

343

Lecture #10 of 18(?)

{{(about) halfway finished... tear}}

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Mass Transfer Processes

Chapters 1 and 4

344

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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

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(UPDATED) 346

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

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

RECALL: 347

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

$N = -\frac{Dc}{RT} \frac{d\bar{\mu}}{dx} + cV$, where again D is diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), c is concentration (mol cm^{-3}), $\bar{\mu}$ is the electrochemical potential (J mol^{-1}), v is velocity (cm s^{-1})

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

$N = -\frac{Dc}{RT} \cdot \frac{d(\mu + zF\phi)}{dx} + cV$... and recall that $\mu_i = \mu_i^0 + RT \ln a_i$ and so,

$N = -\frac{Dc}{RT} \cdot \frac{d(\mu^0 + RT \ln a + zF\phi)}{dx} + cV$... and assuming $a = c$,

$N = -Dc \cdot \frac{d(\ln c)}{dx} - \frac{zFD}{RT} c \cdot \frac{d\phi}{dx} + cV$... and finally...

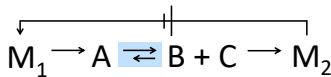
$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)$

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Who cares? ...

RECALL: 348

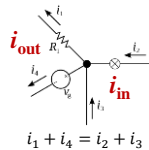
... when the current is at a steady-state, the current is constant, and there is no new capacitive charging!



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

Kirchhoff's Current Law (KCL)

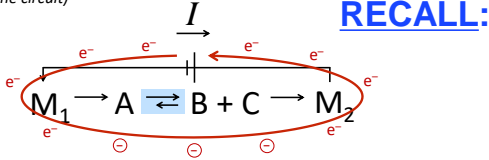
$\sum_{k=1}^n I_k = 0$



http://en.wikipedia.org/wiki/Kirchhoff%27s_circuit_laws

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But KCL applies to the *entire circuit*, including in the potentiostat!
 (when current flows, i.e. due motion of charges, it is the same everywhere in the circuit)



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

Migrating/Drifting Ions!

... we'll get to this shortly

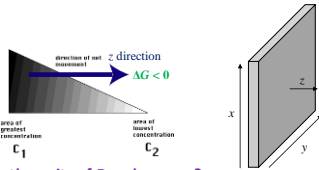
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Back to the first flux term... Diffusion...

RECALL: 350

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



Physician & Physiologist



Adolf Eugen Fick (1829–1901)
from Wiki

Do the units of D make sense?

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

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

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

Huh? zz ? z^2 ? 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!

From B&F

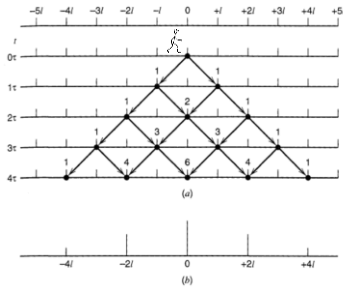
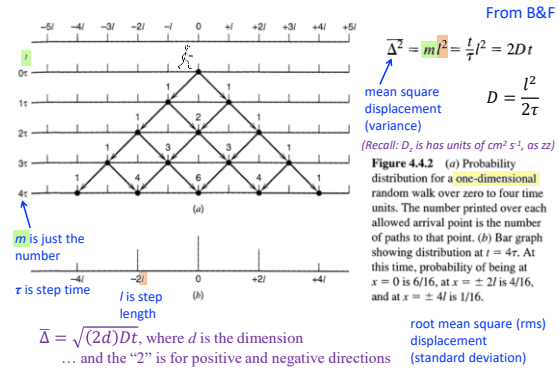


Figure 4.4.2 (a) Probability distribution for a one-dimensional random walk over zero to four time units. The number printed over each allowed arrival point is the number of paths to that point. (b) Bar graph showing distribution at $t = 4\tau$. At this time, probability of being at $x = 0$ is $6/16$, at $x = \pm 2l$ is $4/16$, and at $x = \pm 4l$ is $1/16$.

... Flashback! Pascal's triangle! ...

