Lecture #12 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
We use both of Fick’s laws of diffusion to derive equations for time-dependent (not steady-state) transport-controlled electrochemistry...

\[ -J_0(x, t) = D_0 \frac{\partial C_0(x, t)}{\partial x} \]

B&F, pg. 149

... but taking baby steps toward the Cottrell equation... conceptually, one can derive Fick’s law in a manner similar to how we thought about the diffusion coefficient... grab your favorite beverage and go on a walk!

\[ i(t) = i_d(t) = \frac{nFAD_0^{1/2}C_0^*}{\pi^{1/2}t^{1/2}} \]

... and here’s the conclusion of that derivation... the Cottrell Equation
We use both of Fick’s laws of diffusion to derive equations for time-dependent (not steady-state) transport-controlled electrochemistry...

Fick’s 1st Law of Diffusion:

\[-J_O(x, t) = D_O \frac{\partial C_O(x, t)}{\partial x}\]

This is the net flux (correct dimensions)...
... with half moving right and half moving left

B&F, pg. 149
We use both of Fick’s laws of diffusion to derive equations for time-dependent (not steady-state) transport-controlled electrochemistry...

**Fick’s 1st Law of Diffusion:**

\[-J_O(x, t) = D_O \frac{\partial C_O(x, t)}{\partial x}\]

\[J_O(x, t) = \frac{1}{A} \left( \frac{N_O(x)}{2} - \frac{N_O(x + \Delta x)}{2} \right) \frac{\Delta x^2}{\Delta t} \]

\[-J_O(x, t) = \frac{\Delta x^2}{2\Delta t} \frac{C_O(x + \Delta x) - C_O(x)}{\Delta x}\]

Recall... \[\Delta^2 = ml^2 = \frac{t}{\tau} l^2 = 2D t\]... derived!
We use both of Fick’s laws of diffusion to derive equations for time-dependent (not steady-state) transport-controlled electrochemistry...

Fick’s 1st Law of Diffusion:

\[-J_0(x, t) = D_O \frac{\partial C_O(x, t)}{\partial x}\]

B&F, pg. 149

Fick’s 2nd Law of Diffusion:

\[\frac{\partial C_O(x, t)}{\partial t} = D_O \left( \frac{\partial^2 C_O(x, t)}{\partial x^2} \right)\]

... derive this non-steady-state equation (approximately) in a similar fashion as Fick’s first law...
... the derivation is not so bad...

\[
\frac{\partial C_O(x, t)}{\partial t} = D_O \left( \frac{\partial^2 C_O(x, t)}{\partial x^2} \right)
\]

B&F, pp. 149–150

\[
\frac{\partial C_O(x, t)}{\partial t} = \frac{J(x, t) - J(x + dx, t)}{dx}
\]

Figure 4.4.4 Fluxes into and out of an element at \( x \).
... the derivation is not so bad...

\[
\frac{\partial C_O(x, t)}{\partial t} = D_O \left( \frac{\partial^2 C_O(x, t)}{\partial x^2} \right)
\]

B&F, pp. 149–150

\[
\frac{\partial C_O(x, t)}{\partial t} = \frac{J(x, t) - J(x + dx, t)}{dx}
\]

\[
J(x + dx, t) = J(x, t) + \frac{\partial J(x, t)}{\partial x} \cdot dx
\]

\[-J_O(x, t) = D_O \frac{\partial C_O(x, t)}{\partial x} \]

(First Law)

... derived!
The experiment we will model is a potential step experiment...

key points:
- at $E_1$: no reaction ($C_O(x, 0) = C_O^*$)
- at $E_2$: diffusion-controlled reaction ($C_O(0, t) = 0$)

**Figure 5.1.2**  (a) Waveform for a step experiment in which species O is electroinactive at $E_1$, but is reduced at a diffusion-limited rate at $E_2$. (b) Concentration profiles for various times into the experiment. (c) Current flow vs. time.
How to derive expressions for diffusion-controlled current vs. time:

1. Solve Fick’s Second Law to get $C_0(x, t)$, and in the process of doing this, you will use boundary conditions that “customize” the solution for the particular experiment of interest:

$$\frac{\partial C_0(x, t)}{\partial t} = D_0 \left( \frac{\partial^2 C_0(x, t)}{\partial x^2} \right)$$

