Lecture #10 of 26
Mass Transfer Processes

Chapters 1 and 4
Q: What’s in this set of lectures?
A: B&F Chapters 1 & 4 main concepts:

● 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 diffusive models
- Conductivity
- Transport (Transference) number
- Balance sheets
- Ohmic drop/loss
... well, that must have been incorrect (it’s not!)...

anyway, let’s try this again... Grab a beverage and let’s go on a (random) walk!

(RECALL:)

\[ \overline{\Delta}^2 = ml^2 = \frac{t}{\tau} l^2 = 2Dt \]

\[ D = \frac{l^2}{2\tau} \]

(Recall: \( D_z \) is has units of cm\(^2\) s\(^{-1}\), as \( zz \))

**Figure 4.4.2** (a) Probability distribution for a one-dimensional random walk over zero to four time units. The number printed over each allowed arrival point is the number of paths to that point. (b) Bar graph showing distribution at \( t = 4\tau \). At this time, probability of being at \( x = 0 \) is 6/16, at \( x = \pm 2l \) is 4/16, and at \( x = \pm 4l \) is 1/16.

\[ \overline{\Delta} = \sqrt{(2d)Dt}, \text{ where } d \text{ is the dimension} \]

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

\( m \) is just the number

\( \tau \) is step time

\( l \) is step length

Root mean square (rms) displacement (standard deviation)
... so how far do species diffuse in electrochemistry?

<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>

*the rms displacement

In both directions from a...

... plane

... wire, line, tube

... point, sphere, disk

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

a characteristic "diffusion length"

root mean square (rms) displacement (standard deviation)

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

... and the “2” is for positive and negative directions
... so how far do species diffuse in electrochemistry in 1D?

Given $D = 5 \times 10^{-6}$ cm$^2$ s$^{-1}$ (but memorize $\sim 10^{-5}$ cm$^2$ s$^{-1}$),

<table>
<thead>
<tr>
<th>time</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ms</td>
<td>1 $\mu$m</td>
</tr>
<tr>
<td>0.1 s</td>
<td>10 $\mu$m</td>
</tr>
<tr>
<td>10 s</td>
<td>0.1 mm</td>
</tr>
<tr>
<td>16.7 min</td>
<td>1 mm</td>
</tr>
<tr>
<td>1.157 day</td>
<td>1 cm</td>
</tr>
<tr>
<td>0.32 year</td>
<td>10 cm $\approx$ 3.9&quot;</td>
</tr>
</tbody>
</table>

$\Delta = \sqrt{(2d)D}t$, where $d$ is the dimension

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

a characteristic
"diffusion length"

root mean square (rms) displacement
(standard deviation)
... what are typical values for diffusion coefficients, for species in electrochemistry?

And why are both so... fast?

<table>
<thead>
<tr>
<th>Cation</th>
<th>$D$ x $10^{-5}$ cm$^2$/s</th>
<th>Anion</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H^+$</td>
<td>9.31</td>
<td>$OH^-$</td>
<td>5.28</td>
</tr>
<tr>
<td>$Li^+$</td>
<td>1.03</td>
<td>$F^-$</td>
<td>1.47</td>
</tr>
<tr>
<td>$Na^+$</td>
<td>1.33</td>
<td>$Cl^-$</td>
<td>2.03</td>
</tr>
<tr>
<td>$K^+$</td>
<td>1.96</td>
<td>$Br^-$</td>
<td>2.08</td>
</tr>
<tr>
<td>$Rb^+$</td>
<td>2.07</td>
<td>$I^-$</td>
<td>2.05</td>
</tr>
<tr>
<td>$Cs^+$</td>
<td>2.06</td>
<td>$NO_3^-$</td>
<td>1.90</td>
</tr>
<tr>
<td>$Ag^+$</td>
<td>1.65</td>
<td>$CH_3COO^-$</td>
<td>1.09</td>
</tr>
<tr>
<td>$NH_4^+$</td>
<td>1.96</td>
<td>$CH_3CH_2COO^-$</td>
<td>0.95</td>
</tr>
<tr>
<td>$N(C_4H_9)_4^+$</td>
<td>0.52</td>
<td>$B(C_5H_5)_4^-$</td>
<td>0.53</td>
</tr>
<tr>
<td>$Ca^{2+}$</td>
<td>0.79</td>
<td>$SO_4^{2-}$</td>
<td>1.06</td>
</tr>
<tr>
<td>$Mg^{2+}$</td>
<td>0.71</td>
<td>$CO_3^{2-}$</td>
<td>0.92</td>
</tr>
<tr>
<td>$La^{3+}$</td>
<td>0.62</td>
<td>$Fe(CN)_6^{3-}$</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Note: Values at infinite dilution in $10^{-5}$ cm$^2$/sec. Calculated from data of Robinson and Stokes (1960).

