Lecture #14 of 17

Q: What’s in this set of lectures?
A: B&F Chapter 13 main concepts:

- Section 1.2.3: Double layer structure
- Sections 13.1 & 13.2: Gibbs adsorption isotherm; Electrocapillary / Surface excess / Lippmann’s equation; Point of Zero Charge
- Section 13.3: Models: Helmholtz, Gouy–Chapman (Poisson–Boltzmann), GC–Stern
- Section 13.5: Specific adsorption

RECALL FROM LAST TIME...

For the purposes of this class, we want to understand the microscopic origin of the most prominent features of these $C_d$ vs. $E$ data:

a) A minimum in $C_d$ exists at the pzc.

b) $C_d$ is quasi-constant at potentials well positive and well negative of the pzc.

c) This quasi-constant $C_d$ is larger when $E$ is (+) of pzc than when it is (–) of pzc.

d) $C_d$ increases with salt concentration at all potentials, and the “dip” disappears.
Models of Electrical Double Layer:

1) **The Helmholtz Model**: this is the simplest possible model. It postulates that ions (anions and cations) occupy a plane a distance, $d$, from the electrode surface, and that the effective "dielectric constant" operating in the DL is potential independent:

$$C_d = \frac{\varepsilon \varepsilon_0}{d}$$

... for a parallel plate capacitor, $C$ is independent of $E$ because the permittivity of the capacitor, $\varepsilon_0$, and its spacing, $d$, are both independent of applied potential...

... and a flat $C_d$ is in no way observed... we need a more sophisticated model...

... and specifically one where the model of the double layer captures these elements?

H.H. Girault, Analytical and Physical Electrochemistry, EPFL Press, 2004, Figure 5.13
Three traditional models for double layer structure:

1) Helmholtz
2) Gouy–Chapman (GC)
3) Gouy–Chapman–Stern (GCS)

... let's take a look at each...

Models of Electrical Double Layer:

2) The Gouy–Chapman Model: this model adopts all the same assumptions used in Debye–Hückel Theory, which are the following:

a) ions are considered to be point charges; their polarizability is neglected

b) interactions between ions, and between ions and the electrode are purely electrostatic (i.e. no specific (chemical) adsorption); thus, the IHP and OHP will not exist in this model since these explicitly require finite ion size = polarizability

c) the metal is considered a planar surface with a surface charge density, $\sigma^M$

d) ions are distributed according to Maxwell–Boltzmann statistics...

RECALL: Debye–Hückel equation

(in water at 25 °C) $\log \gamma = \frac{0.51z^2\sqrt{I}}{1 + 3.3\alpha x \sqrt{I}}$

$\alpha$ = effective diameter of hydrated ion (nm)

... the derivation is long and the main idea is that you balance thermal motion (Boltzmann) with electrostatics (Poisson/Gauss)
... d) ions are distributed according to Maxwell–Boltzmann statistics...  
\[ n_i = n_i^0 \exp\left( \frac{-z_ie\phi}{4\mathcal{E}T} \right) \]

where \( e \) is the elementary charge, and \( \phi \) is the electric potential relative to the bulk solution.

![Figure 13.3.2 View of the solution near the electrode surface as a series of laminae.](image)

the charge density, i.e. charge per unit volume, \( \rho(x) \), is defined as:  
\[ \rho(x) = \sum_i n_i z_i e \]

... so substituting from the last slide...  
\[ \rho(x) = \sum_i z_i e n_i^0 \exp\left( \frac{-z_i e\phi}{4\mathcal{E}T} \right) \]

... and now the Poisson Equation gives us another expression for \( \rho(x) \):  
\[ \rho(x) = -\varepsilon\varepsilon_0 \frac{d^2\phi}{dx^2} \]

... substituting, we get the Poisson–Boltzmann Equation (no Maxwell)...  
\[ \frac{d^2\phi}{dx^2} = \frac{e}{\varepsilon\varepsilon_0} \sum_i n_i^0 z_i \exp\left( \frac{-z_i e\phi}{4\mathcal{E}T} \right) \]

