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

- <u>Mass transfer</u>

- **Diffusion**

- **Migration / Drift**

- **Convection**

- **Semi-empirical diffusive models**

- *Conductivity*

- *Transport (Transference) number*

- *Balance sheets*

- *Ohmic drop/loss*

From before, <u>for one species</u> the total flux <u>in one-dimension</u> is

$$N = -\frac{Dc}{RT} \cdot \frac{d\bar{\mu}}{dx} + cv,$$ where again D is diffusion coefficient (cm² s⁻¹), c is
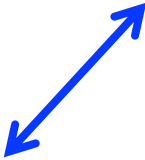
concentration (mol cm⁻³), $\bar{\mu}$ is the electrochemical potential (J mol⁻¹), v is velocity (cm s⁻¹)

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

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

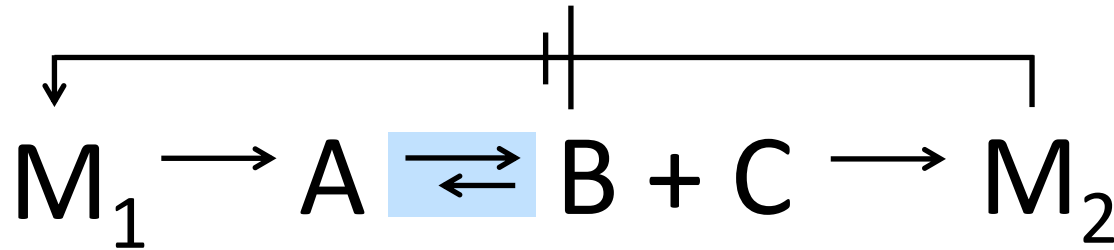$$N = -\frac{Dc}{RT} \cdot \frac{d(\mu^0 + RT \ln a + zF\phi)}{dx} + cv \dots$$ and assuming $a \approx c$,

$$N = -\mathrm{Dc} \cdot \frac{d(\ln c)}{dx} - \frac{zFD}{RT} c \cdot \frac{d\phi}{dx} + cv \dots$$ and finally…

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

Who cares? …

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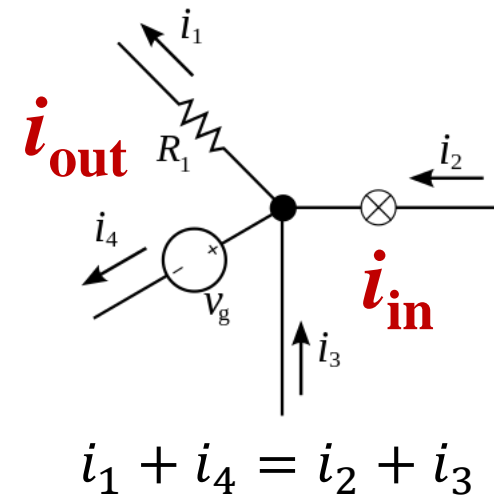
… when the current is at a steady-state, *the current is constant*, and there is no new capacitive charging!

$$M_1 \longrightarrow A \rightleftharpoons B + C \longrightarrow M_2$$

… for steady-state current, KCL applies… no, not KC**I**… but KC**L**!

Kirchhoff's Current Law (KCL)

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

i_{out} R_1 i_1

i_4 i_2

V_g i_{in}

i_3

$$i_1 + i_4 = i_2 + i_3$$

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

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)

RECALL:

I

e^- e^- e^- e^-

e^- e^-

$$M_1 \longrightarrow A \rightleftarrows B + C \longrightarrow M_2$$

e^- e^-
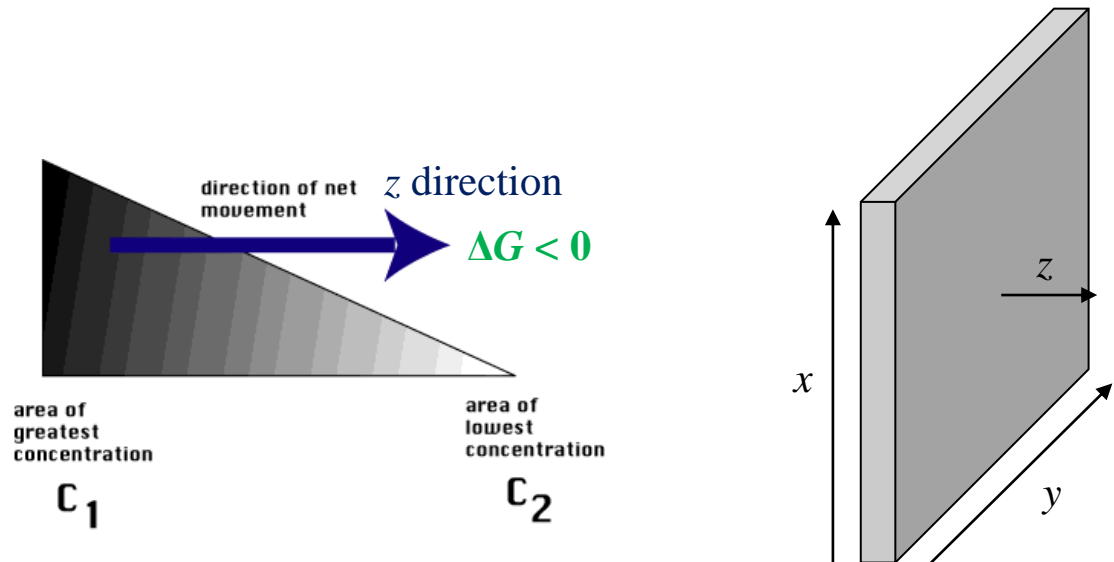
⊖   ⊖   ⊖
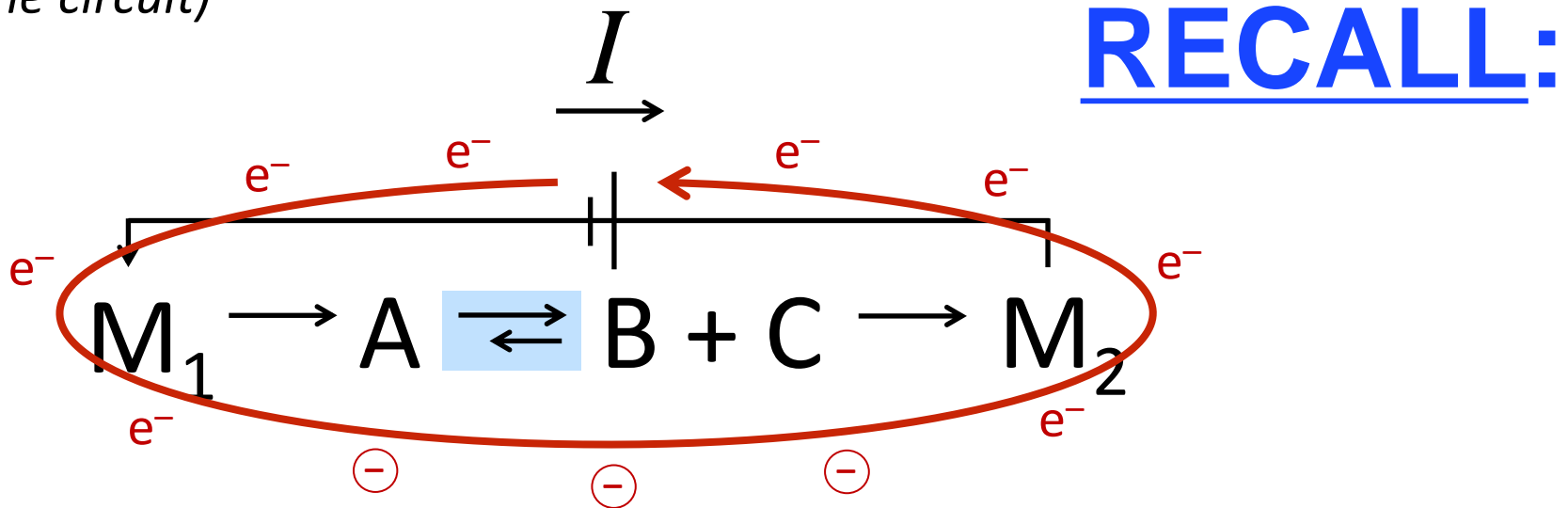
… hey, what are those minus signs at the bottom? …

Migrating/Drifting Ions!

