Lecture #6 of 17
Q: What’s in this set of lectures?
A: B&F Chapters 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
- Conductivity
- Transport (Transference) number
- Balance sheets
We can all label the faradaic and non-faradaic processes…
… but what is this new feature?

What if we just “ran out” of Cl\(^-\) at the electrode to oxidize?

… RECALL FROM LAST TIME…
… mass transfer in electrochemistry is concerned with the movement of material = mass (even species as small as electrons) from one location (in solution) to another, and arises from spatial differences in electric potential, chemical potential, or from volume movement (of solution)…

… *We need to understand mass transfer!* …
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... We need to understand mass transfer! ...

... but first, because it relates directly to mass transfer, I need to introduce the governing equation for the continuity of mass, which is even more stringent than the law of the conservation of mass!
... since the continuity of mass equation is “better than” the conservation of mass law, and it is highly relevant to electrochemistry and in fact all science and engineering fields, we better know it...

... it is introduced to most undergraduate students studying chemical engineering, materials science, and physics, but only partially to chemists (first half) and mechanical engineers (second half)...

... anyway, here it is for species A along dimension $x$… Enjoy!

$$\frac{\partial c_A}{\partial t} = \sum_i R_{A,i} - \frac{\partial N_A}{\partial x}$$

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rate of change of the concentration of species A with respect to time

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rate of change of the concentration of species A with respect to time mass action (R)ate laws that effect species A, e.g. $k_2[A][B]$

... this is what chemists were taught it’s easy!

... and recall that these (R)eactions are driven by differences in chemical potential, $\mu$, of various species, including A

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\frac{\partial c_A}{\partial t} = \sum_i R_{A,i} - \frac{\partial N_A}{\partial x}
\]

rate of change of the (c)oncentration of species A with respect to (t)ime

mass action (R)ate laws that effect species A, e.g. $k_2[A][B]$

rate of change of the flux ($N$) of species A with respect to position ($x$)

https://en.wikipedia.org/wiki/Continuity_equation

... what is mass flux? ... it’s easy!
Mass transfer... *and also* heat transfer... *and momentum transfer*
(1) **Migration / Drift** (not heat as heat is not charged!)

Flux (mol cm$^{-2}$ s$^{-1}$) of **charged** species due to an electric field (electric potential)... in general, stirring does not affect this as cations and anions move in opposite directions.

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Flux of **species** due to a concentration gradient and random thermal motion (no real “force”)

[Diffusion animation]

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Hydrodynamic movement (e.g. forced convection (stirring)) still keeps charged species near each other (Coulombic attraction)

... FYI: electro-convection occurs after ~30 sec of an electrochemical experiment
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Convection here, too!
Mass transfer, for a charged species, sounds like a current!

How is current density ($J$, A cm\(^{-2}\)) is related to flux ($N$, 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? ...
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\[
J_x = zF N_x \quad \text{... the Faraday constant}
\]

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

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

\[
J = zF N = F \sum_i z_i \left( - \frac{D_i c_i}{RT} \cdot \nabla \bar{\mu}_i + c_i \nu_i \right), \text{ where } \nabla \text{ is "del" (nabla)}
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... where \(D_i\) is the diffusion coefficient of species \(i\) (in units of \(\text{cm}^2 \text{ s}^{-1}\)), \(c\) is the concentration (in units of \(\text{mol cm}^{-3}\)), \(\bar{\mu}\) is the electrochemical potential (in units of \(\text{J mol}^{-1}\)), and \(\nu\) is the velocity (in units of \(\text{cm s}^{-1}\))
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The total current density, in one-dimension, due to all charged species is,

$$J_x = zFN_x = F \sum_i z_i \left( -\frac{D_i x c_i}{RT} \cdot \frac{d\mu_i}{dx} + c_i v_{i,x} \right),$$

and in 3D,

$$J = zFN = F \sum_i z_i \left( -\frac{D_i c_i}{RT} \cdot \nabla \mu_i + c_i v_i \right),$$

where $\nabla$ is “del” (nabla)

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For derivation, see Bockris & Reddy, Modern EChem, Vol. 1, 2002, Section 4.4.15
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As we will soon see, this equals mobility, \( J_x = z F N_x \) ... the Faraday constant and thus in the absence of convection...

