Lecture #13 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
... 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

slope = \( nF\pi^{-1/2}D^{1/2}C^* \)

(long time)  (short time)
... use the Cottrell Equation to measure $D$, such as in thin films/coatings!

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

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

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...

\[ Q_d = \frac{2nFAD_O^{1/2}C_O^*t^{1/2}}{\pi^{1/2}} \]

the integrated Cottrell Equation
The integrated Cottrell Equation

\[ Q_d = \frac{2nFAD_O^{1/2}C_0^*t^{1/2}}{\pi^{1/2}} \]

**Figure 5.8.2**
Chronocoulometric response for a double-step experiment performed on 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.

What is this positive intercept?

Figure 5.8.1  Linear plot of chronocoulometric response at a planar platinum disk. System is 0.95 mM 1,4-dicyanobenzene (DCB) in benzonitrile containing 0.1 M tetra-n-butylammonium fluoborate. Initial potential: 0.0 V vs. Pt QRE. Step potential: $-1.892$ V vs. Pt QRE. $T = 25^\circ$C, $A = 0.018$ cm$^2$. $E^{0'}$ for DCB $+ e \rightleftharpoons$ DCB$^-$ is $-1.63$ V vs. QRE. The actual chronocoulometric trace is the part of Figure 5.8.2 corresponding to $t < 250$ ms. [Data courtesy of R. S. Glass.]
... this is called an Anson plot.

\[ Q = \frac{2nFAD_0^{1/2}C^{*}_{O}t^{1/2}}{\pi^{1/2}} + Q_{dl} + nFAG_0 \]  \hspace{1cm} (5.8.2)

with \( \Gamma_0 \), the surface excess of O (mol cm\(^{-2}\))

What is this positive intercept?

**Figure 5.8.1** Linear plot of chronocoulometric response at a planar platinum disk. System is 0.95 mM 1,4-dicyanobenzene (DCB) in benzonitrile containing 0.1 M tetra-n-butylammonium fluoborate. Initial potential: 0.0 V vs. Pt QRE. Step potential: \(-1.892 \) V vs. Pt QRE. \( T = 25^\circ \)C, \( A = 0.018 \) cm\(^2\). \( E^{0'} \) for DCB + \( e \rightleftharpoons \) DCB\(^-\) is \(-1.63 \) V vs. QRE. The actual chronocoulometric trace is the part of Figure 5.8.2 corresponding to \( t < 250 \) ms. [Data courtesy of R. S. Glass.]
Preface
Tribute to Fred Anson and list of publications

Fred’s scientific accomplishments in over 300 publications cover the gamut of inorganic, analytical, and physical electrochemistry. He started out in his Ph.D. work with J.J. Lingane and in his early work at Caltech looking at various reactions at Pt electrodes and in coulometry and coulometric titrations. In his early days at Caltech, he had a number of papers dealing with the ‘rediscovered’ technique of chronopotentiometry. This led, in a classical example of serendipity, to the discovery of what is now termed thin-layer electrochemistry. His interest in surface processes at electrodes led, somewhat later, to the discovery of chronocoulometry. His pioneering contributions to this area eventually led to the naming of the ‘Anson plot’ of $Q$ vs. $t^{1/2}$ after him. While primarily an experimentalist, he has contributed to a theoretical understanding of inner and outer sphere reactions and double layer effects at electrodes. A major theme to be found in Fred’s publications is an interest in the electron 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><strong>Chronoamperometry</strong></td>
<td>meas $I(t)$ (or use $dQ(t)/dt$)</td>
<td>$i_d(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}}$</td>
</tr>
<tr>
<td><em>(or differentiate CC)</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Chronocoulometry</strong></td>
<td>meas $Q(t)$ (or use $I(t)$ area)</td>
<td>$Q = \frac{2nFAD_O^{1/2}C_O^*t^{1/2}}{\pi^{1/2}}$</td>
</tr>
<tr>
<td><em>(or integrate CA)</em></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
... 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.ch.huji.ac.il/nmr/techniques/other/diff/diff.html
http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3003887/
... how else can one calculate $D$? ...
... how about not using electrochemistry, **but NMR instead**... What?
... Yes! **Pulsed-Field Gradient (PFG) NMR**!

... and, **with diffusion**...

http://chem.ch.huji.ac.il/nmr/techniques/other/diff/diff.html
http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3003887/
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

**signal**

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

**noise**

\[ i = \frac{E}{R} \exp\left(\frac{-t}{RC}\right) \]

... here we assume
\[ E = 0.6 \text{ V}, \quad R = 100 \text{ } \Omega \]
we have equations for the “signal” and the “noise,” so...
we can calculate the signal-to-noise ratio for a potential step experiment

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

\[ i = \frac{E}{R} \exp \left( -\frac{t}{RC} \right) \]

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

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

\[
i = \frac{E}{R} \exp \left( -\frac{t}{Rt} \right)
\]

... here we assume \( E = 0.6 \text{ V}, \ R = 100 \text{ } \Omega \)
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 cm$^2$ to 1 cm$^2$.

\[ A = \pi (0.15)^2 = 0.0706 \text{ cm}^2 \approx 7 \text{ mm}^2 \]
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?