… we'll get to this shortly

RECALL:

Diffusion coefficient (D, cm² 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 <u>steady-state</u> Diffusion: $N_z = -D_z \dfrac{dc}{dz}$ in 1D

direction of net movement

z direction

$\Delta G < 0$

area of greatest concentration

area of lowest concentration

c_1

c_2

x

z

y

Physician & Physiologist

Do the units of D make sense?

N_z (mol **cm⁻²** s⁻¹, as ***xy***) = D_z · dc/dz ((mol **cm⁻³**) **cm⁻¹**, as ***xyz z***)

(mol **cm⁻²** s⁻¹, as ***xy***) = D_z · (mol **cm⁻⁴**, as ***xyzz***)

Therefore, D_z is has units of **cm²** s⁻¹… but as ***zz***…

Huh? *zz*? z^2? What?… That was unexpected!… Is it right?…

Adolf Eugen Fick
(1829–1901)

from Wiki

… 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!
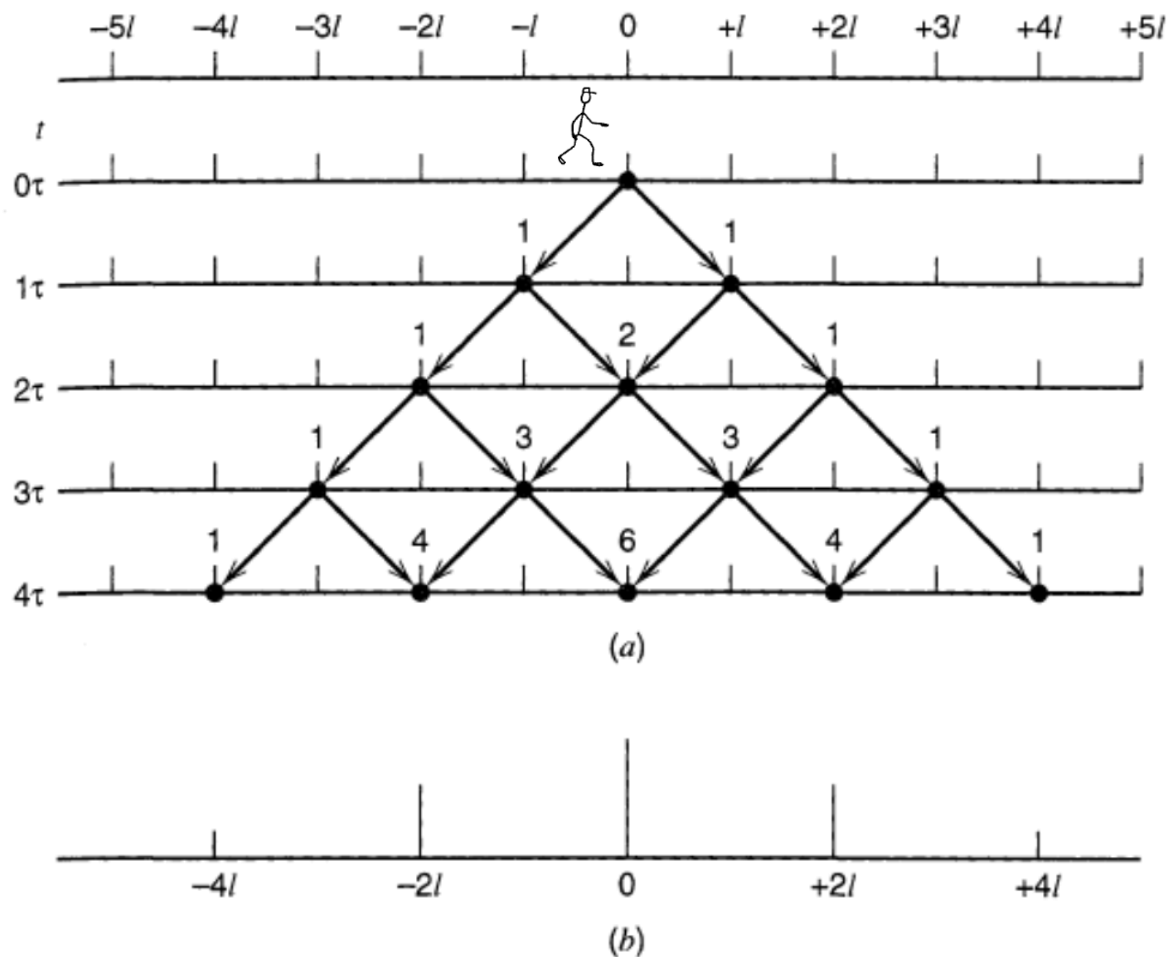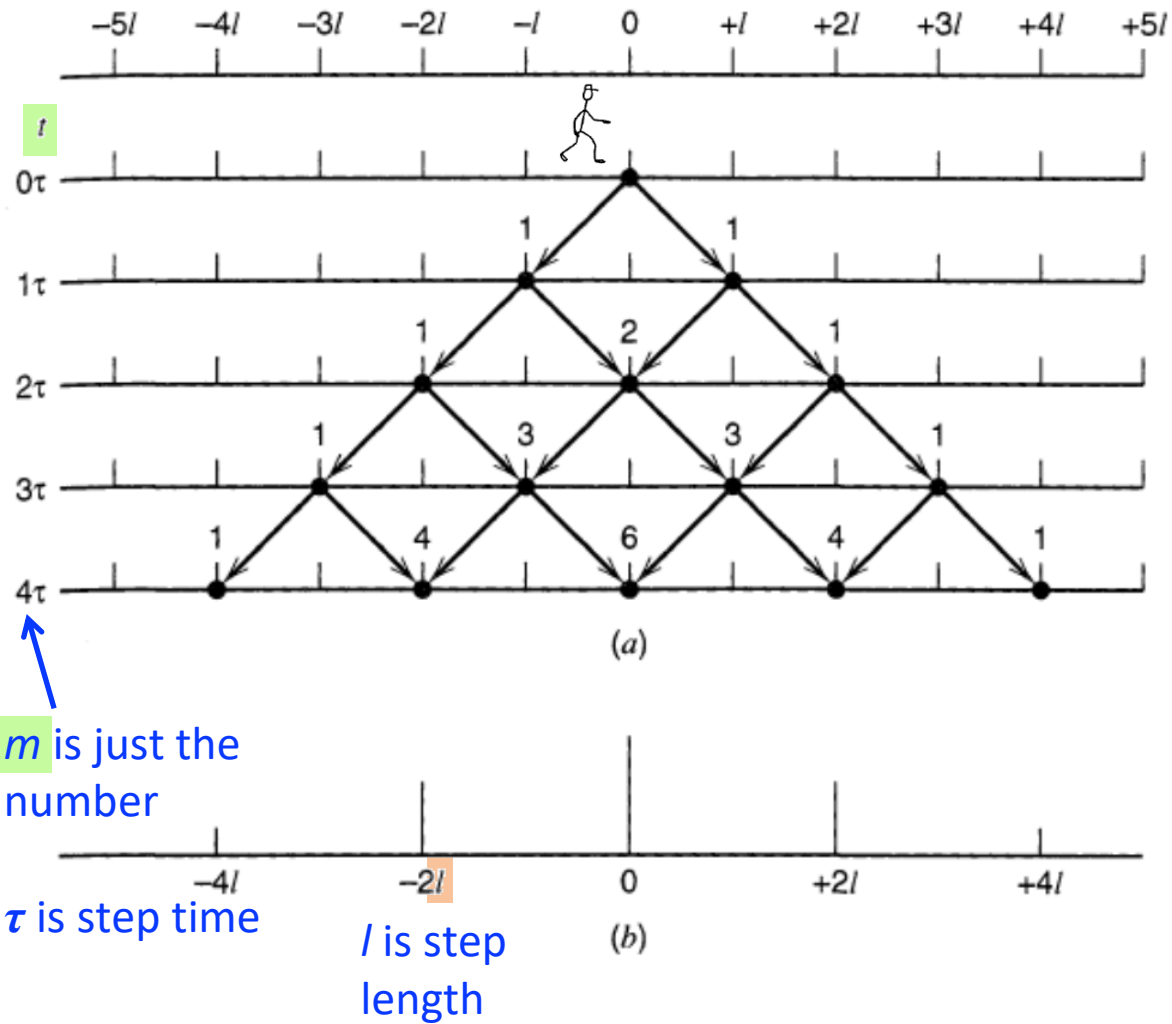
From B&F