... if we apply the P–B eq to a 1:1 electrolyte, we obtain the following (see B&F, pp. 547–548):  
\[ \frac{d\phi}{dx} = -\left( \frac{8\mathcal{E}Tn_i^0}{\varepsilon\varepsilon_0} \right)^{1/2} \sinh\left( \frac{ze\phi}{2\mathcal{E}T} \right) \]

... and if we further assume that \( \phi^0 \) is small, we get...  
\[ \phi = \phi^0 \exp(-\kappa x) \]

... where  
\[ \kappa = \left( \frac{2n_i^0 z_i e^2}{\varepsilon\varepsilon_0 8\mathcal{E}T} \right)^{1/2} \]

... here, \( \kappa \) has units of 1/distance. We commonly refer to \( \kappa \) as \( \lambda_D \), the "Debye (screening) length" characterizing the solution.
… Does a more sophisticated model of the double layer better capture features observed experimentally?  

… the electric potential variation near the electrode under the Gouy–Chapman Model (compare with Helmholtz Model…)

\[ \phi = \phi^0 \exp(-\kappa x) \]

\[ \lambda_D = \frac{1}{\kappa} = \sqrt{\frac{\varepsilon_0 kT}{2n_0^0 z^2 e^2}} \]

Figure 13.3.3 Potential profiles through the diffuse layer in the Gouy–Chapman model.

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 13.3.3

… how does the Gouy–Chapman Model do in terms of predicting the correct value of \( C_d \)?

\[ C_d = \frac{\Delta M}{\Delta \phi} = \left( \frac{2\varepsilon_0 \varepsilon_\infty \phi^0}{4T} \right)^{1/2} \cos^{-1} \left( \frac{2\phi_0}{2\phi_0} \right) \]

Figure 13.3.5 Predicted differential capacitance from the Gouy–Chapman theory. Calculated from (13.3.23) for the indicated concentrations of a 1:1 electrolyte in water at 25°C. Note the very restricted potential scale. The predicted capacitance rises very rapidly at more extreme potentials relative to \( E_c \).

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 13.3.5

About G–C Theory we can say the following:

a) it predicts a “dip” in \( C_d \) that becomes more capacitive with increased ionic strength = Good!

b) but it predicts a \( C_d \) that is WAY too high as the potential becomes far from the pzc = Bad!...

c) and the \( C_d \) is symmetrical about the pzc (why?): this is not what is observed experimentally...
Getting close?

... Notably, near the pzc?

**Fig. 5.13** Capacity of a mercury electrode in a KF solution (pzc = -0.433V) with the respective Gouy-Chapman capacity [Paolo Gallino, EPFL thesis].

... example: How thick is the diffuse layer from an electrode in, say, aqueous 0.1 M NaClO₄ solution?

*Answer:* The diffuse layer thickness is approximated by \( \lambda_D \). Let's calculate it.

\[
\lambda_D = \frac{1}{\kappa} = \sqrt{\frac{\varepsilon \varepsilon_0 k T}{2 n' z^2 e^2}}
\]
Example: How thick is the diffuse layer from an electrode in, say, aqueous 0.1 M NaClO$_4$ solution?

Answer: The diffuse layer thickness is approximated by $\lambda_D$.

Let's calculate it.

$$\lambda_D = \frac{1}{\kappa} = \sqrt{\frac{\varepsilon\epsilon_0 kT}{2n^0 z^2 e^2}}$$

$$= \sqrt{\frac{78 \times 8.854 \times 10^{-12} \text{ C}^2 / \text{ J/m})(1.381 \times 10^{-23} \text{ J/K})(298 \text{ K})}{2 \times (100 \times 6.022 \times 10^{23} / \text{ m}^3)(1)^2(1.602 \times 10^{-19} \text{ C})^2}}$$

$$\approx 1 \text{ nm} \ldots \text{about the same thickness as the compact layer}...$$

Wow!

