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! ...

... 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!

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

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

... 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!

\[
\frac{\partial c_A}{\partial t} = \sum_i R_{A,i}
\]

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

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

... 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!

\[
\frac{\partial c_A}{\partial t} = \sum_i R_{A,i}
\]

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

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

\[
\frac{\partial c_A}{\partial t} = \sum_l R_{A,l} - \frac{\partial N_A}{\partial x}
\]

Mass transfer… and also heat transfer… and momentum transfer

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

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.

2. **Diffusion** (heat transport is down a temperature gradient)
   - Flux of species due to a concentration gradient and random thermal motion (no real "force")
   ![Diffusion](http://en.wikipedia.org/wiki/Diffusion)

3. **Convection** (heat transport is fluid/gas motion)
   - 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.

Mass transfer... and also heat transfer... and momentum transfer
Mass transfer is (mostly) driven by gradients in electrochemical potential...

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

How is current density \( J \) \( (A \text{ cm}^{-2}) \) related to flux \( N \) \( (\text{mol cm}^{-2} \text{s}^{-1}) \)?
... well, current density has units of \( A \text{ cm}^{-2} = C \text{ cm}^{-2} \text{s}^{-1} \)...  
... and flux has units of \( \text{mol cm}^{-2} \text{s}^{-1} \)...  
... So what do we need to equate these? ...

... well, current density has units of \( A \text{ cm}^{-2} = C \text{ cm}^{-2} \text{s}^{-1} \)...  
... and flux has units of \( \text{mol cm}^{-2} \text{s}^{-1} \)...  
... So what do we need to equate these? ...

... something with units of \( C \text{ mol}^{-1} \)...
Mass transfer (mostly) driven by gradients in electrochemical potential... 386

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

How is current density \( (J, \ \text{A cm}^{-2}) \) is related to flux \( (\mathcal{N}, \ \text{mol cm}^{-2} \text{ s}^{-1})? \)
... well, current density has units of \( \text{A cm}^{-2} = \text{C cm}^{-2} \text{ s}^{-1} \)
... and flux has units of \( \text{mol cm}^{-2} \text{ s}^{-1} \)
... So what do we need to equate these? ...
... something with units of \( \text{C mol}^{-1} \)
\[ J_s = z F N_s \] the Faraday constant

The total current density, in one-dimension, due to all charged species is,
\[ J_s = z F N_s = F \sum_i z_i \left( \frac{\partial c_i}{\partial t} + \frac{\partial j_i}{\partial x} \right), \text{ and in 3D,} \]
\[ J_s = z F N_s = F \sum_i z_i \left( \frac{\partial c_i}{\partial t} + \frac{\partial j_i}{\partial x} \right), \text{ where } \Psi \text{ is "del" (nabla)} \]
... 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 \( \text{mol cm}^{-3} \)), \( \rho \) is the electrochemical potential (in units of \( J \text{ mol}^{-1} \)), and \( v \) is the velocity (in units of \( \text{cm s}^{-1} \))

Mass transfer is (mostly) driven by gradients in electrochemical potential... 387

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

How is current density \( (J, \ \text{A cm}^{-2}) \) is related to flux \( (\mathcal{N}, \ \text{mol cm}^{-2} \text{ s}^{-1})? \)
... well, current density has units of \( \text{A cm}^{-2} = \text{C cm}^{-2} \text{ s}^{-1} \)
... and flux has units of \( \text{mol cm}^{-2} \text{ s}^{-1} \)
... So what do we need to equate these? ...
... something with units of \( \text{C mol}^{-1} \)
\[ J_s = z F N_s \] the Faraday constant

The total current density, in one-dimension, due to all charged species is,
\[ J_s = z F N_s = F \sum_i z_i \left( \frac{\partial c_i}{\partial t} + \frac{\partial j_i}{\partial x} \right), \text{ and in 3D,} \]
\[ J_s = z F N_s = F \sum_i z_i \left( \frac{\partial c_i}{\partial t} + \frac{\partial j_i}{\partial x} \right), \text{ where } \Psi \text{ is "del" (nabla)} \]
... 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 \( \text{mol cm}^{-3} \)), \( \rho \) is the electrochemical potential (in units of \( J \text{ mol}^{-1} \)), and \( v \) is the velocity (in units of \( \text{cm s}^{-1} \))

Mass transfer is (mostly) driven by gradients in electrochemical potential... 388

