electrochemical and chemical potentials of neutral species are the same. At equilibrium, it is the electrochemical potential of all charged species that is the same throughout the system.
- The inner or Galvani potential is not the same everywhere even at equilibrium, and it is the Galvani potential that underlies the integrity of the Nernst equation.

- Relating electrochemical potentials to work functions on an absolute scale is a nontrivial but important exercise that allows us to understand how the electronic levels of electrodes and solution species are aligned with respect to one another.