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

RECALL: 
... 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! From B&F

\[ \Delta = \sqrt{2D t} \]

mean square displacement (variance)

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

(Recall: D, is has units of cm² s⁻¹, as x²)

Figure 4.42. (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) The graph, showing distribution at \( r = 4t \). At this time, probability of being at \( x = 0 \) or \( x = 4t \), at \( x = \pm 2t \), or \( x = \pm 4t \) is 1/16.

- how far do species diffuse in electrochemistry?

<table>
<thead>
<tr>
<th>Dimension</th>
<th>( \Delta^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D</td>
<td>( \sqrt{2D t} )</td>
</tr>
<tr>
<td>2D</td>
<td>( \sqrt{4D t} )</td>
</tr>
<tr>
<td>3D</td>
<td>( \sqrt{6D t} )</td>
</tr>
</tbody>
</table>

\[ \Delta = \sqrt{2D t} \] root mean square (rms) displacement

\[ \Delta^* = \sqrt{2D t} \] a characteristic "diffusion length"

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

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

In both directions from a...

- plane
- wire, line, tube
- point, sphere, disk

Recall:

\[ \Delta = \frac{\sqrt{2D t}}{N} \]

\( s = \text{cm} \)
... so how far do species diffuse in electrochemistry in 1D?  

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

<table>
<thead>
<tr>
<th>time</th>
<th>( \Delta )</th>
</tr>
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<tbody>
<tr>
<td>1 ms</td>
<td>1 ( \mu \text{m} )</td>
</tr>
<tr>
<td>0.1 s</td>
<td>10 ( \mu \text{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 = 3.9&quot;</td>
</tr>
</tbody>
</table>

\[ \Delta = \sqrt{\langle D d \rangle t}, \] where \( d \) is the dimension

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

\[ \text{a characteristic "diffusion length"} \]

... what are typical values for diffusion coefficients, for species in electrochemistry?

And why are both so... slow, as examples?

\[ \Delta = \sqrt{\langle D d \rangle t}, \] where \( d \) is the dimension

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

\[ \text{a characteristic "diffusion length"} \]

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

\[ D(\text{H}^+) = 9.31 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \]
\[ D(\text{OH}^-) = 5.28 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \]
Protons (and hydroxide ions, maybe) do not diffuse by normal thermal motion... they hop between molecules... by a Grotthuss mechanism...

\[
\begin{align*}
D(H^+) &= 9.31 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1} \\
D(OH^-) &= 5.28 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}
\end{align*}
\]

a "cartoon"

http://www../../../2mecha.png

Chemist

Theodor von Grotthuss (1785–1822)
from Wiki

... OH\textsuperscript{–} (and even H\textsuperscript{+}) transport mechanisms are not fully agreed upon... Protons transfer is enabled by an additional 0–0 bond contraction, as required in H\textsuperscript{2}O\textsuperscript{-}. This explains why the oxidation energy for hydroxide mobility is larger than that of proton mobility by about 63 kcal/mol. The longer cycle is termed by hydrogen bond formation to the empty oxygen center. Available experimental data, and most of the computational results, can be rationalized in the framework of the above model. (2009 Elsevier Science B.V. All rights reserved.


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- Ohmic drop/loss
Moving on... remember this...
... to seed our next topic, let's assume that the walker is **charged**...

![Flashback! Pascal's triangle! From B&F](image)

... what if we applied an external field to this scenario?...
... then the random walk would no longer be quite so random!

![Flashback! Pascal's triangle! From B&F](image)

... anyway... some very important background "first"...

**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**:

\[
N_z = -D \frac{dc}{dz} \text{ in 1D}
\]

**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**: \( F = ma \)

... \( |e|E = m \cdot \frac{\Delta v}{\Delta t} \) with \( e \), elementary charge (C), \( E \), electric field (V cm\(^{-1}\)), \( \Delta v \), average drift velocity (cm s\(^{-1}\)), \( \tau \), mean time (s) to reset drift motion through collisions (i.e. \( v = 0 \))

Because \( \mu = \frac{|e|E}{m} \)

... and the units of mobility are correct... (cm s\(^{-1}\)) = \( \mu \cdot (V \text{ cm}^{-1}) \)
... 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, $E$:

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

... anyway... some very important background “first”...