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

How is current density \( (J, \ \text{A cm}^{-2}) \) is related to flux \( (\mathcal{N}, \ \text{mol cm}^{-2} \text{ s}^{-1})? \)
... well, current density has units of \( \text{A cm}^{-2} = \text{C cm}^{-2} \text{ s}^{-1} \)
... and flux has units of \( \text{mol cm}^{-2} \text{ s}^{-1} \)
... So what do we need to equate these? ...
... something with units of \( \text{C mol}^{-1} \)
\[ J_s = z F N_s \] the Faraday constant

The total current density, in one-dimension, due to all charged species is,
\[ J_s = z F N_s = F \sum_i z_i \left( \frac{\partial c_i}{\partial t} + \frac{\partial j_i}{\partial x} \right), \text{ and in 3D,} \]
\[ J_s = z F N_s = F \sum_i z_i \left( \frac{\partial c_i}{\partial t} + \frac{\partial j_i}{\partial x} \right), \text{ where } \Psi \text{ is "del" (nabla)} \]
... 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 \( \text{mol cm}^{-3} \)), \( \rho \) is the electrochemical potential (in units of \( J \text{ mol}^{-1} \)), and \( v \) is the velocity (in units of \( \text{cm s}^{-1} \))
mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: diffusion, migration, and convection

the Nernst–Planck Equation:

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

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\(^{-1}\))

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

the Nernst–Planck Equation:

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

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\(^{-1}\))

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

the Nernst–Planck Equation:

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

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

the Nernst–Planck Equation:

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

\( J_i(x) \) is 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:

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

... 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

the Nernst–Planck Equation:

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

... 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?

... 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**: 

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

\( \text{B&F, 1.4.2} \) 

& 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?

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

the **Nernst–Planck Equation**: 

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

\( \text{B&F, 1.4.2} \) 

& 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? \( J_{\text{convection}} \)

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

the **Nernst–Planck Equation**: 

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

\( \text{B&F, 1.4.2} \) 

& 4.1.8

... 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),

$$\mu_i^\beta = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{i,\neq i}} = \mu_i^0 + z_i F \phi^\beta,$$

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 $\mu_i^\beta = \mu_i^0$.

IUPAC Gold (http://goldbook.iupac.org)

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

$$N = -\frac{D}{RT} \frac{dc_i}{dx} + cv,$$

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

**flux**

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

\[ N = \frac{D c}{RT} \frac{d\bar{\mu}}{dx} + CV, \]  

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\(^{-1}\))

Recall that \( \bar{\mu} = \mu + zF \phi \) and so,

\[ N = \frac{D c}{RT} \frac{d\mu}{dx} + CV, \text{ and recall that } \mu = \mu_0 + RT \ln a_i \text{ and so,} \]

\[ N = \frac{D c}{RT} \frac{d\mu_0}{dx} + CV \]

\[ flux \]

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

---

… don’t worry... there are not too many steps...

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

Fick's first law of steady-state Diffusion: $N_x = -D \frac{dc}{dz}$ in 1D

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

where $D_0$ is the maximum $D$ (at infinite $T$)
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:** \( N_x = -D \frac{\partial c}{\partial x} \) in 1D

\( D \) also exhibits Arrhenius behavior: \( D = D_0 e^{-\frac{E_a}{RT}} \) where \( D_0 \) is the maximum \( D \) (at infinite \( T \))

Some very important background “first”… okay, second!

Steady-state? …

… Initial states equilibrate using ICE, ICE Baby!

\[
\begin{align*}
A & \rightleftharpoons B + C \\
| & | \\
\text{Initial Concentrations:} & \text{Reactant} & \text{Product} \\
E & 0.150 \text{ M} & 0.300 \text{ M} \\
C & \text{no M} & \text{no M} \\
E & \text{0.055 - x M} & \text{x M} \\
\text{Equilibrium Concentrations:} & \text{Reactant} & \text{Product} \\
E & ? \text{ M} & ? \text{ M} \\
C & ? \text{ M} & ? \text{ M} \\
E & ? \text{ M} & ? \text{ M}
\end{align*}
\]

A

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…

\[ A \rightleftharpoons B + C \]

… but for how long? …

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

… 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!