---

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$$= 9.589 \times 10^{-10} \text{ m} = 96 \text{ Å}$$

$$\approx 1 \text{ nm} \ldots \text{about the same thickness as the compact layer}...$$

Wow!
… example: How thick is the diffuse layer from an electrode in, say, aqueous 0.1 M NaClO₄ solution?

### Table 13.3.1  Characteristic Thickness of the Diffuse Layer

<table>
<thead>
<tr>
<th>C⁺(M)</th>
<th>1/κ(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.0</td>
</tr>
<tr>
<td>10⁻¹</td>
<td>9.6</td>
</tr>
<tr>
<td>10⁻²</td>
<td>30.4</td>
</tr>
<tr>
<td>10⁻³</td>
<td>96.2</td>
</tr>
<tr>
<td>10⁻⁴</td>
<td>304</td>
</tr>
</tbody>
</table>

*For a 1:1 electrolyte at 25°C in water.

This means that the electrostatic repulsion between charged colloid particles, for example, is very short range at high electrolyte concentrations… suspensions of these particles frequently precipitate.

Three traditional models for double layer structure:

1) Helmholtz
2) Gouy-Chapman (GC)
3) Gouy-Chapman-Stern (GCS)

… let’s take a look at each…
3) The Gouy–Chapman–Stern Model: basically, the idea is to use both the Helmholtz Model and the Gouy–Chapman Model in series:

\[
\frac{1}{C_D} = \frac{1}{C_H} + \frac{1}{C_D}
\]

Wait a minute! This is modeling just one interface with two sides, but there are two capacitors (and thus in total seemingly four sides)... what gives?
Models of Electrical Double Layer:

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Wait a minute! This is modeling just one interface with two sides, but there are two capacitors (and thus in total seemingly four sides)... what gives?

\[
\frac{1}{C_d} = \frac{1}{C_H} + \frac{1}{C_D}
\]

If it barks like a dog, and smells like a dog, then maybe we should call it a dog...

What are the units?

This means that the electric potential drop across the Helmholtz Layer (inside of the OHP) will be linear, and a quasi-exponential potential drop will extend from this point and into the bulk solution...

... our three models for the potential distribution near a charged electrode immersed in an electrolyte solution...

http://electrochem.cwru.edu/
... History...

Hermann Ludwig Ferdinand von Helmholtz
(1821–1894)

Louis Georges Gouy
(1854–1926)

David Leonard Chapman
(1869–1958)

Otto Stern
(1888–1926)
Nobel Prize (Physics, 1943)

Physician & Physicist

Physicist

P-Chemist

... History...

Physician & Physicist

Physicist

P-Chemist

... History...

Physician & Physicist

Physicist

P-Chemist

... History...

Physician & Physicist

Physicist

P-Chemist

splice a Helmholtz capacitor to a GC capacitor, right here... and then thank Stern!

Figure 13.3.6 (a) A view of the differential capacitance in the Gouy-Chapman-Stern (GCS) model as a series network of Helmholtz-layer and diffuse-layer capacitances. (b) Potential profile through the solution side of the double layer, according to GCS theory. Calculations from (13.3.23) for 10^{-2} M LiCl electrolyte in water at 25°C.

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 13.3.6

... the mathematical details are in B&F, pp. 551–552, but qualitatively, what GCS does is it uses the smaller capacitance of either \( C_H \) or \( C_{D(GC)} \)...

\[
\frac{1}{C_d} = \frac{1}{C_H} + \frac{1}{C_D}
\]

Figure 13.3.7 Expected behavior of \( C_d \) according to GCS theory as the electrolyte concentration changes.
... what effect does specific adsorption have on the pzc? The answer is hinted at in the data that we saw earlier...

... but to really reveal specific adsorption, one must look carefully at the concentration dependence of the pzc. If there is one, then specific adsorption is occurring...

The sign of the shift in pzc is the sign of the ion that is adsorbing...

