Lecture #12 of 18(?)

Mass Transfer Processes

Chapters 1 and 4

Q: What's in this set of lectures?
A: B&F Chapters 1 & 4 main concepts:

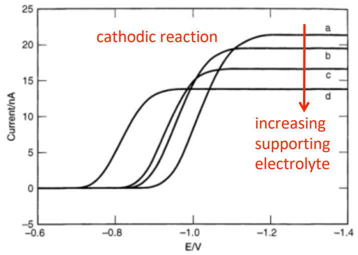
- Section 1.4: Mass transfer and Semi-empirical treatment of electrochemical observations
- Chapter 4: Mass transfer

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**

Now, do the following trends make sense? Reaction is **$Tl^+ + e^- \rightleftharpoons Tl^0$**

RECALL:



We derived the following equation considering diffusive transport only *(i.e. in the presence of large amounts of supporting electrolyte)*…

$$i_l = nFAm_O C_O^*$$

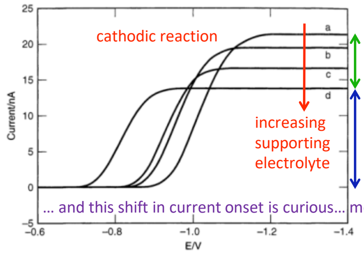
$$m_O = D_O/\delta_O$$

… but this cannot explain the behavior here as none of these variables is changing

Figure 4.3.5 Voltammograms for reduction of 0.65 m*M* Tl_2SO_4 at a mercury film on a silver ultramicroelectrode (radius, 15 μm) in the presence of (*a*) 0, (*b*) 0.1, (*c*) 1, and (*d*) 100 m*M* $LiClO_4$. The potential was controlled *vs.* a Pt wire QRE whose potential was a function of solution composition. This variability is the basis for the shifts in wave position along the potential axis. [Reprinted with permission from M. Ciszkowska and J. G. Osteryoung, *Anal. Chem.*, **67**, 1125 (1995). Copyright 1995, American Chemical Society.]

Now, do the following trends make sense? Reaction is **$Tl^+ + e^- \rightleftharpoons Tl^0$**

… why are the diagonal trends not changing like in the lab?… see next slide…



RECALL:

$I_{m\text{-}Tl+}$, to bring Tl^+ to the electrode

$I_{d\text{-}Tl+}$, to bring Tl^+ to the electrode

… and this shift in current onset is curious… more on that later…

Figure 4.3.5 Voltammograms for reduction of 0.65 m*M* Tl_2SO_4 at a mercury film on a silver ultramicroelectrode (radius, 15 μm) in the presence of (*a*) 0, (*b*) 0.1, (*c*) 1, and (*d*) 100 m*M* $LiClO_4$. The potential was controlled *vs.* a Pt wire QRE whose potential was a function of solution composition. This variability is the basis for the shifts in wave position along the potential axis. [Reprinted with permission from M. Ciszkowska and J. G. Osteryoung, *Anal. Chem.*, **67**, 1125 (1995). Copyright 1995, American Chemical Society.]

… so supporting electrolyte removes (most) migration for redox species of interest… but it also removes iR_u drop from data… a two-for-one!… 428

Materials and Corrosion 2006, 57, No. 6 DOI: 10.1002/maco.200603982

The iR drop – well-known but often underestimated in electrochemical polarization measurements and corrosion testing

W. Oelßner*, F. Berthold and U. Guth

… let's just look at some figures: 1, 4, 5, 7, 14 ,16

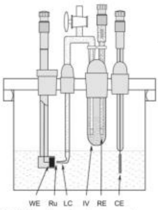


Fig. 1. Electrode configuration in a corrosion test cell (Sensortechnik Meinsberg GmbH, Germany). WE: working electrode, CE: counter electrode, RE: reference electrode, LC: Lugging capillary, IV: intermediate vessel, R_u: uncompensated resistance