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J_x = zF N_x = F \sum_i z_i \left( - \frac{D_{i,x} c_i}{RT} \cdot \frac{d \tilde{\mu}_i}{dx} + c_i v_{i,x} \right), \text{ and in 3D,}
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mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: diffusion, migration, and convection

the \textit{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 \textbf{flux} of reactant \textit{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)

from Wiki
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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 cm\(^2\) s\(^{-1}\)\)
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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.
mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: diffusion, migration, and convection.

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the flux due to convection of reactant \(i\) where \(v(x)\) 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*:

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... 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?
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\( B&F, 1.4.2 \) & \( 4.1.8 \)

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... in parallel... \( J_i(x) = J_1 + J_2 + J_3 \)
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B&F, 1.4.2 & 4.1.8

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

... and now what if there was rapid stirring?
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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 (J/mol),

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

where

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

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

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

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

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

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

\[ N = -\frac{Dc}{RT} \cdot \frac{d(\mu+zF\phi)}{dx} + cv \]

The flux

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and assuming \( a \approx c \),

\[ N = -Dc \cdot \frac{d(\ln c)}{dx} - \frac{z_i F D}{RT} c \cdot \frac{d\phi}{dx} + cv \]

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

\[ J_i(x) = -D_i C_i(x) \cdot \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i(x) \cdot \frac{\partial \phi(x)}{\partial x} + C_i v(x) \]
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:** \(N_z = -D_z \frac{dc}{dz}\), in 1D

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

\( \Delta G < 0 \)
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**Physician & Physiologist**

Adolf Eugen Fick (1829–1901)

from Wiki
Steady-state? …

… Initial states equilibrate using ICE, ICE Baby!

$$A \leftrightarrow B + C$$

<table>
<thead>
<tr>
<th>Reaction:</th>
<th>HA</th>
<th>$A^-$</th>
<th>$H_3O^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.150 M</td>
<td>0.000 M</td>
<td>0.000 M</td>
</tr>
<tr>
<td>C</td>
<td>$-x$ M</td>
<td>$+x$ M</td>
<td>$+x$ M</td>
</tr>
<tr>
<td>E</td>
<td>0.150 - $x$ M</td>
<td>$x$ M</td>
<td>$x$ M</td>
</tr>
</tbody>
</table>

http://chemwiki.ucdavis.edu/Physical_Chemistry/Eq
ulibria/Le_Chatelier%27s_Principle/Ice_Tables

http://buzzworthy.mtv.com/2012/11/14/justin-
bieber-vanilla-ice-photo/
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…

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

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

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

… but for how long? …

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

… 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...

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

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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 \textit{rare} conditions,

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

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

\[
\begin{align*}
M_1 & \rightarrow A \quad \text{↔} \quad B + C \rightarrow M_2
\end{align*}
\]

… for steady-state current, KCL applies… no, not KCI… but KCL!
… 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 KCI… but KCL!

Kirchhoff’s Current Law (KCL)

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

\[ i_1 + i_4 = i_2 + i_3 \]

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)

\[ I \]

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

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

\[ I \]

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

… 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? $N_z$ (mol $\text{cm}^{-2} \text{s}^{-1}$, as $xy$) = ...

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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Do the units of \(D\) make sense?

\[N_z \text{ (mol cm}^{-2} \text{s}^{-1}, \text{as xy}) = D_z \cdot \text{dc/dz (mol cm}^{-3} \text{ cm}^{-1}, \text{as xyz z)} \]
\[\text{mol cm}^{-2} \text{s}^{-1}, \text{as xy) = D_z \cdot (mol cm}^{-4} \text{, as xyzz) …} \]
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)

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

\[
\Delta G < 0
\]

Do the units of \(D\) make sense?

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

\(\text{(mol cm}^{-2} \text{ s}^{-1}, \text{ as } xy) = D_z \cdot (\text{mol cm}^{-4}, \text{ as } xyz\, z)\)

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

Huh? \(zz\)? \(z^2\)? What? …
… 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!

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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From B&F

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 $1/16$.  

$m$ is just the number 

$\tau$ is step time

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

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\[ m \text{ is just the number} \]

\[ \tau \text{ is step time} \]

\[ l \text{ is step length} \]

\[ \text{mean square displacement (variance)} \]

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.

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... 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!

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

mean square displacement (variance)

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

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.

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\[ \Delta z = 2dD \tau \]

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 \( t = 4\tau \). 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.

