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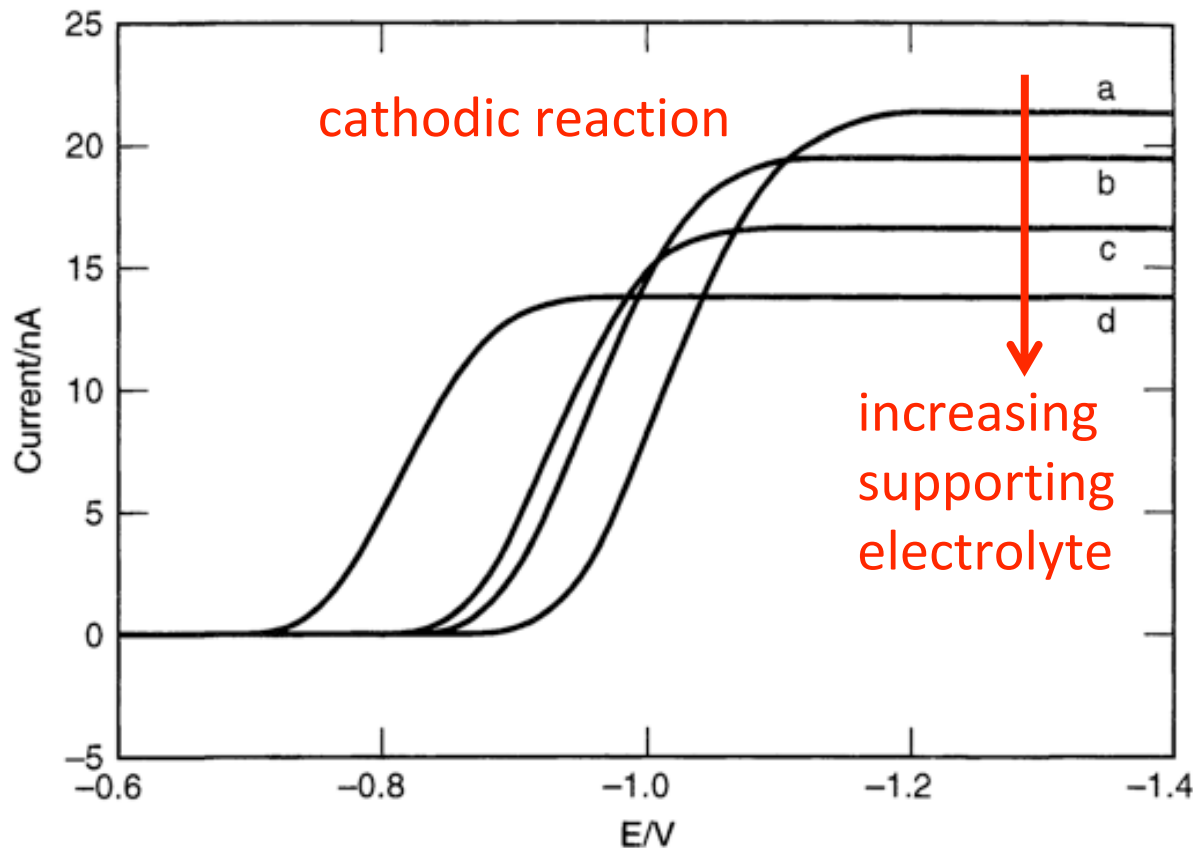
- Section 1.4: Mass transfer and Semi-empirical treatment of electrochemical observations

- Chapter 4:   Mass transfer

Looking forward… Section 1.4 and Chapter 4

- <u>Mass transfer</u>

- <u>Diffusion</u>

- <u>Migration / Drift</u>

- <u>Convection</u>

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

- <u>Conductivity</u>

- <u>Transport (Transference) number</u>

- <u>Balance sheets</u>

- **Ohmic drop/loss**

RECALL:

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

cathodic reaction

increasing 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 mM Tl$_2$SO$_4$ 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 mM 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…

