Lecture #8 of 18
Q: What’s in this set of lectures?
A: Introduction, Review, and B&F Chapter 1, 15 & 4 main concepts:

● Section 1.1: Redox reactions
● Chapter 15: Electrochemical instrumentation
● Section 1.2: Charging interfaces
● Section 1.3: Overview of electrochemical experiments
● Section 1.4: Mass transfer and Semi-empirical treatment of electrochemical observations
● Chapter 4: Mass transfer
Looking forward… Section 1.4 and Chapter 4

- Mass transfer
- Diffusion
- Migration / Drift
- Convection
- Semi-empirical models
- Balance sheets
... B&F's "balance sheets" help us understand the role of migration in steady-state electrolytic mass transport. *Let's break them down:*

![Diagram of electrolysis cell](image)

**0.1 M HCl**

**Figure 4.3.2** Balance sheet for electrolysis of hydrochloric acid solution. (a) Cell schematic. (b) Various contributions to the current when 10e are passed in the external circuit per unit time.
all ions in the bulk of the cell contribute to migration by an amount proportional to their transport number...

\[ t_i = \frac{|z_i|u_iC_i}{\sum_j |z_j|u_jC_j} \]

0.1 M HCl
... B&F’s “balance sheets” help us understand the role of migration in steady-state electrolytic mass transport. Let’s break them down:

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0.1 M HCl

**Figure 4.3.2** Balance sheet for electrolysis of hydrochloric acid solution.
(a) Cell schematic. (b) Various contributions to the current when 10e are passed in the external circuit per unit time.

\[ t_{H^+} = \frac{|1|(3.6 \times 10^{-3} \text{ cm}^2\text{s}^{-1}\text{V}^{-1})(0.1 \times 10^{-3} \text{ mol/cm}^3)}{1|(3.6 \times 10^{-3} \text{ cm}^2\text{s}^{-1}\text{V}^{-1})(0.1 \times 10^{-3} \text{ mol/cm}^3) + 1|(7.9 \times 10^{-4} \text{ cm}^2\text{s}^{-1}\text{V}^{-1})(0.1 \times 10^{-3} \text{ mol/cm}^3)} = 0.82 \]

\[ t_{Cl^-} = 0.18 \approx 2 \]

\[ \sim 8 \]
diffusion occurs only in regions where a concentration gradient exists... near the electrodes...

0.1 M HCl

these coefficients are the values necessary to satisfy the steady-state condition of $i = i_m + i_d$... for example, at the cathode (left):

$10H^+$(needed) = $8H^+$(migration) + $2H^+$(diffusion) + $2Cl^-$ (diffusion) for charge balance
... B&F’s “balance sheets” help us understand the role of migration in steady-state electrolytic mass transport. Let’s break them down:

and at the anode (right):
\[ 10\text{Cl}^-(\text{needed}) = 2\text{Cl}^-(\text{migration}) + 8\text{Cl}^-(\text{diffusion}) + 8\text{H}^+(\text{diffusion}) \] for charge balance
... B&F’s “balance sheets” help us understand the role of migration in steady-state electrolytic mass transport. Let’s break them down:

If we focus on the **cathode H\(^+\) current** and **anode Cl\(^-\) current**...

![Diagram of electrolysis](image)

---

**0.1 M HCl**

---

**cathode (for H\(^+\))**: \(i = -10; \ i_d = -2, \ i_m = -8 \) (80% of the H\(^+\) current is migration)

**anode (for Cl\(^-\))**: \(i = +10; \ i_d = 8, \ i_m = 2 \) (20% of the Cl\(^-\) current is migration)

---

**Figure 4.3.2** Balance sheet for electrolysis of hydrochloric acid solution. 
(a) Cell schematic. (b) Various contributions to the current when 10e are passed in the external circuit per unit time.
... once again, counter ions move to maintain electroneutrality in the diffusion layers.

This is a negative current...

0.001 M Cu$^{2+}$/Cu$^{+}$

... and so is this!

-5(2) + 7(1) = -3

= 3(1) = +3

$6e^-$ needs 6 “+”s, whose ratios are $t_i$

**Figure 4.3.3** Balance sheet for electrolysis of the Cu(II), Cu(I), NH$_3$ system. (a) Cell schematic. (b) Various contributions to the current when 6$e$ are passed in the external circuit per unit time; $i = 6, n = 1$. For Cu(II) at the cathode, $|i_m| = (1/2)(1/3)(6) = 1$ (equation 4.3.3), $i_d = 6 - 1 = 5$ (equation 4.3.4). For Cu(I) at the anode, $|i_m| = (1/1)(1/6)(6) = 1$, $i_d = 6 + 1 = 7$. 

... once again, counter ions move to maintain electroneutrality in the diffusion layers ...