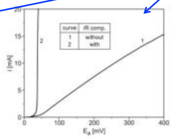


Fig. 14. Polarization curves of zinc in 0.25 M zinc sulphate solution (κ = 19 mS/cm) without (curve 1) and with (curve 2) automatic iR compensation by the interrupter method. Distance Luggin capillary – working electrode z = 0.2 cm, area of the working electrode A = 0.25 cm^2, scan rate sr = 0.2 mV/s, E_a: applied potential, i: polarization current

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Problems

Solutions

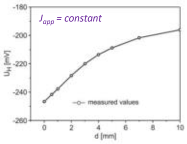


Fig. 4. Measured potentials in dependency on the distance of the Luggin capillary from the electrode surface (*E. Heitz* et al. in [6], p. 236). U_H: potential of the Haber-Luggin probe, d: distance between the Haber-Luggin probe and the working electrode

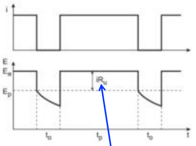
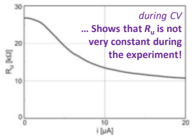


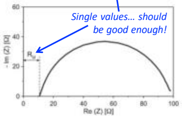
Fig. 7. Characteristic shape of the interrupter pulses. i: polarizing current, iR_u: ohmic drop, E: Electrode potential, E_a: applied potential, E_p: "true" polarization of the working electrode, t_o: interrupter period, t_p: polarization period (duration ratio t_o/t_p not in scale)



during CV

… Shows that R_u is not very constant during the experiment!

Fig. 16. Change of the ohmic resistance R_u in the experiment shown in Fig. 15. i: polarization current



Single values… should be good enough!

Fig. 5. Determination of the resistance R_u for the system steel X20Cr13 in 0.05 M H_2SO_4 from a Nyquist plot. Re (Z): real part of impedance, Im (Z): imaginary part of impedance, R_u: uncompensated resistance

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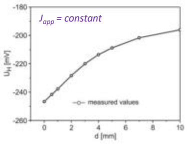
Problems



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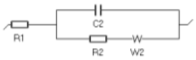

Start by fitting EIS data using this equivalent circuit:
- **What is R1?** Fix it to the clear value for R_u.
- **What is R2?** Charge-transfer resistance; fix it to 0.
- **What is C2?** Cap$_{dl}$; just let it float.
- **What is W2?** Warburg diffusion, σ; **find it!**

https://www.palmsens.com/knowledgebase-topic/warburg-impedance/

$$\sigma = \frac{RT}{n^2F^2A\sqrt{2}}\left(\frac{1}{D_O^{1/2}C_O^b} + \frac{1}{D_R^{1/2}C_R^b}\right)$$

units of Ohm/s$^{1/2}$

assume these are the same value

… so that the units work out most easily…
… use meters as the length in *A*, *D*, and *C*

Solutions

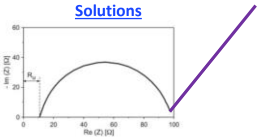

Fig. 5. Determination of the resistance R_u for the system steel X20Cr13 in 0.05 M H_2SO_4 from a Nyquist plot. Re (Z): real part of impedance, Im (Z): imaginary part of impedance, R_u: uncompensated resistance

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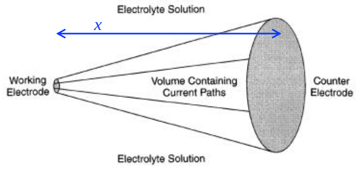
… finally, iR_u drop does not always have a typical length-dependent “*R*”… 431



… current is limited by largest resistor in series… which is at WE

***Uncompensated resistance*:**

$\kappa = \sigma$

Planar WE

$$R_u = x/\kappa A$$

Point WE

$$R_u = \boxed{\frac{1}{4\pi\kappa r_0}}\left(\frac{x}{x + r_0}\right)$$

see B&F, pp. 27–28, and pp. 216–218 for details

Units: Ohm^{-1} cm^{-1}

What happens when *x* → ∞? **Just this term**… with 1/(2 circumference) in place of *x*/*A*