... for this we define the constant Eisin–Markov coefficient for a given $\sigma_M (= 0)$, as follows:

$$\frac{1}{RT} \left( \frac{\partial E_s}{\partial \ln \sigma_{salt}} \right)_{\sigma_M} = \left( \frac{\partial \Delta E}{\partial \sigma_{salt}} \right)_{\sigma_M}$$

Bockris and Reddy, Plenum Press, 1973, Figure 7.57

... why a negative shift with anion adsorption?

here, I am indicating excess charges, not all charges...

Fig. 7.37. Electrocapillary curves from solutions of different electrolyte (HCl) concentration. The symbol RHE stands for a reversible hydrogen electrode referenced, not in a standard solution, but in the same electrolyte as the electrode under study.
... why a negative shift with anion adsorption?

$\text{pzc -}$

$E_{\text{WE}}$

$\text{(+)}$

$\text{(-)}$

... here, I am indicating excess charges, not all charges...

... why a negative shift with anion adsorption?

... at the pzc, $q_M = 0$ and there is no excess positive or negative charge in the solution...
… now, an adsorbing anion is added and thus a fixed negative charge is added to the solution side of the interface… this new $q_n$ is matched by an equal and opposite $q_M$ on the electrode side…

Result: We are no longer at the pzc at this potential

… a new pzc exists, which is the potential required to neutralize charge, due to charges on both sides of the interface

… but to really reveal specific adsorption, one must look carefully at the concentration dependence of the pzc. If there is one, then specific adsorption is occurring…

The sign of the shift in pzc is the sign of the ion that is adsorbing…

… for this we define the constant Esin–Markov coefficient for a given $\sigma$ (= 0), as follows:

$$\frac{1}{RT} \left( \frac{\partial E_c}{\partial \ln \sigma_{ab}} \right)_{\sigma=0} = \left( \frac{\partial E_c}{\partial \sigma_{ab}} \right)_{\sigma=0}$$

Bockris and Reddy, Plenum Press, 1973, Figure 7.5
... a new pzc exists, which is the potential required to neutralize charge, due to charges on both sides of the interface... specific adsorption!

Figure 13.3.8  Cathode potential profiles in the double layer for mercury in contact with 0.1 M NaCl at 29°C. Potential given with respect to the PZC in NaCl. In positive direction towards the mercury-glass junction. Heavily distorted because chloride is specifically adsorbed. Hydrated with ammonia. From B. C. Grahame, Chem. Rev., 41, 441 (1947). Copyright 1947, American Chemical Society.

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 13.3.8

... what about uncharged adsorbates, like organic molecules?


Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 13.9.1

... what about uncharged adsorbates, like organic molecules?

Figure 13.9.2  Differential capacitance curves corresponding to the systems of Figure 13.9.1. (Reprinted with permission from B. C. Grahame, Chem. Rev., 41, 441 (1947). Copyright 1947, American Chemical Society.)

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 13.9.2
… what about uncharged adsorbates, like organic molecules?

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 13.9.2

Figure 13.9.2 Differential capacitance curves corresponding to the systems of Figure 13.9.1. [Reprinted with permission from D. C. Grahame, J. Chem. Soc., 41, 44 (1947). Copyright 1947, American Chemical Society.]

what is the origin of these sharp \( C_d \) peaks?

… Gunk is blocking ~80% of surface!

what is the origin of these sharp \( C_d \) peaks?

… Gunk could be redox-active... and whose capacitance is called the chemical, or quantum, capacitance...
In conclusion, with the GCS Model we have a semi-quantitative understanding of this interface with some predictive power…

Q: What was in this set of lectures?
A: B&F Chapter 13 main concepts:

- Section 1.2.3: Double layer structure
- Sections 13.1 & 13.2: Gibbs adsorption isotherm; Electrocapillary / Surface excess / Lippmann’s equation; Point of Zero Charge
- Section 13.3: Models: Helmholtz, Gouy–Chapman (Poisson–Boltzmann), GC–Stern
- Section 13.5: Specific adsorption

Now what about starting with this behavior…

... plus adding in Faradaic charge-transfer reaction kinetics?!?!?!

... Oh yeah!! ...

