Lecture #15 of 26
Time-Dependence in Electrochemistry

Chapters 4 and 5
Q: What’s in this set of lectures?
A: B&F Chapters 4 & 5 main concepts:

- Section 4.4.2: Fick’s Second Law of Diffusion
- Section 5.1: Overview of step experiments
- Section 5.2: Potential step under diffusion controlled
- Sections 5.3 & 5.9: Ultramicroelectrodes
- Sections 5.7 – 5.8: Chronoamperometry/Chronocoulometry
Looking forward... Section 4.4.2 and Chapter 5

- Fick’s Second Law of Diffusion
- Linear Diffusion = time-dependent current (Cottrell Equation)
- Anson Plots for surface adsorbed species
- Radial Diffusion = time-independent current (at steady-state)
- Ultramicroelectrodes (UMEs)
- Scanning Electrochemical Microscopy (SECM)
- Single molecule electrochemistry
Bard and scanning electrochemical microscopy (SECM)...

http://electrochem.cwru.edu/ed/encycl/art-m04-microscopy.htm
Fig. 5. Substrate imaging. (A) Tip is maintained at constant height while scanning horizontally. (B) SECM image of a portion (1 μm x 1 μm) of a human breast cell membrane acquired with a 47 nm radius ultramicroelectrode.

http://electrochem.cwru.edu/ed/encycl/art-m04-microscopy.htm
Fig. 7. (A) 80 μm × 80 μm atomic force microscopy image of a disk-like region of boron-doped diamond. (B) SECM image over such a region.
Electrochemical Detection of Single Molecules

Fu-Ren F. Fan and Allen J. Bard*

The electrochemical behavior of a single molecule can be observed by trapping a small volume of a dilute solution of the electroactive species between an ultramicroelectrode tip with a diameter of \( \sim 15 \) nanometers and a conductive substrate. A scanning electrochemical microscope was used to adjust the tip-substrate distance (\( \sim 10 \) nanometers), and the oxidation of \([[\text{trimethylammonio}]\text{methyl}]\) ferrocene \((\text{Cp}_2\text{FeTMA}^+)\) to \(\text{Cp}_2\text{FeTMA}^{2+}\) was carried out. The response was stochastic, and anodic current peaks were observed as the molecule moved into and out of the electrode-substrate gap. Similar experiments were performed with a solution containing two redox species, ferrocene carboxylate \((\text{Cp}_2\text{FeCOO}^-)\) and \(\text{Os(bpy)}_3^{2+}\) (bpy is 2,2'-bipyridyl).

**Fig. 1.** Idealized schematic illustration of the tip geometry and the tip-substrate configuration used.
the magic of “thin layer electrochemistry”...

\[ J_i(x) = -D_i \frac{C_o^* - C_o(x = 0)}{\partial_o} \]

... Recalling Section 1.4.2 (Semi-Empirical)
A feasibility assessment... 1 molecule is trapped within a 1 µm x 1 µm x 10 nm volume between an SECM tip and a surface. What’s the value of the limiting current?

\[ i = -nFAD \frac{\Delta C}{\delta} \]

\[ C_{1 \text{ molecule}} = (1 \text{ molecule}) \left( \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ molecules}} \right) \left( \frac{1}{(10 \times 10^{-7} \text{ cm})(1 \times 10^{-4} \text{ cm})^2} \right) \]

\[ C_{1 \text{ molecule}} = 1.66 \times 10^{-10} \text{ mol/cm}^3 \]
A feasibility assessment... 1 molecule is trapped within a 1 µm x 1 µm x 10 nm volume between an SECM tip and a surface. What’s the value of the limiting current?

\[ i = -nFAD \frac{\Delta C}{\delta} \]

\[ i = (1 \text{ eq/mol})(96485 \text{ C/eq})(1 \times 10^{-4} \text{ cm})^2(1 \times 10^{-5} \text{ cm}^2/\text{s}) \left( \frac{1.66 \times 10^{-10} \text{ mol/cm}^3}{10 \times 10^{-7} \text{ cm}} \right) \]

\[ = 1.6 \times 10^{-12} \text{ A} = 1.6 \text{ pA} \]