Němec, *J. Electroanal. Chem.*, 1964, *8*, 166

A review of 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

Time-Dependence in Electrochemistry

Chapters 4 and 5

Q: What's in this set of lectures?
A: B&F Chapters 4 & 5 main concepts:

- Section 4.4.2: Fick's Second Law of Diffusion
- Section 5.1: Overview of step experiments
- Section 5.2: Potential step under diffusion controlled
- Sections 5.3 & 5.9: Ultramicroelectrodes
- Sections 5.7 – 5.8: Chronoamperometry/Chronocoulometry

(UPDATED)

Looking forward... Section 4.4.2 and Chapter 5

- **Fick's Second Law of Diffusion**
- **Linear Diffusion = time-dependent current (Cottrell Equation)**
- *Anson Plots for surface adsorbed species*
- *Radial Diffusion = time-independent current (at steady-state)*
- *Ultramicroelectrodes (UMEs)*
- *Scanning Electrochemical Microscopy (SECM)*
- *Single molecule electrochemistry*

We use <u>both</u> of Fick's laws of diffusion to derive equations for time-dependent (not steady-state) transport-controlled electrochemistry...

Fick's 1st Law of Diffusion:

this is **flux** *(not current density)*

$$-J_O(x, t) = D_O \frac{\partial C_O(x, t)}{\partial x}$$

B&F, pg. 149

... but taking baby steps toward the Cottrell equation... conceptually, one can derive Fick's law in a manner similar to how we thought about the diffusion coefficient... grab your favorite beverage and go on a walk!

$$i(t) = i_d(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}}$$

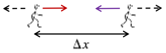
... and here's the conclusion of that derivation... **the Cottrell Equation**

We use <u>both</u> of Fick's laws of diffusion to derive equations for time-dependent (not steady-state) transport-controlled electrochemistry... 437


Adolph Eugen Fick

Fick's 1st Law of Diffusion:

$$-J_O(x,t) = D_O \frac{\partial C_O(x,t)}{\partial x}$$



B&F, pg. 149

this is **number** *(not flux)*

$$J_O(x,t) = \frac{1}{A} \frac{\frac{N_O(x)}{2} - \frac{N_O(x+\Delta x)}{2}}{\Delta t}$$

This is the **net flux** *(correct dimensions)*...
... with half moving right and half moving left

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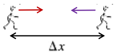
We use <u>both</u> of Fick's laws of diffusion to derive equations for time-dependent (not steady-state) transport-controlled electrochemistry... 438


Adolph Eugen Fick

Fick's 1st Law of Diffusion:

$$-J_O(x,t) = D_O \frac{\partial C_O(x,t)}{\partial x}$$



B&F, pg. 149

$$J_O(x,t) = \frac{1}{A} \frac{\frac{N_O(x)}{2} - \frac{N_O(x+\Delta x)}{2}}{\Delta t} \frac{\Delta x^2}{\Delta x^2}$$

$$-J_O(x,t) = \frac{\Delta x^2}{2\Delta t} \frac{C_O(x+\Delta x) - C_O(x)}{\Delta x}$$

D_O

Recall... $\overline{\Delta^2} = ml^2 = \frac{t}{\tau} l^2 = 2Dt$

... derived!

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We use <u>both</u> of Fick's laws of diffusion to derive equations for time-dependent (not steady-state) transport-controlled electrochemistry... 439


Adolph Eugen Fick

Fick's 1st Law of Diffusion:

$$-J_O(x,t) = D_O \frac{\partial C_O(x,t)}{\partial x}$$

B&F, pg. 149

Fick's 2nd Law of Diffusion:

$$\frac{\partial C_O(x,t)}{\partial t} = D_O \left(\frac{\partial^2 C_O(x,t)}{\partial x^2} \right)$$

... derive this non-steady-state equation (approximately) in a similar fashion as Fick's first law...