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! …

… 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

$$\overline{\Delta^2} = m\,l^2 = \frac{t}{\tau}l^2 = 2Dt$$

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.

m is just the number

τ is step time

l is step length

root mean square (rms) displacement (standard deviation)

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

Dimension	$\overline{\Delta}* =$
1D	$\sqrt{2Dt}$
2D	$\sqrt{4Dt}$
3D	$\sqrt{6Dt}$

*the rms displacement

In both directions from a…

… plane

… wire, line, tube

… point, sphere, disk

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

a characteristic "diffusion length"

root mean square (rms) displacement (standard deviation)

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

Given D = 5 x 10^{-6} cm² s⁻¹ (but memorize ~10^{-5} cm² s⁻¹),

time	$\overline{\Delta}$
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 ≈ 3.9"

a characteristic "diffusion length"

root mean square (rms) displacement (standard deviation)

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

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} cm²/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_3COO^-	1.09
NH_4^+	1.96	$CH_3CH_2COO^-$	0.95
$N(C_4H_9)_4^+$	0.52	$B(C_6H_5)_4^-$	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

Note: 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
* on the order of 10^{-7} cm²/s for proteins

a characteristic **"diffusion length"**

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

root mean square (rms) displacement (standard deviation)

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

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

Chemist

Theodor von Grotthuss
(1785–1822)

from Wiki

a "cartoon"

http://www.snipview.com/q/Grotthuss%20mechanism

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

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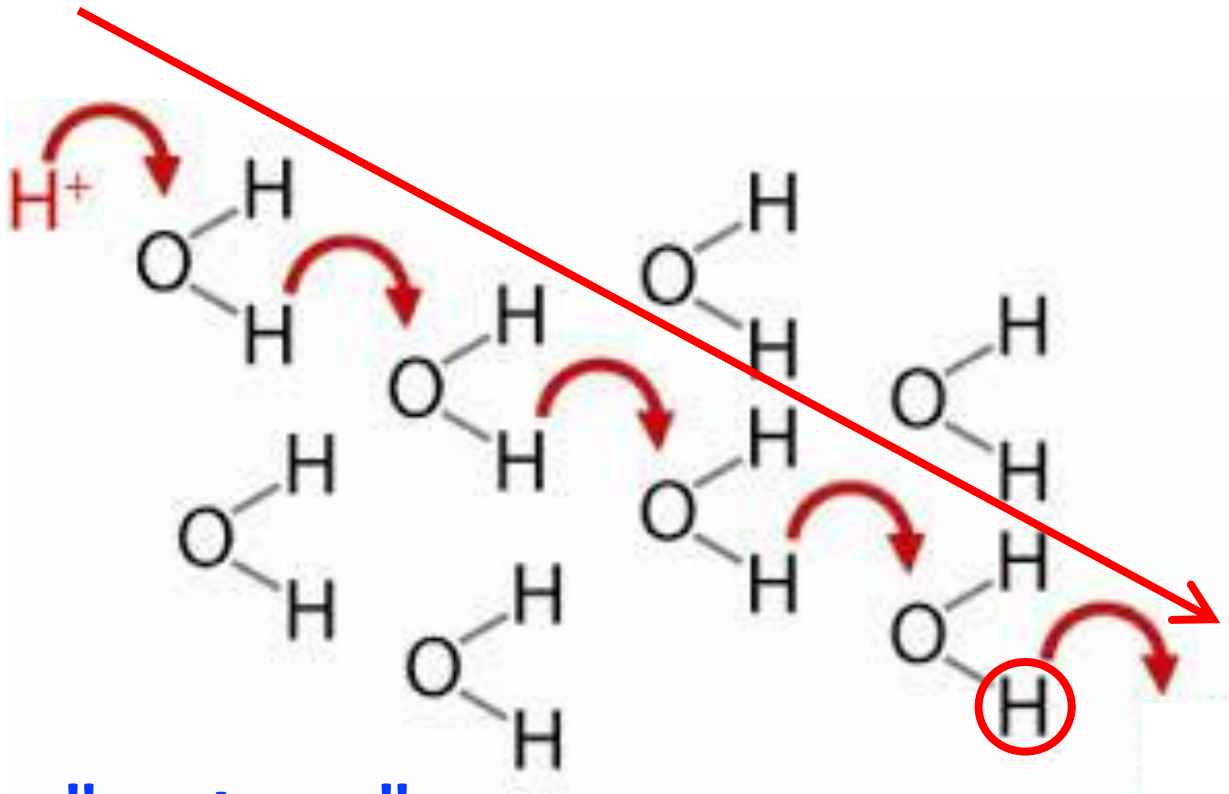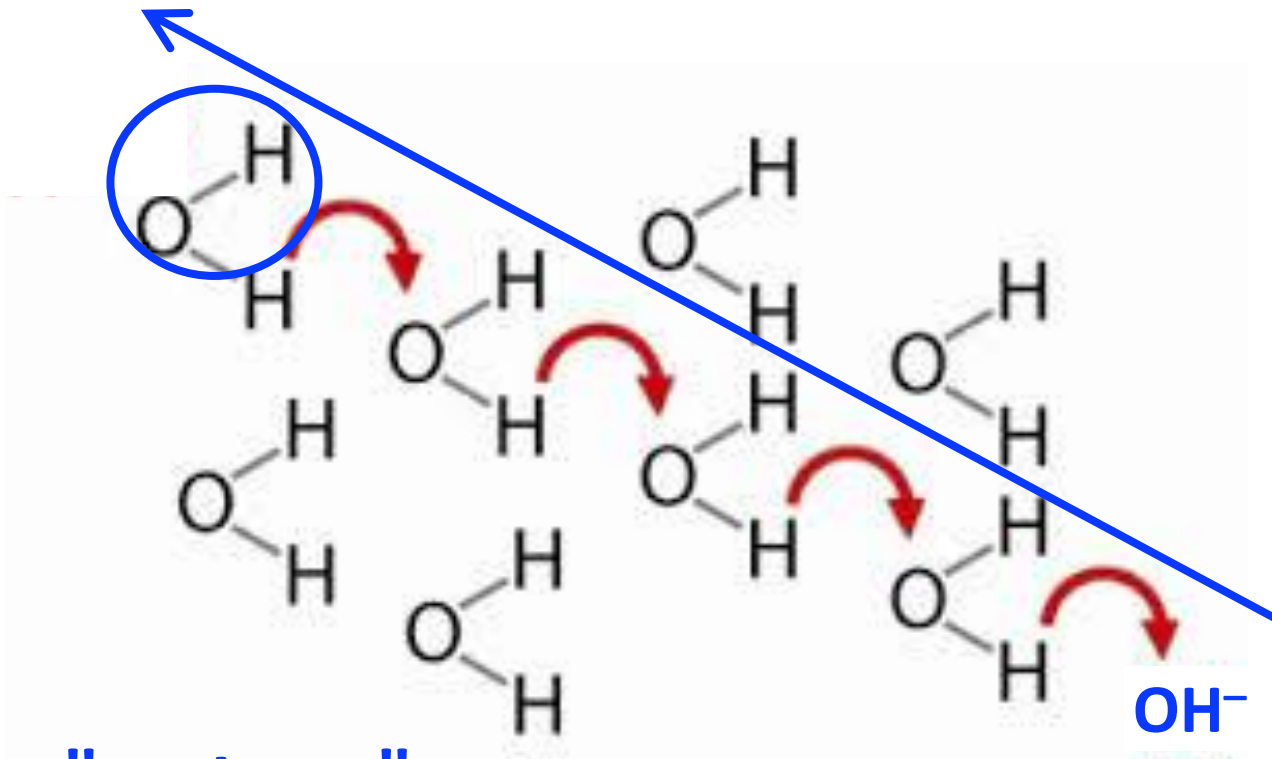$$D(OH^-) = 5.28 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$