“Diffusion: Mass Transfer in Fluid Systems,” 2013, by E. L. Cussler

Why are both so... slow, as examples?

- on the order of $10^{-6}$ cm$^2$/s for molecules
- on the order of $10^{-7}$ cm$^2$/s for proteins

$a$ characteristic "diffusion length"

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

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

root mean square (rms) displacement (standard deviation)
Protons (and hydroxide ions, maybe) do not diffuse by normal thermal motion... they hop between molecules... by a **Grotthuss mechanism**...

\[
D(H^+) = 9.31 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \\
D(OH^-) = 5.28 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}
\]

http://www.snipview.com/q/Grotthuss%20mechanism

**a "cartoon"**

Theodor von Grotthuss (1785–1822)

from Wiki
Protons (and hydroxide ions, maybe) do not diffuse by normal thermal motion... they hop between molecules... by a **Grotthuss mechanism**...

D(H⁺) = 9.31 x 10⁻⁵ cm² s⁻¹
D(OH⁻) = 5.28 x 10⁻⁵ cm² s⁻¹

http://www.snipview.com/q/Grotthuss%20mechanism

"cartoon"
Proton transfer is enabled by an additional O–O bond contraction, not required in H$_5$O$_2^+$. This explains why the activation energy for hydroxide mobility is larger than that of proton mobility by about 0.5 kcal/mol. The transfer cycle is terminated by hydrogen-bond formation to the other oxygen center. Available experimental data, and most of the computational results, can be rationalized in the framework of the above model. © 2000 Elsevier Science B.V. All rights reserved.

at the molecular level$^2$–$^8$. In contrast, hydroxide ion mobility in basic solutions has received far less attention$^2$–$^5$,$^9$,$^{10}$, even though bases and base catalysis play important roles in many organic and biochemical reactions and in the chemical industry. The reason for this may be attributed to the century-old notion$^{11}$ that a hydrated OH$^-$ can be regarded as a water molecule missing a proton, and that the transport mechanism of such a ‘proton hole’ can be inferred from that of an excess proton by simply reversing hydrogen bond polarities$^{11–18}$. However, recent studies$^2$–$^3$ have identified OH$^-$ hydration complexes that bear little structural similarity to proton hydration complexes. Here we report the solution structures and transport mechanisms of hydrated hydroxide, which we obtained from first-principles computer simulations that explicitly treat quantum and thermal fluctuations of all nuclei$^{19–21}$. We find that the transport mechanism, which differs significantly from the proton hole picture, involves an interplay between the previously identified hydration complexes$^2$–$^3$ and is strongly influenced by nuclear quantum effects.


intriguing topics in aqueous chemistry. It is considered that these ions in aqueous solutions move via sequential proton transfer events, known as the Grotthuss mechanisms. Here, we present an experimental study of the diffusion and H/D exchange of hydronium and hydroxide ions in amorphous solid water (ASW) at 140–180 K by using low-energy sputtering (LES) and temperature-programmed desorption (TPD) measurements. The study shows that the two species transport in ASW via fundamentally different molecular mechanisms. Whereas hydronium ions migrate via efficient proton transfer, hydroxide ions move via Brownian molecular diffusion without proton transfer. The molecular hydroxide diffusion in ASW is in stark contrast to the current view of the hydroxide diffusion mechanism in aqueous solution, which involves proton tr

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Moving on... remember this...
... to seed our next topic, let’s assume that the walker is *charged*...