... and this is a positive current (at that electrode)...

\[
0.001 \text{ M } \text{Cu}^{2+}/\text{Cu}^+ 
\]

\[
\begin{align*}
-5(2) + 7(1) &= -3 \\
= 3(1) &= +3 \\
= -3(1) &= -3
\end{align*}
\]

\[6e^- \text{ needs } 6 \text{ "+"s, whose ratios are } t_i \]

... and so is this!

\[5(2) + -7(1) = +3 \]

**Figure 4.3.3** Balance sheet for electrolysis of the Cu(II), Cu(I), NH₃ system. (a) Cell schematic. (b) Various contributions to the current when \(6e\) are passed in the external circuit per unit time; \(i = 6, n = 1\). For Cu(II) at the cathode, \(|i_m| = (1/2)(1/3)(6) = 1\) (equation 4.3.3), \(i_d = 6 - 1 = 5\) (equation 4.3.4). For Cu(I) at the anode, \(|i_m| = (1/1)(1/6)(6) = 1\), \(i_d = 6 + 1 = 7\).
Adding a supporting electrolyte reduces the original \( i_m \) values.

0.001 M \( \text{Cu}^{2+}/\text{Cu}^+ \)

0.1 M \( \text{NaClO}_4 \)

\( \text{Na}^+\text{ClO}_4^- \) dominates because they carry the most current; their contribution to \( \sigma \) is large, and thus their \( t \) is large.

Figure 4.3.4  Balance sheet for the system in Figure 4.3.3, but with excess \( \text{NaClO}_4 \) as a supporting electrolyte. (a) Cell schematic. (b) Various contributions to the current when \( 6e \) are passed in the external circuit per unit time \( (i = 6, n = 1) \). \( t_{\text{Cu(II)}} = [(2 \times 10^{-3})\lambda/(2 \times 10^{-3} + 10^{-3} + 3 \times 10^{-3} + 0.2)\lambda] = 0.0097 \). For \( \text{Cu(II)} \) at the cathode, \( |i_m| = (1/2)(0.0097)(6) = 0.03 \), \( i_d = 6 - 0.03 = 5.97 \).
... adding a supporting electrolyte reduces the original $i_m$ values

0.001 M Cu$^{2+}$/Cu$^+$

0.1 M NaClO$_4$

But this is actually much more complex because of the...

... diffusion effects here →

Na$^+$ClO$_4^-$ dominates because they carry the most current; their contribution to $\sigma$ is large, and thus their $t$ is large

Figure 4.3.4 Balance sheet for the system in Figure 4.3.3, but with excess NaClO$_4$ as a supporting electrolyte. (a) Cell schematic. (b) Various contributions to the current when 6e are passed in the external circuit per unit time ($i = 6, n = 1$). $t_{Cu(II)} = [(2 \times 10^{-3}) \lambda/(2 \times 10^{-3} + 10^{-3} + 3 \times 10^{-3} + 0.2)\lambda] = 0.0097$. For Cu(II) at the cathode, $[i_m] = (1/2)(0.0097)(6) = 0.03$, $i_d = 6 - 0.03 = 5.97$. 
... adding a supporting electrolyte reduces the original $i_m$ values

0.001 M Cu$^{2+}$/Cu$^+$
0.1 M NaClO$_4$

But this is actually much more complex because of the...

... diffusion effects here →

Na$^+$ClO$_4^-$ dominates because they carry the most current; their contribution to $\sigma$ is large, and thus their $t$ is large

Na$^+$, ClO$_4^-$, and Cl$^-$ share the charge balance responsibilities

**Figure 4.3.4** Balance sheet for the system in Figure 4.3.3, but with excess NaClO$_4$ as a supporting electrolyte. (a) Cell schematic. (b) Various contributions to the current when $6e$ are passed in the external circuit per unit time ($i = 6, n = 1$). $t_{\text{Cu(II)}} = [(2 \times 10^{-3}) \lambda/(2 \times 10^{-3} + 10^{-3} + 3 \times 10^{-3} + 0.2)\lambda] = 0.0097$. For Cu(II) at the cathode, $|i_m| = (1/2)(0.0097)(6) = 0.03, i_d = 6 - 0.03 = 5.97.$
... adding a supporting electrolyte reduces the original $i_m$ values

0.001 M Cu$^{2+}$/Cu$^+$

0.1 M NaClO$_4$

But this is actually much more complex because of the...

... diffusion effects here $\rightarrow$

Na$^+$ClO$_4^-$ dominates because they carry the most current; their contribution to $\sigma$ is large, and thus their $t$ is large

Na$^+$, ClO$_4^-$, and Cl$^-$ share the charge balance responsibilities

CHECK: $-5.97(2) + 6.029(1) = -5.911…$

Figure 4.3.4 Balance sheet for the system in Figure 4.3.3, but with excess NaClO$_4$ as a supporting electrolyte. (a) Cell schematic. (b) Various contributions to the current when 6$e$ are passed in the external circuit per unit time ($i = 6, n = 1$). $t_{\text{Cu(II)}} = [(2 \times 10^{-3}) \lambda/(2 \times 10^{-3} + 10^{-3} + 3 \times 10^{-3} + 0.2)\lambda] = 0.0097$. For Cu(II) at the cathode, $[i_m] = (1/2)(0.0097)(6) = 0.03$, $i_d = 6 - 0.03 = 5.97.$
... adding a supporting electrolyte reduces the original $i_m$ values

0.001 M Cu$^{2+}$/Cu$^+$
0.1 M NaClO$_4$

But this is actually much more complex because of the...