... so we’re talking about pA's. We can measure that!
Fig. 2. Dependence of tip current on relative tip displacement over a conductive ITO substrate in a solution containing 2 mM Cp₂FeTMA⁺ and 2.0 M NaNO₃. The ITO substrate was biased at −0.3 V versus SCE and the tip was biased at 0.55 V, where the redox reactions on both electrodes were diffusion-controlled. The tip moved to the substrate surface at a rate of 30 Å/s. The data were 300 points averaged at each location. The significance of points A, B, and E is discussed in the text. See also Fig. 4.
Q: What *was* in this set of lectures?
A: B&F Chapters 4 & 5 main concepts:

- Section 4.4.2: Fick’s Second Law of Diffusion
- Section 5.1: Overview of step experiments
- Section 5.2: Potential step under diffusion controlled
- Sections 5.3 & 5.9: Ultramicroelectrodes
- Sections 5.7 – 5.8: Chronoamperometry/Chronocoulometry
A detailed review of Section 4.4.2 and Chapter 5

- Fick’s Second Law of Diffusion
- **Linear Diffusion** = time-dependent current (Cottrell Equation)
- Anson Plots for surface adsorbed species
- **Radial Diffusion** = time-independent current (at steady-state)
- Ultramicroelectrodes (UME)
- Scanning Electrochemical Microscopy (SECM)
- Single molecule electrochemistry
Liquid-Junction Potentials

Chapter 2
Q: What’s in this set of lectures?
A: B&F Chapter 2 main concepts:

- “Section 2.1”: Salt; Activity; Underpotential deposition
- Section 2.3: Transference numbers; Liquid-junction potentials
- Sections 2.2 & 2.4: Donnan potential; Membrane potentials; pH meter; Ion-selective electrodes
Refresher... the equilibrium potential and the Nernst Equation

$$\text{O} + n\text{e}^- \rightleftharpoons \text{R}$$

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

- activity of R
- activity of O

the standard potential
*(look it up in the back of your book or in the CRC table)*

... the activity is the product of the activity coefficient and the concentration...

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

$$E = E^0 - \frac{RT}{nF} \ln \frac{\gamma_R}{\gamma_O} - \frac{RT}{nF} \ln \frac{C_R}{C_O}$$
Refresher... the equilibrium potential and the Nernst Equation

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

\[E^0\]

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

the formal potential... this depends on the identity and concentration of all ionizable species present in solution
However, equilibrium “constants”... are not constants...

Fig. 10-1, p. 268 in Skoog & West
... let’s focus on the solubility of \( \text{BaSO}_4 \)...

\[
\text{BaSO}_4(s) \rightleftharpoons \text{SO}_4^{2-}(aq) + \text{Ba}^{2+}(aq)
\]

\[
K_{sp} = \frac{A_{\text{SO}_4^{2-}} A_{\text{Ba}^{2+}}}{A_{\text{BaSO}_4}} \approx A_{\text{SO}_4^{2-}} A_{\text{Ba}^{2+}}
\]

\( A \) (activity) = 1.0 for any pure solid compound in its standard state at room temperature
\[ \text{BaSO}_4(s) \rightleftharpoons \text{SO}_4^{2-}(aq) + \text{Ba}^{2+}(aq) \quad K_{sp} = \frac{A_{\text{SO}_4^{2-}} A_{\text{Ba}^{2+}}}{A_{\text{BaSO}_4}} \approx A_{\text{SO}_4^{2-}} A_{\text{Ba}^{2+}} \]

\[ K_{sp} = \gamma_{\text{SO}_4^{2-}} \left[ \text{SO}_4^{2-} \right] \gamma_{\text{Ba}^{2+}} \left[ \text{Ba}^{2+} \right] \]

the activity coefficient for \( \text{SO}_4^{2-} \)

the concentration of \( \text{SO}_4^{2-} \)
... let’s focus on the solubility of $\text{BaSO}_4$...

