Lecture #6 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
Mass transfer is (mostly) driven by gradients in electrochemical potential…

Mass transfer, for a charged species, sounds like a current!

How is current density ($\mathbf{J}$, A cm$^{-2}$) is related to flux ($\mathbf{N}$, mol cm$^{-2}$ s$^{-1}$)?

... well, current density has units of A cm$^{-2}$ = C cm$^{-2}$ s$^{-1}$...

... and flux has units of mol cm$^{-2}$ s$^{-1}$...

... So what do we need to equate these? ...

... something with units of C mol$^{-1}$...

$$J_x = zF N_x$$

The total current density, in one-dimension, due to all charged species is,

$$J_x = zF N_x = zF \sum_i \left(- \frac{D_{i,x} c_i}{RT} \cdot \frac{d\bar{\mu}_i}{dx} + c_i \nu_{i,x} \right), \text{ and in 3D,}$$

$$\mathbf{J} = zF \mathbf{N} = zF \sum_i \left(- \frac{D_i c_i}{RT} \cdot \nabla \bar{\mu}_i + c_i \mathbf{v}_i \right), \text{ where } \nabla \text{ is “del” (nabla)}$$

... where $D_i$ is the diffusion coefficient of species $i$ (in units of cm$^2$ s$^{-1}$), $c$ is the concentration (in units of mol cm$^{-3}$), $\bar{\mu}$ is the electrochemical potential (in units of J mol$^{-1}$), and $\nu$ is the velocity (in units of cm s$^{-1}$)
Mass transfer is (mostly) driven by gradients in electrochemical potential...

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How is current density \( (J, \text{A cm}^{-2}) \) related to flux \( (N, \text{mol cm}^{-2} \text{s}^{-1}) \)?

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... where \( D_i \) is the diffusion coefficient of species \( i \) (in units of cm\(^2 \text{s}^{-1} \)), \( c \) is the concentration (in units of mol cm\(^{-3} \)), \( \bar{\mu} \) is the electrochemical potential (in units of J mol\(^{-1} \)), and \( \nu \) is the velocity (in units of cm s\(^{-1} \))
mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: diffusion, migration, and convection

the *Nernst-Planck Equation*:

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

the total **flux** of reactant *i* to a flat electrode (this is *N_i(x)* in many textbooks, especially engineering ones; it has units of mol cm\(^{-2}\) s\(^{-1}\))

Walther Hermann Nernst (1864–1941) Nobel Prize (Chemistry, 1920)
Max Karl Ernst Ludwig Planck (1858–1947) Nobel Prize (Physics, 1918)
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the diffusive flux of reactant \( i \) to a flat electrode where \( D_i \) is the diffusion coefficient for species, \( i \) (\( D \) has units of \( \text{cm}^2 \text{ s}^{-1} \))

B&F, 1.4.2 & 4.1.8
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\]

the flux due to migration/drift of reactant \(i\)

where \(z_i\) is the charge on species \(i\),

and \(\partial \phi/\partial x\) is the gradient in electric potential

B&F, 1.4.2 & 4.1.8
mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: diffusion, migration, and convection.

the *Nernst-Planck Equation*:

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\]

the flux due to convection of reactant \( i \) where \( \nu(x) \) is the velocity profile of the solution.
mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: diffusion, migration, and convection.

the *Nernst-Planck Equation*:

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

... so, because we are adding up three contributions to the flux, which is proportional to the current (density), if we drew a circuit to represent these terms, would these be in series or in parallel?
mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: diffusion, migration, and convection

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In parallel... $J_i(x) = J_1 + J_2 + J_3$
mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: diffusion, migration, and convection.

the Nernst-Planck Equation:

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

B&F, 1.4.2 & 4.1.8

… so, if \( J_{\text{drift}} \) is huge and \( J_{\text{diffusion}} \) is small, what process dictates \( J \)?

… and now what if there was rapid stirring?
mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: diffusion, migration, and convection

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mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: diffusion, migration, and convection.

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... again... but where did this equation for flux come from?