... diffusion effects here →

Na$^+$ClO$_4^-$ dominates because they carry the most current; their contribution to $\sigma$ is large, and thus their $t$ is large

Na$^+$, ClO$_4^-$, and Cl$^-$ share the charge balance responsibilities

CHECK: $-5.97(2) + 6.029(1) = -5.911... +2.92(1) + 2.92(1) = 5.84...$

**Figure 4.3.4** Balance sheet for the system in Figure 4.3.3, but with excess NaClO$_4$ as a supporting electrolyte. (a) Cell schematic. (b) Various contributions to the current when 6$e$ are passed in the external circuit per unit time ($i = 6$, $n = 1$). $i_{Cu(II)} = [(2 \times 10^{-3}) \lambda/(2 \times 10^{-3} + 10^{-3} + 3 \times 10^{-3} + 0.2)\lambda] = 0.0097$. For Cu(II) at the cathode, $|i_m| = (1/2)(0.0097)(6) = 0.03$, $i_d = 6 - 0.03 = 5.97$. 
... adding a supporting electrolyte reduces the original $i_m$ values

$0.001 \text{ M Cu}^{2+}/\text{Cu}^+$

$0.1 \text{ M NaClO}_4$

But this is actually much more complex because of the...

... diffusion effects here →

CHECK: $-5.97(2) + 6.029(1) = -5.911... +2.92(1) + 2.92(1) = 5.84...$ so, $+0.071$ for $\text{Cl}^-$ toward the cathode

... and $-0.071$ for $\text{Cl}^-$ away from the anode

$\text{Na}^+\text{ClO}_4^-$ dominates because they carry the most current; their contribution to $\sigma$ is large, and thus their $t$ is large

$\text{Na}^+$, $\text{ClO}_4^-$, and $\text{Cl}^-$ share the charge balance responsibilities

Figure 4.3.4 Balance sheet for the system in Figure 4.3.3, but electrolyte. (a) Cell schematic. (b) Various contributions to the current when $6e$ are passed in the external circuit per unit time ($i = 6$, $n = 1$). $t_{\text{Cu(II)}} = [(2 \times 10^{-3}) \lambda/(2 \times 10^{-3} + 10^{-3} + 3 \times 10^{-3} + 0.2)\lambda] = 0.0097$. For Cu(II) at the cathode, $[i_m] = (1/2)(0.0097)(6) = 0.03$, $i_d = 6 - 0.03 = 5.97$. 
… adding a supporting electrolyte reduces the original \( i_m \) values

### 0.001 M Cu\(^{2+}\)/Cu\(^+\)  
### 0.1 M NaClO\(_4\)

![Electrolyte Diagram](image)

### FOR YOUR REFERENCE

<table>
<thead>
<tr>
<th>Diffusion</th>
<th>Diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.9709 Cu((II))</td>
<td>5.9709</td>
</tr>
<tr>
<td>6.0291 Cu((I))</td>
<td>6.0291</td>
</tr>
<tr>
<td>2.92Na(^+)</td>
<td>2.91</td>
</tr>
<tr>
<td>2.92ClO(_4) (^-)</td>
<td>2.91</td>
</tr>
</tbody>
</table>

**CHECK:** 
-5.9709(2) + 6.0291(1) = -5.9127...  
+2.91(1) + 2.91(1) = 5.82... so, +0.0927 for Cl\(^-\) toward the cathode

**Figure 4.3.4** Balance sheet for the system in Figure 4.3.3, t ... and -0.0927 for Cl\(^-\) away from the anode

*Balance sheet now balances*  
*This is a very challenging sign convention, so don’t worry about it. Just use absolute numbers!*
Okay, let’s end with doing our own example… Consider a 0.10 M equimolar solution of K₃Fe(CN)₆ and K₄Fe(CN)₆:

\[
\text{Fe}^{\text{III}}(\text{CN})_6^{3-} + 1\text{e}^- \rightleftharpoons \text{Fe}^{\text{II}}(\text{CN})_6^{4-}
\]

* anions move toward the anode
* cations move toward the cathode
1) Calculate all $t$’s *(for now, assume mobilities are equal, and thus cancel)*.

\[ t_{\text{Fe(CN)}_6^{3-}} = \frac{|3| \times (0.1 \times 10^{-3} \text{ mol/cm}^3)}{|3| \times (0.1 \times 10^{-3} \text{ mol/cm}^3) + |4| \times (0.1 \times 10^{-3} \text{ mol/cm}^3) + |1| \times (0.7 \times 10^{-3} \text{ mol/cm}^3)} \]

\[ t_{\text{Fe(CN)}_6^{3-}} = \frac{|3| \times (0.1)}{|3| \times (0.1) + |4| \times (0.1) + |1| \times (0.7)} = 0.214 \approx 0.2 \]

\[ t_{\text{Fe(CN)}_6^{4-}} = \frac{|4| \times (0.1)}{|3| \times (0.1) + |4| \times (0.1) + |1| \times (0.7)} = 0.286 \approx 0.3 \]

\[ t_i = \frac{|z_i| u_i C_i}{\sum_j |z_j| u_j C_j} \quad t_{K^+} = \frac{|1| \times (0.7)}{|3| \times (0.1) + |4| \times (0.1) + |1| \times (0.7)} \approx 0.5 \]