$$\text{BaSO}_4(s) \rightleftharpoons \text{SO}_4^{2-}(aq) + \text{Ba}^{2+}(aq)$$

$$K_{sp} = \frac{A_{\text{SO}_4^{2-}} A_{\text{Ba}^{2+}}}{A_{\text{BaSO}_4}} \approx A_{\text{SO}_4^{2-}} A_{\text{Ba}^{2+}}$$

$$K_{sp} = \gamma_{\text{SO}_4^{2-}} \left[ \text{SO}_4^{2-} \right] \gamma_{\text{Ba}^{2+}} \left[ \text{Ba}^{2+} \right]$$

the *thermodynamic* equilibrium constant

$$K_{sp}' = \frac{K_{sp}}{\gamma_{\text{SO}_4^{2-}} \gamma_{\text{Ba}^{2+}}} = \left[ \text{SO}_4^{2-} \right] \left[ \text{Ba}^{2+} \right]$$

the *concentration* equilibrium constant
... the greater the charge on an ion, the greater the **depression** of its activity coefficient by an inert salt...

... so, for NaCl, what is $I$? [NaCl]!

Ionic strength, $I = 0.5(z_A^2[A] + z_B^2[B] + z_C^2[C] + ...)$

Fig. 10-3, p. 272 in Skoog & West
... the greater the charge on an ion, the greater the *depression* of its activity coefficient by an inert salt... but at high concentration, this trend flips!

**Fig. 2.18.** Schematic of the observed trend of $\gamma_\pm$ versus $\sqrt{c}$ curve for salts showing a minimum.
... let’s focus on the solubility of BaSO₄...

$$\text{BaSO}_4(s) \rightleftharpoons \text{SO}_4^{2-}(aq) + \text{Ba}^{2+}(aq) \quad K_{sp} = \frac{A_{\text{SO}_4^{2-}} A_{\text{Ba}^{2+}}}{A_{\text{BaSO}_4}} \approx A_{\text{SO}_4^{2-}} A_{\text{Ba}^{2+}}$$

$$K_{sp} = \gamma_{\text{SO}_4^{2-}} \left[ \text{SO}_4^{2-} \right] \gamma_{\text{Ba}^{2+}} \left[ \text{Ba}^{2+} \right]$$

$$K_{sp}' = \frac{K_{sp}}{\gamma_{\text{SO}_4^{2-}} \gamma_{\text{Ba}^{2+}}} = \left[ \text{SO}_4^{2-} \right] \left[ \text{Ba}^{2+} \right]$$

... but what are these values? That is, how do we calculate them... ... and why do they depend on the concentration of salt?
... in all three of these cases, \( K' > K \), at not too large of an ionic strength.

![Chemical reactions and equilibrium equations](image)

**General Observation:** \( K' \) always shifts (from \( K \)) to favor the **most ionic state** of the equilibrium.
Refresher... the equilibrium potential and the Nernst Equation

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

**Question:** How, qualitatively, is the equilibrium potential for Fe\(^{2+}/\text{Fe}^{3+}\) affected by the addition of a supporting electrolyte, KF, at a concentration of 0.1 M?

\[ \text{Fe}^{3+} + 1\text{e}^- \Leftrightarrow \text{Fe}^{2+} \]
Refresher... the equilibrium potential and the Nernst Equation

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

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\[ \text{Fe}^{3+} + \text{1e}^- \rightleftharpoons \text{Fe}^{2+} \]

\[ E = E^0 - \frac{RT}{nF} \ln \frac{\gamma_R}{\gamma_O} - \frac{RT}{nF} \ln \frac{C_R}{C_O} \]
Refresher... the equilibrium potential and the Nernst Equation

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\[ \text{Fe}^{3+} + \text{1e}^- \rightleftharpoons \text{Fe}^{2+} \]