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… the derivation is not so bad…

$$\frac{\partial C_O(x,t)}{\partial t} = D_O\left(\frac{\partial^2 C_O(x,t)}{\partial x^2}\right)$$

B&F, pp. 149–150

$$\frac{\partial C_O(x,t)}{\partial t} = \frac{J(x,t) - J(x+dx,t)}{dx}$$

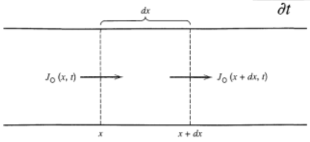


Figure 4.4.4 Fluxes into and out of an element at x.

… the derivation is not so bad…

$$\frac{\partial C_O(x,t)}{\partial t} = D_O\left(\frac{\partial^2 C_O(x,t)}{\partial x^2}\right)$$

B&F, pp. 149–150

$$\frac{\partial C_O(x,t)}{\partial t} = \frac{J(x,t) - J(x+dx,t)}{dx}$$

$$J(x+dx,t) = J(x,t) + \frac{\partial J(x,t)}{\partial x}dx$$

$$-J_O(x,t) = D_O\frac{\partial C_O(x,t)}{\partial x}$$

(First Law)

… derived!

The experiment we will model is a *potential step experiment*…

key points: *at E_1: no reaction ($C_O(x, 0) = C_O{}^*$)*

at E_2: diffusion-controlled reaction ($C_O(0, t) = 0$)

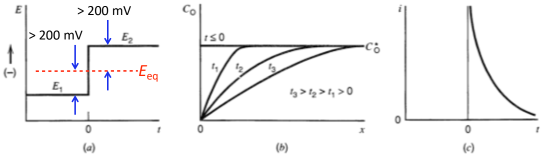


Figure 5.1.2 (*a*) Waveform for a step experiment in which species O is electroinactive at E_1, but is reduced at a diffusion-limited rate at E_2. (*b*) Concentration profiles for various times into the experiment. (*c*) Current flow *vs*. time.

How to derive expressions for diffusion-controlled current vs. time:

1. Solve Fick's Second Law to get $C_O(x, t)$, and in the process of doing this, you will use boundary conditions that "customize" the solution for the particular experiment of interest:

$$\frac{\partial C_O(x,t)}{\partial t} = D_O\left(\frac{\partial^2 C_O(x,t)}{\partial x^2}\right)$$

2. Use Fick's First Law to calculate $J_O(0, t)$ from $C_O(x, t)$:

flux

$$-J_O(x,t) = D_O\frac{\partial C_O(x,t)}{\partial x}$$

3. Calculate the time-dependent diffusion-limited current:

$i = nFAJ_O(0, t)$

… using the… Laplace transform, integration by parts, L'Hôpital's rule, Schrödinger equation, complementary error function, Leibniz rule, chain rule… **Wow! Cool!**

Step 1 is the kicker… we'll use the *Laplace Transform* to solve the linear partial differential equation

The Laplace transform of any function $F(t)$ is:

$$L\{F(t)\} \equiv \int_0^\infty e^{-st}F(t)dt$$

how about $F(t) = 1$?

$$L\{1\} = \int_0^\infty e^{-st}(1)dt = \left.\frac{e^{-st}}{-s}\right|_0^\infty = 0 - \left(\frac{1}{-s}\right) = \frac{1}{s}$$

how about $F(t) = kt$?

$$L\{kt\} = \int_0^\infty e^{-st}(kt)dt = k\int_0^\infty te^{-st}dt = k\left.\left(\frac{e^{-st}}{s^2}(-st-1)\right)\right|_0^\infty$$

how about $F(t) = kt$?