cathodic reaction

increasing supporting electrolyte
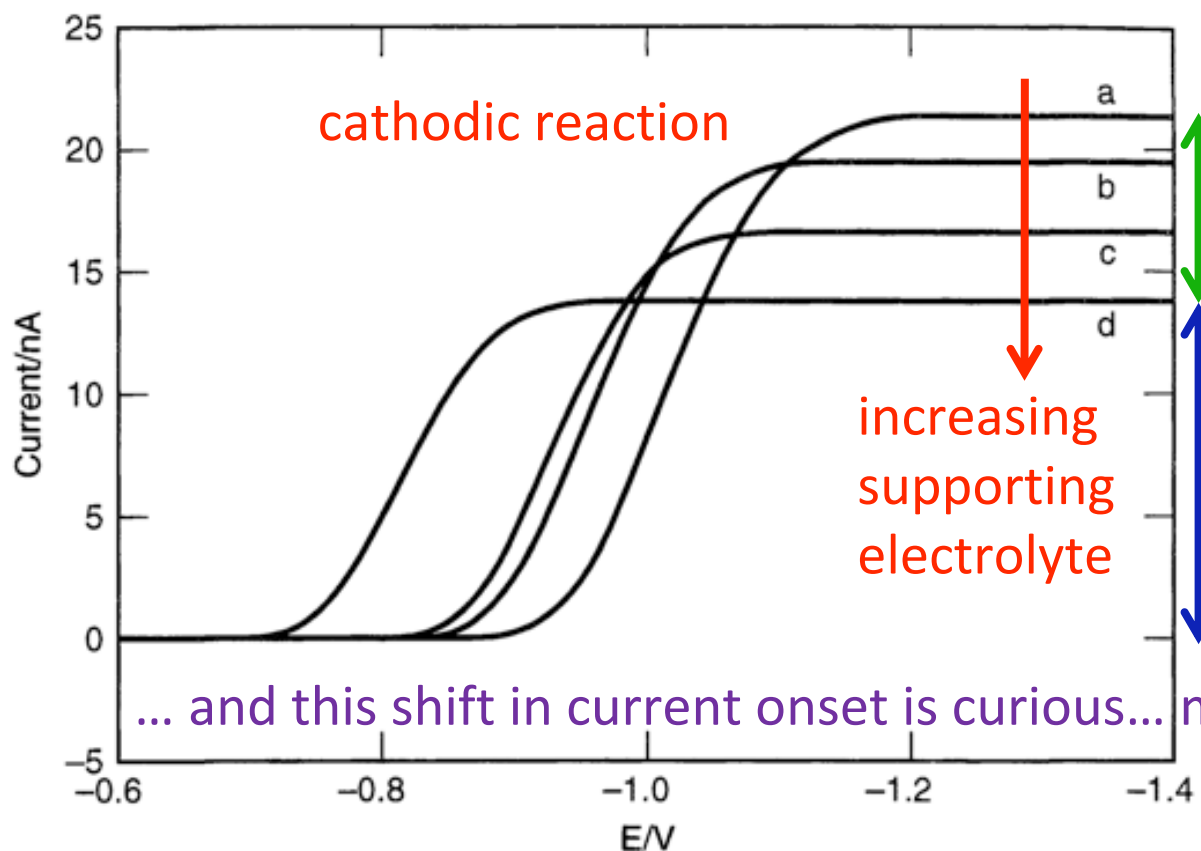
RECALL:

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

I_{d-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 mM 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 mM 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!…

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

W. Oelßner*, F. Berthold and U. Guth

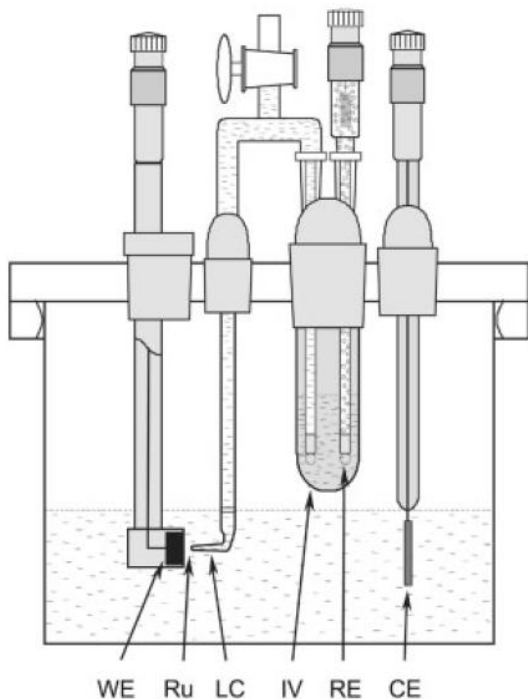… let's just look at some figures: 1, 4, 5, 7, 14 ,16

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
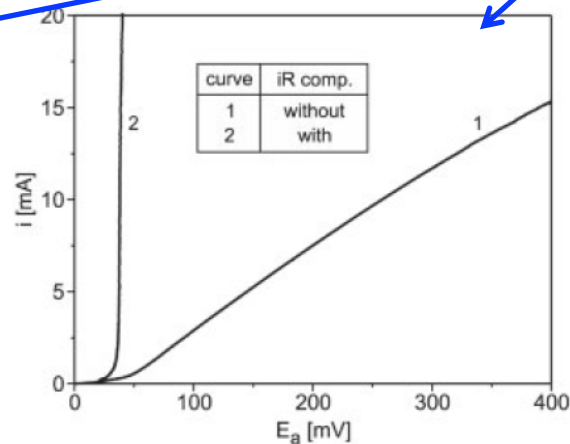
WE   Ru   LC   IV   RE   CE

Fig. 14. Polarization curves of zinc in 0.25 M zinc sulphate solution ($\kappa = 19$ 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

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

Problems

Solutions

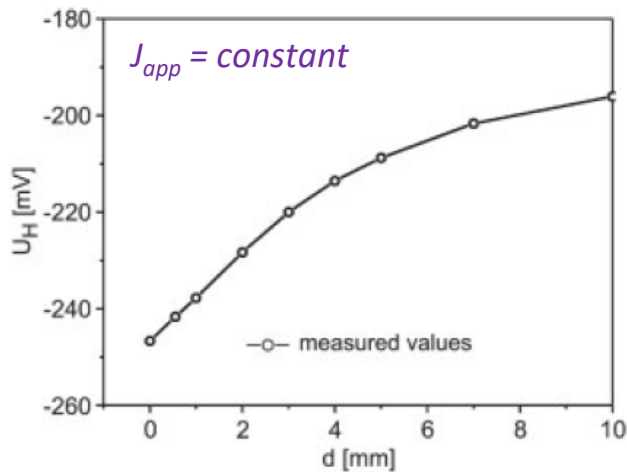J_{app} = constant

—o— measured values

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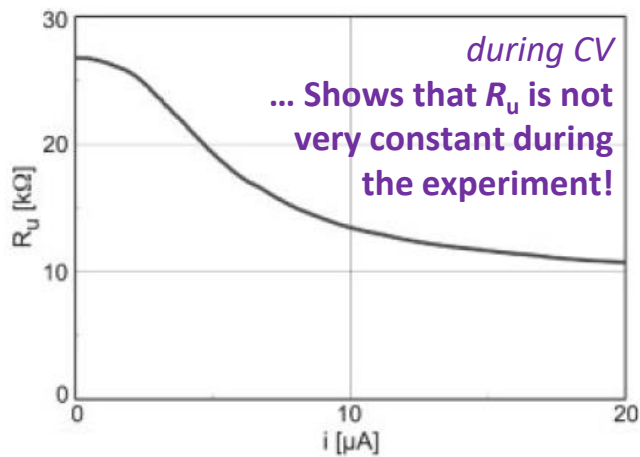
during CV
… Shows that R_u is not very constant during the experiment!