... who’s comfortable with me just giving you this equation?
Electrochemical potential of species $i$ in phase $\beta$ is an energy ($\text{J/mol}$),

$$\bar{\mu}_i^\beta = \left( \frac{\partial G}{\partial n_i^\beta} \right)_{T,p,n_j\neq i} = \mu_i^\beta + z_i F \phi^\beta,$$

where

- $G$ (Gibbs free energy ($\text{J}$))
- $n_i$ (amount of species $i$ ($\text{mol}$))
- $\mu_i = \mu_i^0 + RT \ln a_i$ (chemical potential ($\text{J/mol}$))
- $z_i$ (valancy of species $i$)
- $F \approx 10^5$ (Faraday constant ($\text{C/mol}$))
- $\phi^\beta$ (Galvani/inner electric potential ($\text{V}$))
- $a_i$ (activity of species $i$)

For an uncharged species $\bar{\mu}_i^\beta = \mu_i^\beta$.


IUPAC Gold (http://goldbook.iupac.org)
From before, for one species the total flux in one-dimension is

\[ N = -\frac{Dc}{RT} \cdot \frac{d\mu}{dx} + cv, \]

where again \( D \) is diffusion coefficient (cm\(^2\) s\(^{-1}\)), \( c \) is concentration (mol cm\(^{-3}\)), \( \mu \) is the electrochemical potential (J mol\(^{-1}\)), \( v \) is velocity (cm s\(^{-1}\))

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Recall that \( \bar{\mu}_i^\beta = \mu_i^\beta + z_i F_\beta \) and so,

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flux

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and finally...

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i \nu(x) \]
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Some very important background “first”… okay, second!

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

(The second law is for non-steady-state conditions, where time is another independent variable.)
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)

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\(D\) also exhibits Arrhenius behavior: \(D = D_0 e^{-\frac{E_a}{RT}}\)

where \(D_0\) is the maximum \(D\) (at infinite \(T\)
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Steady-state? …
… Initial states equilibrate using ICE, ICE Baby!

\[
\begin{align*}
A & \iff B + C
\end{align*}
\]

<table>
<thead>
<tr>
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<tr>
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[http://chemwiki.ucdavis.edu/Physical_Chemistry/Equilibria/Le_Chatelier%27s_Principle/Ice_Tables](http://chemwiki.ucdavis.edu/Physical_Chemistry/Equilibria/Le_Chatelier%27s_Principle/Ice_Tables)

Steady-state? …

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\[ A \overset{\Leftrightarrow}{\underset{\text{ICE}}{\longrightarrow}} B + C \]

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Vanilla Ice wants to know, “What happens if, as the initial state progresses, you keep supplying A and pulling B and C away?” …
… Le Chatelier’s Principle keeps the reaction going…

\[
\rightarrow \text{A} \xleftrightarrow{\text{B + C}} \rightarrow
\]

… but for how long? …
… Le Chatelier’s Principle keeps the reaction going…

\[ \rightarrow A \iff B + C \rightarrow \]

… but for how long? …

\[ M_1 \rightarrow A \iff B + C \rightarrow M_2 \]

… as long as the supply in and the flow out is constant…

… and in electrochemical systems, as long as a constant potential bias is applied!
Le Chatelier’s Principle keeps the reaction going…

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… and in electrochemical systems, as long as a constant potential bias is applied!

In an ideal world, i.e. under certain *rare* conditions,

\[
\frac{\partial c_A}{\partial t} = \frac{\partial c_B}{\partial t} = \frac{\partial c_C}{\partial t} = 0, \text{ and the system is in a *steady state* where there is a net flux of species (generation of A and loss of B and C) but the concentrations in the cell do not change with time.}
\]
Who cares? …

… when the current is at a steady state, *the current is constant*, and there is no new capacitive charging!

\[
M_1 \rightarrow A \leftrightarrow B + C \rightarrow M_2
\]

… for steady-state current, KCL applies… no, not KCl… but KCL!
Who cares? …

… when the current is at a steady state, *the current is constant*, and there is no new capacitive charging!

For steady-state current, KCL applies… no, not KCl… but KCL!

**Kirchhoff’s Current Law (KCL)**

\[
\sum_{k=1}^{n} I_k = 0
\]

\[
i_{\text{out}} = i_{\text{in}}
\]

\[
i_1 + i_4 = i_2 + i_3
\]

But KCL applies to the *entire circuit*, including in the potentiostat! (when the current flow, i.e. due motion of charges, is at steady state)

... hey, what are those minus signs at the bottom? ...
But KCL applies to the *entire circuit*, including in the potentiostat! (when the current flow, i.e. due motion of charges, is at steady state)

\[ I \]

\[ \text{M}_1 \rightarrow \text{A} \leftrightarrow \text{B} + \text{C} \rightarrow \text{M}_2 \]

... hey, what are those minus signs at the bottom? ...

