Lecture #10 of 18(?)
(about) halfway finished... tear

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

... don’t worry... there aren’t too many steps...

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

\[ N = -D \frac{\partial C}{\partial x} + CV \]

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\(^{-1}\))

Recall that \( \mu_i = \mu_i^0 + z_i R T \ln a_i \) and so,

\[ N = -D \frac{\partial \ln a_i}{\partial x} + CV \]

... and finally...

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

Who cares? ...

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

\[ M_1 \xrightarrow{A} B + C \rightarrow M_2 \]

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

**Kirchhoff's Current Law (KCL)**

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

But KCL applies to the entire circuit, including in the potentiostat!

\[ \text{RECALL:} \quad I \]
\[ \text{M}_1 \rightarrow A \rightarrow B + C \rightarrow \text{M}_2 \]

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

**Migrating/Drifting Ions!**

... we’ll get to this shortly

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RECALL:

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

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

\[ N_z \text{ (mol cm}^{-3} \text{s}^{-1}, \text{as} x y) = D_z \text{ (mol cm}^{-3} \text{s}^{-1}, \text{as} x y z) \]

\[ D_z \text{ is has units of cm}^2 \text{s}^{-1} \text{... but so zz...} \]

Huh? zz? ?? What?? That was unexpected!... Is it right?...

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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!

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*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!

From B&F

\[ \overline{\Delta} = \sqrt{(2D)D_t} \]

where \( D \) is the number \( \tau \) is step time \( l \) is step length

Recall: \( D \) has units of cm\(^2\) s\(^{-1}\), as does \( \Delta \) (root mean square (rms) displacement (standard deviation))

\[ \Delta = \sqrt{(2d)D_t} \]

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

\( \overline{\Delta} = \sqrt{(2d)D_t} \)

... the rms displacement

In both directions from a...

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

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

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

\( \Delta = \sqrt{(2d)D_t} = \frac{\text{cm}^2}{s} = \text{cm} \)

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

a characteristic “diffusion length”

root mean square (rms) displacement (standard deviation)

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

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

\[
\begin{array}{|c|c|}
\hline
\text{time} & \overline{\Delta} \\
\hline
1 \text{ ms} & 1 \mu \text{m} \\
0.1 \text{ s} & 10 \mu \text{m} \\
10 \text{ s} & 0.1 \text{ mm} \\
16.7 \text{ min} & 1 \text{ mm} \\
1.157 \text{ day} & 1 \text{ cm} \\
0.32 \text{ year} & 10 \text{ cm} \approx 3.9” \\
\hline
\end{array}
\]

\( \overline{\Delta} = \sqrt{(2d)D_t} \)

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

a characteristic “diffusion length”

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

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

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

$$\Delta = \sqrt{\langle 2d D t \rangle}$$
where $d$ is the dimension

... and the "2" is for positive and negative directions

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

$D(H^+) = 9.31 \times 10^{-5}$ cm$^2$/s

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

http://www.snipview.com/q/Grotthuss%20mechanism
... OH$^-$ (and even H$^+$) transport mechanisms are not fully agreed upon...

Proton transfer is enabled by an additional $\text{H}_{\text{B}}$–$\text{H}_{\text{A}}$ bond contraction, not required in II (6). This explains why the activation energy for hydroxide mobility is larger than that of proton mobility by about 0.1 kcal/mol. The proton cycle is terminated by hydrogen/carbon formation to the near oxygen center. Available experimental data, and most of the computational results, can be rationalized in the framework of the above model. © 2000 Elsevier Science B.V. All rights reserved.


At the molecular level (5), in contrast, hydroxide ion mobility in both solutions has reached low values (<1) (5), even though the ionic strength of both solutions is comparable. The low mobility of hydroxide ions in the chemical industry is due to the presence of hydroxide ions, which form a solid phase that is not easily ionized or transformed into the hydroxide ion. The reason for this may be attributed to the concept of a “conservation of the solid phase” that a hydroxide ion can be regarded as a water molecule minus a proton, and that the transport mechanism of such a “proton hole” is clearly different from that of a free proton. The concept of a proton hole is also supported by the fact that hydroxide ions are known to act as a bridge in phase transitions (6). Hence, proton mobility has been observed in solid state electrolyte solutions that explicitly have a proton transport phase (5-7) and are strongly influenced by molecular quantum effects.


Looking forward... Section 1.4 and Chapter 4

- Mass transfer
- Diffusion
- Migration / Drift
- Convection
- Semi-empirical diffusive models
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Moving on... remember this...

... to seed our next topic, let’s assume that the walker is charged...

... Flashback! Pascal’s triangle! ...

From B&F
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!...