2) Convert $t$’s to migrational ion displacements…
2) Convert t’s to *migrational* ion displacements...

\[
10 \times 0.5 \times 1 = 5 \text{ K}^+
\]

\[
10 \times 0.2 \times 1/3 = 2/3 \text{ Fe(CN)}_6^{3-}
\]

\[
10 \times 0.3 \times 1/4 = 3/4 \text{ Fe(CN)}_6^{4-}
\]

3) Calculate *diffusional* ion displacements by difference:
Okay, let’s end with doing our own example…

Consider a 0.10 M equimolar solution of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$:

$$Fe^{III}(CN)_6^{3-} + 1e^- \rightleftharpoons Fe^{II}(CN)_6^{4-}$$

- **Cathode:**
  - $10 e^- \rightarrow 10 Fe(CN)_6^{4-}$
  - $10 Fe(CN)_6^{3-} \leftarrow 10 e^-$
  - $10 \times 0.5 \times 1 = 5 K^+$
  - $10 \times 0.2 \times \frac{1}{3} = \frac{2}{3} Fe(CN)_6^{3-}$
  - $10 \times 0.3 \times \frac{1}{4} = \frac{3}{4} Fe(CN)_6^{4-}$

- **Anode:**
  - $10 e^- \rightarrow 10 Fe(CN)_6^{4-}$
  - $10 Fe(CN)_6^{3-} \leftarrow 10 e^-$
2) Convert t’s to *migrational* ion displacements...

\[
\begin{align*}
10 \times 0.5 \times 1 &= 5 \text{ K}^+ \\
10 \times 0.2 \times 1/3 &= 2/3 \text{ Fe(CN)}_6^{3-} \\
10 \times 0.3 \times 1/4 &= 3/4 \text{ Fe(CN)}_6^{4-}
\end{align*}
\]

3) Calculate *diffusional* ion displacements by difference:

**cathode**
\[
10 \text{ Fe(CN)}_6^{3-} (\text{needed}) = -2/3 \text{ Fe(CN)}_6^{3-} (\text{mig}) + 10 \frac{2}{3} \text{ Fe(CN)}_6^{3-} (\text{diff}) \\
-10 \text{ Fe(CN)}_6^{4-} (\text{needed}) = -3/4 \text{ Fe(CN)}_6^{4-} (\text{mig}) - 9 \frac{1}{4} \text{ Fe(CN)}_6^{4-} (\text{diff})
\]

**anode**
\[
-10 \text{ Fe(CN)}_6^{3-} (\text{needed}) = 2/3 \text{ Fe(CN)}_6^{3-} (\text{mig}) - 10 \frac{2}{3} \text{ Fe(CN)}_6^{3-} (\text{diff}) \\
10 \text{ Fe(CN)}_6^{4-} (\text{needed}) = 3/4 \text{ Fe(CN)}_6^{4-} (\text{mig}) + 9 \frac{1}{4} \text{ Fe(CN)}_6^{4-} (\text{diff})
\]
Okay, let’s end with doing our own example…
Consider a 0.10 M equimolar solution of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$:

$$Fe^{III}(CN)_6^{3-} + 1e^- \rightleftharpoons Fe^{II}(CN)_6^{4-}$$

\[
\begin{align*}
\text{cathode} & : \\
10 \text{ e}^- & \rightarrow 10 \text{ Fe(CN)}_6^{4-} & 10 \text{ e}^- & \rightarrow 10 \text{ Fe(CN)}_6^{4-} \\
10 \text{ Fe(CN)}_6^{3-} & \rightarrow 10 \text{ Fe(CN)}_6^{4-} & 10 \text{ Fe(CN)}_6^{3-} & \rightarrow 10 \text{ Fe(CN)}_6^{4-}
\end{align*}
\]

\[
\begin{align*}
10 \times 0.5 \times 1 &= 5 \text{ K}^+ \\
10 \times 0.2 \times 1/3 &= \frac{2}{3} \text{ Fe(CN)}_6^{3-} \\
10 \times 0.3 \times 1/4 &= \frac{3}{4} \text{ Fe(CN)}_6^{4-}
\end{align*}
\]

\[
\begin{align*}
-9 \frac{1}{4} \text{ Fe(CN)}_6^{4-} & \rightarrow 10 \frac{2}{3} \text{ Fe(CN)}_6^{3-} & 9 \frac{1}{4} \text{ Fe(CN)}_6^{4-} & \rightarrow -10 \frac{2}{3} \text{ Fe(CN)}_6^{3-}
\end{align*}
\]
3) Calculate *diffusional* ion displacements by difference:

**cathode**

\[
10 \text{Fe(CN)}_6^{3-} \text{(needed)} = -\frac{2}{3} \text{Fe(CN)}_6^{3-} \text{(mig)} + 10 \frac{2}{3} \text{Fe(CN)}_6^{3-} \text{(diff)}
\]

\[
-10 \text{Fe(CN)}_6^{4-} \text{(needed)} = -\frac{3}{4} \text{Fe(CN)}_6^{4-} \text{(mig)} - 9 \frac{1}{4} \text{Fe(CN)}_6^{4-} \text{(diff)}
\]

**anode**

\[
-10 \text{Fe(CN)}_6^{3-} \text{(needed)} = 2\frac{1}{3} \text{Fe(CN)}_6^{3-} \text{(mig)} - 10 \frac{2}{3} \text{Fe(CN)}_6^{3-} \text{(diff)}
\]

\[
10 \text{Fe(CN)}_6^{4-} \text{(needed)} = 3\frac{1}{4} \text{Fe(CN)}_6^{4-} \text{(mig)} + 9 \frac{1}{4} \text{Fe(CN)}_6^{4-} \text{(diff)}
\]

4) Counter ions move to maintain electroneutrality in diffusion layers:

**cathode**

\[
(+10 2\frac{2}{3} \text{Fe(CN)}_6^{3-})(3) + (-9 1\frac{1}{4} \text{Fe(CN)}_6^{4-})(4)
\]

\[
32 - 37 = -5 \text{ (means +5 counterion diffusion... away from the electrode)}
\]

**anode**

\[
(+9 1\frac{1}{4} \text{Fe(CN)}_6^{4-})(4) + (-10 2\frac{2}{3} \text{Fe(CN)}_6^{3-})(3)
\]

\[
37 - 32 = +5 \text{ (means -5 counterion diffusion... toward the electrode)}
\]
Okay, let’s end with doing our own example…

Consider a 0.10 M equimolar solution of $\text{K}_3\text{Fe(CN)}_6$ and $\text{K}_4\text{Fe(CN)}_6$:

$$\text{Fe}^{\text{III}}(\text{CN})_6^{3-} + 1\text{e}^- \rightleftharpoons \text{Fe}^{\text{II}}(\text{CN})_6^{4-}$$

\[
\begin{align*}
\text{cathode} & \quad \text{anode} \\
10 \text{ Fe(CN)}_6^{3-} & \quad 10 \text{ Fe(CN)}_6^{3-} \\
10 \text{ e}^- & \quad 10 \text{ e}^- \\
10 \times 0.5 \times 1 &= 5 \text{ K}^+ \\
10 \times 0.2 \times \frac{1}{3} &= \frac{2}{3} \text{ Fe(CN)}_6^{3-} \\
10 \times 0.3 \times \frac{1}{4} &= \frac{3}{4} \text{ Fe(CN)}_6^{4-} \\
-9 \frac{1}{4} \text{ Fe(CN)}_6^{4-} & \quad 9 \frac{1}{4} \text{ Fe(CN)}_6^{4-} \\
10 \frac{2}{3} \text{ Fe(CN)}_6^{3-} & \quad -10 \frac{2}{3} \text{ Fe(CN)}_6^{3-} \\
5 \text{ K}^+ & \quad -5 \text{ K}^+ 
\end{align*}
\]
5. Finally, tally $i_m$ and $i_d$:

so, for the reaction of Fe(CN)$_6^{3-}$ at the cathode:

$$i_m = \frac{-\frac{2}{3}}{-\frac{2}{3} + 10 \cdot \frac{2}{3}} = -0.066$$

(–) means migration will "reduce" the total current
5. Finally, tally $i_m$ and $i_d$:

so, for the reaction of $\text{Fe(CN)}_6^{3-}$ at the cathode:

$$i_m = \frac{-2/3}{-2/3 + 10^{2/3}} = -0.066$$  \((-) \text{ means migration will "reduce" the total current}

$$i_d = \frac{10^{2/3}}{-2/3 + 10^{2/3}} = +1.066$$  \((+) \text{ … the diffusional current should always be positive}

and, for the reaction of $\text{Fe(CN)}_6^{4-}$ at the anode:
Okay, let’s end with doing our own example…
Consider a 0.10 M equimolar solution of K₃Fe(CN)₆ and K₄Fe(CN)₆:

\[
\text{Fe}^{\text{III}}(\text{CN})_6^{3-} + 1e^- \rightleftharpoons \text{Fe}^{\text{II}}(\text{CN})_6^{4-}
\]
5. Finally, tally $i_m$ and $i_d$:

so, for the reaction of $\text{Fe(CN)}_6^{3-}$ at the cathode:

$$i_m = \frac{-\frac{2}{3}}{-\frac{2}{3} + 10 \frac{2}{3}} = -0.066$$

(−) means migration will "reduce" the total current

$$i_d = \frac{10 \frac{2}{3}}{-\frac{2}{3} + 10 \frac{2}{3}} = +1.066$$

$I_d$ will be larger by 6.6% as compared to its value in the absence of migration

and, for the reaction of $\text{Fe(CN)}_6^{4-}$ at the anode:

$$i_m = \frac{+\frac{3}{4}}{+\frac{3}{4} + 9 \frac{1}{4}} = +0.075$$

(+ means migration will "add to" the total current

$$i_d = \frac{9 \frac{1}{4}}{+\frac{3}{4} + 9 \frac{1}{4}} = +0.925$$

$I_d$ will be smaller by 7.5% as compared to its value in the absence of migration
5. Finally, tally $i_m$ and $i_d$: **Boom! ... Problem analyzed!**

so, for the reaction of $\text{Fe(CN)}_6^{3-}$ at the cathode:

\[
i_m = \frac{-2/3}{-2/3 + 10 \cdot 2/3} = -0.066
\]