2. Use Fick’s First Law to calculate $J_0(0, t)$ from $C_0(x, t)$:

$$-J_0(x, t) = D_0 \frac{\partial C_0(x, t)}{\partial x}$$

3. Calculate the time-dependent diffusion-limited current:

$$i = nF A J_0(0, t)$$

... using the... Laplace transform, integration by parts, L’Hôpital’s rule, Schrödinger equation, complementary error function, Leibniz rule, chain rule... Wow! Cool!
Step 1 is the kicker... we’ll use the *Laplace Transform* to solve the linear partial differential equation

The Laplace transform of any function $F(t)$ is:

$$L\{F(t)\} = \int_0^\infty e^{-st}F(t)\,dt$$

how about $F(t) = 1$?

$$L\{1\} = \int_0^\infty e^{-st}(1)\,dt = \left[\frac{e^{-st}}{-s}\right]_0^\infty = 0 - \left(\frac{1}{-s}\right) = \frac{1}{s}$$

how about $F(t) = kt$?

$$L\{kt\} = \int_0^\infty e^{-st}(kt)\,dt = k \int_0^\infty te^{-st}\,dt = k \left(\frac{e^{-st}}{s^2}(-st - 1)\right)_0^\infty$$
how about \( F(t) = kt \)?

\[
L\{kt\} = \int_0^\infty e^{-st} (kt) \, dt = k \int_0^\infty te^{-st} \, dt = k \left( \int_0^\infty \frac{e^{-st}}{s^2} (-st - 1) \right)_{0}^{\infty} = k \left( 0 - \frac{1}{s^2} (-1) \right) = \frac{k}{s^2}
\]

Integrated by parts

Used L’Hôpital’s rule

how about \( F(t) = e^{-at} \)?

\[
L\{e^{-at}\} = \int_0^\infty e^{-st} e^{-at} \, dt = \int_0^\infty e^{-(s+a)t} \, dt = \frac{e^{-(s+a)t}}{-(s+a)} \Bigg|_0^\infty = 0 - \frac{1}{-(s + a)} = \frac{1}{s + a}
\]
OK, now for our case:

\[ F(t) = \frac{\partial C_O(x, t)}{\partial t} - D_O \left( \frac{\partial^2 C_O(x, t)}{\partial x^2} \right) \]

Recall, Second Law:

\[ \frac{\partial C_O(x, t)}{\partial t} = D_O \left( \frac{\partial^2 C_O(x, t)}{\partial x^2} \right) \]
OK, now for our case: \[ F(t) = \frac{\partial C_O(x, t)}{\partial t} - D_O \left( \frac{\partial^2 C_O(x, t)}{\partial x^2} \right) \]

\[ L \left\{ \frac{\partial C_O(x, t)}{\partial t} - D_O \left( \frac{\partial^2 C_O(x, t)}{\partial x^2} \right) \right\} = ? \]

\[ \int_0^\infty e^{-st} D \frac{\partial^2 C(x, t)}{\partial x^2} \, dt = D \frac{\partial^2}{\partial x^2} \int_0^\infty e^{-st} C(x, t) \, dt = D \frac{\partial^2}{\partial x^2} \tilde{C}(x, s) \]

well, wait a second, this term is not so bad...

the Laplace transform of \( C(x, t) \)? ... Isn’t this cheating?

Well, ahem, no!
OK, now for our case:

\[
F(t) = \frac{\partial C_O(x, t)}{\partial t} - D_O \left( \frac{\partial^2 C_O(x, t)}{\partial x^2} \right)
\]

\[
L \left\{ \frac{\partial C_O(x, t)}{\partial t} - D_O \left( \frac{\partial^2 C_O(x, t)}{\partial x^2} \right) \right\} = \text{?}
\]

not so lucky with this term...

\[-D \frac{\partial^2}{\partial x^2} \bar{C}(x, s)\]
and at time = 0, what is the value of \( C \), anywhere? Integration, by parts, again!

\[
\int_{a}^{b} g(x)f'(x) \, dx = [g(x)f(x)]_{a}^{b} - \int_{a}^{b} f(x)g'(x) \, dx
\]

\[
\int_{0}^{\infty} e^{-st} \frac{\partial C_{0}(x, t)}{\partial t} \, dt = \left[ e^{-st} C(x, t) \right]_{0}^{\infty} - \int_{0}^{\infty} C(x, t)(-se^{-st}) \, dx
\]

\[
= 0 - C(x, 0) + s\bar{C}(x, s)
\]

... and at time = 0, what is the value of \( C \), anywhere? ... just \( C^{*} \)!
L.T. of Fick’s 2nd Law...

\[ F(t) = \frac{\partial C_o(x, t)}{\partial t} - D_0 \left( \frac{\partial^2 C_o(x, t)}{\partial x^2} \right) \]

now is turns out that the L.T. of this...

\[ L \left\{ \frac{\partial C_o(x, t)}{\partial t} - D_0 \left( \frac{\partial^2 C_o(x, t)}{\partial x^2} \right) \right\} \]

is this...

\[ s \tilde{C}(x, s) - C^* - D \frac{\partial^2}{\partial x^2} \tilde{C}(x, s) \]

see B&F, pg. 775, for details

Now what? Well, recall these terms are equal to each other (= 0), then rearrange...