Chemist

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OH⁻

a "cartoon"

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Proton transfer is enabled by an additional O–O bond contraction, not required in $H_5O_2^+$. 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.

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

at the molecular level[2–8]. In contrast, hydroxide ion mobility in basic solutions has received far less attention[2,3,9,10], 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 notion[11] 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 polarities[11–18]. However, recent studies[2,3] 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 nuclei[19–21]. We find that the transport mechanism, which differs significantly from the proton hole picture, involves an interplay between the previously identified hydration complexes[2,3] and is strongly influenced by nuclear quantum effects.

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 tr

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

Looking forward… Section 1.4 and Chapter 4

- <u>Mass transfer</u>

- <u>Diffusion</u>

- **Migration / Drift**

- **Convection**

- **Semi-empirical diffusive models**

- *Conductivity*

- *Transport (Transference) number*

- *Balance sheets*

- *Ohmic drop/loss*

Moving on… remember this…
    … to seed our next topic, let's assume that the walker is *charged*…
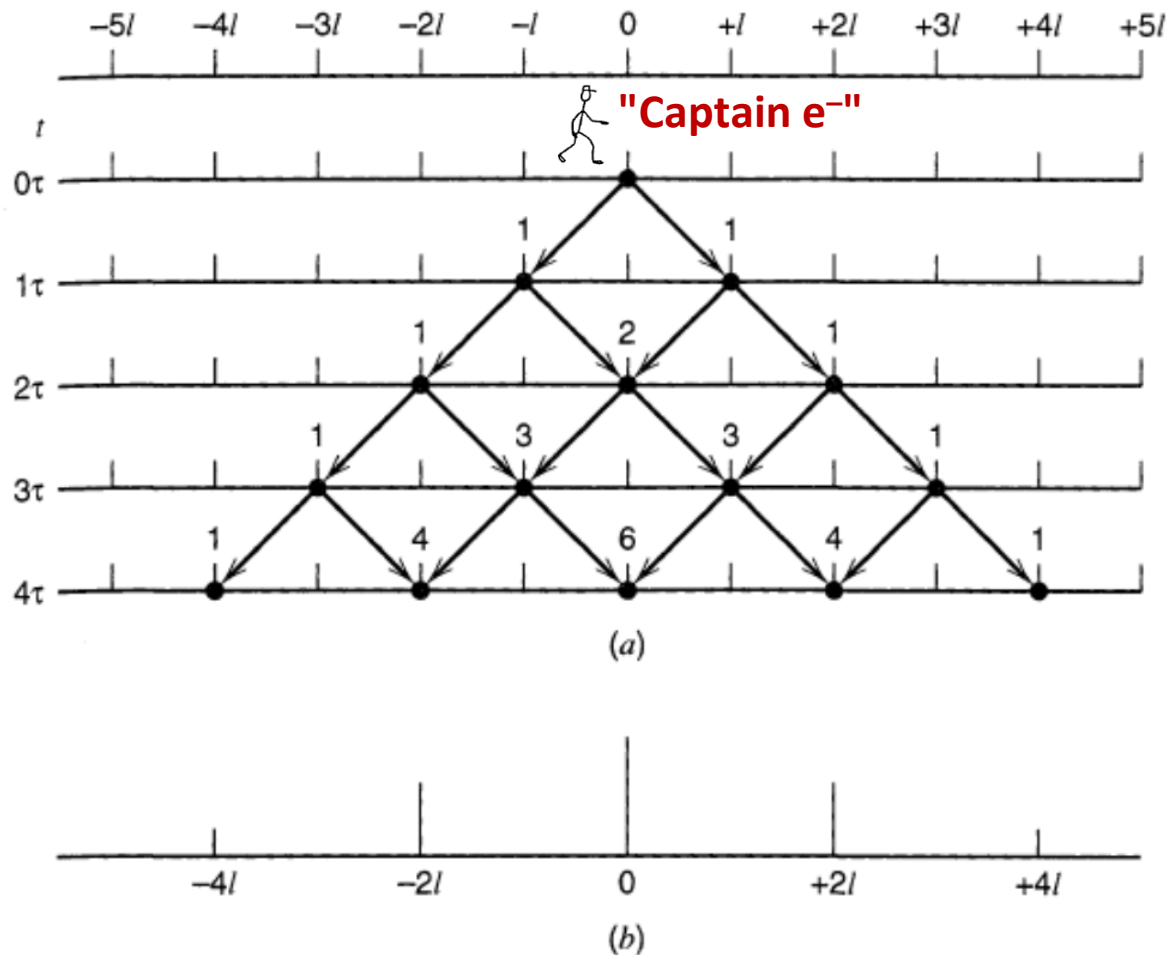

"Captain e⁻"

(a)

(b)

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.