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

root mean square (rms) displacement (standard deviation)
… 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

From a…

… plane

… wire, line, tube

… point, sphere, disk

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

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

a characteristic "diffusion length"

root mean square (rms) displacement (standard deviation)
... so how far do species diffuse in electrochemistry in 1D?

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

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

<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>$10 \text{ cm} \approx 3.9''$</td>
</tr>
</tbody>
</table>
what are typical values for diffusion coefficients, for species in electrochemistry?

Table 6.1-1 Diffusion coefficients of ions in water at 25 °C

<table>
<thead>
<tr>
<th>Cation</th>
<th>( D ) (x 10^{-5} \text{ cm}^2/\text{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>
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<td>Br(^-)</td>
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<tr>
<td>Rb(^+)</td>
<td>2.07</td>
<td>I(^-)</td>
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</tr>
<tr>
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<td>NO(_3^)</td>
<td>1.90</td>
</tr>
<tr>
<td>Ag(^+)</td>
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<td>CH(_3)COO(^-)</td>
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<td>N(C(_4)H(_9))(_4^+)</td>
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<td>B(C(_5)H(_5))(_4^\text{-})</td>
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</tr>
<tr>
<td>Mg(_2^+)</td>
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<td>CO(_3^2^-)</td>
<td>0.92</td>
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<td>0.62</td>
<td>Fe(CN)(_6^3^-)</td>
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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

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

\[ \bar{\Delta} = \sqrt{(2d)Dt} \], where \( d \) is the dimension
… what are typical values for diffusion coefficients, for species in electrochemistry?

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$a$ characteristic "diffusion length"

root mean square (rms) displacement (standard deviation)

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

Why are both so… slow (for example)?

"Diffusion: Mass Transfer in Fluid Systems," 2013, by E. L. Cussler
... what are typical values for diffusion coefficients, for species in electrochemistry?

Why are both so... fast?

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

Why are both so... slow (for example)?

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

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

a characteristic "diffusion length"

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

\[ D(H^+) = 9.31 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \]
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http://www.snipview.com/q/Grotthuss%20mechanism
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*Theodor von Grotthuss (1785–1822)*

from Wiki

**a "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.


**ABSTRACT:** The diffusion of hydronium (H$_3$O$^+$) 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 trans...
... remember this... but now let's say 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 \( 1/16 \).
... what if we applied an external field to this scenario...

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... 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!

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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

… start with **Newton’s second law of motion:** \[ F = m \cdot a \]
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… \(|z|eE = m \cdot \frac{v_d}{\tau}\), 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. \(v = 0\))
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Because $v_{d-z} = \mu_z \cdot E_z$, this means that $\mu = |z|e \frac{\tau}{m}$
Diffusion coefficient \((D, \text{ cm}^2 \text{ s}^{-1})\) – “proportionality constant relating the flux of [the] amount of [an entity to its] concentration gradient…”

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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 … (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, $E$:

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

Mathematician, Physicist, Politician, and Theologian

Sir George Gabriel Stokes (1819–1903)

Physicist & Philosopher

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

---

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Albert Einstein (1879–1955)

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)

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

Newton’s second law of motion: \(F = ma, \quad v_d = \mu \cdot E\)

Stokes’ law: \(F = |z|eE = 6\pi \eta r v_d\), 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)

… anyway… some very important background “first”…

Sir George Gabriel Stokes (1819–1903) from Wiki
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… and a very important point is that these two parameters, \(D\) and \(\mu\), are related!
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… and what is the value of \(\frac{RT}{F}\)?

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**Scientist**

Marian Smoluchowski (1872–1917)

**Physicist & Philosopher**

Albert Einstein (1879–1955)

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

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

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

\[ J_i(x) = \pm \sigma_i \frac{d\mu_i}{dx} \]

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... then, the Nernst–Planck equation for an anion can be defined as:

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

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... 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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Bockris & Reddy, Fig. 4.62
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\[ D \left( -\frac{1}{RT} \cdot \frac{dU}{dx} \right) = \mu \cdot \frac{d\phi}{dx}, \text{ and because the electric potential component of the (free) energy is } zF\phi, \text{ then } \frac{dU}{d\phi} = zF, \]

\[ D \left( -\frac{1}{RT} \cdot zF \right) = \mu = \frac{|z|FD}{RT} \ldots \]
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\[ D \left( -\frac{1}{RT} \cdot zF \right) = \mu = \frac{|z|FD}{RT} \] ... the Einstein–Smoluchowski eqn.