(−) means migration will "reduce" the total current

\[
i_d = \frac{10 \cdot 2/3}{-2/3 + 10 \cdot 2/3} = +1.066
\]

$I_d$ will be larger by 6.6% as compared to its value in the absence of migration

and, for the reaction of $\text{Fe(CN)}_6^{4-}$ at the anode:

\[
i_m = \frac{+3/4}{+3/4 + 9 \cdot 1/4} = +0.075
\]

(+) means migration will "add to" the total current

\[
i_d = \frac{9 \cdot 1/4}{+3/4 + 9 \cdot 1/4} = +0.925
\]

$I_d$ will be smaller by 7.5% as compared to its value in the absence of migration
Does the following make sense? Reaction is: \( \text{Tl}^+ + e^- \rightleftharpoons \text{Tl}^0 \)

Equation derived from diffusive transport only:

\[
i_l = nFAM_{\text{O}}C^*_{\text{O}}
\]

\[
m_{\text{O}} = D_{\text{O}}/\delta_{\text{O}}
\]

Figure 4.3.5 Voltammograms for reduction of 0.65 mM \( \text{Tl}_2\text{SO}_4 \) at a mercury film on a silver ultramicroelectrode (radius, 15 \( \mu \)m) in the presence of (a) 0, (b) 0.1, (c) 1, and (d) 100 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 shifts in wave position along the potential axis. [Reprinted with permission from M. Ciszkowska and J. G. Osteryoung, Anal. Chem., 67, 1125 (1995). Copyright 1995, American Chemical Society.]
Does the following make sense? Reaction is: $\text{Tl}^+ + e^- \rightleftharpoons \text{Tl}^0$

**Figure 4.3.5** Voltammograms for reduction of 0.65 mM Tl$_2$SO$_4$ at a mercury film on a silver ultramicroelectrode (radius, 15 µm) in the presence of (a) 0, (b) 0.1, (c) 1, and (d) 100 mM 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 shifts in wave position along the potential axis. [Reprinted with permission from M. Ciszkowska and J. G. Osteryoung, *Anal. Chem.*, 67, 1125 (1995). Copyright 1995, American Chemical Society.]
... so, supporting electrolyte removes (most) drift of redox species of interest... but it also removes $iR_u$ drop from data (2 for 1)...

The $iR$ drop – well-known but often underestimated in electrochemical polarization measurements and corrosion testing

W. Oelßner*, F. Berthold and U. Guth

... let’s just open the paper and look at figures: 1, 4, 5, 7, 14, 16
... and finally, iR drop is not always of the form “iR”...

Uncompensated resistance:

\[ \kappa = \sigma \quad \text{Planar WE} \]

\[ R_u = \frac{x}{\kappa A} \]
... and finally, iR drop is not always of the form “iR”...

Uncompensated resistance:

\[ \kappa = \sigma \]

**Planar WE**

\[ R_u = \frac{x}{\kappa A} \]

**Point WE**

\[ R_u = \frac{1}{4\pi \kappa r_0} \left( \frac{x}{x + r_0} \right) \]

What happens when \( x \to \infty \)?

Němec, *J. Electroanal. Chem.*, 1964, 8, 166
A review of Section 1.4 (and Chapter 4)

- Mass transfer
- Diffusion
- Migration / Drift
- Convection
- Semi-empirical models
- Balance sheets
Q: What was in that **HUGE** (first, and second) set of lectures?
A: Introduction, Review, and B&F Chapter 1, 15 & 4 main concepts:

- Section 1.1: Redox reactions
- Chapter 15: Electrochemical instrumentation
- Section 1.2: Charging interfaces
- Section 1.3: Overview of electrochemical experiments
- Section 1.4: Mass transfer and Semi-empirical treatment of electrochemical observations
- Chapter 4: Mass transfer
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
- Section 5.3 & 5.9: Ultramicroelectrodes
- Sections 5.7 – 5.8: Chronoamperometry/Chronocoulometry
we use both of Fick’s laws to derive equations for transport-controlled electrochemistry...

Fick’s 1st Law of Diffusion:

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

... derive it (approximately) in a similar fashion as the diffusion coefficient... get your favorite beverage!
we use both of Fick’s laws to derive equations for transport-controlled electrochemistry...