351

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352

... so how far do species diffuse in electrochemistry? 353

Dimension	$\bar{\Delta}^* =$	*the rms displacement In both directions from a...
1D	$\sqrt{2Dt}$... plane
2D	$\sqrt{4Dt}$... wire, line, tube
3D	$\sqrt{6Dt}$... point, sphere, disk

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

a characteristic "diffusion length"

root mean square (rms) displacement (standard deviation)

$\bar{\Delta} = \sqrt{(2d)Dt}$, where d is the dimension
... and the "2" is for positive and negative directions

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... so how far do species diffuse in electrochemistry in 1D? 354

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

time	$\bar{\Delta}$
1 ms	1 μm
0.1 s	10 μm
10 s	0.1 mm
16.7 min	1 mm
1.157 day	1 cm
0.32 year	10 cm \approx 3.9"

a characteristic "diffusion length"

root mean square (rms) displacement (standard deviation)

$\bar{\Delta} = \sqrt{(2d)Dt}$, where d is the dimension
... and the "2" is for positive and negative directions

354

... what are typical values for diffusion coefficients, for species in electrochemistry? 355

And why are both so... fast? -1 Diffusion coefficients of ions in water at 25 °C

Cation	D	Anion	D
H ⁺	9.31 x 10 ⁻⁵ cm ² /s	OH ⁻	5.28
Li ⁺	1.03	F ⁻	1.47
Na ⁺	1.33	Cl ⁻	2.03
K ⁺	1.96	Br ⁻	2.08
Rb ⁺	2.07	I ⁻	2.05
Cs ⁺	2.06	NO ₃ ⁻	1.90
Ag ⁺	1.65	CH ₃ COO ⁻	1.09
NH ₄ ⁺	1.96	CH ₃ CH ₂ COO ⁻	0.95
N(C ₂ H ₅) ₄ ⁺	0.52	B(C ₆ H ₅) ₄ ⁻	0.53
Ca ²⁺	0.79	SO ₄ ²⁻	1.06
Mg ²⁺	0.71	CO ₃ ²⁻	0.92
La ³⁺	0.62	Fe(CN) ₆ ³⁻	0.98

Notes: Values at infinite dilution in 10⁻⁵ cm²/sec. Calculated from data of Robinson and Stokes (1960). "Diffusion: Mass Transfer in Fluid Systems," 2013, by E. L. Cussler

Why are both so... slow, as examples? * on the order of 10⁻⁶ cm²/s for molecules a characteristic "diffusion length" * on the order of 10⁻⁷ cm²/s for proteins

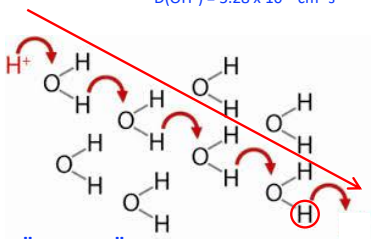
$\bar{\Delta} = \sqrt{(2d)Dt}$, where *d* is the dimension root mean square (rms) displacement ... and the "2" is for positive and negative directions (standard deviation)

355

Protons (and hydroxide ions, maybe) do not just diffuse by normal thermal motion... they also hop between molecules... by a Grotthuss mechanism... 356

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

Chemist



Theodor von Grothuss (1785-1822) from Wiki

a "cartoon"

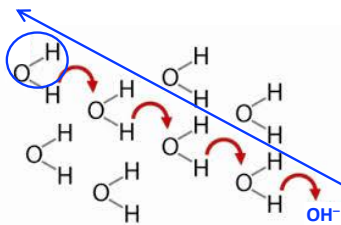
<http://www.snipview.com/q/Grothuss%20mechanism>

356

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<http://www.snipview.com/q/Grothuss%20mechanism>

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... OH⁻ (and even H⁺) transport mechanisms are not fully agreed upon... 358

Proton transfer is enabled by an additional O-O bond contraction, not required in H₂O₂. 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.

at the molecular level¹⁶. In contrast, hydroxide ion mobility in basic solutions has received far less attention^{17,18}, even though bases and base catalysis play important roles in many organic and biochemical reactions and in the chemical industry. The reason for this may be attributed to the century-old notion¹⁹ that a hydrated OH⁻ can be regarded as a water molecule missing a proton, and that the transport mechanism of such a 'proton hole' can be inferred from that of an excess proton by simply reversing hydrogen bond polarities²⁰⁻²². However, recent studies²³ have identified OH⁻ hydration complexes that bear little structural similarity to proton hydration complexes. Here we report the solution structures and transport mechanisms of hydrated hydroxide, which we obtained from first-principles computer simulations that explicitly treat quantum and thermal fluctuations of all nuclei²⁴⁻²⁶. We find that the transport mechanism, which differs significantly from the proton hole picture, involves an interplay between the previously identified hydration complexes²⁷ and is strongly influenced by nuclear quantum effects.