**Migrating/Drifting Ions!**  
... we’ll get to this shortly
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

Do the units of \(D\) make sense? \(N_z \text{ (mol cm}^{-2} \text{ s}^{-1}, \text{ as } xy) = \ldots\)

**Physician & Physiologist**

Adolf Eugen Fick
(1829–1901)

from Wiki
**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)

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\[ N_z \text{ (mol cm}^{-2} \text{ s}^{-1}, \text{ as } xy) = D_z \cdot \frac{dc}{dz} \text{ (mol cm}^{-3} \text{ cm}^{-1}, \text{ as } xyz \ z) \]

\[ \text{(mol cm}^{-2} \text{ s}^{-1}, \text{ as } xy) = D_z \cdot \text{(mol cm}^{-4}, \text{ as } xyzz) \] …
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)

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Therefore, \(D_z\) is has units of \(\text{cm}^2 \text{ s}^{-1}\)… but as \(zz\…\)

Huh? \(zz\? \ z^2\? \text{ What? …}\)
... well, that must have been incorrect... let's try this again...

Get your favorite beverage and let's go on a (random) walk!

---

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! ...
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$m$ is just the number

$\tau$ is step time

$l$ is step length
... well, that must have been incorrect... let's try this again... Get your favorite beverage and let's go on a (random) walk!

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

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From B&F
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mean square displacement (variance)

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

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mean square displacement (variance)

Recall, \( D \) is has units of cm² s⁻¹, as \( zz \Delta = 2dD \tau \).

**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 \( \tau = 4 \). 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.
… so how far do species diffuse in electrochemistry in 1D?

<table>
<thead>
<tr>
<th>D</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

A characteristic "diffusion length"

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

$$\bar{\Delta} = \sqrt{(2d)Dt}, \text{ where } d \text{ is the dimension}$$
so how far do species diffuse in electrochemistry in 1D?

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

$$\bar{\Delta} = \sqrt{(2d)Dt},$$

where $d$ is the dimension.

<table>
<thead>
<tr>
<th>time</th>
<th>$\bar{\Delta}$</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>

A characteristic "diffusion length" root mean square (rms) displacement (standard deviation)
… what are typical values for diffusion coefficients, for species in electrochemistry?

<table>
<thead>
<tr>
<th>Cation</th>
<th>$D$</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>$B(C_6H_5)_4^-$</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>

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

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

* 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"

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

Why are both so… slow (for example)?

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$x 10^{-5} \text{ cm}^2/\text{s}$

Why are both so… fast?

Why are both so… slow (for example)?

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

\[
\bar{\Delta} = \sqrt{(2d)Dt}, \text{ where } d \text{ is the dimension}
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a characteristic "diffusion length"

root mean square (rms) displacement (standard deviation)
Proton (and hydroxide) ions do not diffuse by normal Brownian motion… they hop between molecules… by a Grotthuss mechanism.

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$$D(\text{OH}^-) = 5.28 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$

http://www.snipview.com/q/Grotthuss%20mechanism
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\end{align*}
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[http://www.snipview.com/q/Grotthuss%20mechanism](http://www.snipview.com/q/Grotthuss%20mechanism)
Proton transfer is enabled by an additional O–O bond contraction, not required in H₅O₂⁺. 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.


ABSTRACT: The diffusion of hydronium (H₃O⁺) and hydroxide (OH⁻) ions is one of the most 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 transfer.
… remember this... but now let’s say the walker is charged...

**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...

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From B&F
… 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 drift

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(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! …
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: \(F = m \cdot a\)
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... anyway… some very important background “first”...
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So, \(\mu = |z|e \frac{\tau}{m}\), because \(v_{d-z} = \mu_z \cdot E_z\)
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\[ |z| eE = m \cdot \frac{v_d}{\tau}, \]
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So, \( \mu = |z| e \frac{\tau}{m} \), because \( v_{d-z} = \mu_z \cdot E_z \)

… and the units of mobility are correct … (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, $E$:

$$6\pi \eta rv \leftrightarrow ze \rightarrow |z_i| eE$$

Mathematician, Physicist, Politician, and Theologian

Physicist & Philosopher

Sir George Gabriel Stokes (1819–1903)  
Albert Einstein (1879–1955)  
(from Wiki)
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\[
6\pi\eta rv \quad \text{viscous drag} \quad \text{electrophoretic force} \quad |z_i|eE
\]

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

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

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

---

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… and a very important point is that these two parameters, \(D\) and \(\mu\), are related!
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… Einstein–Smoluchowski equation,

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

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

… and what is the value of \(\frac{RT}{F}\)?