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

... now, \( \gamma_{\text{Fe}^{3+}} < \gamma_{\text{Fe}^{2+}} \), agreed?...
**Debye–Hückel equation**  
* (in water at 25 °C)  
\[
-\log \gamma_x = \frac{0.51z_x^2\sqrt{I}}{1 + 3.3\alpha_x\sqrt{I}}
\]

\( \alpha = \text{effective diameter of hydrated ion (nm)} \)

---

**Table 10-2**

<table>
<thead>
<tr>
<th>Ion</th>
<th>Activity Coefficient at Indicated Ionic Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \alpha_x, \text{nm} )</td>
</tr>
<tr>
<td>H(_3)O(^+)</td>
<td>0.9</td>
</tr>
<tr>
<td>Li(^+), C(_6)H(_5)COO(^-)</td>
<td>0.6</td>
</tr>
<tr>
<td>Na(^+), IO(_3), HSO(_3), HCO(_3), H(_2)PO(_4), H(_2)AsO(_4), OAc(^-)</td>
<td>0.4–0.45</td>
</tr>
<tr>
<td>OH(^-), F(^-), SCN(^-), HS(^-), ClO(_3), ClO(_4), BrO(_3), IO(_3), MnO(_4)</td>
<td>0.35</td>
</tr>
<tr>
<td>K(^+), Cl(^-), Br(^-), I(^-), CN(^-), NO(_2), NO(_3), HCOO(^-)</td>
<td>0.3</td>
</tr>
<tr>
<td>Rb(^+), Cs(^+), Ti(^+), Ag(^+), NH(_4)</td>
<td>0.25</td>
</tr>
<tr>
<td>Mg(^2+), Be(^2+)</td>
<td>0.8</td>
</tr>
<tr>
<td>Ca(^2+), Cu(^2+), Zn(^2+), Sn(^2+), Mn(^2+), Fe(^2+)</td>
<td>0.6</td>
</tr>
<tr>
<td>Ni(^2+), Co(^2+), Phthalate(^{2-})</td>
<td>0.5</td>
</tr>
<tr>
<td>Sr(^2+), Ba(^2+), Cd(^2+), Hg(^2+), S(^2-)</td>
<td>0.45</td>
</tr>
<tr>
<td>Pb(^2+), CO(_3)^{2-}, SO(_3)^{-}, C(_2)O(_4)^{-}</td>
<td>0.40</td>
</tr>
<tr>
<td>Hg(_2^{2+}), SO(_4^{2-}), S(_2)O(_3^{2-}), Cr(_2^{3-}), HPO(_4^{2-})</td>
<td>0.9</td>
</tr>
<tr>
<td>Al(^3+), Fe(^3+), Cr(^3+), La(^3+), Ce(^3+)</td>
<td>0.4</td>
</tr>
<tr>
<td>PO(_4^{3-}), Fe(CN)(_6^{3-})</td>
<td>1.1</td>
</tr>
<tr>
<td>Th(^4+), Zr(^4+), Ce(^4+), Sn(^4+)</td>
<td>0.5</td>
</tr>
</tbody>
</table>


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Table 10-2, p. 274 in Skoog & West
Debye–Hückel equation
(in water at 25 °C)

\[-\log \gamma_x = \frac{0.51z_x^2 \sqrt{I}}{1 + 3.3\alpha_x \sqrt{I}}\]

\(\alpha = \text{effective diameter of hydrated ion (nm)}\)

... the derivation is long... but the main idea is that you balance thermal motion (Boltzmann) with electrostatics (Poisson/Gauss)...

Physicist & P-Chemist

Peter Joseph William Debye
(1884–1966)

Erich Armand Arthur Joseph Hückel
(1896–1980)

from Wiki
Debye–Hückel equation

\[ \text{(in water at 25 °C)} \]

\[ -\log \gamma_x = \frac{0.51 z_x^2 \sqrt{I}}{1 + 3.3 \alpha_x \sqrt{I}} \]

\( \alpha = \text{effective diameter of hydrated ion (nm)} \)

... the “limiting law” is when \( I \to 0 \) (< 10 mM)...