Agmon, *Chem. Phys. Lett.*, 2000, 319, 247

Tuckerman, Marx, and Parrinello, *Nature*, 2002, 417, 925

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 t

Lee, Choi, Choi, Sung, and Kang, *J. Phys. Chem. Lett.*, 2014, 5, 2568

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(UPDATED) 359

Looking forward... Section 1.4 and Chapter 4

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- Diffusion
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Moving on... remember this...

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

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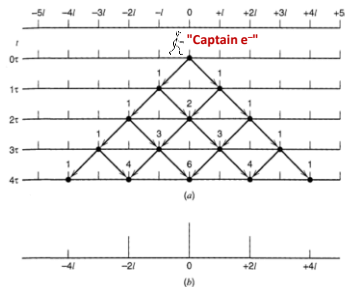


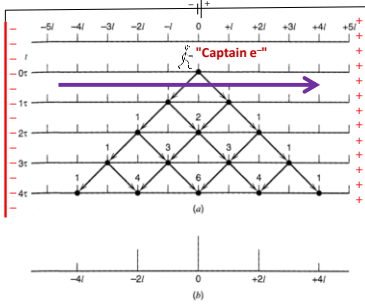
Figure 4.4.2 (a) Probability distribution for a one-dimensional random walk over zero to four time units. The number printed over each allowed arrival point is the number of paths to that point. (b) Bar graph showing distribution at $t = 4\tau$. At this time, probability of being at $x = 0$ is $6/16$, at $x = \pm 2l$ is $4/16$, and at $x = \pm 4l$ is $1/16$.

... Flashback! Pascal's triangle! ...

From B&F

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... 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 migration/drift

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 $x = \pm 2$ is 4/16, and at $x = \pm 4$ is 1/16.

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361

... anyway... some very important background "first" ... 362

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 (μ , $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) – "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:** $F = m \cdot a$

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

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}) = $\mu \cdot (\text{V cm}^{-1})$

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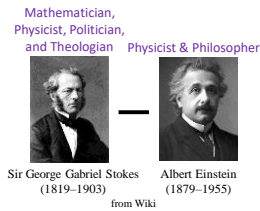
... and another formula for ionic mobility, μ_i 363

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 :

$$6\pi\eta r v \left(\begin{array}{l} \text{viscous drag} \\ \leftarrow \end{array} \right) + \left(\begin{array}{l} \text{electrophoretic force} \\ \rightarrow \end{array} \right) |z_i|eE = 0$$

\leftarrow particle velocity \rightarrow

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



363

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

Stokes' law: $F = |z|eE = 6\pi\eta r v_d$, 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 η (dynamic viscosity of the medium) and r (radius of the spherical ion)

Mathematician,
Physicist, Politician,
and Theologian



Sir George Gabriel Stokes
(1819–1903)
from Wiki

364

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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 μ , are related!

... Einstein–Smoluchowski equation,

$$\mu_i = \frac{|z_i|FD_i}{RT}$$

... and what is the value of $\frac{RT}{F}$? **25.7 mV!**

Physicist & Philosopher Scientist



Albert Einstein
(1879–1955)
from Wiki



Marian Smoluchowski
(1872–1917)

365

... some textbooks (Bockris) initially define the migration/drift term in terms of mobility based on straightforward physical reasoning... 366

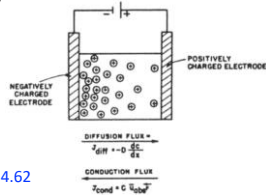
... use the Nernst–Planck equation for one species, i , which is defined as...

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

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

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

$$0 = -D_i \frac{dc_i}{dx} - \frac{|z_i|}{z_i} \mu_i c_i \frac{d\phi}{dx} + c_i v$$



Bockris & Reddy, Fig. 4.62

366

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... use the Nernst–Planck equation ^{mobility} for one species, i , which is defined as...

