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...

**Fick’s 1st Law of Diffusion:**

\[-J(x, t) = D \frac{\partial C(x, t)}{\partial x}\]

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!

\[i(t) = \frac{niFADx}{\pi^{1/2}t^{1/2}}\]

... 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:**

\[-J(x, t) = D \frac{\partial C(x, t)}{\partial x}\]

B&F, pg. 149

\[N(x) - \frac{N(x + \Delta x)}{\Delta t}\]

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

\[-J_Q(x, t) = D_O \frac{\partial C_Q(x, t)}{\partial x}\]

\[\begin{array}{c}
\text{Recall... } \\
\Delta^2 = m t^2 = \frac{1}{4} \Delta^2 = 2D t
\end{array}\]

Fick's 1st Law of Diffusion:

\[-J_Q(x, t) = D_O \frac{\partial C_Q(x, t)}{\partial x} \]

B&F, pg. 149

Fick's 2nd Law of Diffusion:

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

... derive this non-steady-state equation (approximately) in a similar fashion as Fick's first law...

... the derivation is not so bad...

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

B&F, pp. 149–150

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

\[\Delta x \]

\[J_1(x, t) \rightarrow J_2(\Delta x, t) \]

Figure 4.44: 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

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

\[\begin{align*}
-J_O(x, t) &= D_O \frac{\partial C_O(x, t)}{\partial x} \quad \text{[First Law]} \\
&\quad \text{... derived!}
\end{align*}\]

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 8.1.2](image)

(a) Waveform for a step experiment in which species O is electroactive at $E_1$, but is reduced at a diffusion-controlled 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 $C_O(x, t)$, and in the process of doing this, you will use boundary conditions that “customize” the solution for the particular experiment of interest:

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

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

\[\begin{align*}
-J_O(x, t) &= D_O \frac{\partial C_O(x, t)}{\partial x} \\
i &= nFAlO(0, t)
\end{align*}\]

... 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 \( F(t) = kt \)?

\[
L(kt) = \int_0^\infty e^{-st}(kt)\,dt = k \int_0^\infty t e^{-st}dt = k \left[ \frac{e^{-st}(-st - 1)}{s^2} \right]_0^\infty
\]

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

\[
L(e^{-at}) = \int_0^\infty e^{-st}e^{-at}dt = \int_0^\infty e^{-(s+a)t}dt = \left[ \frac{e^{-(s+a)t}}{-s-a} \right]_0^\infty = 0 - \left( \frac{1}{-s-a} \right) = \frac{1}{s+a}
\]

OK, now for our case:

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

Recall, Second Law:

\[
\frac{\partial C_0(x, t)}{\partial t} - D_0 \left( \frac{\partial^2 C_0(x, t)}{\partial x^2} \right)
\]
OK, now for our case:

\[ F(t) = \frac{\partial C(x, t)}{\partial t} - D \frac{\partial^2 C(x, t)}{\partial x^2} \]

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

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

\[ \int_0^\infty e^{-st} D \frac{\partial^2 C(x, t)}{\partial x^2} \, dt = D \frac{\partial^2 \mathcal{L}^{-1} C(x, s)}{\partial x^2} \]

Isn't this cheating? Isn't this cheating? Well, ahem, no!

OK, now for our case:

\[ F(t) = \frac{\partial C(x, t)}{\partial t} - D \frac{\partial^2 C(x, t)}{\partial x^2} \]

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

not so lucky with this term...

\[ -D \frac{\partial^2 \mathcal{L}^{-1} C(x, s)}{\partial x^2} \]

Integration, by parts, again!

\[ \int_a^b g(x) f'(x) \, dx = [g(x) f(x)]_a^b - \int_a^b f(x) g'(x) \, dx \]

\[ \int_0^\infty e^{-st} g(x) \frac{\partial C(x, t)}{\partial t} \, dt \]

\[ g(x) \quad f'(x) \]

\[ = [e^{-st} C(x, t)]_0^\infty - \int_0^\infty C(x, t) (-se^{-st}) \, dx \]

\[ = 0 - C(x, 0) + s \mathcal{L}^{-1} C(x, s) \]

... 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 it 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...
\[ s \overline{C}(x, s) - \overline{C}^* = -D \frac{\partial^2 \overline{C}(x, s)}{\partial x^2} \]

Now what? Well, recall these terms are equal to each other \((= 0)\), then rearrange...
... and what does it look like?

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

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

... and by analogy, the solution of our equation is:
\[ \overline{C}(x, s) = \frac{\overline{C}^*}{s} + A'(s) \exp \left( -\frac{i}{\sqrt{D}} x \right) + B'(s) \exp \left( \frac{i}{\sqrt{D}} x \right) \]

Now, what are \(A'\) and \(B'\) (to simplify), and how do we get rid of the “s”?
... first, we need some boundary conditions!

