Lecture #13 of 18(?)

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

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

key points:
- at \( E_1 \): no reaction (\( C_0(x, 0) = C_0^* \))
- at \( E_2 \): diffusion-controlled reaction (\( C_0(0, t) = 0 \))

RECALL:

\[
C_0(x, t) = C_0^* \left[ 1 - \text{erfc} \left( \frac{x}{2(D_0t)^{1/2}} \right) \right]
\]

\[
C_0^*(x, t) = C_0^* \text{erf} \left( \frac{x}{2(D_0t)^{1/2}} \right)
\]

... 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 \( C(0, t) = 0 \) ... Check!

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

**RECALL:**

\[ C(x, t) = C^* \text{ eff} \left( \frac{x}{2(Dt)^{1/2}} \right) \]

\[ C^* = 1 \times 10^{-6} \text{ mol cm}^{-3} \]
\[ D = 0.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \]

\[ x = (100 \mu\text{m}) \]

---

How large is the diffusion layer? Recall the rms displacement...

**RECALL:**

<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>

\( \bar{\Delta} = (Dd) \sqrt{\text{Dt}} \)

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

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

... plane

... wire, line, tube

... point, sphere, disk

---

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

**RECALL:**

Why is 52% of the bulk concentration noteworthy?

Plug in \( x = (Dt)^{1/2} \)...

... Ah ha!

\[ \sqrt{D}t = 2.2 \mu\text{m} \]

---
OK... that's Step #1... Whoa! That was deep!... The last two steps are not...

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:

\[
i = nFAl_O(0, t)
\]

... now Step #2...

RECALL:

\[
-J_O(x, t) = D_O \frac{\partial C_O(x, t)}{\partial x} \quad \text{(Fick's First Law)}
\]

... 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:

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

... now Step #3...

RECALL:

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

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

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

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...

... 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...

RECALL:

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

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

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

$$J(x, t) = D_0 \frac{\partial C(x, t)}{\partial x}$$

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

$$i = nFAJ(0, t)$$

... and finally, Step #3 using Step #2...

RECALL:

$$-J(0, t) = \frac{D_0}{\sqrt{\pi t}}$$

... and with $i = nFAJ(0, t)$...
... OK, so what does it predict?

---

### 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?
... OK, so what does it predict?

\[ \dot{I}(t) = I_d(t) = \frac{nFAD_0^{1/2}C^*}{\pi^{1/2}D^{1/2}} \]

(long time) (short time)

slope = \( nFAR^{1/2}D^{1/2}C^* \)

... use the Cottrell Equation to measure \( D \), such as in thin films/coatings!

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

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...

\[ Q_d = \frac{2nFAD_0^{1/2}C^*}{\pi^{1/2}} \]

Figure 5.8.2 Chronocoulometric response for a double-step experiment performed in the system of Figure 5.8.1. The reversal step was made to 0.0 V vs. QRE. [Data courtesy of R. S. Glass.]

... this is called an Anson plot.

**Figure 5.8.1** Linear plot of chromo-electrochemical response at a planar platinum disk. System is 0.95 molar 1,4-dicyanobenzene (DCB) in benzonitrile containing 0.1 M tetra-n-butylammonium fluoroborate. Initial potential: 0.0 V vs. Pt QRE. Step potential: −1.892 V vs. Pt QRE. T = 25°C, A = 0.018 cm². E' for DCB + e = DCB⁻ + 1.85 V vs. QRE. The actual chromo-electrochemical trace is the part of Figure 5.8.2 corresponding to t < 250 ms. (Data courtesy of R. S. Glass.)


![Diagram](image1.png)

**Figure 5.8.1**

\[ Q = \frac{2neAD[\Gamma^{O}(t)]}{\Delta t} + Q_R = \alpha A\Gamma^{O} \] (5.8.2)

with \( \Gamma^{O} \), the surface excess of O (mol cm\(^{-2}\))

**Figure 5.8.1** Linear plot of chromo-electrochemical response at a planar platinum disk. System is 0.95 molar 1,4-dicyanobenzene (DCB) in benzonitrile containing 0.1 M tetra-n-butylammonium fluoroborate. Initial potential: 0.0 V vs. Pt QRE. Step potential: −1.892 V vs. Pt QRE. T = 25°C, A = 0.018 cm². E' for DCB + e = DCB⁻ + 1.85 V vs. QRE. The actual chromo-electrochemical trace is the part of Figure 5.8.2 corresponding to t < 250 ms. (Data courtesy of R. S. Glass.)