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... 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...

$$0 = -D_i \frac{dc_i}{dx} - \frac{|z_i|}{z_i} \mu_i c_i \frac{d\phi}{dx} + c_i v$$

electrochemical potential

$$D_i \frac{dc_i}{dx} = -\frac{|z_i|}{z_i} \mu_i c_i \frac{d\phi}{dx}$$

and using the "Boltzmann law," $c_i = c_{0,i} e^{-\frac{\bar{\mu}_i}{RT}}$,

$$D_i \left(-\frac{1}{RT} c_{0,i} e^{-\frac{\bar{\mu}_i}{RT}} \cdot \frac{d\bar{\mu}_i}{dx} \right) = -\frac{|z_i|}{z_i} \mu_i \left(c_{0,i} e^{-\frac{\bar{\mu}_i}{RT}} \right) \cdot \frac{d\phi}{dx}$$

and (flip the z_i term),

$$D_i \left(\frac{|z_i|}{z_i} \frac{1}{RT} \cdot \frac{d\bar{\mu}_i}{dx} \right) = \mu_i \cdot \frac{d\phi}{dx}$$

and because the electric potential component of the electrochemical potential equals $z_i F \phi$, then $\frac{d\bar{\mu}_i}{d\phi} = z_i F$,

$$\mu_i = \frac{|z_i| F D_i}{RT} \dots \text{the Einstein–Smoluchowski equation}$$

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... and now lastly, a simplified (cleaner) Nernst–Planck equation... 368

From before, ^{electrochemical potential} for one species the total flux in one-dimension is

$$N = -\frac{Dc}{RT} \frac{d\bar{\mu}}{dx} + cv, \dots$$

Never subscript i , as it is species independent

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

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

$$N = -D \cdot \frac{dc}{dx} - \frac{|z|}{z} \mu c \cdot \frac{d\phi}{dx} + cv$$

mobility

$$\mu_i = \frac{|z_i| F D_i}{RT}$$

$$D_i = \frac{RT \mu_i}{|z_i| F}$$

B&F, 4.2.2

flux

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

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

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

mobility

$$\mu_i = \frac{|z_i| F D_i}{RT}$$

$$D_i = \frac{RT \mu_i}{|z_i| F}$$

B&F, 4.2.2

flux

As again, recall that the current density can be simplified even further... in the absence of convection... $J_{x,i} = \frac{\sigma_i}{z_i F} \frac{d\bar{\mu}_i}{dx}$

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

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(UPDATED) 370

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Wow, those were some hefty equations... there is some value in thinking 371
 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.*

371

Wow, those were some hefty equations... there is some value in thinking 372
 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...**

$$N_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)$$

do not stir near the electrode...
... which you can't actually do anyway!

add supporting electrolyte

$$N_i(x) = -D_i \frac{\partial C_i(x)}{\partial x}$$

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...)

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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):

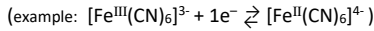
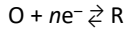
first, let's eliminate contributions to transport from migration/drift and convection **SO WE CAN FOCUS ON DIFFUSIONAL EFFECTS...**

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do not stir near the electrode...
 ... which you can't actually do anyway!
 add supporting electrolyte

$$N_i(x) = -D_i \frac{\partial C_i(x)}{\partial x}$$

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



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... 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, δ is the Nernst diffusion layer thickness

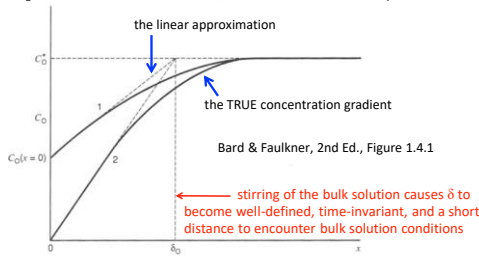


Figure 1.4.1 Concentration profiles (solid lines) and diffusion layer approximation (dashed lines). $x = 0$ corresponds to the electrode surface and δ_O is the diffusion layer thickness. Concentration profiles are shown at two different electrode potentials: (1) where $C_O(x=0)$ is about $C_O^*/2$, (2) where $C_O(x=0) = 0$ and $i = i_L$.

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... 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, δ is the Nernst diffusion layer thickness

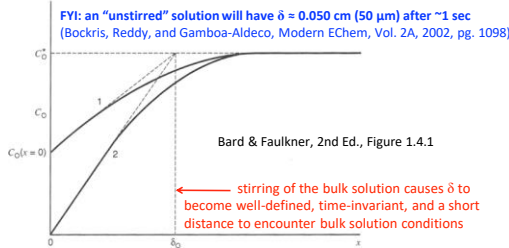


Figure 1.4.1 Concentration profiles (solid lines) and diffusion layer approximation (dashed lines). $x = 0$ corresponds to the electrode surface and δ_O is the diffusion layer thickness. Concentration profiles are shown at two different electrode potentials: (1) where $C_O(x=0)$ is about $C_O^*/2$, (2) where $C_O(x=0) = 0$ and $i = i_L$.