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

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: \( N_z = -D \frac{dc}{dz} \) 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: \( F = ma \)

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

Because \( v_d \mu = \mu z_i e E, \) this means that \( \mu = \frac{|z_i|e}{6\pi \eta r} \)

... 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, \( z_i, \) and moving in an electric field, \( E: \)

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

Mathematician, Physicist, Politician, and Theologian

Physicist & Philosopher

Sir George Gabriel Stokes (1819–1903)
Albert Einstein (1879–1955)
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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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: \( F = m \cdot a, \nu_d = \mu \cdot E \)

Stokes’ law: \( F = \pi \eta r^2 \nu_d \), and so by solving \( \mu = \frac{\pi \eta r}{6} \) which gives a physical meaning to the mobility, with \( \eta \) (dynamic viscosity of the medium) and \( r \) (radius of the spherical ion)

Sir George Gabriel Stokes (1819–1903) from Wiki

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

Scientist Marian Smoluchowski (1872–1917) from Wiki

Physicist & Philosopher Albert Einstein (1879–1955)

and what is the value of \( m \nu_d \)? \( \text{25.7 mV} \)

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

Einstein–Smoluchowski equation,

\[
\mu_I = \frac{|z_I| FD_I}{RT}
\]

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

… use the Nernst–Planck equation for one species, \( i \), which is defined as…

\[
N_i = -D_i \frac{dc_i}{dx} - \frac{z_i e}{K T} \left( \frac{\partial \mu_i}{\partial c_i} \right)^{eq} \frac{dc_i}{dx} + c_i \nu_d
\]

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

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

\[
0 = -D_i \frac{dc_i}{dx} - \frac{z_i e}{K T} \left( \frac{\partial \mu_i}{\partial c_i} \right)^{eq} \frac{dc_i}{dx} + c_i \nu_d
\]

Bockris & Reddy, Fig. 4.62

… some textbooks (Bockris) initially define the migration/drift term in terms of mobility based on straightforward physical reasoning…
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0 = -D_i \frac{\partial c_i}{\partial x} + \frac{|z_i|}{RT} \mu_i \frac{\partial \phi}{\partial x} + c_i \nu + \frac{F}{RT} \sigma
\]

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

\[
\sigma R T = z_i c_i e^{\frac{z_i F \phi}{RT}} \frac{\partial \phi}{\partial x}
\]

... 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...

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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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Wow, those were some hefty equations... there is some value in thinking semi-quantitatively about mass transport and B&F developed a formalism for this (pp. 29–35):

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

\[ N_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{x_i F}{RT} \frac{\partial \rho(x)}{\partial x} + \frac{C_{\text{int}}}{} \]

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

And imagine a scenario where not only this is true, but where \( dC/dx \) is time invariant, meaning at steady-state, and thus you should see no hysteresis. (Ironically, this situation is encountered when the bulk solution is stirred... more on that in a bit...)
10/31/2023

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

\[ N_O(x) = -D_o \frac{C_O^* - C_O(x = 0)}{\delta_o} \]

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

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

\[ N_O(x) = -D_o \frac{C_O^* - C_O(x = 0)}{\delta_o} \]

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

FYI: an "unstirred" solution will have \( \delta \approx 0.050 \text{ cm (50 µm)} \) after ~1 sec (Bockris, Reddy, and Gamboa-Aldeco, Modern EChem, Vol. 2A, 2002, pg. 1098)
... because it will be convenient later, group the diffusion coefficient with the diffusion layer thickness:

\[ m_O = \frac{D_O}{\delta_O} \]

where \( m_O \) is the mass transfer coefficient (units: cm s\(^{-1}\); a velocity)

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

... substituting...

\[ N_O(x) = -m_O \left[ C_o(x) - C_o(x = 0) \right] \]

moles s\(^{-1}\) cm\(^2\) cm s\(^{-1}\) moles cm\(^{-3}\)

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

\[ \frac{i}{nF_A} = m_O \left[ C_o(x = 0) - C_o^* \right] \] (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...

\[ \frac{i}{nF_A} = m_R \left[ C_R^* - C_R(x = 0) \right] \]

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... and to simply the process, define the fastest rate, \( i_o \), as when \( C_o(x = 0) = 0 \)

\[ \frac{i}{nF_A} = m_o \left[ C_o(x = 0) - C_o^* \right] \]

\[ \frac{i}{nF_A} = m_o \left[ 0 - C_o^* \right] = -m_o C_o^* \]

\[ \frac{i}{nF_A} = m_o C_o(x = 0) \]

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

\[ \frac{i}{nF_A} = m_R \left[ C_R^* - C_R(x = 0) \right] = -m_o C_R^* \]

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

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

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

Formal potential = experimentally measured \( E^0 \)

... this will show up again...

Figure 14.2: (a) Current-potential curve for a nernstian reaction involving two soluble species with only oxidant present initially. (b) \( \log (i_l) \) vs. \( F \) for this system.

What happens to the potential when \( i \to i_l/2 \)? \( E \to -\infty \)
What happens to the potential when \( i \to 0 \)? \( E \to +\infty \)
... and when $C^* \neq 0$...

$$E = E^0 - \frac{RT}{nF} \ln \left( \frac{m_D}{m_R} \right) + \frac{RT}{nF} \ln \left( \frac{i_{1c} - i}{i - i_{1a}} \right)$$

Looks linear...

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

We could also define a linearized overpotential formula here... $\eta_{lin}$ (or $\eta_{act}$)

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

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

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

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