![Diagram](image2.png)

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with \( \Gamma^{O} \), the surface excess of O (mol cm\(^{-2}\))

![Diagram](image3.png)

**Figure 5.8.1** Linear plot of chromo-electrochemical response at a planar platinum disk. System is 0.95 molar 1,4-dicyanobenzene (DCB) in benzonitrile containing 0.1 M tetra-n-butylammonium fluoroborate. Initial potential: 0.0 V vs. Pt QRE. Step potential: −1.892 V vs. Pt QRE. T = 25°C, A = 0.018 cm². E' for DCB + e = DCB⁻ + 1.85 V vs. QRE. The actual chromo-electrochemical trace is the part of Figure 5.8.2 corresponding to t < 250 ms. (Data courtesy of R. S. Glass.)


![Image](image4.png)

**Figure 5.8.1**

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with \( \Gamma^{O} \), the surface excess of O (mol cm\(^{-2}\))

Prelude

**Tribute to Fred Anson and list of publications**

Fred Anson

Fred’s scientific accomplishments in over 300 publications cover the gamut of inorganic, analytical, and physical electrochemistry. His early PhD work with J. J. Lingane laid the foundation for his research at Caltech looking at various reactions at Pt electrodes and in continuity with electrochromic titrations. In the early days at Caltech, he led a number of papers delving into the realm of physical chemistry, especially those dealing with surface science, which is a classic example of symmetry. To the discovery of what is now termed short-time electrochemistry, his interest in surface processes at electrodes led to the discovery of short-time chronoamperometry. His pioneering contributions in this area eventually led to the naming of the “Anson plot” or its \( t \) after him. While primarily an experimentalist, he has contributed to a theoretical understanding of inner and outer sphere reactions and multiple layer effects at electrodes. A major theme to be found in Fred’s publications is an interest in the direct transfer kinetics and mechanisms of...
... one data set, from “one” experiment...  
... where either plot allows you to calculate $D$!

<table>
<thead>
<tr>
<th>experiment</th>
<th>observable</th>
<th>governing equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chronoamperometry (or differentiate CC)</td>
<td>meas $i(t)$ (or use $dQ(t)/dt$)</td>
<td>$i_d(t) = \frac{nFAD_0^2C^*_0}{\pi^{1/2}D^{1/2}}$</td>
</tr>
<tr>
<td>Chronocoulometry (or integrate CA)</td>
<td>meas $Q(t)$ (or use $lt$ area)</td>
<td>$Q = \frac{2nFAD_0^2C^*_0\lambda^{1/2}}{\pi^{1/2}}$</td>
</tr>
</tbody>
</table>

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... how else can one calculate $D$? ...  
... how about not using electrochemistry, but NMR instead... What?  
... Yes! Pulsed-Field Gradient (PFG) NMR!  
... so, without diffusion...

http://chem.uchicago.edu/nmr/techniques/other/diff/diff.html  
http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3003887/

495

... how else can one calculate $D$? ...  
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http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3003887/

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So, where is the non-ideal data in a Cottrell and Anson plot?

Short times... check!

we have equations for the “signal” and the “noise,” so...

we can calculate the signal-to-noise ratio for a potential step experiment

\[ \frac{S}{N} \approx \frac{i_{\text{signal}}}{i_{\text{noise}}} \]

Here we assume

\[ E = 0.6 \text{ V}, \quad R = 100 \Omega \]
... the RC time constant of the cell imposes a lower limit on the accessible time window (~100 µs) for a potential step experiment... but what is the origin of the long time limit?

... we assume \( E = 0.6 \text{ V}, \quad R = 100 \Omega \)

So, where is the non-ideal data in a Cottrell and Anson plot?

Short times... check!

long times...
... what is this due to again?
... let's see...