375

... because it will be convenient later, group the diffusion coefficient with the diffusion layer thickness: 376

$$m_o = \frac{D_o}{\delta_o} \text{ where } m_o \text{ is the mass transfer coefficient (units: cm s}^{-1}\text{; a velocity)}$$

* Note: dimensionally we have (cm² s⁻¹)/cm

... substituting...

$$N_o(x) = -m_o [C_o^* - C_o(x=0)]$$

↑ moles s⁻¹ cm⁻²
↑ cm s⁻¹
↑ moles cm⁻³

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... because it will be convenient later, group the diffusion coefficient with the diffusion layer thickness: 377

$$m_o = \frac{D_o}{\delta_o} \text{ where } m_o \text{ is the mass transfer coefficient (units: cm s}^{-1}\text{; a velocity)}$$

* Note: dimensionally we have (cm² s⁻¹)/cm

... substituting...

$$N_o(x) = -m_o [C_o^* - C_o(x=0)]$$

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

$$\frac{i}{nFA} = m_o [C_o(x=0) - C_o^*] \tag{1.4.6}$$

... since this was assumed to be at steady-state, the flux for the transport of "R" must be opposite and at the same rate...

$$\frac{i}{nFA} = m_R [C_R^* - C_R(x=0)]$$

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... and to simply the process, define the fastest rate, *i_f*, as when **C_O(x=0) = 0** 378

$$\frac{i}{nFA} = m_o [C_o(x=0) - C_o^*]$$

$$\frac{i_f}{nFA} = m_o [0 - C_o^*] = -m_o C_o^*$$

$$\frac{i - i_f}{nFA} = m_o C_o(x=0)$$

... and, as an example, if no R is present initially then **C_R^{*} = 0**

$$\frac{i}{nFA} = m_R [C_R^* - C_R(x=0)] = -m_R C_R(x=0)$$

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

$$E = E^0 + \frac{RT}{nF} \ln \left(\frac{C_o(x=0)}{C_R(x=0)} \right)$$

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$$E = E^{0'} - \frac{RT}{nF} \ln \left(\frac{m_O}{m_R} \right) + \frac{RT}{nF} \ln \left(\frac{i_l - i}{i} \right)$$

formal potential = experimentally measured E^0

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

$$E_{1/2} = E^{0'} - \frac{RT}{nF} \ln \left(\frac{m_O}{m_R} \right) + \frac{RT}{nF} \ln \left(\frac{i_l - i_{l/2}}{i_{l/2}} \right)$$

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$$E = E^{0'} - \frac{RT}{nF} \ln \left(\frac{m_O}{m_R} \right) + \frac{RT}{nF} \ln \left(\frac{i_l - i}{i} \right)$$

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$$E_{1/2} = E^{0'} - \frac{RT}{nF} \ln \left(\frac{m_O}{m_R} \right)$$

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$$E = E_{1/2} + \frac{RT}{nF} \ln \left(\frac{i_l - i}{i} \right)$$

... this will show up again...

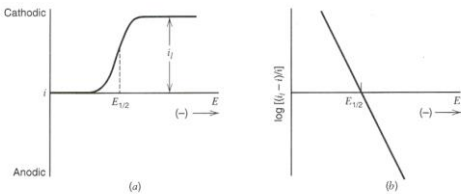


Figure 1.4.2 (a) Current-potential curve for a Nernstian reaction involving two soluble species with only oxidant present initially. (b) $\log[(i_l - i)/i]$ vs. E for this system.

What happens to the potential when $i \rightarrow i_l$? $E \rightarrow -\infty$
 What happens to the potential when $i \rightarrow 0$? $E \rightarrow +\infty$

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... and when $C_R^* \neq 0$...

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$$E = E^{0'} - \frac{RT}{nF} \ln \left(\frac{m_O}{m_R} \right) + \frac{RT}{nF} \ln \left(\frac{i_{l,c} - i}{i - i_{l,a}} \right)$$

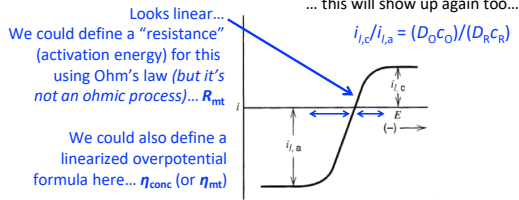


Figure 1.4.3 Current-potential curve for a Nernstian system involving two soluble species with both forms initially present.

... 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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(UPDATED) 383

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

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