... and what does it look like?

our equation:

\[ \frac{d^2 \tilde{C}(x, s)}{dx^2} - \frac{s}{D} \tilde{C}(x, s) = - \frac{C^*}{D} \]

the time-independent Schrödinger Eq. in 1D...

\[ \frac{d^2 \psi(x)}{dx^2} - \frac{2m}{\hbar^2} \left( E - V(x) \right) \psi(x) = 0 \]
the solution of the Schrödinger Eq. in 1D...

\[
\frac{d^2 C(x, s)}{dx^2} - \frac{s}{D} C(x, s) = -\frac{C^*}{D}
\]

... and by analogy, the solution of our equation is:

\[
\psi(x) = A' \exp \left( -\sqrt{2m(E - V(x))} \frac{1}{\hbar} x \right) + B' \exp \left( \sqrt{2m(E - V(x))} \frac{1}{\hbar} x \right)
\]

\[
\bar{C}(x, s) = \frac{C^*}{s} + A'(s) \exp \left( -\sqrt{\frac{s}{D}} x \right) + B'(s) \exp \left( \sqrt{\frac{s}{D}} x \right)
\]
\[
\tilde{C}(x, s) = \frac{C^*}{s} + A'(s) \exp\left(-\sqrt{\frac{s}{D}} x\right) + B'(s) \exp\left(\sqrt{\frac{s}{D}} x\right)
\]

Now, what are \(A'\) and \(B'\) (to simplify), and how do we get rid of the “\(s\)”?

... first, we need some boundary conditions!

1. \(\lim_{x \to \infty} C_0(x, t) = C^*_0\)

called semi-infinite linear (because of \(x\)) diffusion

\[
\lim_{x \to \infty} \tilde{C}(x, s) = \frac{C^*}{s}
\]

What does this do for us?

\[
\tilde{C}(x, s) = \frac{C^*}{s} + A'(s) \exp\left(-\sqrt{\frac{s}{D}} x\right) + B'(s) \exp\left(\sqrt{\frac{s}{D}} x\right)
\]

... and so \(B'\) must be equal to 0
\[ \tilde{C}(x, s) = \frac{C^*}{s} + A'(s) \exp \left( -\sqrt{\frac{s}{D}} x \right) \]

**some more boundary conditions...**

2. \( C(0, t) = 0 \)

\[ \tilde{C}(0, s) = 0 \]

L.T.

What does this do for us?

\[ \tilde{C}(x, s) = \frac{C^*}{s} + A'(s) \exp \left( -\sqrt{\frac{s}{D}} x \right) \]

... and so \( A'(s) = \frac{C^*}{s} \)
now our solution is fully constrained... and we need “t” back!!

\[
\overline{C}_O(x, s) = \frac{C_0^*}{s} - \frac{C_0^*}{s} e^{-\sqrt{s/D_0}x}
\]

inverse L.T. using Table A.1.1 in B&F

\[
e^{-\beta x/s} = \text{erfc}\left[\frac{x}{2(kt)^{1/2}}\right]
\]

where \(\beta = (s/k)^{1/2}\)

\[
C_0(x, t) = C_0^* \left\{ 1 - \text{erfc} \left[ \frac{x}{2(D_0 t)^{1/2}} \right] \right\}
\]
What's efrc?... Well, first of all, what's the error function: erf?

\[ \text{erf}(x) \equiv \frac{2}{\pi^{1/2}} \int_0^x e^{-y^2} dy \]
Now... what’s erf_c?

Complementary Error Function

\[ \text{erfc}(x) \equiv 1 - \text{erf}(x) \]

Gaussian distribution, with mean = 0 and std. dev. = \( \frac{1}{\sqrt{2}} \)
Does this make sense?

\[ C_0(x, t) = C^*_0 \left\{ 1 - \text{erfc} \left( \frac{x}{2(D_0 t)^{1/2}} \right) \right\} \]

\[ C_0(x, t) = C^*_0 \text{erf} \left( \frac{x}{2(D_0 t)^{1/2}} \right) \]

... well, for large \( x \), \( \text{erf} = 1 \) (\( \text{erfc} = 0 \)) and so \( C(x, t) = C^* \) ... Check!