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

$D = 0.5 \times 10^{-5}$ cm$^2$/s  
_lower bound for typical value_

$r_0 = 0.15$ cm  
_value from previous slide_

Answer: < $\sim 1 - 10$ 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.

\[ t \approx 0.1 - 1 \text{ s} \]  
linear diffusion

\[ t \approx 1 - 100 \text{ s} \]  
mixed diffusion

\[ t > \sim 100 \text{ s} \]  
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”) limit the data acquisition time window to ~1 s.

3. charging imposes a lower limit of 0.1 – 0.5 µs on this data acquisition time window.

4. maximum current densities are > 60 mA cm$^{-2}$ initially, but just 100 µA cm$^{-2}$ at S/N $\approx$ 10.

... but, why do we care?
Why do we care? One reason...

we need to push this up in order to perform meaningful measurements of the kinetics of fast reactions.

Figure 3.4.1  Current-overpotential curves for the system $O + e \rightleftharpoons R$ with $\alpha = 0.5$, $T = 298$ K, $i_{l,c} = -i_{l,a} = i_{l}$ and $i_0/i_l = 0.2$. The dashed lines show the component currents $i_c$ and $i_a$. 
... but deleterious edge effects also suggest an opportunity:

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

$\begin{align*}
t &\approx 0.1 - 1 \text{ s} \\
t &\approx 1 - 100 \text{ s} \\
t &> \sim 100 \text{ s}
\end{align*}$

linear diffusion

mixed diffusion

spherical diffusion

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...

... 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)...

Why is 52% of the bulk concentration noteworthy?

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

... Ah ha!

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

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

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

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

$7.1 \mu \text{m}, 22 \mu \text{m}, (100 \mu \text{m})$

... use the geometric area for calculations
... and thus linear-diffusion-controlled currents decay with time ("indefinately")...

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

the Cottrell Equation

![Graph showing current decay with time for different diffusion coefficients](image)

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

(10 ms)
... but the same is **not true** for purely spherical diffusion:

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

... 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...

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

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

\[
B = C^*
\]

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 2\textsuperscript{nd} 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 \textit{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!

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

* This spatial behavior is independent of time...

... the insulating shroud surrounding the electrode should be $> \sim 10r_0$ to observe stable hemispherical diffusion

$r_0 = 10 \mu m$
... the diffusion layer “thickness” is \(2r_0\), no matter how small \(r_0\) is!

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

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

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

\[
\Delta = \sqrt{(2d)Dt} = \sqrt{\left(\frac{\text{cm}^2}{s}\right)s} = \text{cm}
\]

\(10 \text{ nm}
\)

\(100 \text{ nm}
\)

\(1 \mu\text{m}
\)

\((100 \mu\text{m})\)
the UME: You can buy one from BASi

Ordering Information

| MF-2005   | 10 µm diameter Platinum Microelectrode |
| MF-2006   | 10 µm diameter Gold Microelectrode      |
| MF-2007   | 11 µm (±2 µm) diameter Carbon Fiber Microelectrode |
| MF-2150   | 100 µm diameter Platinum Microelectrode |

Custom fabrication is available, e.g., 33 µm carbon, 25 µm silver, 25 µm gold, etc. Please contact requirements.
... steady-state is “often” reached at each applied potential at a UME during a sweep

... Let’s quantify it... steady-state occurs when $\nu << \frac{RTD}{(nF r_0^2)}$

... $\nu$ (mV s$^{-1}$) $<< 26 \text{ mV} x (D/r_0^2)$... for a BASi UME with $r_0 = 5 \mu m$...

... $26 \text{ mV} x \left(\frac{(0.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})}{(0.5 \times 10^{-3} \text{ cm})^2}\right) = 26 \text{ mV} x (20 \text{ s}^{-1})$

... $\nu << 0.5 \text{ V s}^{-1}$... Wow!
(1) Change sign of currents, because B&F indicates that positive current is cathodic
... this is likely because electrons are the charge carrier of current
... but physicists disagree; also, ions can be + or – so no need to focus on e⁻

(2) Mirror image the plot through the origin so that the axes look like math axes
… and back by popular demand: “Steps to convert TX to IUPAC”…

Figure 1. Cyclic voltammogram of ferrocene (1.0 mM) in acetonitrile with 0.1 M tetra-n-butylammonium perchlorate at a gold microdisk electrode (r = 6.5 μm). (a) 10 V s⁻¹ scan rate. (b) 0.1 V s⁻¹ scan rate