**Fick’s 1st Law of Diffusion:**

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

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

\[J_0(x, t) = \frac{1}{A} \left( \frac{N_O(x)}{2} - \frac{N_O(x + \Delta x)}{2} \right) \frac{1}{\Delta t}\]
we use both of Fick’s laws to derive equations for transport-controlled electrochemistry...

Fick’s 1st Law of Diffusion:

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

\[J_O(x, t) = \frac{1}{A} \frac{N_O(x) - N_O(x + \Delta x)}{2} \frac{2}{\Delta t} \frac{\Delta x^2}{\Delta x^2}\]
Fick’s 1st Law of Diffusion:

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

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

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

\[D_O \]

… derived!
we use both of Fick’s laws to derive equations for transport-controlled electrochemistry...

Fick’s 1\textsuperscript{st} Law of Diffusion:

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

B&F, pg. 149

Fick’s 2\textsuperscript{nd} 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 it (approximately) in a similar fashion as Fick’s first law…
... derivation is not so bad...

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

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

**Figure 4.4.4** Fluxes into and out of an element at \( x \).
\[
\frac{\partial C_O(x, t)}{\partial t} = D_O \left( \frac{\partial^2 C_O(x, t)}{\partial x^2} \right)
\]

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

\[
J(x + dx, t) = J(x, t) + \frac{\partial J(x, t)}{\partial x} dx
\]
... derivation is not so bad...

FOR YOUR REFERENCE

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

\[ \frac{\partial C_0(x, t)}{\partial t} = \frac{J(x, t) - J(x + dx, t)}{dx} \]

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

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

(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* ($C_O(0, t) = 0$)

![Diagram](image)  

**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.
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:

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

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

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

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

$$i = nFAJ_O(0, t)$$
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:

$$L\{F(t)\} \equiv \int_0^\infty e^{-st}F(t)\,dt$$
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 $F(t) = 1$?

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

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

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

how about $F(t) = kt$?

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

$$L\{kt\} = \int_0^\infty e^{-st}(kt)\,dt = k \int_0^\infty te^{-st}\,dt = k \left( \frac{e^{-st}}{s^2} (-st - 1) \right) \bigg|_0^\infty$$

Integrated by parts
how about $F(t) = kt$?

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

\[ = k \left( 0 - \frac{1}{s^2} (-1) \right) = \frac{k}{s^2} \]

Integrated by parts

Used L’Hôpital’s rule
how about $F(t) = kt$?

$$L\{kt\} = \int_0^\infty e^{-st}(kt)\,dt = k \int_0^\infty te^{-st}\,dt = k \left. \left( \frac{e^{-st}}{s^2} (-st - 1) \right) \right|_0^\infty$$

Integrated by parts

Used L’Hôpital’s rule

$$= k \left( 0 - \frac{1}{s^2} (-1) \right) = \frac{k}{s^2}$$

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

$$L\{e^{-at}\} = \int_0^\infty e^{-st} e^{-at}\,dt = \int_0^\infty e^{-(s+a)t}\,dt = \left. \frac{e^{-(s+a)t}}{-(s + a)} \right|_0^\infty$$
how about $F(t) = kt$?

$$L\{kt\} = \int_0^\infty e^{-st}(kt)\,dt = k \int_0^\infty te^{-st}\,dt = k \left( \frac{e^{-st}}{s^2} (-st - 1) \right) \bigg|_0^\infty$$

Integrated by parts

Used L'Hôpital's rule

$$= k \left( 0 - \frac{1}{s^2} (-1) \right) = \frac{k}{s^2}$$

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

$$L\{e^{-at}\} = \int_0^\infty e^{-st} e^{-at}\,dt = \int_0^\infty e^{-(s+a)t}\,dt = \left. \frac{e^{-(s+a)t}}{-(s+a)} \right|_0^\infty$$

$$= 0 - \frac{1}{-(s + a)} = \frac{1}{s + a}$$
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: \[ F(t) = \frac{\partial C_O(x, t)}{\partial t} - D_O \left( \frac{\partial^2 C_O(x, t)}{\partial x^2} \right) \]

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

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

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

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

the Laplace transform of \( C(x, t) \)? … Isn’t this cheating?
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: \[ F(t) = \frac{\partial C_O(x, t)}{\partial t} - D_O \left( \frac{\partial^2 C_O(x, t)}{\partial x^2} \right) \]

\[
L \left\{ \frac{\partial C_O(x, t)}{\partial t} - D_O \left( \frac{\partial^2 C_O(x, t)}{\partial x^2} \right) \right\} = \bar{C}(x, s)
\]
\[ \int_{a}^{b} g(x)f'(x)\,dx = [g(x)f(x)]_{a}^{b} - \int_{a}^{b} f(x)g'(x)\,dx \]

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

Integration, by parts, again!

\[ \int_{0}^{\infty} e^{-st} \frac{\partial C_{0}(x, t)}{\partial t} dt \]

\[ = [e^{-st}C(x, t)]_{0}^{\infty} - \int_{0}^{\infty} C(x, t)(-se^{-st})dx \]

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

... and at time = 0, what is the value of \( C \), anywhere?
Integration, by parts, again!