Integrated by parts

$$L\{kt\} = \int_0^\infty e^{-st}(kt)dt = k\int_0^\infty te^{-st}dt = k\left.\left(\frac{e^{-st}}{s^2}(-st-1)\right)\right|_0^\infty$$

Used L'Hôpital's rule

$$= k\left(0 - \frac{1}{s^2}(-1)\right) = \frac{k}{s^2}$$

how about $F(t) = e^{-at}$?

$$L\{e^{-at}\} = \int_0^\infty e^{-st}e^{-at}dt = \int_0^\infty e^{-(s+a)t}dt = \left.\frac{e^{-(s+a)t}}{-(s+a)}\right|_0^\infty$$

$$= 0 - \frac{1}{-(s+a)} = \frac{1}{s+a}$$

OK, now for our case: $F(t) = \frac{\partial C_O(x,t)}{\partial t} - D_O\left(\frac{\partial^2 C_O(x,t)}{\partial x^2}\right)$

Recall, Second Law:

$$\frac{\partial C_O(x,t)}{\partial t} = D_O\left(\frac{\partial^2 C_O(x,t)}{\partial x^2}\right)$$

OK, now for our case: $F(t) = \frac{\partial C_O(x,t)}{\partial t} - D_O\left(\frac{\partial^2 C_O(x,t)}{\partial x^2}\right)$

$$L\left\{\frac{\partial C_O(x,t)}{\partial t} - D_O\left(\frac{\partial^2 C_O(x,t)}{\partial x^2}\right)\right\} = ?$$

well, wait a second, this term is not so bad…

$$\int_0^\infty e^{-st} D\frac{\partial^2 C(x,t)}{\partial x^2}dt = D\frac{\partial^2}{\partial x^2}\int_0^\infty e^{-st}C(x,t)dt = D\frac{\partial^2}{\partial x^2}\bar{C}(x,s)$$

the Laplace transform of *C*(*x*, *t*)? … Isn't this cheating?

Well, ahem, no!

OK, now for our case: $F(t) = \frac{\partial C_O(x,t)}{\partial t} - D_O\left(\frac{\partial^2 C_O(x,t)}{\partial x^2}\right)$

$$L\left\{\frac{\partial C_O(x,t)}{\partial t} - D_O\left(\frac{\partial^2 C_O(x,t)}{\partial x^2}\right)\right\} = ?$$

not so lucky with this term…

?

$$-D\frac{\partial^2}{\partial x^2}\bar{C}(x,s)$$

$$\int_a^b g(x)f'(x)dx = [g(x)f(x)]\Big|_a^b - \int_a^b f(x)g'(x)dx$$

Integration, by parts, again!

$$\int_0^\infty e^{-st}\frac{\partial C_O(x,t)}{\partial t}dt$$

g(x) f'(x)

$$= \left[e^{-st}C(x,t)\right]\Big|_0^\infty - \int_0^\infty C(x,t)\left(-se^{-st}\right)dx$$

$$= 0 - C(x,0) + s\bar{C}(x,s)$$

... and at time = 0, what is the value of *C*, anywhere?

... **just C^*!**

L.T. of Fick's 2nd Law... $F(t) = \frac{\partial C_O(x,t)}{\partial t} - D_O\left(\frac{\partial^2 C_O(x,t)}{\partial x^2}\right)$

now is turns out that the L.T. of this... $L\left\{\frac{\partial C_O(x,t)}{\partial t} - D_O\left(\frac{\partial^2 C_O(x,t)}{\partial x^2}\right)\right\}$

is this... $s\bar{C}(x,s) - C^* - D\frac{\partial^2}{\partial x^2}\bar{C}(x,s)$

see B&F, pg. 775, for details

Now what? Well, recall these terms are equal to each other (= 0), then rearrange...