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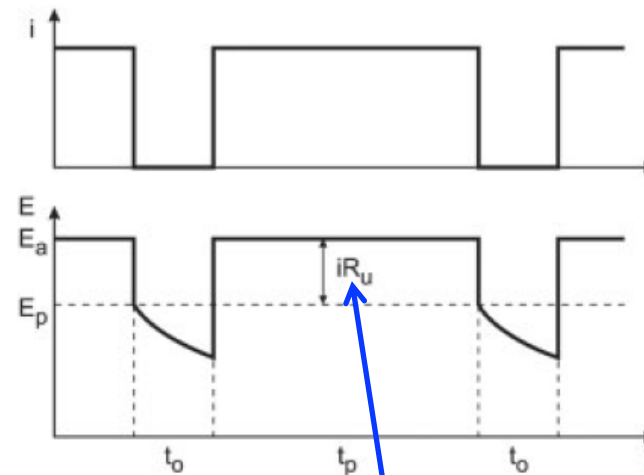
iR_u

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)

Single values… should be good enough!

R_u

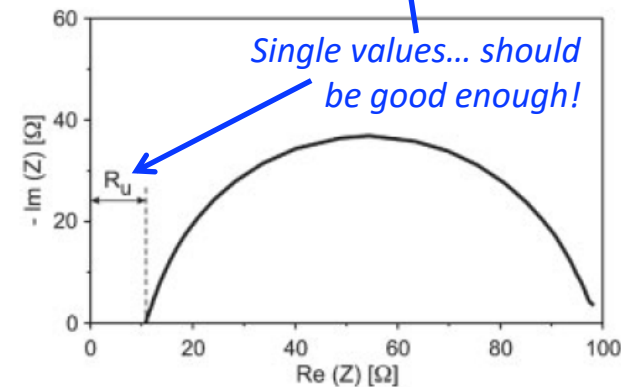**Fig. 5.** Determination of the resistance R_u for the system steel X20Cr13 in 0.05 M H_2SO_4 from a Nyquist plot. Re (Z): real part of impedance, Im (Z): imaginary part of impedance, R_u: uncompensated resistance

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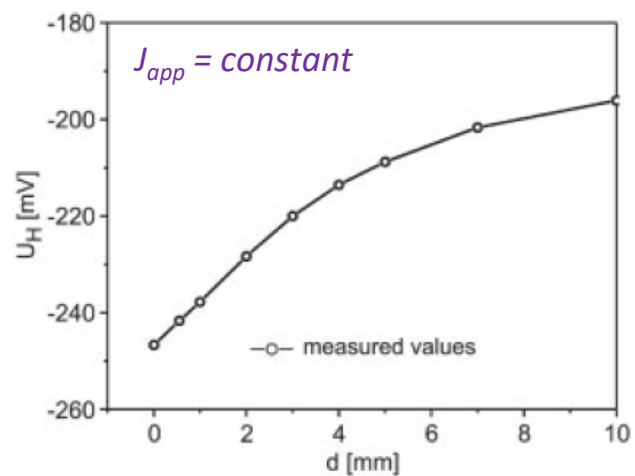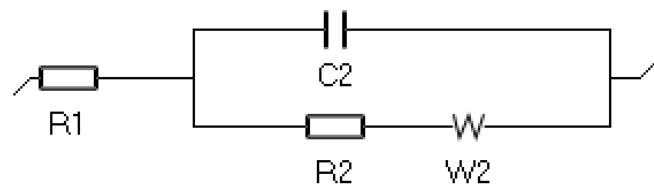of interest… but it also removes iR_u drop from data… a two-for-one!…