From B&F

… Flashback! Pascal's triangle! …

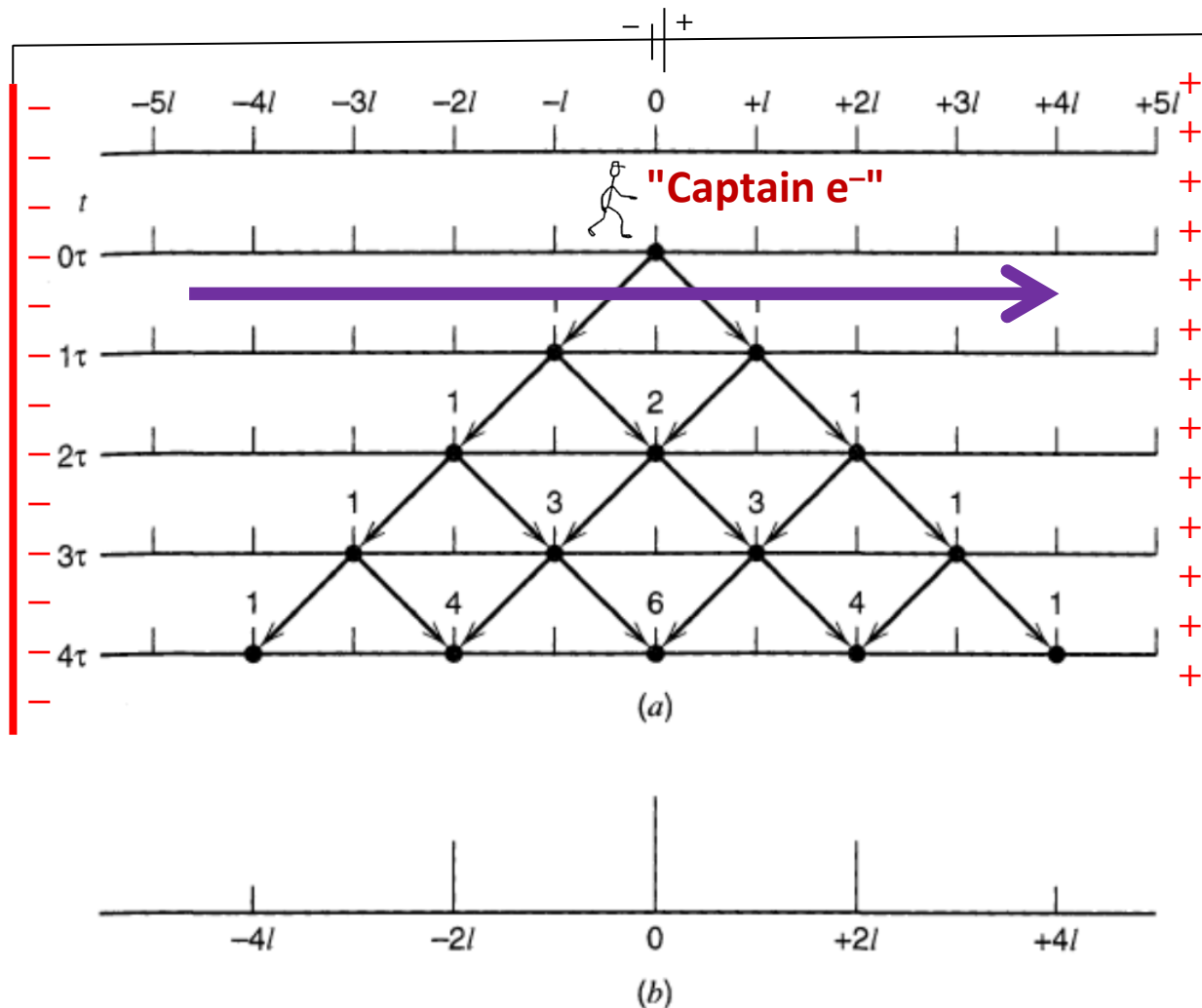**… then the random walk would no longer be quite so random!**

"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.

… welcome to the concept of ionic **migration/drift**

From B&F

… Flashback! Pascal's triangle! …

Diffusion coefficient (D, cm² s⁻¹) – "<u>proportionality constant relating the flux of [the] amount of [an entity to its] concentration gradient</u>…" (IUPAC Gold Book)

$\qquad$ **Fick's first law of steady-state Diffusion**: $N_z = -D_z \dfrac{dc}{dz}$ in 1D

Mobility (μ, cm² V⁻¹ s⁻¹) – "the limiting velocity of an ion in an electric field of unit strength" (B&F, pg. 66)… or <u>a proportionality constant relating the velocity of an ion to the electric field strength</u>

$\qquad$ … start with **Newton's second law of motion**: $F = m \cdot a$

$\qquad$ … $|z|e\mathbf{E} = m \cdot \dfrac{v_d}{\tau}$, with e, elementary charge (C),

$\qquad\qquad\qquad\qquad\qquad$ $\mathbf{E}$, electric field (V cm⁻¹)),

$\qquad\qquad\qquad\qquad\qquad$ v_d, average drift velocity (cm s⁻¹),

$\qquad\qquad\qquad\qquad\qquad$ τ, mean time (s) to reset drift motion through collisions (i.e. $v = 0$)

$\qquad$ Because $\underline{v_{d,z} = \mu_z \cdot \mathbf{E}_z}$, this means that $\boldsymbol{\mu} = |\boldsymbol{z}|\boldsymbol{e}\dfrac{\boldsymbol{\tau}}{\boldsymbol{m}}$

$\qquad$ … and the units of mobility are correct … $(\text{cm s}^{-1}) = \mu \cdot (\text{V cm}^{-1})$
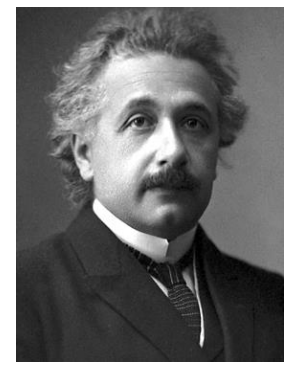
the mobility is defined from **Stokes' law** by the **Stokes–Einstein equation** based on the balance of forces acting on a particle, with charge, ze, and moving in an electric field, **E**:

$6\pi\eta rv$ — viscous drag

ze

electrophoretic force — $|z_i|e\mathbf{E}$

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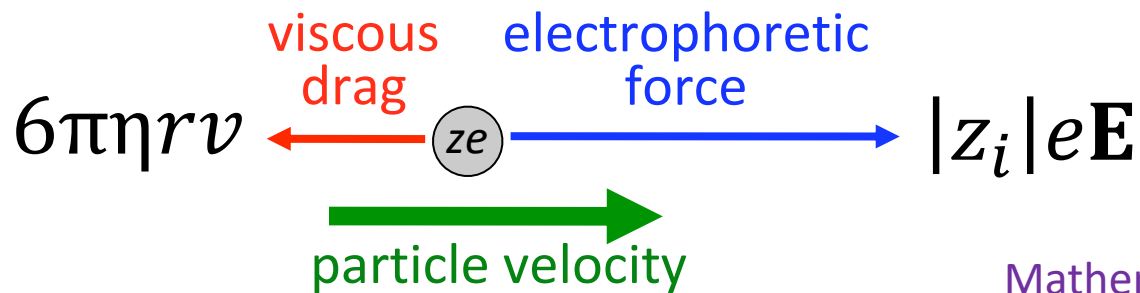
$$\mu_i = \frac{v}{\mathbf{E}} = \frac{|z_i|e}{6\pi\eta r}$$

Mathematician, Physicist, Politician, and Theologian

Physicist & Philosopher
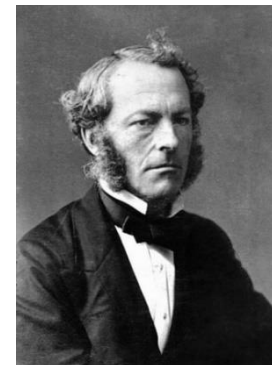
Sir George Gabriel Stokes (1819–1903)