... and what does it look like?

our equation: $$\frac{d^2\bar{C}(x,s)}{dx^2} - \frac{s}{D}\bar{C}(x,s) = -\frac{C^*}{D}$$

the time-independent *Schrödinger Eq.* in 1D... $$\frac{d^2}{dx^2}\psi(x) - \frac{2m}{\hbar^2}\left(E - V(x)\right)\psi(x) = 0$$

our equation: $$\frac{d^2\bar{C}(x,s)}{dx^2} - \frac{s}{D}\bar{C}(x,s) = -\frac{C^*}{D}$$

the time-independent *Schrödinger Eq.* in 1D... $$\frac{d^2}{dx^2}\psi(x) - \frac{2m}{\hbar^2}\left(E - V(x)\right)\psi(x) = 0$$

the solution of the *Schrödinger Eq.* is:

$$\psi(x) = A'\exp\left(\frac{-\sqrt{2m\left(E - V(x)\right)}}{\hbar}x\right) + B'\exp\left(\frac{\sqrt{2m\left(E - V(x)\right)}}{\hbar}x\right)$$

... and by analogy, the solution of our equation is:

$$\bar{C}(x,s) = \frac{C^*}{s} + A'(s)\exp\left(-\sqrt{\frac{s}{D}}x\right) + B'(s)\exp\left(\sqrt{\frac{s}{D}}x\right)$$

$$\bar{C}(x,s) = \frac{C^*}{s} + A'(s)\exp\left(-\sqrt{\frac{s}{D}}x\right) + B'(s)\exp\left(\sqrt{\frac{s}{D}}x\right)$$

Now, what are A' and B' (to simplify), and how do we get rid of the "s"?
… just like in any calculus problem, we need some *boundary conditions*!

1. $$\lim_{x\to\infty} C_O(x,t) = C_O^*$$

called *semi-infinite linear (because of x) diffusion*

$$\Big\downarrow \text{L.T.}$$

$$\lim_{x\to\infty} \bar{C}(x,s) = \frac{C^*}{s}$$

What does this do for us?

$$\bar{C}(x,s) = \frac{C^*}{s} + A'(s)\underset{0}{\exp\left(-\sqrt{\frac{s}{D}}x\right)} + B'(s)\overset{\infty}{\exp\left(\sqrt{\frac{s}{D}}x\right)}$$

… and so B' must be equal to 0

$$\bar{C}(x,s) = \frac{C^*}{s} + A'(s)\exp\left(-\sqrt{\frac{s}{D}}x\right)$$

some more boundary conditions…

2. $$C(0,t) = 0$$

$$\Big\downarrow \text{L.T.}$$

$$\bar{C}(0,s) = 0$$

What does this do for us?

$$\bar{C}(x,s) = \frac{C^*}{s} + A'(s)\overset{1}{\exp\left(-\sqrt{\frac{s}{D}}x\right)}$$

… and so $A'(s) = -\frac{C^*}{s}$

now our solution is fully constrained… *but we still need "t" back!!*

$$\bar{C}_O(x,s) = \frac{C_O^*}{s} - \frac{C_O^*}{s}e^{-\sqrt{s/D_O}\,x}$$

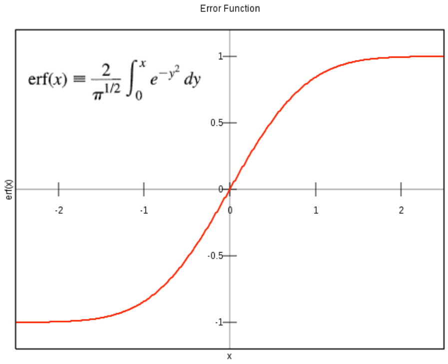
inverse L.T. $\Big\downarrow$ using Table A.1.1 in B&F

$$e^{-\beta x}/s = \operatorname{erfc}[x/2(kt)^{1/2}]$$ where $\beta = (s/k)^{1/2}$

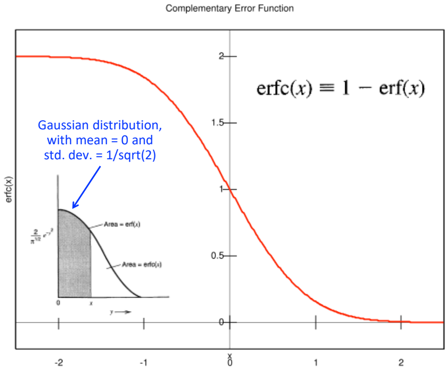
$$\Big\downarrow$$

$$C_O(x,t) = C_O^*\left\{1 - \operatorname{erfc}\left[\frac{x}{2(D_O t)^{1/2}}\right]\right\}$$

What's efrc?... Well, first of all, what's the error function: erf?