... and for \( x = 0 \), \( \text{erf} = 0 \) (\( \text{erfc} = 1 \)) and so \( C(x, t) = 0 \) ... Check!

... Let’s plot it!
Hey, these look completely reasonable... and they are not exponential!

\[ C^* = 1 \times 10^{-6} \text{ M} \]
\[ D = 0.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \]

\[ C_O(x, t) = C^*_O \text{ erf} \left[ \frac{x}{2(D_O t)^{1/2}} \right] \]

(100 µm)
How large is the diffusion layer? Recall the rms displacement...

<table>
<thead>
<tr>
<th>Dimension</th>
<th>$\bar{\Delta}*$ =</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D</td>
<td>$\sqrt{2Dt}$</td>
</tr>
<tr>
<td>2D</td>
<td>$\sqrt{4Dt}$</td>
</tr>
<tr>
<td>3D</td>
<td>$\sqrt{6Dt}$</td>
</tr>
</tbody>
</table>

The rms displacement

*the rms displacement

In both directions from a...

... plane

... wire, line, tube

... point, sphere, disk

$\bar{\Delta} = \sqrt{2dDt} = \sqrt{\left(\frac{\text{cm}^2}{s}\right)s} = \text{cm}$

$\bar{\Delta} = \sqrt{(2d)Dt}$, where $d$ is the dimension

... and the “2” is for positive and negative directions

a characteristic
“diffusion length”

root mean square (rms) displacement (standard deviation)
Hey, these look completely reasonable for 1D diffusion in one direction!

Why is 52% of the bulk concentration noteworthy?

Plug in $x = (Dt)^{0.5}$!
... Ah ha!

$C^* = 1 \times 10^{-6} \text{ M}$

$D = 0.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$

$C_O(x, t) = C^*_O \text{ erf} \left[ \frac{x}{2(D_O t)^{1/2}} \right]$}

$\sqrt{Dt} = 2.2 \mu m$

... use the geometric area for calculations
OK... that’s Step #1... Whoa! That was deep!... The last two steps are not...

1. Solve Fick’s Second Law to get $C_0(x, t)$, and in the process of doing this, you will use boundary conditions that “customize” the solution for the particular experiment of interest:

$$\frac{\partial C_0(x, t)}{\partial t} = D_0 \left( \frac{\partial^2 C_0(x, t)}{\partial x^2} \right)$$

2. Use Fick’s First Law to calculate $J_0(0, t)$ from $C_0(x, t)$:

$$-J_0(x, t) = D_0 \frac{\partial C_0(x, t)}{\partial x}$$

3. Calculate the time-dependent diffusion-limited current:

$$i = nF A J_0(0, t)$$
... now Step #2...

\[-J_O(x, t) = D_O \frac{\partial C_O(x, t)}{\partial x}\]  

(Fick’s First Law)

... but we just derived \(C_O(x, t)\):

\[C_O(x, t) = C_O^* \text{ erf} \left[ \frac{x}{2(D_O t)^{1/2}} \right]\]

... and so we need to evaluate:

\[-J_O(x, t) = D_O \frac{\partial}{\partial x} \left[ C_O^* \text{ erf} \left( \frac{x}{2\sqrt{D_O t}} \right) \right]\]
\[-J_0(x, t) = D_0 \frac{\partial}{\partial x} \left[ C^* \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right] \]

... we use the **Leibniz rule**, to get \( \frac{d}{dx}(\text{erf}(x)) \) as follows:

\[
\frac{d}{dx} \text{erf}(x) = \frac{2}{\pi^{1/2}} \frac{d}{dx} \int_0^x e^{-y^2} \, dy = \frac{2}{\pi^{1/2}} e^{-x^2}
\]

... and using this in conjunction with the chain rule, we get:

\[-J_0(x, t) = D_0 C^* \left( \frac{1}{2\sqrt{D_0 t}} \right) \frac{2}{\sqrt{\pi}} \exp \left( \frac{-x^2}{4D_0 t} \right) \]

... and when \( x = 0 \) (at the electrode), we get:

\[-J_0(0, t) = C^* \frac{D_0}{\sqrt{\pi t}} \]

... which is what we needed for Step #3...
1. Solve Fick’s Second Law to get $C_0(x, t)$, and in the process of doing this, you will use boundary conditions that “customize” the solution for the particular experiment of interest:

\[
\frac{\partial C_0(x, t)}{\partial t} = D_0 \left( \frac{\partial^2 C_0(x, t)}{\partial x^2} \right)
\]