Problems

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

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/

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

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

assume these are the same value
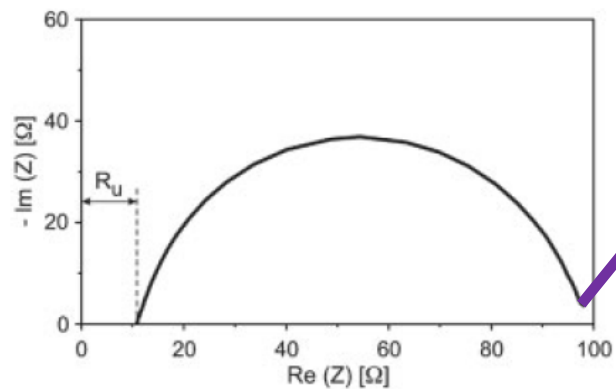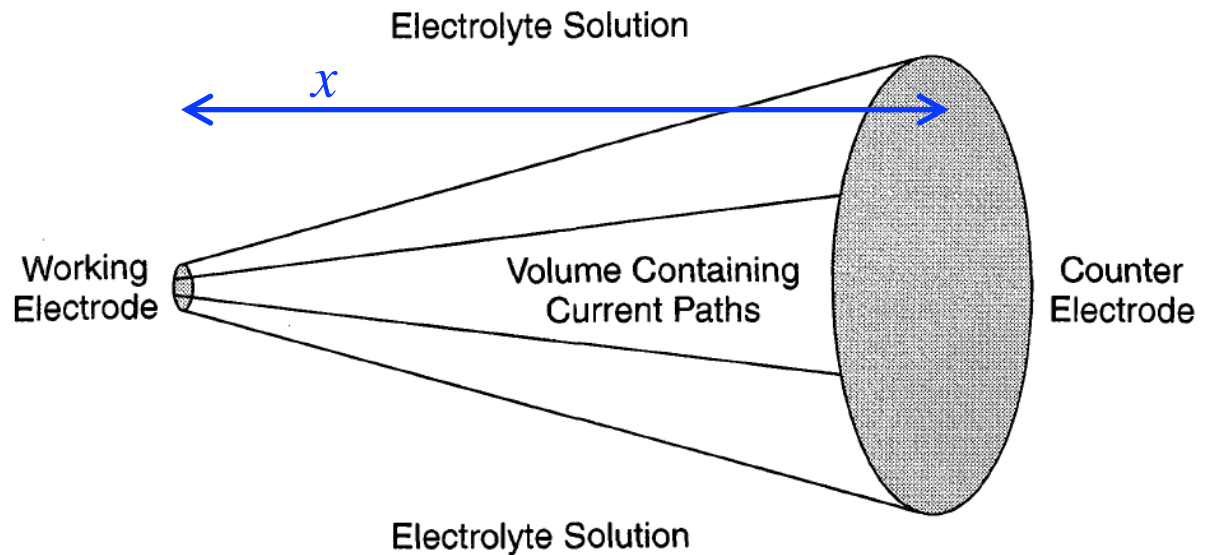
Solutions

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

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

Electrolyte Solution

Working Electrode

Volume Containing Current Paths

Counter Electrode

Electrolyte Solution

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

Uncompensated resistance:

$\kappa = \sigma$

Planar WE

$$R_u = x/\kappa A$$

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

Point WE

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

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

What happens when $x \to \infty$? **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

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...

Adolph Eugen Fick

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!

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

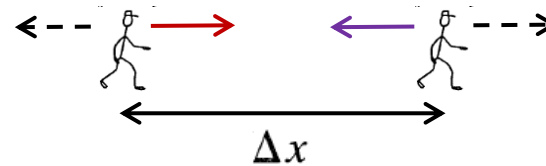... and here's the conclusion of that derivation...   **the Cottrell Equation**

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

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)*

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

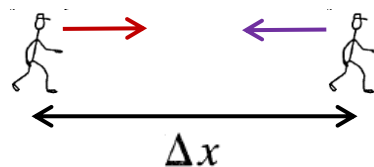This is the **net flux** *(correct dimensions)*...
... with half moving right and half moving left

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

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

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

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

D_O

... derived!

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

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

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…

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

B&F, pp. 149–150

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

dx

$J_O(x, t)$ → → $J_O(x + dx, t)$

x $x + dx$

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

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

B&F, pp. 149–150

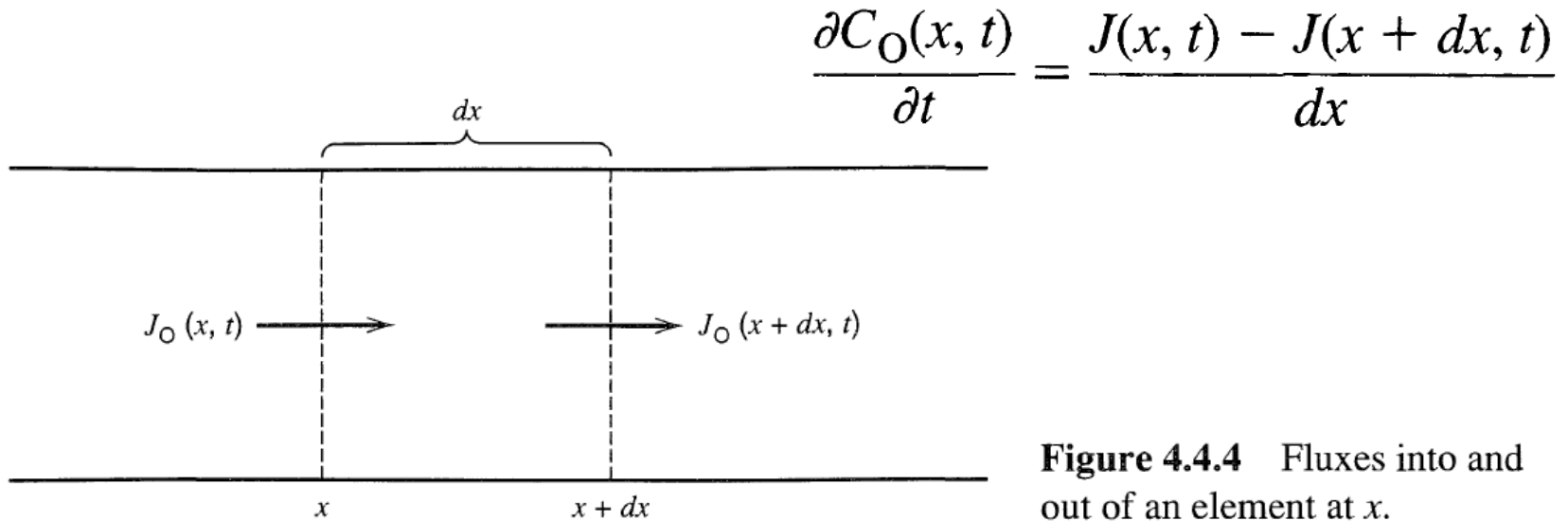$$\frac{\partial C_O(x, t)}{\partial t} = \frac{J(x, t) - J(x + dx, t)}{dx}$$