... Now we're talking!
Q: What’s in this set of lectures?
A: B&F Chapter 3 main concepts:

- Sections 3.1 & 3.6: Homogeneous Electron-Transfer (Arrhenius, Eyring, TST (ACT), Marcus Theory)
- Sections 3.2, 3.3, 3.4 & 3.6: Heterogeneous ET (Butler–Volmer Eq, Tafel Eq, Volcano Plot, Gerischer Theory, Quantum Mechanical Tunneling)
- Section 3.5: Multistep ET Mechanisms

RECALL… since the continuity of mass equation is “better than” the conservation of mass law, and it is highly relevant to electrochemistry and in fact all science and engineering fields, we better know it…

… it is introduced to most undergraduate students studying chemical engineering, materials science, and physics, but only partially to chemists (first half) and mechanical engineers (second half)…

… anyway, here it is for species A along dimension x… Enjoy!

\[ \frac{\partial c_A}{\partial t} = \sum_i R_{A,i} - \frac{\partial N_A}{\partial x} \]

https://en.wikipedia.org/wiki/Continuity_equation

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\[ \frac{\partial c_A}{\partial t} = \sum_i R_{A,i} - \frac{\partial N_A}{\partial x} \]

rate of change of the (concentration of species A with respect to (time)
rate of change of the (mass action of the laws that effect species A, e.g. \( k_i[A][B] \))
rate of change of the (flux (\(N\)) of species A with respect to position (x))

… differences in chemical potential, \( \mu \), drive (Reactions… differences in electrochemical potential, \( \mu \), drive volumetric fluxes (RBCs)

https://en.wikipedia.org/wiki/Continuity_equation
From transition state theory (TST) (activated complex theory (ACT)), the standard Gibb’s free energy of activation, $\Delta G^\ddagger$ is defined as... and there is something really neat about ET rxns!

... Marcus Theory... the idea...

- Has anyone ever told you that the overall thermodynamics of a reaction are not related to the kinetics of the reaction? ... Well, this is not true for (at least) electron-transfer reactions!

- What we know
  - KINETICS: Kinetics of a reaction are dependent on the activation energy, and temperature, by the empirical Arrhenius equation... and are related to the free energy of the transition state by the Eyring equation and transition-state theory (activated-complex theory):
    \[ k_{ET} = A e^{-\frac{\Delta G^\ddagger}{RT}} \]
    \[ k_{ET} = \frac{A}{B} e^{-\frac{\Delta E}{RT}} \]
  - THERMODYNAMICS: A reaction is favorable if the $\Delta G$ is negative, and thus $\Delta E$ is positive

• Has anyone ever told you that the overall thermodynamics of a reaction are not related to the kinetics of the reaction? Well, this is not true for (at least) electron-transfer reactions!

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    \[ k_{ET} = A e^{-\frac{E_A}{RT}} \]
    \[ k_{ET} = \kappa \kappa^* T \frac{\exp}{\exp} \frac{\Delta G^*}{RT} \]

• THERMODYNAMICS: A reaction is favorable if the \( \Delta G \) is negative, and thus \( \Delta G (E_{cell}) \) is positive

• What is new
  The kinetics of an electron-transfer reaction (\( k_{ET} \)) are dependent on the driving force for the overall reaction (i.e. \( \Delta G^0 (\Delta E^0, E_{cell}) \))
  Marcus Theory (Nobel Prize in Chemistry in 1992)

Rudy asked: For an electron-transfer event, how does one satisfy the Franck-Condon principle and the conservation of energy?