1. \( \lim_{x \to \infty} C_o(x, t) = C^* \)
called semi-infinite linear (because of x diffusion)

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

What does this do for us?
\[ \overline{C}(x, s) = \frac{\overline{C}^*}{s} + A'(s) \exp \left( -\frac{i}{\sqrt{D}} x \right) + B'(s) \exp \left( \frac{i}{\sqrt{D}} x \right) \]
... and so \(B'\) must be equal to 0
some more boundary conditions...

2. \( \mathcal{C}(0, s) = 0 \)

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

What does this do for us?

... and so \( A'(s) = -\frac{C^*}{s} \)

now our solution is fully constrained... and we need “t” back!!

\[
\tilde{C}_0(x, s) = \frac{C_0^m}{s} - \frac{C_0^m}{s} e^{-\sqrt{D} x}
\]

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

\[
e^{-\sqrt{D} x} = \text{erf}[\sqrt{D} \sqrt{t}]\frac{1}{\sqrt{\pi}}
\]

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

\[
C_0(x, t) = C_0^m \left[ 1 - \text{erf} \left( \frac{x}{2D(t)^{1/2}} \right) \right]
\]

What’s erf?... Well, first of all, what’s the error function: erf?
Now... what's efrc?

Gaussian distribution, with mean = 0 and std. dev. = 1/√2

Does this make sense?

\[ C_{O}(x, t) = C_{O}\left\{ 1 - \text{erfc}\left( \frac{x}{2(D_{O})^{1/2}} \right) \right\} \]

\[ C_{O}(x, t) = C_{O}\text{ erf}\left( \frac{x}{2(D_{O})^{1/2}} \right) \]

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

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

... Let's plot it!

Hey, these look completely reasonable... and they are not exponential!
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>

$\bar{\Delta} = \sqrt{\langle d^2 \rangle Dt}$ = \sqrt{\left( \frac{cm^2}{s} \right)} s = cm

Hey, these look completely reasonable for 1D diffusion in one direction!

Hey, these look completely reasonable for 1D diffusion in one direction!

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:

   $$i = nFAl_0(0, t)$$
... 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 \(C_o(x, t)\):

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

... and so we need to evaluate:

\[-J_O(x, t) = D_O \frac{\partial}{\partial x}\left[C^*_\operatorname{erf}\left(\frac{x}{2\sqrt{D_O t}}\right)\right]\]

... now Step #2...

\[-J_O(x, t) = D_O \frac{\partial}{\partial x}\left[C^*_\operatorname{erf}\left(\frac{x}{2\sqrt{D_O t}}\right)\right]\]

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

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

see B&F, pg. 780, for details

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

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

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

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

... which is what we needed for Step #3...

OK... that's Steps #1 and 2...

1. Solve Fick's Second Law to get \(C_o(x, t)\), and in the process of doing this, you will use boundary conditions that "customize" the solution for the particular experiment of interest:

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

2. Use Fick's First Law to calculate \(J_O(0, t)\) from \(C_o(x, t)\):

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

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

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

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

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

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

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

> 1 kV neutral particles corona discharge capture plates charged particles
... OK, so what does it predict?

\[ \frac{\dot{I}(t)}{I_0} = \frac{nFAD_{\text{eq}}}{D_{\text{eq}} C_{\text{O}}^2} \]

the Cottrell Equation

- \( D = 1.5 \times 10^{-6} \text{ cm}^2 \text{s}^{-1} \)
- \( D = 1 \times 10^{-5} \text{ cm}^2 \text{s}^{-1} \)

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.

... OK, so what does it predict?

\[ \frac{\dot{I}(t)}{I_0} = \frac{nFAD_{\text{eq}}}{D_{\text{eq}} C_{\text{O}}^2} \]

the Cottrell Equation

- \( D = 1.5 \times 10^{-5} \text{ cm}^2 \text{s}^{-1} \)
- \( D = 1 \times 10^{-4} \text{ cm}^2 \text{s}^{-1} \)

... OK, so what does it predict?

\[ \frac{\dot{I}(t)}{I_0} = \frac{nFAD_{\text{eq}}}{D_{\text{eq}} C_{\text{O}}^2} \]

the Cottrell Equation

- \( \text{slope} = \frac{nFA}{\sqrt{2D_{\text{eq}}}} \frac{1}{\sqrt{C_{\text{O}}}} \)

???

Best wishes and Robert A. M. Doole\*
Department of Chemistry, UMIST (P.O.Box 88), Manchester, U.K. M60 1QD (e-mail: r.a.doole@umist.ac.uk; Fax: +44 0161 2084539)
use the Cottrell Equation to measure $D$, such as in thin films/coatings!

but what are the problems with this approach?

\[ \dot{i}(t) = \frac{nFAD_0^2C_0}{w^{1/2}D^{1/2}} \]

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...

\[ Q_d = \frac{2nFAD_0^{1/2}C_0^{3/2}}{w^{1/2}} \]