Albert Einstein (1879–1955)

from Wiki

Diffusion coefficient (D, cm² 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 (μ, cm² V⁻¹ s⁻¹) – "the limiting velocity of an ion in an electric field of unit strength" (B&F, pg. 66)… or <u>a proportionality constant relating the velocity of an ion to the electric field strength</u>

> **Newton's second law of motion**: $F = m \cdot a$, $v_d = \mu \cdot \mathbf{E}$

Stokes' law: $F = |z|e\mathbf{E} = 6\pi\eta r v_d$, and so by solving $\mu = \frac{v_d}{\mathbf{E}}$ 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
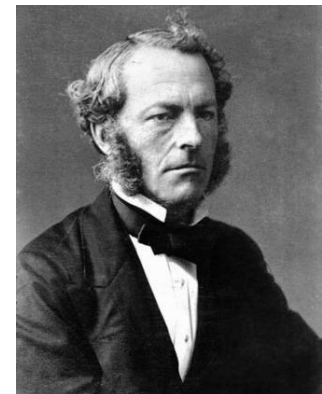
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Newton's second law of motion: $F = m \cdot a$, $v_d = \mu \cdot \mathbf{E}$
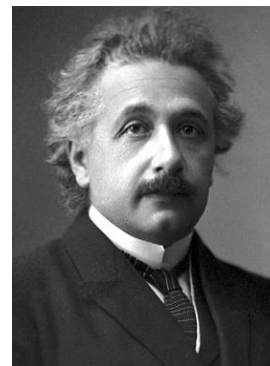
… and a *very* important point is that these two parameters, D and μ, are related!

… Einstein–Smoluchowski equation,

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

… and what is the value of $^{RT}/_F$? **25.7 mV!**

Physicist & Philosopher   Scientist

Albert Einstein   Marian Smoluchowski
(1879–1955)   (1872–1917)
from Wiki

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

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

mobility

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

… 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…

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

POSITIVELY CHARGED ELECTRODE

NEGATIVELY CHARGED ELECTRODE

DIFFUSION FLUX =

$$J_{diff} = -D \frac{dc}{dx}$$

CONDUCTION FLUX

$$J_{cond} = C \, \bar{u}_{obs} \vec{F}$$

Bockris & Reddy, Fig. 4.62

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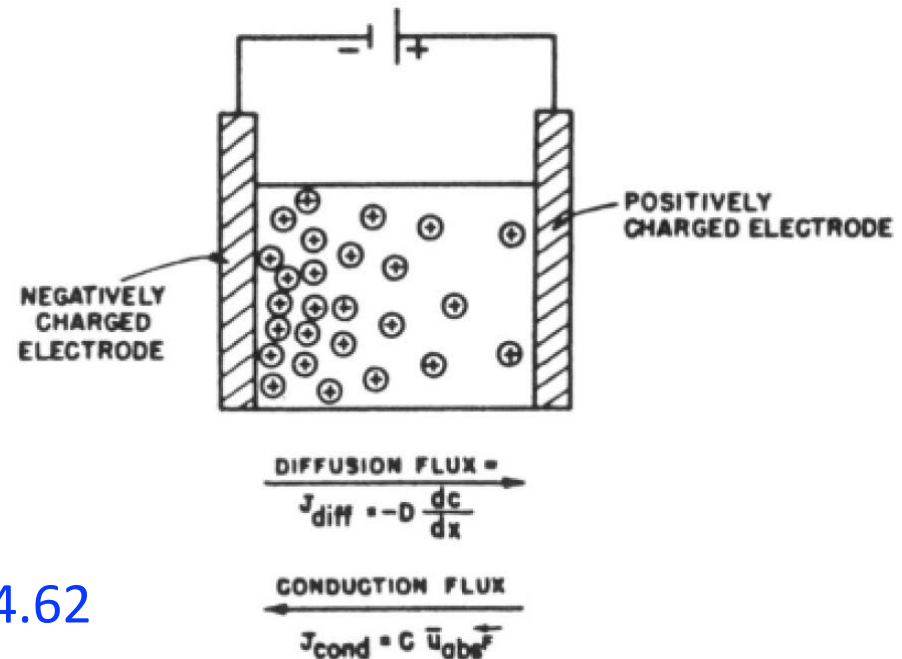
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$$N_i = -D_i \frac{dc_i}{dx} - \frac{|z_i|}{z_i} \mu_i c_i \frac{d\phi}{dx} + c_i v$$

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

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

electrochemical potential

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

$D_i \frac{dc_i}{dx} = -\frac{|z_i|}{z_i} \mu_i c_i \frac{d\phi}{dx}$, and using the "Boltzmann law," $c_i = c_{0,i} e^{-\frac{\overline{\mu}_i}{RT}}$,

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

$D_i \left(\frac{|z_i|}{z_i} \frac{1}{RT} \cdot \frac{d\overline{\mu}_i}{dx} \right) = \mu_i \cdot \frac{d\phi}{dx}$, and because the electric potential component

of the electrochemical potential equals $z_i F \phi$, then $\frac{d\overline{\mu}_i}{d\phi} = z_i F$,

$\boldsymbol{\mu_i = \frac{|z_i| F D_i}{RT}}$... **the Einstein–Smoluchowski equation**

electrochemical potential

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

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

Never subscript *i*, as it is species independent

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

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

mobility

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

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

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

B&F, 4.2.2

flux

$$J_i(x) = -D_i\frac{\partial C_i(x)}{\partial x} - \frac{z_iF}{RT}D_iC_i\frac{\partial \phi(x)}{\partial x} + C_iv(x)$$

electrochemical potential

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

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

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

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

mobility

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

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

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

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

$$J_{x,i} = \frac{\sigma_i}{z_i F}\frac{d\bar{\mu}_i}{dx}$$

B&F, 4.2.2

flux

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

Looking forward… Section 1.4 and Chapter 4

- <u>Mass transfer</u>

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- **Convection**

- **Semi-empirical diffusive models**

- *Conductivity*

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- *Balance sheets*

- *Ohmic drop/loss*

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.*

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**…

do not stir near the electrode…

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

add supporting electrolyte

… which you can't actually do anyway!

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

And imagine a scenario where not only this is true, but where *dC/dx* is time invariant, meaning <u>at steady-state</u>, 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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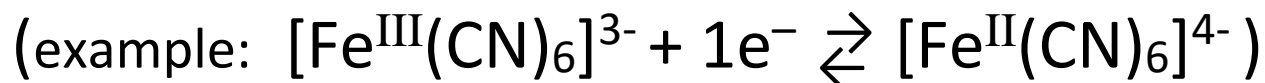
add supporting electrolyte

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

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

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

$$O + n e^- \rightleftarrows R$$

(example: $[Fe^{III}(CN)_6]^{3-} + 1e^- \rightleftarrows [Fe^{II}(CN)_6]^{4-}$)