![Image of Albert Einstein (1879–1955) and Scientist Marian Smoluchowski (1872–1917) from Wiki]
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\[\mu_i = \frac{|z_i|FD_i}{RT}\]

... and what is the value of \(\frac{RT}{F}\)? **25.7 mV**
... now, a simplified Nernst–Planck equation...

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i \nu(x) \]
From before, for one species the total flux in one-dimension is

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

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

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... 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

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_iF}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i \nu(x) \]
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… which can also be written using the E–S equation

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

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

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

B&F, 4.2.2

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_iF}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i \nu(x) \]
… some textbooks (Bockris) initially define the migration term in terms of mobility based on straightforward physical reasoning…
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… then, the Nernst–Planck equation for an anion can be defined as…

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… and the E–S equation can be derived using this version…

FOR YOUR REFERENCE
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... and the E–S equation can be derived using this version...

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

\[ 0 = -D \cdot \frac{dc}{dx} + \mu c \cdot \frac{d\phi}{dx} + cv \]
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\[ N = -D \frac{dc}{dx} + \mu c \frac{d\phi}{dx} + cv \]

… and the E–S equation can be derived using this version…

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

\[ 0 = -D \frac{dc}{dx} + \mu c \frac{d\phi}{dx} + cv \]

\[ D \frac{dc}{dx} = \mu c \frac{d\phi}{dx} \], and using the “Boltzmann law,” \( c = c_0 e^{-\frac{U}{RT}} \),
... then, the Nernst–Planck equation for an anion can be defined as...

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

... and the E–S equation can be derived using this version...

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\[ 0 = -D \frac{dc}{dx} + \mu c \frac{d\phi}{dx} + cv \]

\[ D \frac{dc}{dx} = \mu c \frac{d\phi}{dx}, \text{ and using the “Boltzmann law,” } c = c_0 e^{-\frac{U}{RT}}, \]

\[ D \left( -\frac{1}{RT} c_0 e^{-\frac{U}{RT}} \frac{dU}{dx} \right) = \mu \left( c_0 e^{-\frac{U}{RT}} \right) \frac{d\phi}{dx} \]

\[ D \left( -\frac{1}{RT} \frac{dU}{dx} \right) = \mu \frac{d\phi}{dx} \]
... then, the Nernst–Planck equation for an anion can be defined as...

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

... and the E–S equation can be derived using this version...

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

\[ 0 = -D \cdot \frac{dc}{dx} + \mu c \cdot \frac{d\phi}{dx} + cv \]

\[ D \cdot \frac{dc}{dx} = \mu c \cdot \frac{d\phi}{dx} \]

and using the “Boltzmann law,” \( c = c_0 e^{-\frac{U}{RT}} \),

\[ D \left( -\frac{1}{RT} c_0 e^{-\frac{U}{RT}} \cdot \frac{dU}{dx} \right) = \mu \left( c_0 e^{-\frac{U}{RT}} \right) \cdot \frac{d\phi}{dx} \]

\[ D \left( -\frac{1}{RT} \cdot \frac{dU}{dx} \right) = \mu \cdot \frac{d\phi}{dx} \]

and because the electric potential component of the (free) energy is \( zF\phi \), then \( \frac{dU}{d\phi} = zF \),

\[ D \left( -\frac{1}{RT} \cdot zF \right) = \mu = \frac{|z|FD}{RT} \]
... then, the Nernst–Planck equation for an anion can be defined as...

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

... and the E–S equation can be derived using this version...

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D \left( -\frac{1}{RT} \cdot \frac{dU}{dx} \right) = \mu \cdot \frac{d\phi}{dx}, \quad \text{and because the electric potential component of the (free) energy is } zF\phi, \text{ then } \frac{dU}{d\phi} = zF,
\]

\[
D \left( -\frac{1}{RT} \cdot zF \right) = \mu = \frac{|z|FD}{RT} \quad \text{... the Einstein–Smoluchowski eqn.}
\]
Looking forward… Section 1.4 and Chapter 4

- Mass transfer
- Diffusion
- Migration / Drift
- Convection
- Semi-empirical models
- Balance sheets