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

RECALL FROM LAST TIME... Step #3 using Step #2...

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

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

\[i(t) = i_d(t) = \frac{nFAJ_0(0, t)^2 C^*}{\pi D_0 t^{3/2}}\]

the Cottrell Equation

Frederick Gardner Cottrell, in 1920
b. January 10, 1877, Oakland, California, U.S.A.
d. November 18, 1948, Berkeley, California, U.S.A.

... established Research Corp. 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

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

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… OK, so what does it predict?

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Enviotech

Air Pollution Control Innovations

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\[ \frac{\dot{d}(t)}{d(t)} = \frac{nFAD(D)}{v_{d}(t)C} \]

- **Cottrell Equation**

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

\[ D = 1.5 \times 10^{-4} \text{ cm}^2 \text{s}^{-1} \]

* 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.
... use the Cottrell Equation to measure $D$!

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

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

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... Solution: Integrate it, with respect to time...

$Q_d = \frac{2nFAD_0^{1/2}C_{O^2}^{1/2}}{\pi^{1/2}}$

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Figure 5.8.2

Chromatographic 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. QSE.
[Data courtesy of R. S. Glass.]

... this is called an Anson plot.

![](image1)


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**Anson, Anal. Chem., 1966, 38, 54**

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Fred Anson

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**Fred Anson**

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reversal methods allow you to get data on both O and R, even if you start with just one in solution.

\[
\begin{align*}
Q &= \frac{2nFAD_{D}^{1/2}C_{O}^{0}}{n^{1/2} + nF\Gamma_{O}} \\
Q(t > \tau) &= \frac{2nFAD_{O}^{1/2}C_{O}^{0}}{\pi^{1/2}} \left[ \tau^{1/2} + \left( t - \tau \right)^{1/2} - \tau^{1/2} \right] + Q_{dl} + nF\Gamma_{O}
\end{align*}
\]

For your reference:
… back to one potential step = one data set, from “one” experiment…651
… where either plot allows you to calculate DI!

<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>$i_{d}(t) = \frac{nFAD_{D}^{1/2}C_{O}^{0}}{n^{1/2}\pi^{1/2}}$</td>
</tr>
<tr>
<td>chronocoulometry (or integrate CA)</td>
<td>meas $Q(t)$ (or use $I(t)$ area)</td>
<td>$Q = \frac{2nFAD_{D}^{1/2}C_{O}^{0}^{1/2}}{\pi^{1/2}}$</td>
</tr>
</tbody>
</table>
... how else can one calculate $D$? ...
... how about not using electrochemistry, **but NMR**... What?
... Yes! **Pulsed-Field Gradient (PFG) NMR!**

[Diagram of PFG NMR process]

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

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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!

[Graphs showing Cottrell and Anson plot]

Long times...
... what is this due to again?
we have equations for the "signal" and the "noise," so…

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

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

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

… 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 µs) for a potential step experiment…

… but what is the origin of the long time limit?

\[ S/N = \frac{I_{\text{signal}}}{I_{\text{noise}}} \]

for S/N = 10, \[ t > 100 \ \mu\text{s} \]
A typical electrode used in a laboratory electrochemistry experiment has an area of 0.05 cm\(^2\) to 1 cm\(^2\).

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

The Cottrell Equation can be used to describe the behavior during a potential step experiment as long as the thickness of the diffusion layer is small relative to the electrode dimension (and, of course, the boundary layer / stagnant layer / Nernst diffusion layer \(\delta\))...

... So, how long is that?

<table>
<thead>
<tr>
<th>( t ) (s)</th>
<th>( \sqrt{2Dt} )</th>
<th>( \frac{\sqrt{2Dt}}{\tau_0} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.0014</td>
<td>0.009</td>
</tr>
<tr>
<td>1</td>
<td>0.0045</td>
<td>0.03</td>
</tr>
<tr>
<td>10</td>
<td>0.014</td>
<td>0.09</td>
</tr>
<tr>
<td>100</td>
<td>0.045</td>
<td>0.3</td>
</tr>
</tbody>
</table>

\[ D = 10^{-5} \text{ cm}^2/\text{s} \]
\[ \tau_0 = 0.15 \text{ cm} \]

(value from previous slide)

Answer: < 1 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.
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 \(\sim 1\) s.

3. charging imposes a lower limit of 100 – 500 \(\mu\)s on this data acquisition time window.

4. maximum current densities are >60 mA cm\(^{-2}\) initially, but just 100 \(\mu\)A cm\(^{-2}\) at S/N = 10.

… but, why do we care?

Why do we care? One reason…

… but deleterious edge effects also suggest an opportunity:

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

![Diagram showing current changes with time and diffusion types](image)
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 and top view of an insulator with Au, C, Pt](image)

... 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 boundary layer / stagnant layer / Nernst diffusion layer (\(\delta\)) ends up reaching a steady-state distance due to natural convection...

... anyway, this doesn't help us simplify our experiment...

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

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

\[ D = 1.5 \times 10^4 \text{ cm}^2 \text{s}^{-1} \]

\[ D = 1 \times 10^5 \text{ cm}^2 \text{s}^{-1} \]

... but the same is not true for purely spherical diffusion:

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

... which has solutions:

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

... 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 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 $10r_0$, no matter how small $r_0$ is! 