"Captain e-"

Figure 4.4.2  (a) Probability distribution for a one-dimensional random walk over zero to four time units. The number printed over each allowed arrival point is the number of paths to that point. (b) Bar graph showing distribution at \( t = 4\tau \). At this time, probability of being at \( x = 0 \) is 6/16, at \( x = \pm 2l \) is 4/16, and at \( x = \pm 4l \) is 1/16.

... Flashback! Pascal’s triangle! ...
… what if we applied an external field to this scenario?…
… then the random walk would no longer be quite so random!

... welcome to the concept of ionic migration/drift

Figure 4.4.2 (a) Probability distribution for a one-dimensional random walk over zero to four time units. The number printed over each allowed arrival point is the number of paths to that point. (b) Bar graph showing distribution at \( t = 4\tau \). At this time, probability of being at \( x = 0 \) is 6/16, at \( x = \pm 2\ell \) is 4/16, and at \( x = \pm 4\ell \) is 1/16.

… Flashback! Pascal’s triangle! …
Diffusion coefficient \((D, \text{cm}^2 \text{s}^{-1})\) – “proportionality constant relating the flux of [the] amount of [an entity to its] concentration gradient...” (IUPAC Gold Book)

**Fick’s first law of steady-state Diffusion:** \(N_z = -D_z \frac{dc}{dz}\) in 1D

Mobility \((\mu, \text{cm}^2 \text{V}^{-1} \text{s}^{-1})\) – “the limiting velocity of an ion in an electric field of unit strength” (B&F, pg. 66)... or a proportionality constant relating the velocity of an ion to the electric field strength

... start with **Newton’s second law of motion:** \(F = m \cdot a\)

... \(|z|eE = m \cdot \frac{v_d}{\tau}\), with \(e\), elementary charge (C),

\[E\], electric field (V cm\(^{-1}\)),

\(v_d\), average drift velocity (cm s\(^{-1}\)),

\(\tau\), mean time (s) to reset drift motion through collisions (i.e. \(v = 0\))

Because \(v_{d,z} = \mu_z \cdot E_z\), this means that \(\mu = |z|e \frac{\tau}{m}\)

... and the units of mobility are correct \((\text{cm s}^{-1}) = \mu \cdot (\text{V cm}^{-1})\)
... and another formula for ionic mobility, $\mu_i$

the mobility is defined from **Stokes' law** by the **Stokes–Einstein equation**

based on the balance of forces acting on a particle, with charge, $ze$, and moving in an electric field, $E$:

$$6\pi \eta rv \overset{\text{viscous drag}}{\longrightarrow} ze \overset{\text{electrophoretic force}}{\longrightarrow} |z_i|eE$$

$$\mu_i = \frac{v}{E} = \frac{|z_i|e}{6\pi \eta r}$$

Mathematician, Physicist, Politician, and Theologian

Physicist & Philosopher

Sir George Gabriel Stokes (1819–1903)

Albert Einstein (1879–1955)
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Newton's second law of motion: 

\[
F = m \cdot a, \quad v_d = \mu \cdot E
\]

Stokes' law: 

\[
F = |z|eE = 6\pi \eta r v_d, \text{ and so by solving } \\
\mu = \frac{v_d}{E} \text{ above, one gets } \mu = \frac{|z|e}{6\pi \eta r} \text{ which gives a physical meaning to the mobility, with } \eta \text{ (dynamic viscosity of the medium) and } r \text{ (radius of the spherical ion)}
\]

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Mathematician, Physicist, Politician, and Theologian

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**Newton’s second law of motion:** \( F = m \cdot a, v_d = \mu \cdot E \)

... and a very important point is that these two parameters, \( D \) and \( \mu \), are related!

... Einstein–Smoluchowski equation,

\[
\mu_i = \frac{|z_i|FD_i}{RT}
\]

... and what is the value of \( \frac{RT}{F} \)? **25.7 mV**!
... some textbooks (Bockris) initially define the migration/drift term in terms of mobility based on straightforward physical reasoning...