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

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

… 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 ($C_O(0, t) = 0$)

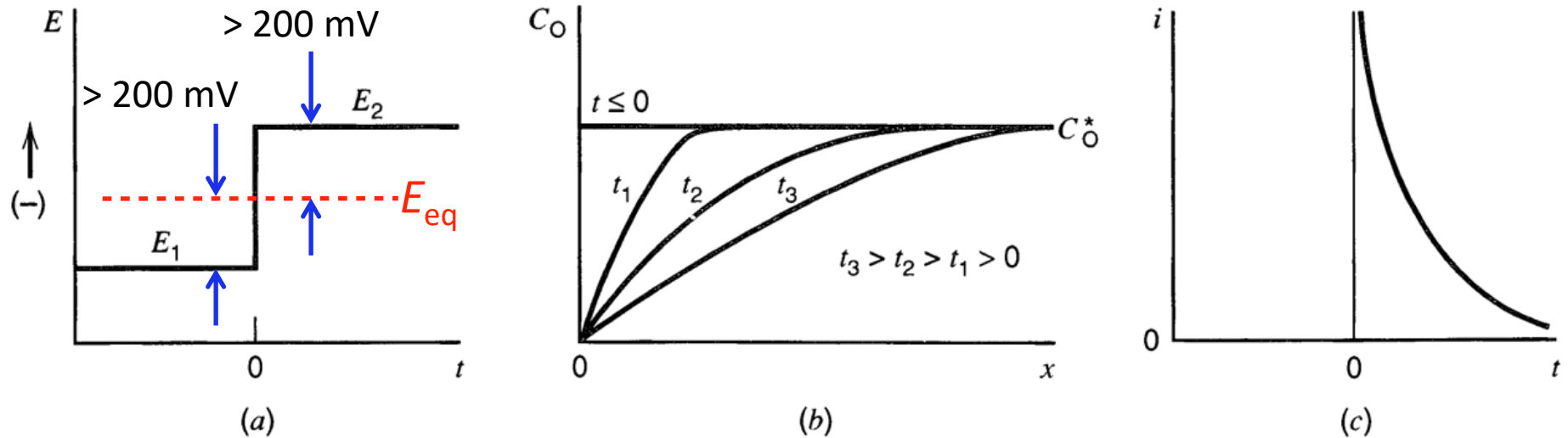(a)   (b)   (c)

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.

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 $F(t) = kt$?

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

Integrated by parts

Used L'Hôpital's rule

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

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

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

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

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

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

the solution of the
Schrödinger Eq. is:

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

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

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

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

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*

L.T.

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

What does this do for us?

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

0   ∞

... 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 <u>more</u> boundary conditions...

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

L.T.

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

What does this do for us?

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

... and so $A'(s) = -\dfrac{C^*}{s}$

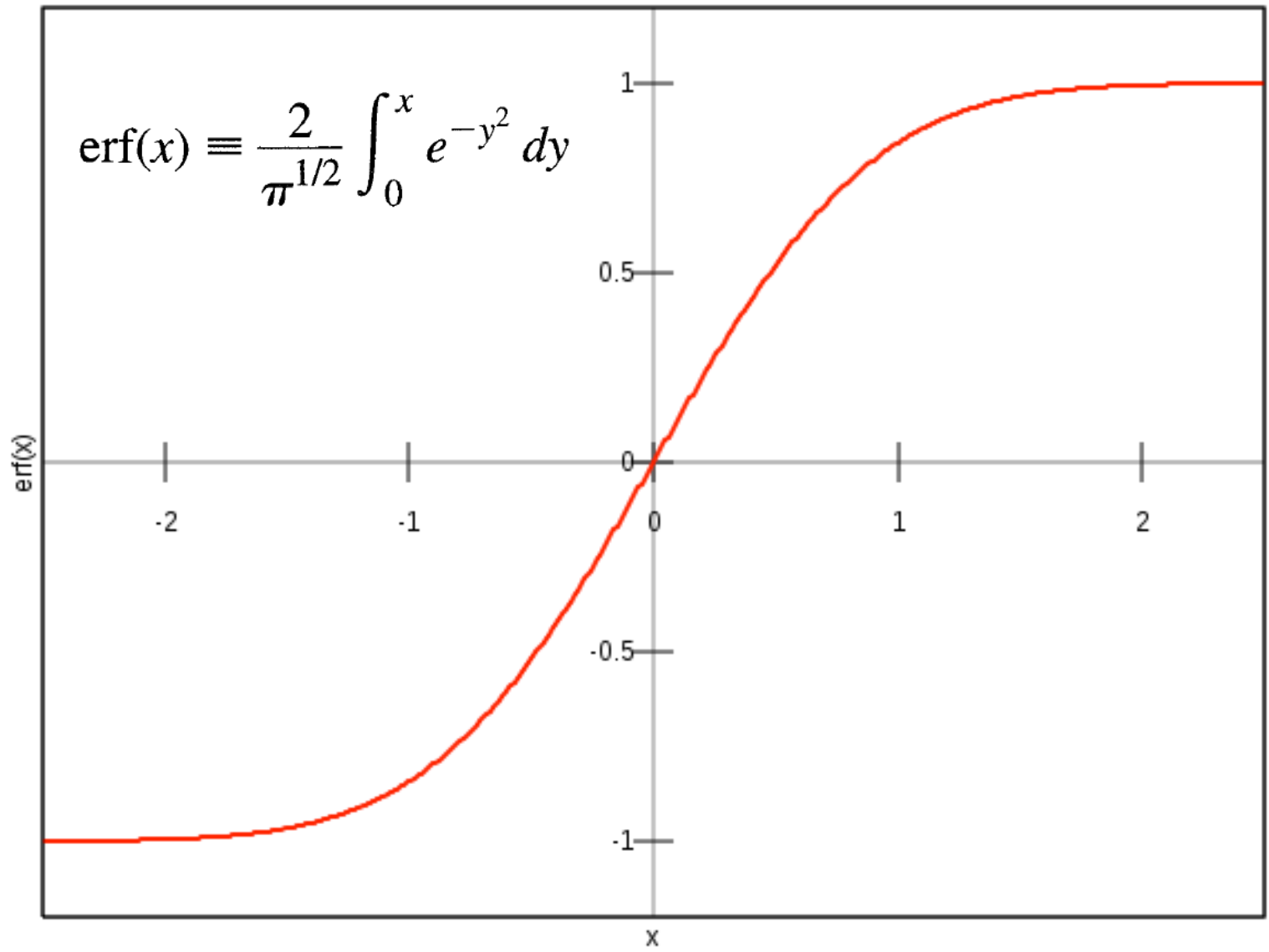$$\overline{C}_O(x, s) = \frac{C_O^*}{s} - \frac{C_O^*}{s} e^{-\sqrt{s/D_O}\,x}$$