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

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Mobility ($\mu$, cm$^2$ V$^{-1}$ 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

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

Stokes’ law: $F = \frac{|z|eE}{6\pi \eta r}$, and so by solving $\mu = \frac{|z|eE}{6\pi \eta r}$ above, one gets $\mu = \frac{|z|eE}{6\pi \eta r}$, which gives a physical meaning to the mobility, with $\eta$ (dynamic viscosity of the medium) and $r$ (radius of the spherical ion)

... and what is the value of $RT/F$?

Scientist Marian Smoluchowski (1872–1917)

... 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 $RT/F$? 25.7 mV!
... use the Nernst–Planck equation for one species, \( i \), which is defined as...

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

... 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} - z_i \mu_i c_i \frac{d\phi}{dx} + c_i v
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... some textbooks (Bockris) initially define the migration/drift term in terms of mobility based on straightforward physical reasoning...

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\]
... and now lastly, a simplified (cleaner) Nernst–Planck equation...

electrochemical potential

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

\[ N = \frac{dc}{dx} \mu c \frac{d\phi}{dx} + cv \]  

... several math steps from before

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

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

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

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

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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...)

\[ \frac{J_i}{x} = -D_i \frac{\partial C_i}{\partial x} - \frac{z_i F}{R T} \frac{\partial \phi}{\partial x} + \frac{C_i(x)}{\delta} \]

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

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

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

\[ \text{(example: } [\text{Fe}^{III}(CN)_{6}]^{3-} + 1e^{-} \rightarrow [\text{Fe}^{II}(CN)_{6}]^{4-} \text{) } \]

... because we are at steady-state, let’s approximate the concentration gradient near the WE as a linear function:

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

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

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

... 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 \( \delta_0 \) is the diffusion layer thickness. Concentration profiles are shown at two different electrode potentials: (1) where \( C_i(x = 0) \) is about \( \frac{C_i^0}{2} \), (2) where \( C_i(x = 0) \approx 0 \) and \( i = i_0 \).
... because we are at steady-state, let’s approximate the concentration gradient near the WE as a linear function:

\[ I_O(x) = -D_O \frac{C_O - C_O(x = 0)}{\delta_O} \]

where \( C_O \) is the bulk concentration of O, \( \delta \) is the Nernst diffusion layer thickness.

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

... 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 \((\text{cm}^2 \text{s}^{-1})/\text{cm}\)

... substituting...

\[ I_O(x) = -m_O[C_O - C_O(x = 0)] \]

... 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, \( i \), as when \( C_\text{O}(x = 0) = 0 \):

\[
\frac{i}{nF} = m_0[0 - C_\text{O}^*] = -m_0C_\text{O}^* \\
\frac{i}{nFA} = m_0C_\text{O}(x = 0)
\]

... and, as an example, if no \( R \) is present initially then \( C_\text{R}^* = 0 \):

\[
\frac{i}{nFA} = m_\text{R}[C_\text{R} - C_\text{R}(x = 0)] = -m_\text{R}C_\text{R}(x = 0)
\]

... 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...

\[
E = E^0 + \frac{RT}{nF} \ln \frac{C_\text{O}(x = 0)}{C_\text{R}(x = 0)}
\]

... and this equation is further simplified by using the definition for the half-wave potential: \( E = E_{1/2} \) when \( i = i/2 \).

\[
E_{1/2} = E^0 - \frac{RT}{nF} \ln \frac{m_0}{m_\text{R}} + \frac{RT}{nF} \ln \left( \frac{m_\text{O}}{m_\text{R}} \right) \\
E_{1/2} = E^0 - \frac{RT}{nF} \ln \left( \frac{m_0}{m_\text{R}} \right)
\]

... and this equation is further simplified by using the definition for the half-wave potential: \( E = E_{1/2} \) when \( i = i/2 \).

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

... this will show up again...

Figure 1.4.2: (a) Current-potential curve for a nernstian reaction involving two soluble species with only oxidant present initially. (b) log(\(i_l - \hat{i}\)) 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 \(C_R^* \neq 0\)...

\[ E = E^0' - \frac{RT}{nF} \ln \left( \frac{m_O}{m_R} \right) + \frac{RT}{nF} \ln \left( \frac{i_{lc} - l}{l - i_{in}} \right) \]

... this will show up again too...

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... \(\eta_{conc}\) (or \(\eta_{mt}\))

Looks linear...

\[ i_{lc}/i_{in} = (D_O\hat{C}_O)/(D_R\hat{C}_R) \]

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

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