• Franck-Condon principle: Nuclei are fixed during electron-transfer between orbitals (IUPAC Gold Book); Born-Oppenheimer approximation is relevant

• Minor assumptions to go from internal (potential) energy to free energy (\( \Delta G = \Delta H - T \Delta S \))

• Three regions of electron transfer
  • (I) Normal, (II) Barrierless, (III) Inverted

Marcus Theory... the idea...
• Minor assumptions to go from internal (potential) energy to free energy
  \( \Delta G = \Delta H - T \Delta S \)
• Three regions of electron transfer
  1. (I) Normal, (II) Barrierless, (III) Inverted

  The nuclear reorganization energy, \( \lambda \), is the free energy required to reorganize the solvent (outer) and bonds (inner) when the electron moves from the reactant to product energy potential energy well... but at the nuclear arrangement of the reactant and for \( \Delta G = 0 \)

\[
\lambda = \frac{2\pi}{h} |H_{ab}|^2 \sqrt{\frac{1}{4\pi \hbar^2 m_b \alpha}} \exp \left( \frac{\lambda + \Delta G^0}{4\Delta G^0} \right)
\]

Closs & Miller, Science, 1988, 240, 440


… Marcus Theory... Experimental Confirmation!
Phenomenological electrochemical kinetics:

**The Butler–Volmer Reaction (current as a function of potential)**

Derivation... start with the generic reaction:

\[ \text{O} + \text{n} \text{e}^- \overset{k_b}{\longrightarrow} \text{R}^{n-} \]

the rate of the forward and backward reactions are:

\[ v_f = k_f C_{O}(0, t) = \frac{-i_c}{nF} \]
\[ v_b = k_b C_{R}(0, t) = \frac{i_a}{nF} \]

The units of \( v \) are moles \( \text{cm}^{-2} \text{s}^{-1} \), and that means \( k_f \) and \( k_b \) have units of...

The concentration of \( R \) at the electrode surface \((x = 0)\) as a function of time
the overall reaction rate, \( v_{\text{net}} \), will therefore be given by the difference between the forward and backward rates:

\[
v_{\text{net}} = v_f - v_b = k_f C_O(0, t) - k_b C_R(0, t) = \frac{-i}{nFA}
\]

or, in terms of the current:

\[
i = i_c - i_a = nFA[k_f C_O(0, t) - k_b C_R(0, t)]
\]

next we need expressions for \( k_f \) and \( k_b \) in terms of \( \eta = (E - E_{eq}) \)…

Again, from transition state theory (TST) (activated complex theory (ACT)), the standard Gibb’s free energy of activation, \( \Delta G^\ddagger \) is defined as…
... and here is the effect of electrode potential on the product and reactant free energy (Marcus) curves (Not inverted)...

\[ E = E_{eq} \]
\[ E < E_{eq} \]
\[ E > E_{eq} \]

Here's a thought experiment that gets us an expression for \( k_f \):

What happens to \( \Delta G^c \) and \( \Delta G^a \) when the potential is changed by \( E \)?

* Marcus Theory

\[ \text{Reaction coordinate} \]
Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 3.3.2

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\[ \text{Reaction coordinate} \]
Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 3.3.2
here's a thought experiment that gets us an expression for $k_f$:

What happens to $\Delta G^\circ$ and $\Delta G_{a}$ when the potential is changed by $E$?

1) "O" is stabilized (i.e. lowered) by $FE$...

2) ... and the barrier height decreased by $(1 - \alpha)FE$...

3) ... the net change in the cathodic barrier is the difference:

$$FE - \alpha FE = \alpha FE$$

NOTE: It's positive; the cathodic barrier became larger (to the right)
here's a thought experiment that gets us an expression for \( k_f \):

What happens to \( \Delta G_c^\ddagger \) and \( \Delta G_a^\dagger \) when the potential is changed by \( E \)?

1) \( \cdot \circ \) is stabilized (i.e. lowered) by \( F(E - E_0^\ddagger) \)
2) \( \cdot \) and the barrier height decreased by \( (1 - \alpha)F(E - E_0^\ddagger) \)
3) \( \cdot \) the net change in the cathodic barrier is the difference:
   \( F(E - E_0^\ddagger) - (1 - \alpha)F(E - E_0^\ddagger) = \alpha F(E - E_0^\ddagger) \)
   
   NOTE: It's positive; the cathodic barrier became larger (to the right)
4) \( \cdot \) and the anodic barrier just decreased by \( (1 - \alpha)F(E - E_0^\ddagger) \) (to the left)...