Now... what's efrc?



Gaussian distribution, with mean = 0 and std. dev. = 1/sqrt(2)

Does this make sense?

$$C_O(x, t) = C_O^*\left\{1 - \mathrm{erfc}\left[\frac{x}{2(D_O t)^{1/2}}\right]\right\}$$

$$C_O(x, t) = C_O^*\,\mathrm{erf}\left[\frac{x}{2(D_O t)^{1/2}}\right]$$

... well, for large *x*, erf = 1 (erfc = 0) and so *C*(*x*, *t*) = *C** ... Check!

... and for *x* = 0, erf = 0 (erfc = 1) and so *C*(*x*, *t*) = 0 ... Check!

... so, it seems reasonable... Let's plot it!

The experiment we will model is a *potential step experiment…*

key points: *at E_1: no reaction ($C_O(x, 0) = C_O^*$)*
at E_2: diffusion-controlled reaction ($C_O(0, t) = 0$)

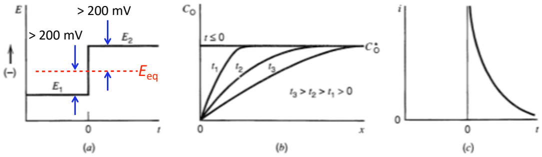
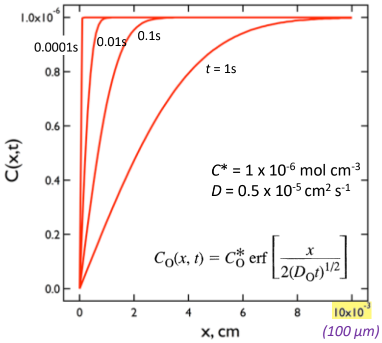


Figure 5.1.2 (*a*) Waveform for a step experiment in which species O is electroinactive at E_1, but is reduced at a diffusion-limited rate at E_2. (*b*) Concentration profiles for various times into the experiment. (*c*) Current flow *vs.* time.

… oh right… and this is the condition that we were deriving…

Hey, these look completely reasonable… and they are not exponential!



How large is the diffusion layer? Recall the rms displacement… **(BRIEFLY)**

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

*the rms displacement

In both directions from a…

… plane

… wire, line, tube

… point, sphere, disk

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

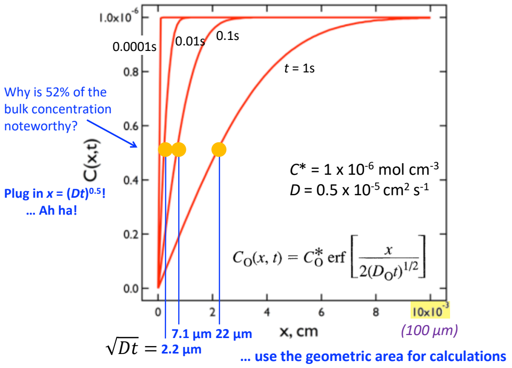
a characteristic "diffusion length"

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

root mean square (rms) displacement (standard deviation)

Hey, these look completely reasonable for 1D diffusion in one direction!

(BRIEFLY)



Why is 52% of the bulk concentration noteworthy?

Plug in $x = (Dt)^{0.5}$! … Ah ha!