A typical electrode used in a laboratory electrochemistry experiment has an area of 0.05 cm² to 1 cm².

\[
A = \pi (0.15)^2 = 0.0706 \text{ cm}^2 = 7 \text{ mm}^2
\]
The Cottrell Equation can be used to describe the behavior during a potential step experiment as long as the thickness of the Nernst diffusion layer is small relative to the electrode dimension (and, of course, the boundary layer / stagnant layer).

So, how long is that, based on $S/N \approx 10:1$?

<table>
<thead>
<tr>
<th>$t$ (s)</th>
<th>$\sqrt{Dt}$ (cm)</th>
<th>$\frac{\sqrt{Dt}}{r_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.0007</td>
<td>0.005</td>
</tr>
<tr>
<td>1</td>
<td>0.0022</td>
<td>0.015</td>
</tr>
<tr>
<td>10</td>
<td>0.0071</td>
<td>0.047</td>
</tr>
<tr>
<td>100</td>
<td>0.022 (220 µm)</td>
<td>0.15</td>
</tr>
</tbody>
</table>

$D = 0.5 \times 10^{-5} \text{ cm}^2/\text{s}$ (lower bound for typical value)

$r_0 = 0.15 \text{ cm}$ (value from previous slide)

Answer: $< \sim 10 \text{ s}$

When the diffusion layer approaches the dimensions of the electrode diameter, radial diffusion to the edges of the electrode cause the flux to be larger than predicted by the Cottrell Equation, and non-uniform.

$t = 0.1 - 1 \text{ s}$
linear diffusion

$t = 1 - 100 \text{ s}$
mixed diffusion

$t > \sim 100 \text{ s}$
with spherical diffusion

How is current affected, relative to the Cottrell prediction?

... so in a potential step experiment...

1. current changes continuously with time.
2. radial diffusion (AKA “edge effects”) limits the data acquisition time window to $\sim 1 - 10 \text{ s}$.
3. charging imposes a lower limit of $0.1 - 0.5 \mu\text{s}$ on this data acquisition time window.
4. theoretically, maximum current densities are $> 60 \text{ mA cm}^{-2}$ initially, but just $100 \text{ µA cm}^{-2}$ at $S/N = 10$.

... but, why do we care?
we need to push this up in order to perform meaningful measurements of the kinetics of rapid redox reactions

**Figure 3.4.1** Current-potential curves for the system O + e ⇌ R with \( n = 0.5, T = 298 \text{ K} \), \( \bar{v}_0 = -\bar{v}_0 = \bar{v} \) and \( \bar{v}_0 = 0.2 \). The dashed lines show the component currents \( i_0 \) and \( i_e \).

... but deleterious edge effects also suggest an opportunity: (UPDATED)

*What if instead of avoiding radial diffusion, we exploit it?... Wait, what?*

<table>
<thead>
<tr>
<th>( t = 0.1 \text{ to } 1 \text{ s} )</th>
<th>( t = 1 \text{ to } 100 \text{ s} )</th>
<th>( t &gt; \sim 100 \text{ s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear diffusion</td>
<td>mixed diffusion</td>
<td>mixed unknown diffusion</td>
</tr>
<tr>
<td>3 mm insulator</td>
<td>[Diagram of insulator]</td>
<td>[Diagram of insulator]</td>
</tr>
<tr>
<td>Au tip on metal rod</td>
<td>[Diagram of Au tip on metal rod]</td>
<td>[Diagram of Au tip on metal rod]</td>
</tr>
</tbody>
</table>

How is current affected, relative to the Cottrell prediction?

Let's design an experiment in which we intentionally operate in this radial diffusion limit the "entire" time!

... well we actually start in the linear regime, and then switch over quickly...

side view top view

[Diagram of side view and top view]

... called "ultramicroelectrodes" or "UMEs"
Recall that for linear diffusion from a plane, current changes continuously with time...
... this means:
\[
\frac{\partial C(x,t)}{\partial t} = 0 = D\left(\frac{\partial^2 C(x,t)}{\partial x^2}\right)
\]
has no solution

... but recall from Section 1.4.2 that the Nernst diffusion layer \(\delta\) ends up reaching a steady-state distance due to natural convection that sets the boundary layer / stagnant layer...
... anyway, this doesn’t help us simplify our experiment...