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

\[
\int_0^\infty e^{-st} \frac{\partial C_0(x, t)}{\partial t} \,dt
\]

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

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

... and at time = 0, what is the value of $C$, anywhere?

... Just $C^*$!
L.T. of Fick’s 2nd Law...

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

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

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

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
L.T. of Fick’s 2nd Law...

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

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

$$L \left\{ \frac{\partial C_O(x, t)}{\partial t} - D_O \left( \frac{\partial^2 C_O(x, t)}{\partial x^2} \right) \right\}$$

is this...

$$s \bar{C}(x, s) - C^* - D \frac{\partial^2 \bar{C}(x, s)}{\partial x^2}$$

Now what? Well, recall they are equal to each other, then rearrange...

... and what does it look like?

our equation:

$$\frac{d^2 \bar{C}(x, s)}{dx^2} - \frac{s}{D} \bar{C}(x, s) = -\frac{C^*}{D}$$
L.T. of Fick's 2nd Law...

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

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

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

is this...

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

Now what? Well, recall they are equal to each other, then rearrange...

... and what does it look like?

our equation:

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

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

\[ \frac{d^2}{dx^2} \psi(x) - \frac{2m}{\hbar^2} (E - V(x)) \psi(x) = 0 \]
our equation:
\[
\frac{d^2C(x, s)}{dx^2} - \frac{s}{D} C(x, s) = -\frac{C^*}{D}
\]

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

\[
\frac{d^2}{dx^2} \psi(x) - \frac{2m}{\hbar^2} (E - V(x)) \psi(x) = 0
\]

the solution of the Schrödinger Eq. is:

\[
\psi(x) = A' \exp \left( -\sqrt{\frac{2m(E - V(x))}{\hbar}} x \right) + B' \exp \left( \sqrt{\frac{2m(E - V(x))}{\hbar}} x \right)
\]
our equation: \[
\frac{d^2 \overline{C}(x, s)}{dx^2} - \frac{s}{D} \overline{C}(x, s) = -\frac{C^*}{D}
\]

the time-independent \textit{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 the \textit{Schrödinger Eq.} is:

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

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

\[
\overline{C}(x, s) = \frac{C^*}{s} + A'(s) \exp \left( -\sqrt{\frac{s}{D}} x \right) + B'(s) \exp \left( \sqrt{\frac{s}{D}} x \right)
\]
Now, what are $A'$ and $B'$ and how do we get rid of the “s”?
… We need some boundary conditions!
Now, what are $A'$ and $B'$ and how do we get rid of the “s”?

... We need some **boundary conditions**!

1. \[
\lim_{x \to \infty} C_O(x, t) = C^*_O
\]

   \[
   \text{L.T.}
   \]

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

   called **semi-infinite linear (because of $x$) diffusion**
\( \bar{C}(x, s) = \frac{C^*}{s} + A'(s)\exp\left(-\sqrt{\frac{S}{D}}x\right) + B'(s)\exp\left(\sqrt{\frac{S}{D}}x\right) \)

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

... We need some boundary conditions!

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

L.T.

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

What does this do for us?

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

... and so \( B' \) must be 0
some boundary conditions...

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

L.T.

\( \lim_{x \to \infty} \overline{C}(x, s) = \frac{C^*}{s} \)
some boundary conditions...

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

\[
\text{L.T.}
\]

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

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

\[
\text{L.T.}
\]

\[ \bar{C}(0, s) = 0 \]
some boundary conditions...

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

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

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

What does this do for us?
\[ \bar{C}(x, s) = \frac{C^*}{s} + A'(s)\exp\left(-\sqrt{\frac{s}{D}}x\right) \]

\[ 0 = \frac{\bar{C}(0, s)}{s} + A'(s)\exp\left(-\sqrt{\frac{s}{D}}0\right) = \frac{C^*}{s} + A'(s) \]

\[ A'(s) = -\frac{C^*}{s} \]

now our solution is fully constrained...

\[ \bar{C}_O(x, s) = \frac{C^*_O}{s} - \frac{C^*_O}{s} e^{-\sqrt{s/D_O}x} \]
now our solution is fully constrained… and we need “t” back!!

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

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

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

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

\[ \text{erfc}(x) \equiv 1 - \text{erf}(x) \]
Now... what's erf c?

Complementary Error Function

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

Gaussian distribution, with mean = 0 and std. dev. = $1/\sqrt{2}$
\[ C_O(x, t) = C_O^* \left\{ 1 - \text{erfc} \left[ \frac{x}{2(D_O t)^{1/2}} \right] \right\} \]

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

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

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

... Let's plot it!
Hey, these look completely reasonable!

\( C^* = 1 \times 10^{-6} \text{ M} \)
\( D = 1 \times 10^{-5} \text{ M} \)

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

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

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

... and with \( i = nF A J(0, t) ... \)

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

the Cottrell Equation
... and finally, Step #3 using Step #2...

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

... and with \( i = nF AJ(0, t) \)...

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

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 Corp. in 1912

... initial funding from profits on patents for the electrostatic precipitator, used to clear smokestacks of charged soot particles