... use the Nernst–Planck equation for one species, $i$, which is defined as:

$$
N_i = -D_i \frac{dc_i}{dx} - \frac{|z_i|}{z_i} \mu_i c_i \frac{d\phi}{dx} + c_i v
$$

... and the E–S equation can be derived by the following reasoning...

... evaluate the condition where the net flux is zero in a quiescent solution, meaning transport due to thermal motion and that from the force of an electric field cancel each other out...

$$
0 = -D_i \frac{dc_i}{dx} - \frac{|z_i|}{z_i} \mu_i c_i \frac{d\phi}{dx} + c_i v
$$

Bockris & Reddy, Fig. 4.62
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$$0 = -D_i \frac{dc_i}{dx} - \frac{|z_i|}{z_i} \mu_i c_i \frac{d\phi}{dx} + c_i v$$

$$D_i \frac{dc_i}{dx} = - \frac{|z_i|}{z_i} \mu_i c_i \frac{d\phi}{dx}$$

and using the “Boltzmann law,” $c_i = c_{0,i} e^{-\frac{\bar{\mu}_i}{RT}}$,

$$D_i \left(- \frac{1}{RT} c_{0,i} e^{-\frac{\bar{\mu}_i}{RT}} \cdot \frac{d\bar{\mu}_i}{dx}\right) = - \frac{|z_i|}{z_i} \mu_i \left(c_{0,i} e^{-\frac{\bar{\mu}_i}{RT}}\right) \cdot \frac{d\phi}{dx}, \text{ and (flip the } z_i \text{ term)},$$

$$D_i \left(\frac{|z_i|}{z_i} \frac{1}{RT} \cdot \frac{d\bar{\mu}_i}{dx}\right) = \mu_i \cdot \frac{d\phi}{dx}, \text{ and because the electric potential component of the electrochemical potential equals } z_i F \phi, \text{ then } \frac{d\bar{\mu}_i}{d\phi} = z_i F,$$

$$\mu_i = \frac{|z_i| F D_i}{RT} \ldots \text{ the Einstein–Smoluchowski equation}$$
... and now lastly, a simplified (cleaner) Nernst–Planck equation...

From before, for one species the total flux in one-dimension is

\[ N = -\frac{Dc}{RT} \cdot \frac{d\mu}{dx} + cv, \ldots \text{\{several math steps from before\}} \]

\[ N = -D \cdot \frac{dc}{dx} \cdot \frac{zFD}{RT} c \cdot \frac{d\phi}{dx} + cv \ldots \]

... which can also be written using the E–S equation

\[ \mu_i = \frac{|z_i|FD_i}{RT} \]

\[ D_i = \frac{RT\mu_i}{|z_i|F} \]

B&F, 4.2.2

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_iF}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i \nu(x) \]
... and now lastly, a simplified (cleaner) Nernst–Planck equation...

From before, for one species the total flux in one-dimension is

\[
N = - \frac{D c}{RT} \frac{d \mu}{dx} + c v, \quad \text{... \{several math steps from before\}}
\]

\[
N = -D \frac{dc}{dx} - \frac{z F D}{RT} c \frac{d\phi}{dx} + cv \ldots
\]

... which can also be written using the E–S equation

\[
\begin{align*}
N &= -D \frac{dc}{dx} + \mu c \frac{d\phi}{dx} + cv \\
&= -D_i \frac{dc_i}{dx} + \frac{|z_i| F D_i}{RT} \frac{d\mu_i}{dx} + c v
\end{align*}
\]

As again, recall that the current density can be simplified even further... in the absence of convection...

\[
J_{x,i} = \frac{\sigma_i d \bar{\mu}_i}{z_i F} dx
\]

\[
J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)
\]
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Wow, those were some hefty equations... there is some value in thinking semi-quantitatively about mass transport and B&F developed a formalism for this (pp. 29–35):

Why?