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

\[ \frac{\partial A}{\partial t} = \frac{\partial B}{\partial t} = \frac{\partial C}{\partial t} = 0 \]

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 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!

\[ \dot{M}_1 \rightarrow A \rightarrow B + C \rightarrow M_2 \]

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

Who cares? ...

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

\[ \dot{M}_1 \rightarrow A \rightarrow B + C \rightarrow M_2 \]

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

Kirchhoff's Current Law (KCL)

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

\[ i_{out} + i_{in} = i_1 + i_4 \]


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)

\[ \dot{M}_1 \rightarrow A \rightarrow B + C \rightarrow M_2 \]

... 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)

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

**Migrating/Drifting Ions!**

*... we'll get to this shortly*

---

Back to the first flux term... Diffusion...

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:**

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

---

Back to the first flux term... Diffusion...

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:**

\[
N_z = -D_z \frac{dc}{dz}, \text{ in 1D}
\]
Diffusion coefficient ($D$, cm$^2$/s) – “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: $\dot{N}_z = -D_z \frac{dc}{dz}$ in 1D

Do the units of $D$ make sense?

$\dot{N}_z$ (mol cm$^{-2}$/s$^{-1}$, as $x$ $y$ $z$)

$D_z$ (mol cm$^{-4}$/s$^{-1}$, as $x$ $y$ $z$)

Therefore, $D_z$ has units of cm$^2$/s$^{-1}$ but as $x$ $y$ $z$ ...

Huh? $x$? $z$? 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 starting point is the number of paths to that point. (b) bar graph showing distribution at $t = 4$. At this time, probability of being at $x = 0$ is 6/32, at $x = 2$ is 0/32, and $ax = \pm 4$ is 3/32.

… Flashback! Pascal’s triangle! …

… 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 starting point is the number of paths to that point. (b) bar graph showing distribution at $t = 4$. At this time, probability of being at $x = 0$ is 6/32, at $x = 2$ is 0/32, and $ax = \pm 4$ is 3/32.

From B&F
\[ D = \frac{l^2}{2\tau} \]

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

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

From B&F
so how far do species diffuse in electrochemistry in 1D?

D    \( \overline{\Delta}^* \)

1D    \( \sqrt{2Dt} \)

2D    \( \sqrt{4Dt} \)

3D    \( \sqrt{6Dt} \)

From a…

... plane

... wire, line, tube

... point, sphere, disk

\[ \overline{\Delta} = \sqrt{\frac{<x^2>}{t}} = \frac{1}{c} \text{ cm} \]

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

\[ \Delta = \sqrt{(2d)Dt} \text{ on the order of } 10^{-6} \text{ cm}^2/\text{s for molecules} \]

\[ \Delta = \sqrt{(2d)Dt} \text{ on the order of } 10^{-7} \text{ cm}^2/\text{s for proteins} \]

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

<table>
<thead>
<tr>
<th>time</th>
<th>( \overline{\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 = 3.9”</td>
</tr>
</tbody>
</table>

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

... so how far do species diffuse in electrochemistry in 1D?

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

<table>
<thead>
<tr>
<th>time</th>
<th>( \overline{\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 = 3.9”</td>
</tr>
</tbody>
</table>

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

\[ \Delta = \sqrt{2d \bar{D} t}, \text{ where } d \text{ is the dimension} \]

Why are both so… slow (for example)?

* on the order of \(10^4\) cm/s for molecules
* on the order of \(10^7\) cm/s for proteins

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

Proton (and hydroxide) ions do not diffuse by normal thermal or Brownian motion… they hop between molecules… by a Grothuss mechanism

\[ D(H^+) = 9.31 \times 10^{-5} \text{ cm}^2\text{s}^{-1} \]
\[ D(OH^-) = 5.28 \times 10^{-6} \text{ cm}^2\text{s}^{-1} \]

http://www.smithweb.com/p/Grothuss%20mechanism

"Diffusion: Mass Transfer in Fluid Systems," 2013, by E. L. Cussler
Proton (and hydroxide) ions do not diffuse by normal thermal or Brownian motion—they hop between molecules by a Grotthuss mechanism.

Proton transfer is enabled by an additional O-O bond formation, not required in H$_2$O. This explains why the activation energy for hydroxide mobility is larger than that of proton mobility by about 0.5 kcal/mol. The hydrogen cycle is sustained by hydrogen bond formation in the other oxygen corner. Available experimental data, and more if the computational results, can be formulated in the framework of the above model. © 2000 Elsevier Science B.V. All rights reserved.