... the linear diffusion layer grows with time (indefinitely)...

... and thus linear-diffusion-controlled currents decay with time ("indefinitely")...
… but the same is not true for purely spherical diffusion:

\[
\frac{\partial C(r,t)}{\partial t} = 0 = D \left( \frac{\partial^2 C(r,t)}{\partial r^2} + \frac{2 \partial C(r,t)}{r \partial r} \right)
\]

… which has solutions:

\[
C(r,t) = B + \frac{A}{r}
\]

… so, for a spherical diffusion field:

\[
\frac{\partial^2 C(r,t)}{\partial r^2} = \frac{2A}{r^3} \quad \frac{\partial C(r,t)}{\partial t} = \frac{-A}{r^2}
\]

and so...

\[
\frac{\partial C(r,t)}{\partial t} = 0 = D \left( \frac{2A}{r^3} + \frac{2(-A)}{r^2} \right)
\]

1. semi-infinite boundary condition...

\[
\lim_{r \to \infty} C(r,t) = C^* = B + 0 \quad C(r,t) = B + \frac{A}{r}
\]

2. electrode surface (edge/circumference) boundary condition...

\[
C(r_0,t) = 0 \quad 0 = C^* + \frac{A}{r_0} \\
A = -C^* r_0
\]

… so Fick’s 2nd Law predicts that the steady-state concentration gradient is:

\[
C(r,t) = C^* - \frac{C^* r_0}{r} = C^* \left[ 1 - \frac{r_0}{r} \right]
\]

… notice that here we can reach a time-independent condition!

… What?

… the diffusion layer “thickness” is 2r_0, no matter how small r_0 is!

at this distance, the concentration is 50% of the bulk… Plug it in! … Ah ha!

… the insulating shroud surrounding the electrode should be \( \sim 10r_0 \) to observe stable hemispherical diffusion

* This spatial behavior is independent of time…
... the diffusion layer “thickness” is $2r_0$, no matter how small $r_0$ is!

$$C(r, t) = C_0 \left[ 1 - \frac{r_0}{r} \right]$$

... recall, that for transient linear diffusion...

$C_0(x, t) = C_0 e^{-x^2 / 4D_f t}$

$\Delta = \sqrt{2D_f t}$

the UME: You can buy one from BASi

... steady-state is “often” reached at each applied potential at a UME during a sweep

... Let’s quantify it... steady-state occurs when $v << RT/(nF^2)$

... $v [mV s^{-1}] << 26 mV x (5/0.5) ...$ for a BASi UME with $r_0 = 5 \mu m$

... 26 mV x ((0.5 x 10^{-8} cm^2 s^{-1}) / (0.5 x 10^{-5} cm^2 s^{-1})) = 26 mV x (20 s^{-1})

... $v << 0.5 V s^{-1}$... Wow, you can still scan quite fast!

Wals, Lovelock, & Licence, Chem. Soc. Rev., 2010, 39, 4185
… and back by popular demand: “Steps to convert TX to IUPAC”, (BRIEFLY) 518

... akin to the semi-empirical model of mass transfer (Section 1.4.2), UMEs have no scan-rate dependence to \(I_v\), which is unlike CVs at traditional disk electrodes...

... this is because we can attain steady-state, mass-transport-limited currents at UMEs...

... without stirring at all...

and the diffusion-limited current pre-factor depends on electrode geometry... 521

\[ i_i = "x"nFDCr_0 \]  \space \text{... but not scan rate!}

<table>
<thead>
<tr>
<th>electrode geometry</th>
<th>&quot;x&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>sphere</td>
<td>4π</td>
</tr>
<tr>
<td>hemisphere</td>
<td>2π</td>
</tr>
<tr>
<td>disk</td>
<td>4</td>
</tr>
<tr>
<td>ring</td>
<td>( \frac{\pi^2(b + a)}{r_0 \ln \left( \frac{16(b + a)}{(b - a)} \right)} )</td>
</tr>
</tbody>
</table>

... disk and ring-disk electrodes are real things that we will cover later