inverse L.T. using Table A.1.1 in B&F

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

where $\beta = (s/k)^{1/2}$

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

Error Function

$$\text{erf}(x) \equiv \frac{2}{\pi^{1/2}} \int_0^x e^{-y^2} \, dy$$

Complementary Error Function

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

$$\mathrm{erfc}(x) \equiv 1 - \mathrm{erf}(x)$$

$\frac{2}{\pi^{1/2}} e^{-y^2}$

Area = erf(x)

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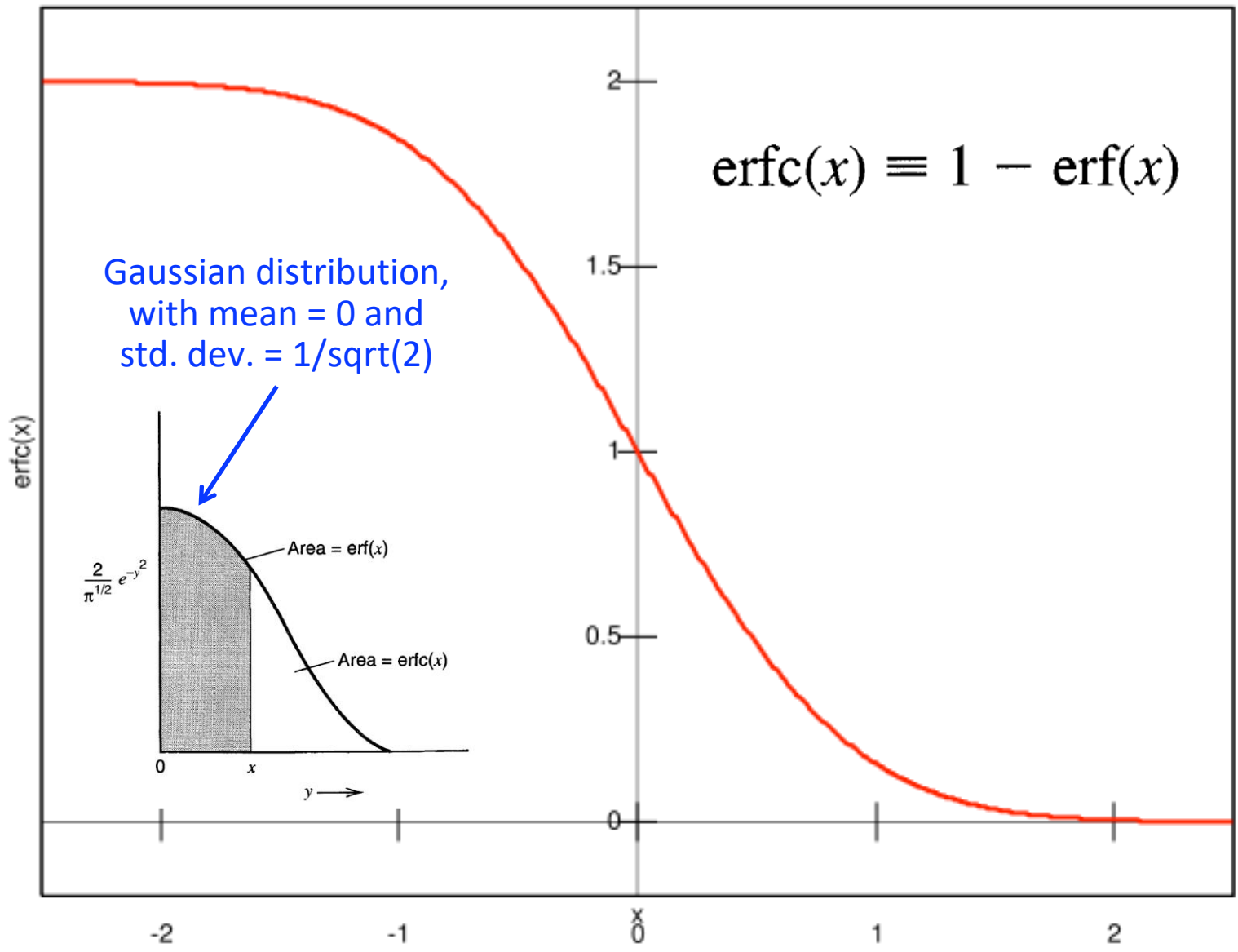
$$C_O(x, t) = C_O^* \left\{ 1 - \text{erfc}\left[\frac{x}{2(D_O t)^{1/2}} \right] \right\}$$