2. Use Fick’s First Law to calculate $J_0(0, t)$ from $C_0(x, t)$:

\[
-J_0(x, t) = D_0 \frac{\partial C_0(x, t)}{\partial x}
\]

3. Calculate the time-dependent diffusion-limited current:

\[
i = nFAJ_0(0, t)
\]
... and finally, Step #3 using Step #2...

\[-J_0(0, t) = C^* \sqrt{\frac{D_0}{\pi t}}\]

... and with \(i = nFAJ_0(0, t)\)...

\[i(t) = i_d(t) = \frac{nFAD_0^{1/2}C^*_0}{\pi^{1/2}t^{1/2}}\]

the Cottrell Equation

Frederick Gardner Cottrell, in 1920

\(b.\) January 10, 1877, Oakland, California, U.S.A.
\(d.\) November 16, 1948, Berkeley, California, U.S.A.

... established Research Corporation for Science Advancement in 1912

... initial funding from profits on patents for the electrostatic precipitator, used to clear smokestacks of charged soot particles
Cottrell, then at UC Berkeley, invented the *electrostatic precipitator* used to clear smokestacks of charged soot particles...

http://en.wikipedia.org/wiki/Electrostatic_precipitator
http://en.wikipedia.org/wiki/Corona_discharge
Air Pollution Control Innovations

Wet electrostatic precipitator technology

Posted by Ron Patterson on Fri, Jul 10, 2009 @ 03:10 PM

In 1824, the German mathematician M. Hohfeld described the removal of particles from gas streams by electrical forces. However, it was almost a century later when Dr. Frederick G. Cottrell at the University of California, Berkeley commercialized the technology by building the first wet electrostatic precipitator.

A wet electrostatic precipitator uses electrical forces to move particles entrained in a gas stream onto collection surfaces. Electrodes in the wet electrostatic precipitator are held at high voltage which creates a corona discharge. Particles receive an electrical charge as they pass through the corona. The charged particles then follow electric field lines from the charging electrodes to collection surfaces, where they are removed from the gas stream.

Dr. Cottrell applied wet electrostatic precipitator technology to the removal of sulfuric acid mist and lead oxide dust emitted from various acid-making and smelting activities. At the time, vineyards in Northern California were being adversely affected by the lead emissions. Dr. Cottrell's innovative wet electrostatic precipitator solved their problem.

Fast forward to the 2000's. Envitech brought the control of lead and sulfur dioxide to a new level by installing our most advanced wet electrostatic precipitator technology on a secondary lead smelting facility in Southern California. The resulting wet electrostatic precipitator system which removes both sulfur dioxide and lead particles is said to set a new standard in air emission control at lead smelting facilities worldwide.

With over thirty years in the industry, we wanted to start sharing the knowledge and expertise that we have gained from cleaning gas streams of unwanted contaminants. Look for future postings that examine various aspects of state-of-the-art air pollution control technologies.

Tags: wet electrostatic precipitators
... OK, so what does it predict?

\[ i(t) = i_d(t) = \frac{nFAD_{O}^{1/2}C_{O}^*}{\pi^{1/2}t^{1/2}} \]

the Cottrell Equation

\[ D = 1.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \]

\[ D = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \]
... OK, so what does it predict?

The Cottrell Equation

\[ i(t) = i_d(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}} \]

Plot data like this only for visualization purposes, and not for fitting the data as your statistics and thus best-fit values will be affected and incorrect.

\( D = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \)

\( D = 1.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \)

(long time) (short time)
... OK, so what does it predict?

\[ i(t) = i_d(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}} \]

the Cottrell Equation

- (long time)
- (short time)

slope = \( nFA\pi^{-1/2}D^{1/2}C^* \)
... use the Cottrell Equation to measure $D$, such as in thin films/coatings!

... but what are the problems with this approach?

The Cottrell Equation

$$i(t) = i_d(t) = \frac{nFAD_O^{1/2}C^*_O}{\pi^{1/2}t^{1/2}}$$

1) Huge initial currents... beware of compliance current!
2) Noise.
3) $RC$ time limitations decrease expected current at really short times.
4) Roughness factor increases expected current at short times.
5) Adsorbed (electrolyzable) gunk increases expected current at short times.
6) Convection, “edge effects,” and thin pathlengths impose a “long” time limit to these types of experiments.

... Solution: Integrate the Cottrell equation with respect to time...

The integrated Cottrell Equation

$$Q_d = \frac{2nFAD_O^{1/2}C^*_O t^{1/2}}{\pi^{1/2}}$$