$C^* = 1 \times 10^{-6}$ mol cm^{-3}
$D = 0.5 \times 10^{-5}$ cm^2 s^{-1}

$$C_O(x,t) = C_O^* \operatorname{erf}\left[\frac{x}{2(D_O t)^{1/2}}\right]$$

$\sqrt{Dt} =$ **2.2 µm** **7.1 µm** **22 µm**

(100 µm)

… use the geometric area for calculations

OK… that's Step #1… Whoa! That was deep!… The last two steps are not…

(BRIEFLY)

1. Solve Fick's Second Law to get $C_O(x, t)$, and in the process of doing this, you will use boundary conditions that "customize" the solution for the particular experiment of interest:

$$\frac{\partial C_O(x,t)}{\partial t} = D_O\left(\frac{\partial^2 C_O(x,t)}{\partial x^2}\right)$$

2. Use Fick's First Law to calculate $J_O(0, t)$ from $C_O(x, t)$:

flux

$$-J_O(x,t) = D_O \frac{\partial C_O(x,t)}{\partial x}$$

3. Calculate the time-dependent diffusion-limited current:

$i = nFAJ_O(0, t)$

… now Step #2… **(BRIEFLY)**

$$-J_O(x,t) = D_O \frac{\partial C_O(x,t)}{\partial x}$$ (Fick's First Law)

… but we just derived $C_O(x, t)$:

$$C_O(x,t) = C_O^* \operatorname{erf}\left[\frac{x}{2(D_O t)^{1/2}}\right]$$

… and so we need to evaluate:

$$-J_O(x,t) = D_O \frac{\partial}{\partial x}\left[C^* \operatorname{erf}\left(\frac{x}{2\sqrt{D_O t}}\right)\right]$$

… now Step #2… **(BRIEFLY)**

$$-J_O(x,t) = D_O \frac{\partial}{\partial x}\left[C^* \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

… we use the *Leibniz rule*, to get d/dx(erf(x)) as follows:

$$\frac{d}{dx}\operatorname{erf}(x) = \frac{2}{\pi^{1/2}}\frac{d}{dx}\int_0^x e^{-y^2}\,dy = \frac{2}{\pi^{1/2}}e^{-x^2}$$

see B&F, pg. 780, for details

… and using this in conjunction with the chain rule, we get:

$$-J_O(x,t) = D_O C^* \left(\frac{1}{2\sqrt{D_O t}}\right)\frac{2}{\sqrt{\pi}}\exp\left(\frac{-x^2}{4D_O t}\right)$$

… and when $x = 0$ (at the electrode), we get:

$$-J_O(0,t) = C^* \sqrt{\frac{D_O}{\pi t}}$$

… which is what we needed for Step #3…

OK… that's Steps #1 and 2… **(BRIEFLY)**

1. Solve Fick's Second Law to get $C_O(x, t)$, and in the process of doing this, you will use boundary conditions that "customize" the solution for the particular experiment of interest:

$$\frac{\partial C_O(x,t)}{\partial t} = D_O\left(\frac{\partial^2 C_O(x,t)}{\partial x^2}\right)$$

2. Use Fick's First Law to calculate $J_O(0, t)$ from $C_O(x, t)$:

flux

$$-J_O(x,t) = D_O\frac{\partial C_O(x,t)}{\partial x}$$

3. Calculate the time-dependent diffusion-limited current:

$i = nFAJ_O(0, t)$

… and finally, Step #3 using Step #2…

$$-J_O(0,t) = C^* \sqrt{\frac{D_O}{\pi t}}$$

… and with $i = nFAJ_O(0, t)$…

$$i(t) = i_d(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}}$$

the Cottrell Equation

Frederick Gardner Cottrell, in 1920
b. January 10, 1877, Oakland, California, U.S.A.
d. November 16, 1948, Berkeley, California, U.S.A.

… established Research Corporation for Science Advancement in 1912

… initial funding from profits on patents for the *electrostatic precipitator*, used to clear smokestacks of charged soot particles