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

… 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 ($C_O(0, t) = 0$)
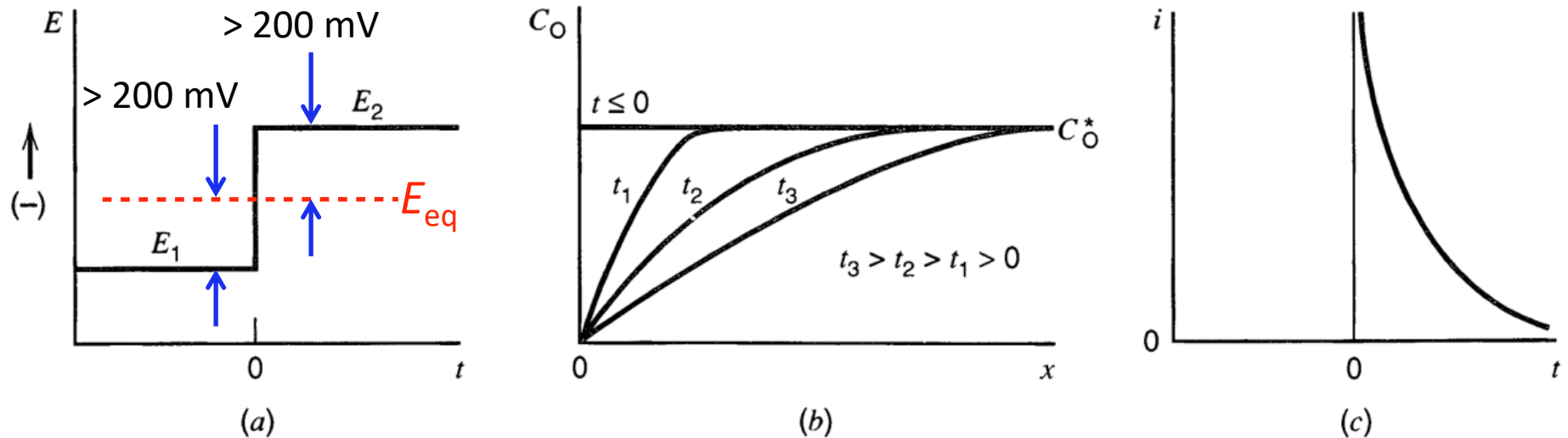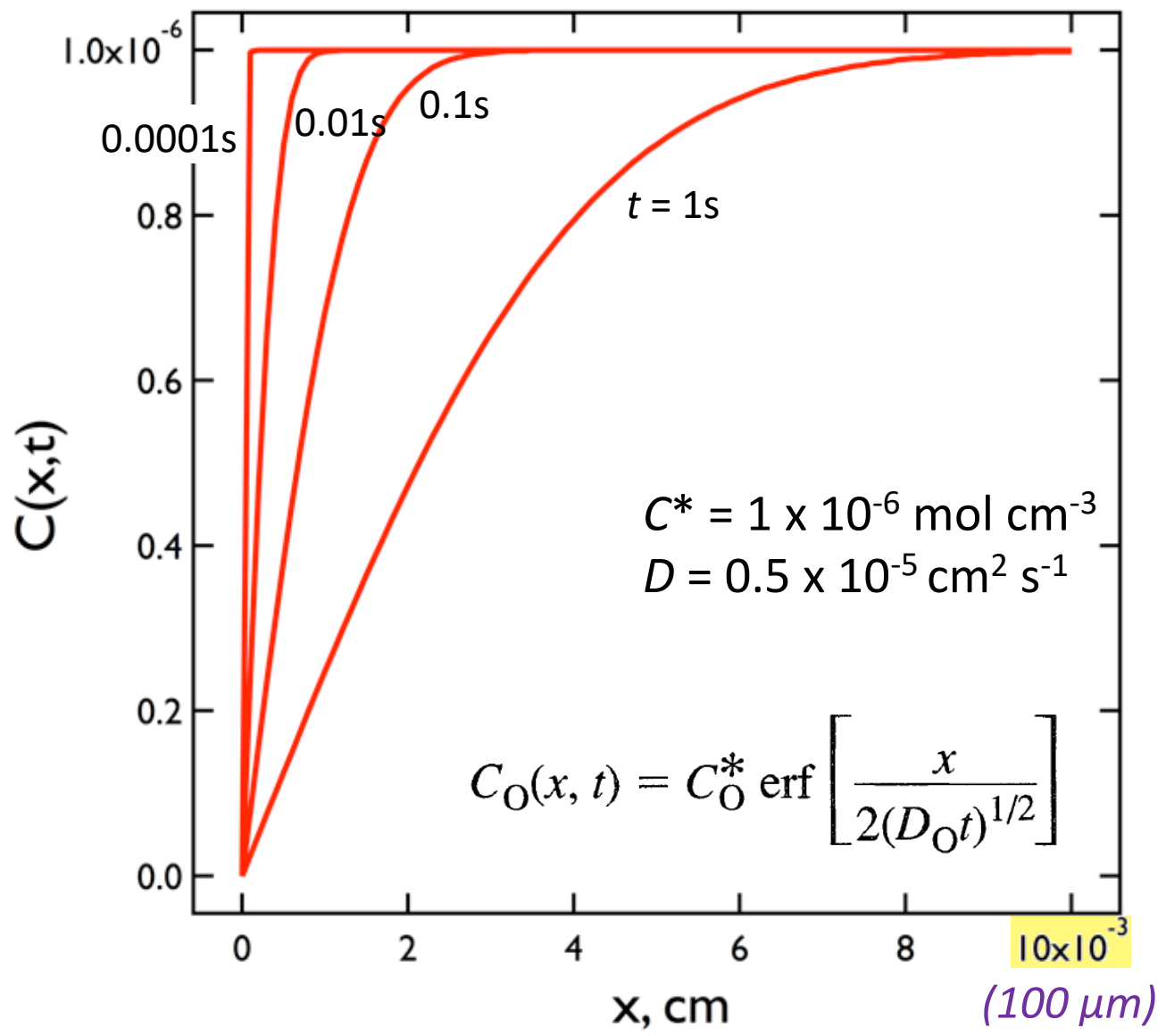