The goal: Derive a (simple) expression for the current as a function of the applied potential in our electrochemical cell.
first, let’s eliminate contributions to transport from migration/drift and convection **SO WE CAN FOCUS ON DIFFUSIONAL EFFECTS**...

\[
J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)
\]

... which you can’t actually do anyway!

And imagine a scenario where not only this is true, but where \(dC/dx\) is time invariant, meaning **at steady-state**, and thus you should see no hysteresis. (Ironically, this situation is encountered when the bulk solution *is* stirred... more on that in a bit...)
Wow, those were some hefty equations... there is some value in thinking semi-quantitatively about mass transport and B&F developed a formalism for this (pp. 29–35):

first, let’s eliminate contributions to transport from migration/drift and convection **SO WE CAN FOCUS ON DIFFUSIONAL EFFECTS**...

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i \nu(x) \]

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} \]

now, consider specifically the reduction of some molecule "O" (first w/o "R"):

\[ \text{O} + n\text{e}^- \rightleftharpoons \text{R} \]

(example: \([\text{Fe}^{III}(\text{CN})_6]^{3-} + 1\text{e}^- \rightleftharpoons [\text{Fe}^{II}(\text{CN})_6]^{4-}\))
... because we are at steady-state, let’s approximate the concentration gradient near the WE as a linear function:

\[ J_0(x) = -D_0 \frac{C^*_O - C_O(x = 0)}{\delta_O} \]

where \( C^*_O \) is the bulk concentration of O, \( \delta \) is the Nernst diffusion layer thickness

the linear approximation

the TRUE concentration gradient

Bard & Faulkner, 2nd Ed., Figure 1.4.1

stirring of the bulk solution causes \( \delta \) to become well-defined, time-invariant, and a short distance to encounter bulk solution conditions

**Figure 1.4.1**  Concentration profiles (solid lines) and diffusion layer approximation (dashed lines). \( x = 0 \) corresponds to the electrode surface and \( \delta_O \) is the diffusion layer thickness. Concentration profiles are shown at two different electrode potentials: (1) where \( C_O(x = 0) \) is about \( C^*_O/2 \), (2) where \( C_O(x = 0) \approx 0 \) and \( i = i_l \).
... because we are at steady-state, let’s approximate the concentration gradient near the WE as a linear function:

\[
J_0(x) = -D_0 \frac{C_0^* - C_0(x = 0)}{\delta_0}
\]

where \(C_0^*\) is the bulk concentration of O, \(\delta\) is the Nernst diffusion layer thickness

FYI: an “unstirred” solution will have \(\delta \approx 0.050\) cm (50 µm) after \(\sim 1\) sec (Bockris, Reddy, and Gamboa-Aldeco, Modern EChem, Vol. 2A, 2002, pg. 1098)

stirring of the bulk solution causes \(\delta\) to become well-defined, time-invariant, and a short distance to encounter bulk solution conditions

**Figure 1.4.1** Concentration profiles (solid lines) and diffusion layer approximation (dashed lines). \(x = 0\) corresponds to the electrode surface and \(\delta_0\) is the diffusion layer thickness. Concentration profiles are shown at two different electrode potentials: (1) where \(C_0(x = 0)\) is about \(C_0^*/2\), (2) where \(C_0(x = 0) \approx 0\) and \(i = i_l\).
... because it will be convenient later, group the diffusion coefficient with the diffusion layer thickness:

\[ m_0 = \frac{D_0}{\delta_0} \]

where \( m_0 \) is the mass transfer coefficient (units: \( \text{cm s}^{-1} \))

* Note: dimensionally we have \( (\text{cm}^2 \text{s}^{-1})/\text{cm} \)

... substituting...

\[ J_0(x) = -m_0 [C_0^* - C_0(x = 0)] \]

moles s\(^{-1}\) cm\(^{-2}\)  \hspace{1cm} \text{cm s}^{-1}  \hspace{1cm} \text{moles cm}^{-3}
... because it will be convenient later, group the diffusion coefficient with the diffusion layer thickness:

\[ m_o = \frac{D_o}{\delta_o} \]

where \( m_o \) is the mass transfer coefficient (units: cm \( s^{-1} \))