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

The spatial behavior is independent of time… 

\[
r_0 = 10 \text{ µm}
\]

$1 \text{ µm}$ $100 \text{ nm}$ $10 \text{ nm}$ 

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

… recall, that for transient linear diffusion… 

\[
C_0(x, t) = C_0^0 \text{ erf} \left[ \frac{x}{2(D_Ct)^{1/2}} \right]
\]

$\Delta = \sqrt{(2d)D_C t} = \left( \frac{\text{cm}^2}{s} \right)^{1/2} = \text{cm}$

the diffusion-limited current pre-factor depends on electrode geometry… 

\[
i = "x" nFDC^*r_0 \quad \text{but not scan rate!}
\]

<table>
<thead>
<tr>
<th>geometry</th>
<th>&quot;x&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>sphere</td>
<td>$4\pi$</td>
</tr>
<tr>
<td>hemisphere</td>
<td>$2\pi$</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>
the UME: You can buy one from BASi

... each potential during a sweep using a UME "often" reaches steady-state
... steady-state occurs when \( v \ll RTD/(nF_0^2) \)

Walsh, Lovelock, & Licence, Chem. Soc. Rev., 2010, 39, 4185

... each potential during a sweep using a UME "often" reaches steady-state
... steady-state occurs when \( v \ll RTD/(nF_0^2) \)
... \( v \) (mV s\(^{-1}\)) << 26 mV x (D/r\(^2\)) ... for a BASi UME with \( d_0 = 5 \mu m \)
... \( (1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}) / (0.5 \times 10^{-3} \text{ cm})^2 = 26 \times 40 \text{ mV s}^{-1} \)

Walsh, Lovelock, & Licence, Chem. Soc. Rev., 2010, 39, 4185
... each potential during a sweep using a UME "often" reaches steady-state

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... $v \ll 1 \text{ V s}^{-1}$... Wow!

Walsh, Lovelock, & Licence, Chem. Soc. Rev., 2010, 39, 4185

... and based on popular demand: "Steps to convert TX to IUPAC"... 677

(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 plot through the origin so that the axes look standard as $+$, $+$, $+$, $-$

Walsh, Lovelock, & Licence, Chem. Soc. Rev., 2010, 39, 4185

... scanning is "often" steady-state at a UME

... steady-state occurs when $v \ll RTD/(nF\bar{\nu})$

... $v (\text{mV s}^{-1}) \ll 26 \text{ mV} \times (D/\bar{\nu})$... for a BASi UME with $\bar{\nu} = 5 \mu m$

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

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

**WITHOUT STIRRING!**

... how tiny (large) is this diffusion-limited current (density)?

Let's assume \( D = 10^{-5} \) cm\(^2\) s\(^{-1}\) and \( C^* = 10^4 \) moles cm\(^{-3}\) (1 mM)

<table>
<thead>
<tr>
<th>( r_0 ) (µm)</th>
<th>( i ) (nA)</th>
<th>( i/A )</th>
</tr>
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<tbody>
<tr>
<td>100</td>
<td>120</td>
<td>386 µA/cm(^2)</td>
</tr>
<tr>
<td>10</td>
<td>12</td>
<td>3.86 mA/cm(^2)</td>
</tr>
<tr>
<td>1</td>
<td>1.2</td>
<td>38.6 mA/cm(^2)</td>
</tr>
<tr>
<td>100 nm</td>
<td>120 pA</td>
<td>386 mA/cm(^2)</td>
</tr>
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... super tiny currents... but huge current densities... = AWESOME... for studies of electrocatalysis!
Again, Why do we care? One reason…

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

Figure 3.4.1 Current-overpotential curves for the system O + e = R with \( \alpha = 0.5, T = 298 \text{ K} \). \( i_0 = i_\infty = i \) and \( \eta_i / \eta_0 = 0.2 \). The dashed lines show the component currents \( i_0 \) and \( i_\infty \).

… how tiny (large) is this diffusion-limited current (density)?
Let's assume \( D = 10^{-5} \text{ cm}^2 \text{ s}^{-1} \) and \( C^* = 10^6 \text{ moles cm}^{-3} (1 \text{ mM}) \)

<table>
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<th>( i = 4\pi n F D^* r_0 ) (nA)</th>
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… so what is \( i R_\infty \) for these electrodes?

… well \( R_\infty \) is fairly large, but \( i R_\infty \) is nearly constant…

\[ R_\infty = \left( \frac{1}{4\pi n F D^* r_0} \right) \]
Recall... Does the following make sense? Reaction is: \( \text{Tl}^+ + e^- \rightleftharpoons \text{Tl} \)

\[ \text{I}_d \text{Tl}^+ \rightarrow \text{I}_m \text{Tl}^+ \] to bring \( \text{Tl}^+ \) to the electrode

**Figure 4.35** Voltammograms for addition of 0.65 mmol/L \( \text{HgI}_2 \) to a mercury film on a silver ultramicro electrode (radius, 15 μm) in the presence of (a) 0.1 M (b) 0.01 M, and (c) 50 mM \( \text{LiClO}_4 \). The potential was controlled vs. a Pt wire QRE whose potential was a function of solution composition. This variability is the basis for the shift in wave position along the potential axis.


... and here is another example of this...

\[ \text{V} vs. \text{As}^+/\text{As}^- \]

**Figure 2** Voltammograms for addition of \( 10^{-3} \) M \( \text{AsH}_3 \) to acetonitrile at 18 °C using a 25 μm Pt microelectrode in (a) presence and (b) absence of 0.1 M \( \text{LiClO}_4 \). Scan rate = 0.09 V/s.


... additional/final points to address about UMEs:

1) You can buy them; how do you make them?
2) UME arrays and ensembles
3) Potential step experiments with UMEs...
4) How rapidly is steady-state attained?