Theodor von Grotthuss (1785–1822)

http://www.snipview.com/p/Grotthuss%20Mechanism

Chemist

Theodor von Grotthuss (1785–1822)
from Wiki

… OH$^-$ diffusion mechanisms are not yet agreed upon…

… remember this… but now let’s say the walker is charged…

… Flashback! Pascal’s triangle! … From B&F
… what if we applied an external field to this scenario…

… Flashback! Pascal’s triangle! …

… welcome to the concept of ionic drift

… Flashback! Pascal’s triangle! …

… 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: \( \dot{N}_x = -D \frac{dc}{dx} \) 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: \( F = m \cdot a \)
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: \( N_x = -D \frac{dc}{dz} \) 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: \( F = m \cdot a \)

\[ \mu = \frac{|z| e E}{\tau} \]

Because \( \nu_{dr}=\mu \cdot E \), this means that \( \mu = \frac{|z| e}{\tau} \)

… and the units of mobility are correct \( \text{(cm s}^{-1} \text{)} = \mu \cdot (\text{V cm}^{-1}) \)

… anyway… some very important background “first”…
... 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, $E$:

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

with viscous drag and electrophoretic force:

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

Viscous drag
Electrophoretic force
Particle velocity

Fick's first law of steady-state diffusion: $N_x = -D \frac{dc}{dx}$, in 1D

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)

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: $F = ma$, $v_x = \mu \cdot E$

Stokes' law: $F = |z_i|eE = 6\pi\eta rv$, and so by solving $\mu = \frac{v}{E}$ above, one gets $\mu = \frac{|z_i|e}{6\pi\eta r}$ which gives a physical meaning to the mobility, with $\eta$ (dynamic viscosity of the medium) and $r$ (radius of the spherical ion).
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: \( \dot{N}_z = -D \frac{dc}{dz} \) 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: \( F = m \cdot a \), \( v_d = \mu \cdot E \)

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

Einstein–Smoluchowski equation, \( \mu_i = \frac{|z_i| F D_i}{RT} \)

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

Faraday constant

Scientist Marian Smoluchowski (1872–1917)

Physicist & Philosopher Albert Einstein (1879–1955)

4/23/2019
 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: \(N_x = -D_x \frac{dC_x}{dx}\) 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: \(F = m \cdot a, \; v_x = \mu \cdot E\)

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

... Einstein–Smoluchowski equation,

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

... and what is the value of \(RT/\mu_i\)? \(25.7 \text{ mV}\)

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

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

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

\[
N = -D \frac{dc}{dx} + cv, \; \ldots \; (\text{several math steps from before})
\]

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

electrochemical potential

flux

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

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

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

... (several math steps from before)

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

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

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

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

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

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

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

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

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

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

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

... and now lastly, a simplified (cleaner) Nernst–Planck equation...
… some textbooks (Bockris) initially define the migration term in terms of mobility based on straightforward physical reasoning…

FOR YOUR REFERENCE

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

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

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

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

... 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...

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

\[ D - R T c_0 e^\frac{-U}{RT} \frac{dU}{dx} = \mu c_0 e^\frac{-U}{RT} \frac{d\phi}{dx} \]

... some textbooks (Bockris) initially define the migration term in terms of mobility based on straightforward physical reasoning...

\[ \frac{d\phi}{dx} = \frac{zF}{RT} \]

\[ D - R T \frac{zF}{RT} = \mu \frac{d\phi}{dx} \]
... then, the Nernst–Planck equation for an anion can be defined as...
\[ N = -D \frac{dc}{dx} + \mu c \frac{d\phi}{dx} + c \nu \]

... 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...
\[ \theta = -D \frac{dc}{dx} + \mu c \frac{d\phi}{dx} + c \nu \]
\[ D \left( \frac{1}{RT} \frac{dc}{dx} \right) = \mu \left( \frac{c}{RT} \frac{d\phi}{dx} \right) \]
\[ D \left( \frac{1}{RT} \frac{d\phi}{dx} \right) = \mu \frac{d\phi}{dx} \]

and because the electric potential component of the (free) energy is \( zF \phi \), then \( \frac{d\phi}{dx} = zF \),
\[ D \left( \frac{1}{RT} \cdot zF \right) = \mu = \frac{RT \mu}{zF} \]... the Einstein–Smoluchowski eqn.