... and then the Debye–Hückel equation simplifies to just the numerator:

\[ -\log \gamma_x = 0.51 z_x^2 \sqrt{I} \]

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Fig. 3.23. The comparison of the experimentally observed mean activity coefficients of HCl and those that are calculated from the Debye–Hückel limiting law.

Bockris & Reddy, Fig. 3.23
Question: How, qualitatively, is the equilibrium potential for Fe\(^{2+}/\)Fe\(^{3+}\) affected by the addition of a supporting electrolyte, KF, at a concentration of 0.1 M?

\[
\text{Fe}^{3+} + 1\text{e}^- \rightleftharpoons \text{Fe}^{2+}
\]

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

... now, \(\gamma_{\text{Fe}^3+} < \gamma_{\text{Fe}^{2+}}\), agreed?... So...

\[
\frac{\gamma_R}{\gamma_O} > 1.0 \quad \text{and} \quad \ln \frac{\gamma_R}{\gamma_O} > 0
\]

... and we conclude that in the presence of added salt... you tell me!
**Question**: How, qualitatively, is the equilibrium potential for Fe$^{2+}$/Fe$^{3+}$ affected by the addition of a supporting electrolyte, KF, at a concentration of 0.1 M?

Fe$^{3+} + 1e^- \rightleftharpoons$ Fe$^{2+}$

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

no added salt...

\[ \gamma_O \approx \gamma_R \approx 1.0 \]

\[ \ln \frac{\gamma_R}{\gamma_O} \approx 0 \]
Question: How, qualitatively, is the equilibrium potential for Fe$^{2+}$/Fe$^{3+}$ affected by the addition of a supporting electrolyte, KF, at a concentration of 0.1 M?

\[ \text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+} \]

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

\(\gamma_O \approx \gamma_R \approx 1.0\)

\[ \ln \frac{\gamma_R}{\gamma_O} \approx 0 \]

\[ \frac{\gamma_R}{\gamma_O} > 1.0 \quad \text{and} \quad \ln \frac{\gamma_R}{\gamma_O} > 0 \]

\textit{ANSWER:} $E^0'$ shifts to more negative potentials
**Question:** What if the redox species were positive/neutral charged, like $\text{Tl}^{+/0}$, and we increased the concentration of supporting electrolyte to $\sim 0.1$ M?

$$
\text{Tl}^+ + 1e^- \rightleftharpoons \text{Tl}^0
$$

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

**ANSWER:** $E^0$ shifts to more negative potentials.
**Question:** What if the redox species were negatively charged, like $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}/[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$, and we increased the concentration of supporting electrolyte to $\sim0.1\text{ M}$? *(FROM e-LAB!)*

$$[\text{Fe}^{\text{III}}]^{3-} + 1\text{e}^- \rightleftharpoons [\text{Fe}^{\text{II}}]^{4-}$$

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

*with added salt...*

No added salt (note $i_{pc}$ and $iR$)  

$$\frac{\gamma_R}{\gamma_O} < 1.0 \text{ and } \ln \frac{\gamma_R}{\gamma_O} < 0$$

**Answer:** $E^0$ shifts to more positive potentials
... practical “activity”... even of solids!  Underpotential deposition (UPD)  

\[ \text{Co}^{2+} + 2e^- \rightleftharpoons \text{Co}^0 \]  

\[ E_{eq} \]  

... \( a_{\text{Co(s)}} < 1 \) ... because the activity of a solid is proportional to its surface coverage!

\[ \text{Co}^0 \rightleftharpoons \text{Co}^{2+} + 2e^- \]  

... but what are these small cathodic current "bumps" that occur at \( E_{\text{app}} > E_{eq} \)?

B&F, pg. 420
Underpotential deposition (UPD) ... practical “activity” ... even of solids! ... $a_{\text{Co(s)}} < 1$ ... because the activity of a solid is proportional to its surface coverage!

Co$^0 \rightleftharpoons$ Co$^{2+} + 2e^-$

B&F, pg. 420