* Note: dimensionally we have (cm\(^2\) s\(^{-1}\))/cm

... substituting...

\[ J_o(x) = -m_o[C_o^* - C_o(x = 0)] \]

... writing the flux (i.e. areal rate) in terms of the current...

\[ \frac{i}{nFA} = m_o[C_o(x = 0) - C_o^*] \] (1.4.6)

... since this was assumed to be at steady-state, the flux for the transport of "R" must be opposite and at the same rate...

\[ \frac{i}{nFA} = m_R[C_R^* - C_R(x = 0)] \]
... and to simply the process, define the fastest rate, \( i_l \), as when \( C_0(x = 0) = 0 \)

\[
\frac{i}{nFA} = m_o [C_0(x = 0) - C^*_o]
\]

\[
\frac{i_l}{nFA} = m_o [0 - C^*_o] = -m_o C^*_o
\]

\[
\frac{i - i_l}{nFA} = m_o C_0(x = 0)
\]

... and, as an example, if no R is present initially then \( C^*_R = 0 \)

\[
\frac{i}{nFA} = m_R [C^*_R - C_R(x = 0)] = -m_R C_R(x = 0)
\]

... now we can obtain the potential dependence of the current by making two substitutions into the Nernst Equation, which we assume holds given that electron-transfer from/to the electrode to/from O/R is rapid enough that equilibrium concentrations are maintained at the electrode surface...

\[
E = E^0 + \frac{RT}{nF} \ln \left( \frac{C_O(x = 0)}{C_R(x = 0)} \right)
\]
...and this equation is further simplified by using the definition for the half-wave potential: $E = E_{1/2}$ when $i = i_l/2$.

$$E_{1/2} = E^{0'} - \frac{RT}{nF} \ln \left( \frac{m_0}{m_R} \right) + \frac{RT}{nF} \ln \left( \frac{i_l - i_l/2}{i_l/2} \right)$$
and this equation is further simplified by using the definition for the half-wave potential: \( E = E_{1/2} \) when \( i = i_l/2 \).

\[
E = E^0' - \frac{RT}{nF} \ln \left( \frac{m_0}{m_R} \right) + \frac{RT}{nF} \ln \left( \frac{i_l - i}{i} \right)
\]

**formal potential** = experimentally measured \( E^0 \)

\[
E_{1/2} = E^0' - \frac{RT}{nF} \ln \left( \frac{m_0}{m_R} \right) + \frac{RT}{nF} \ln \left( \frac{i_l - i_{l/2}}{i_{l/2}} \right)
\]

\[
E_{1/2} = E^0' - \frac{RT}{nF} \ln \left( \frac{m_0}{m_R} \right)
\]
$E = E_{1/2} + \frac{RT}{nF} \ln \left( \frac{i_l - i}{i} \right)$

... this will show up again...

![Diagram](image)

**Figure 1.4.2**  (a) Current-potential curve for a nernstian reaction involving two soluble species with only oxidant present initially. (b) $\log[(i_l - i)/i]$ vs. $E$ for this system.

What happens to the potential when $i \rightarrow i_l$? $E \rightarrow -\infty$

What happens to the potential when $i \rightarrow 0$? $E \rightarrow +\infty$
... and when \( C_R^* \neq 0 \ldots \)

\[
E = E^{0'} - \frac{RT}{nF} \ln \left( \frac{m_0}{m_R} \right) + \frac{RT}{nF} \ln \left( \frac{i_{l,c} - i}{i - i_{l,a}} \right)
\]

Looks linear...

We could define a “resistance” (activation energy) for this using Ohm’s law (but it’s not an ohmic process)...

\( R_{mt} \)

We could also define a linearized overpotential formula here... \( \eta_{\text{conc}} \) (or \( \eta_{mt} \))

\[
i_{l,c}/i_{l,a} = \frac{D_O c_O}{D_R c_R}
\]

**Figure 1.4.3** Current-potential curve for a nernstian system involving two soluble species with both forms initially present.

... but recall that this is all due to mass transport by **diffusion** only...

... what if we now also include mass transport by migration/drift?...