Figure 5.1.2 (*a*) Waveform for a step experiment in which species O is electroinactive at E_1, but is reduced at a diffusion-limited rate at E_2. (*b*) Concentration profiles for various times into the experiment. (*c*) Current flow *vs.* time.

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

$C^* = 1 \times 10^{-6}$ mol cm^{-3}

$D = 0.5 \times 10^{-5}$ cm^2 s^{-1}

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

0.0001s   0.01s   0.1s

$t = 1$s

x, cm

10×10^{-3}

(100 μm)

How large is the diffusion layer? Recall the rms displacement… **(BRIEFLY)** 460

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

*the rms displacement

<u>In both directions</u> 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

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}

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

0.0001s   0.01s   0.1s

$t = 1$s

C(x,t)

x, cm

7.1 µm   22 µm

$\sqrt{Dt} = 2.2$ µm
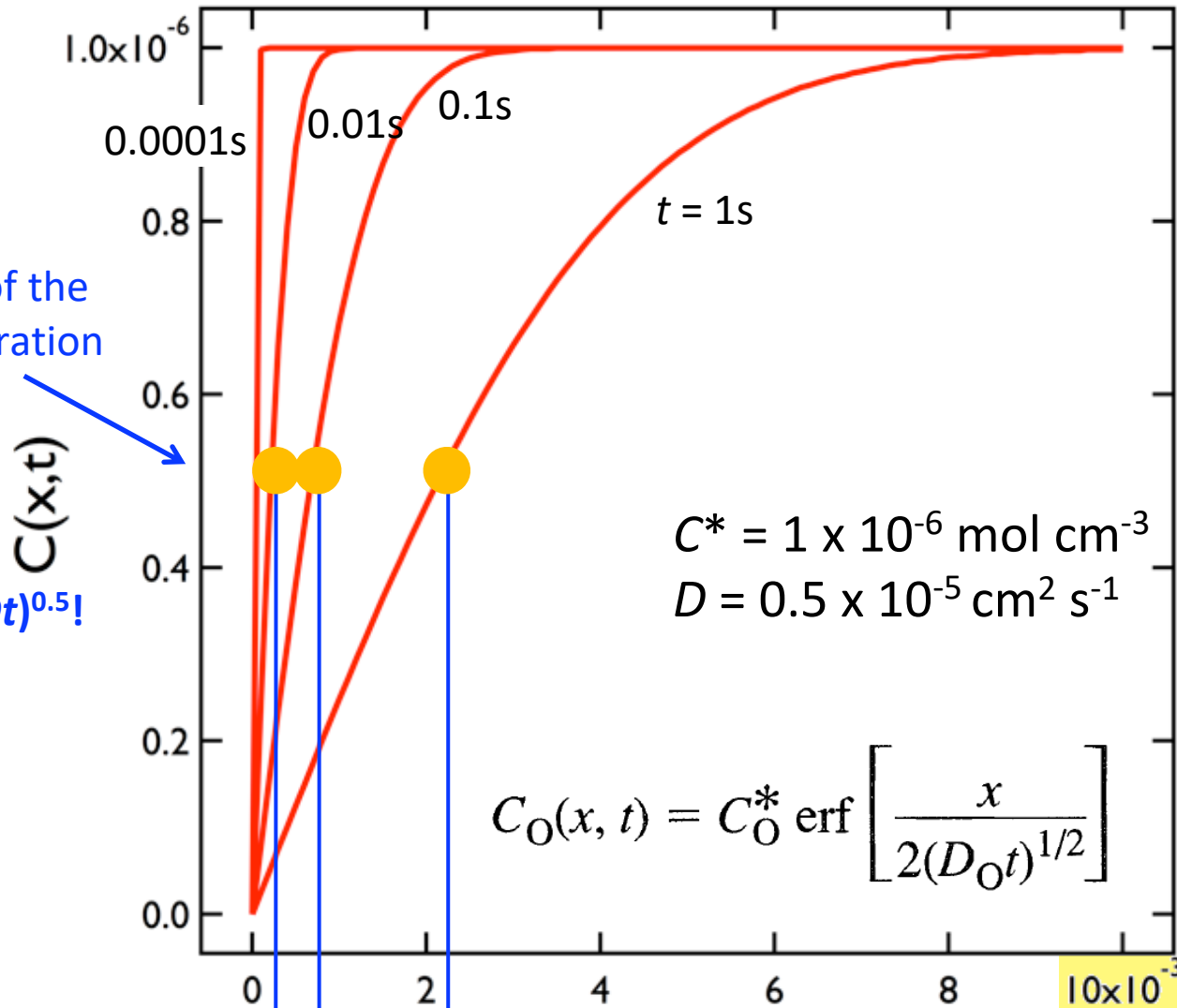
(100 µm)

… use the geometric area for calculations

(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...

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

... 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:

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

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

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

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

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…

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:

$$i = nFAJ_O(0, t)$$

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

… 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