… 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

the linear approximation

the TRUE concentration gradient

Bard & Faulkner, 2nd Ed., Figure 1.4.1

stirring of the bulk solution causes δ to become well-defined, time-invariant, and a short distance to encounter bulk solution conditions
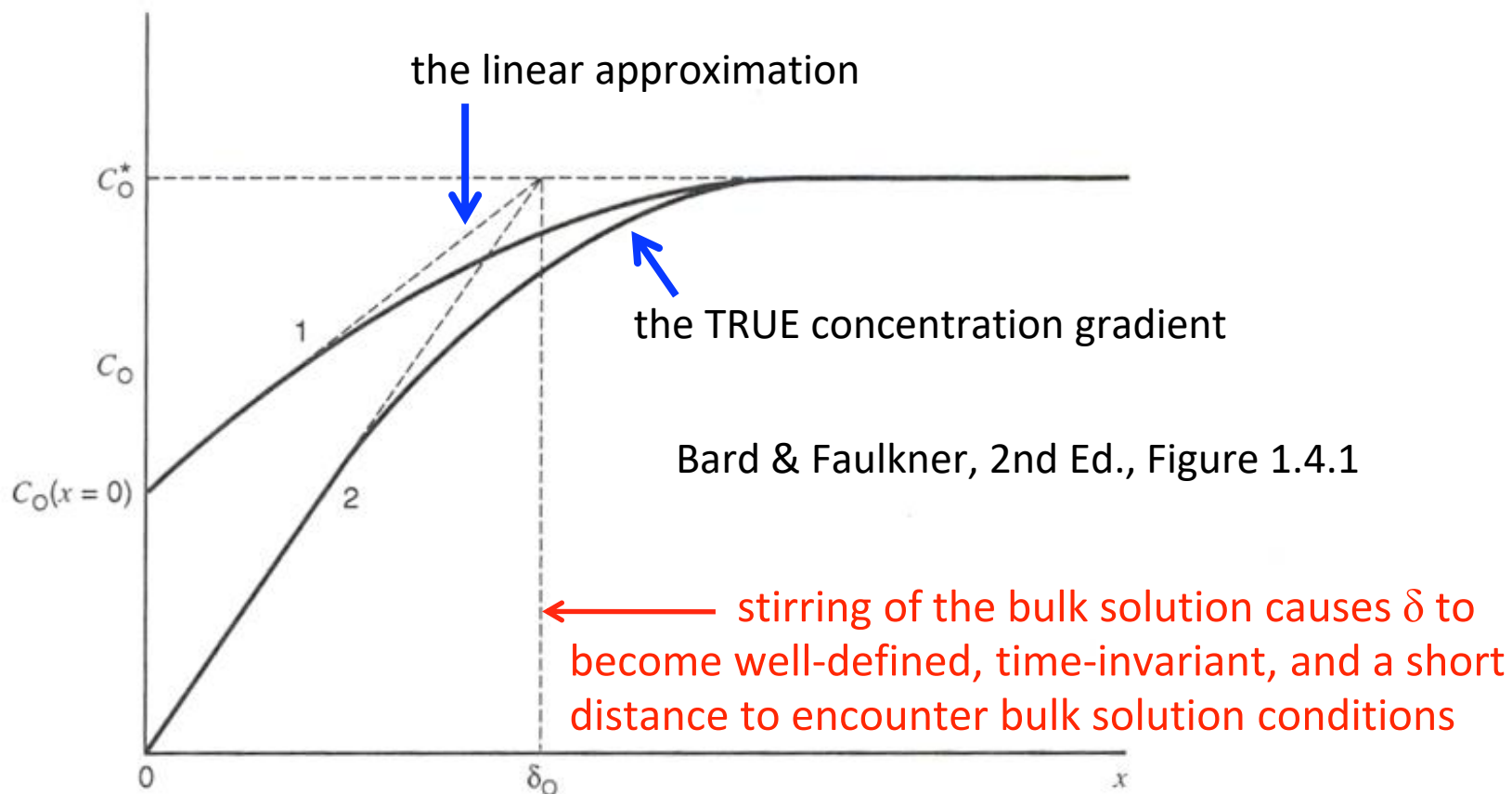
Figure 1.4.1 Concentration profiles (solid lines) and diffusion layer approximation (dashed lines). $x = 0$ corresponds to the electrode surface and δ_O is the diffusion layer thickness. Concentration profiles are shown at two different electrode potentials: (1) where $C_O(x=0)$ is about $C_O^*/2$, (2) where $C_O(x=0) \approx 0$ and $i = i_l$.

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FYI: an "unstirred" solution will have $\delta \approx 0.050$ cm (50 μm) after ~1 sec (Bockris, Reddy, and Gamboa-Aldeco, Modern EChem, Vol. 2A, 2002, pg. 1098)

Bard & Faulkner, 2nd Ed., Figure 1.4.1

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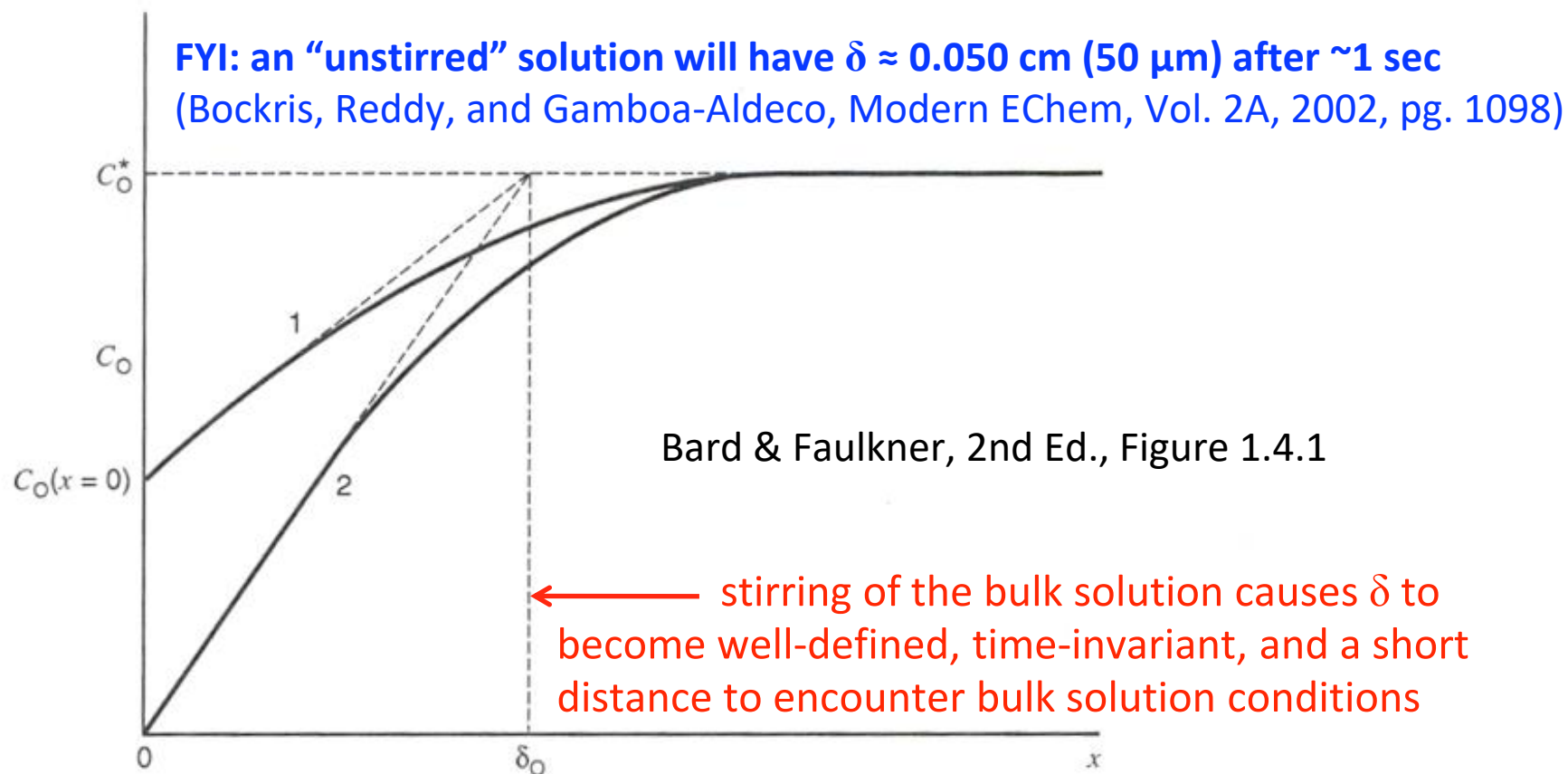
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… because it will be convenient later, group the diffusion coefficient with the diffusion layer thickness:

$$m_O = \frac{D_O}{\delta_O}$$

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

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

… substituting…

$$N_O(x) = -m_O\left[C_O^* - C_O(x = 0)\right]$$

moles s^{-1} cm^{-2} cm s^{-1} moles cm^{-3}

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

… substituting…

$$N_O(x) = -m_O\left[C_O^* - C_O(x = 0)\right]$$

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

$$\frac{i}{nFA} = m_O\left[C_O(x = 0) - C_O^*\right] \tag{1.4.6}$$

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

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

… and to simply the process, define the fastest rate, i_l, as when $C_O(x = 0) = 0$

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

$$\frac{i_l}{nFA} = m_O[0 - C_O^*] = -m_O C_O^*$$

$$\frac{i - i_l}{nFA} = m_O C_O(x = 0)$$

… 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…

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

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

formal potential = experimentally measured E^o

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

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

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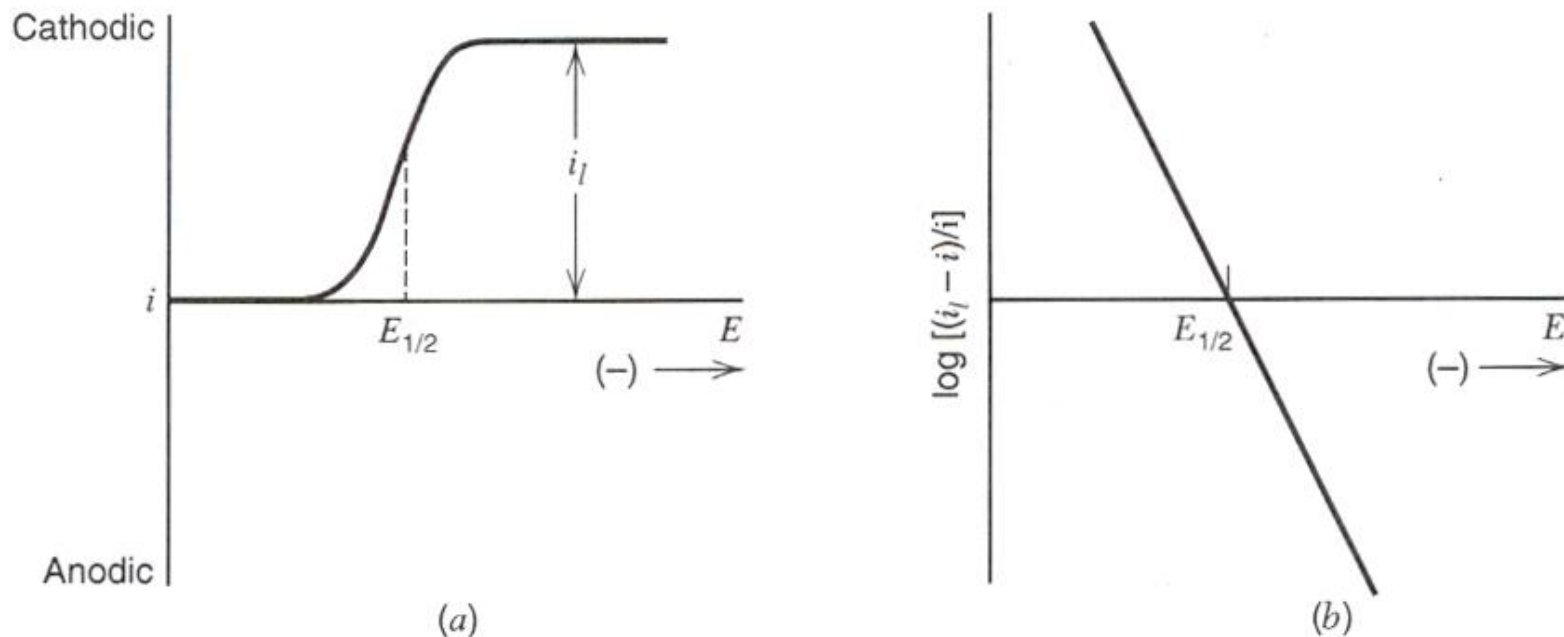
… this will show up again…

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 $i \rightarrow 0$? $E \rightarrow +\infty$

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

… this will show up again too…

$i_{l,c}/i_{l,a} = (D_O c_O)/(D_R c_R)$

Looks linear…
We could define a "resistance" (activation energy) for this using Ohm's law *(but it's not an ohmic process)*… R_{mt}

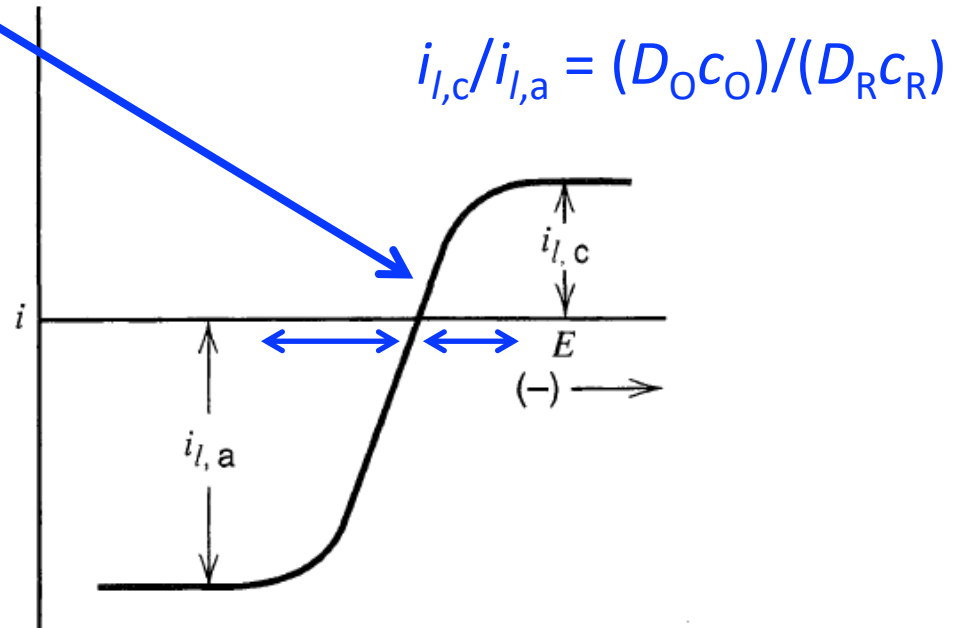We could also define a linearized overpotential formula here… η_{conc} (or η_{mt})

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 <u>diffusion</u> only…
… **what if we now also include mass transport by migration/drift?**…

Looking forward… Section 1.4 and Chapter 4

- <u>Mass transfer</u>

- <u>Diffusion</u>

- <u>Migration / Drift</u>

- <u>Convection</u>

- <u>Semi-empirical diffusive models</u>

- *Conductivity*

- *Transport (Transference) number*

- *Balance sheets*

- *Ohmic drop/loss*