Lecture #13 of 18(?)

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

- <u>Fick's Second Law of Diffusion</u>

- <u>Linear Diffusion = time-dependent current (Cottrell Equation)</u>

- **Anson Plots for surface adsorbed species**

- **Radial Diffusion = time-independent current (at steady-state)**

- **Ultramicroelectrodes (UMEs)**

- *Scanning Electrochemical Microscopy (SECM)*

- *Single molecule electrochemistry*

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 ($C_O(0, t) = 0$)
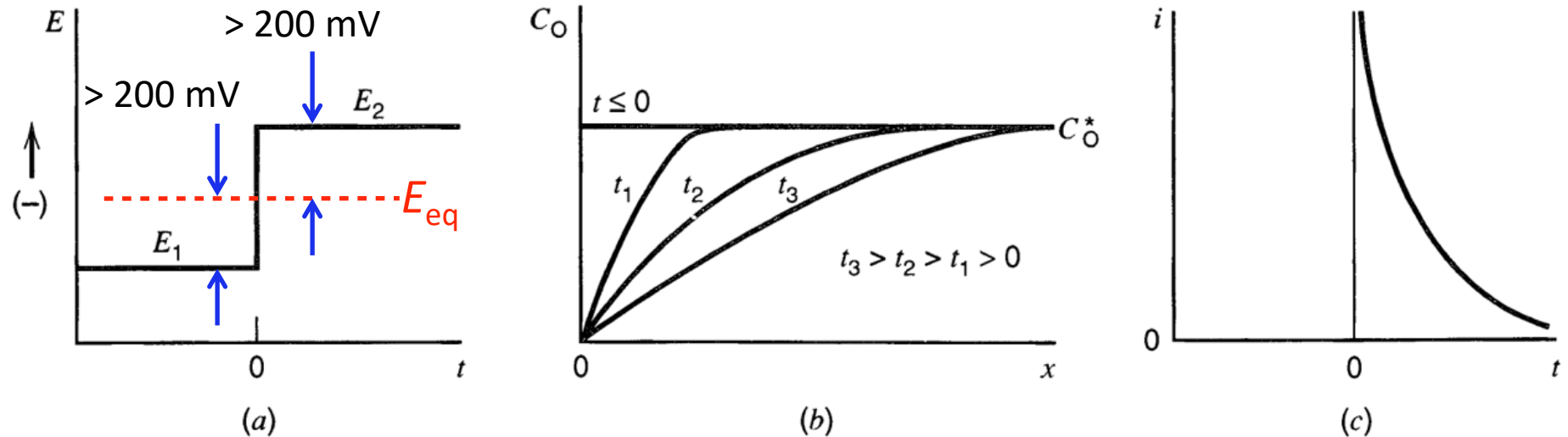
RECALL:

> 200 mV

> 200 mV

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…

RECALL:

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

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

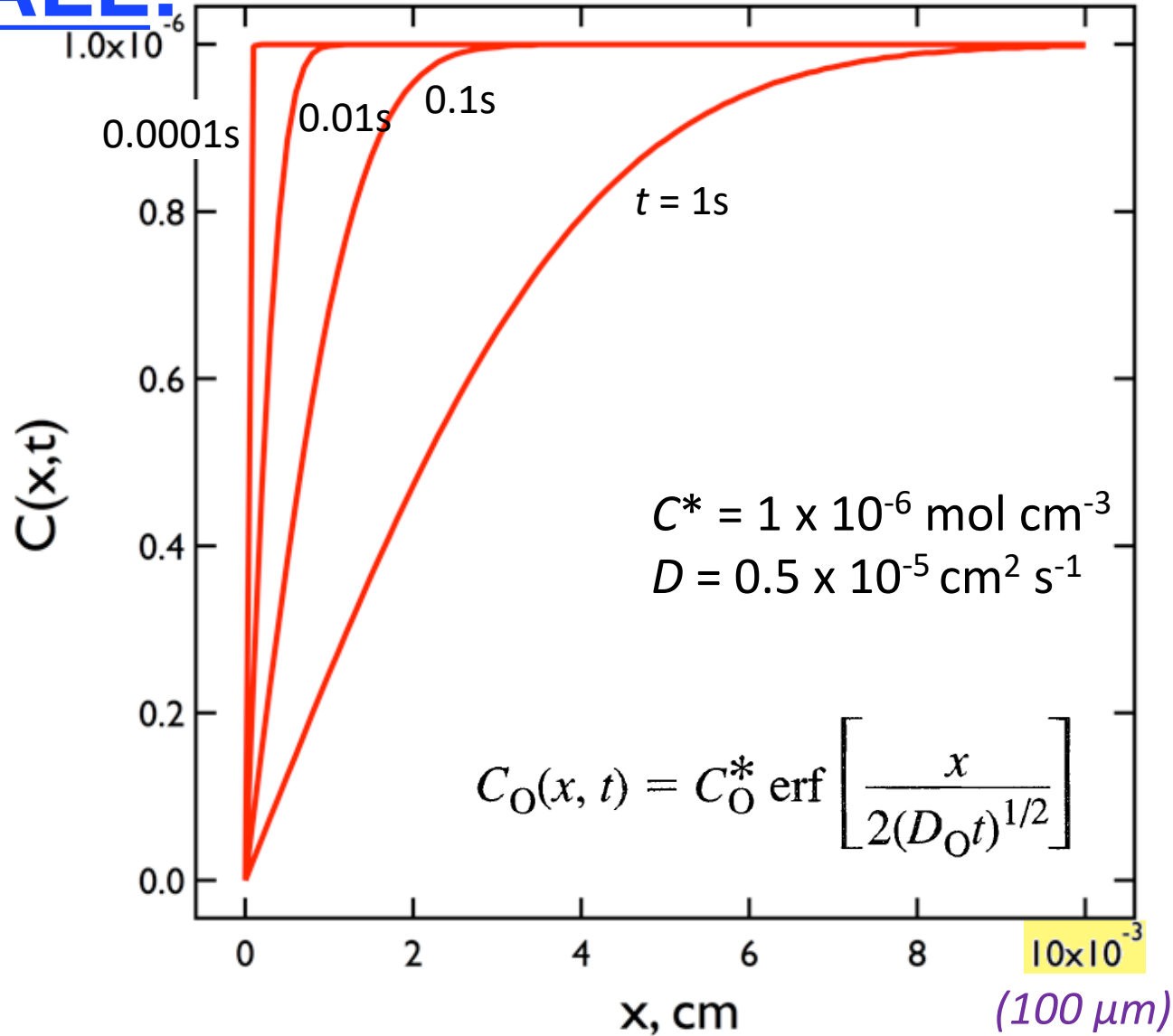… well, for large x, erf = 1 (erfc = 0) and so $C(x, t) = C^*$ … Check!

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

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

RECALL:

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

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

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

C(x,t)

x, cm

(100 μm)

RECALL:

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

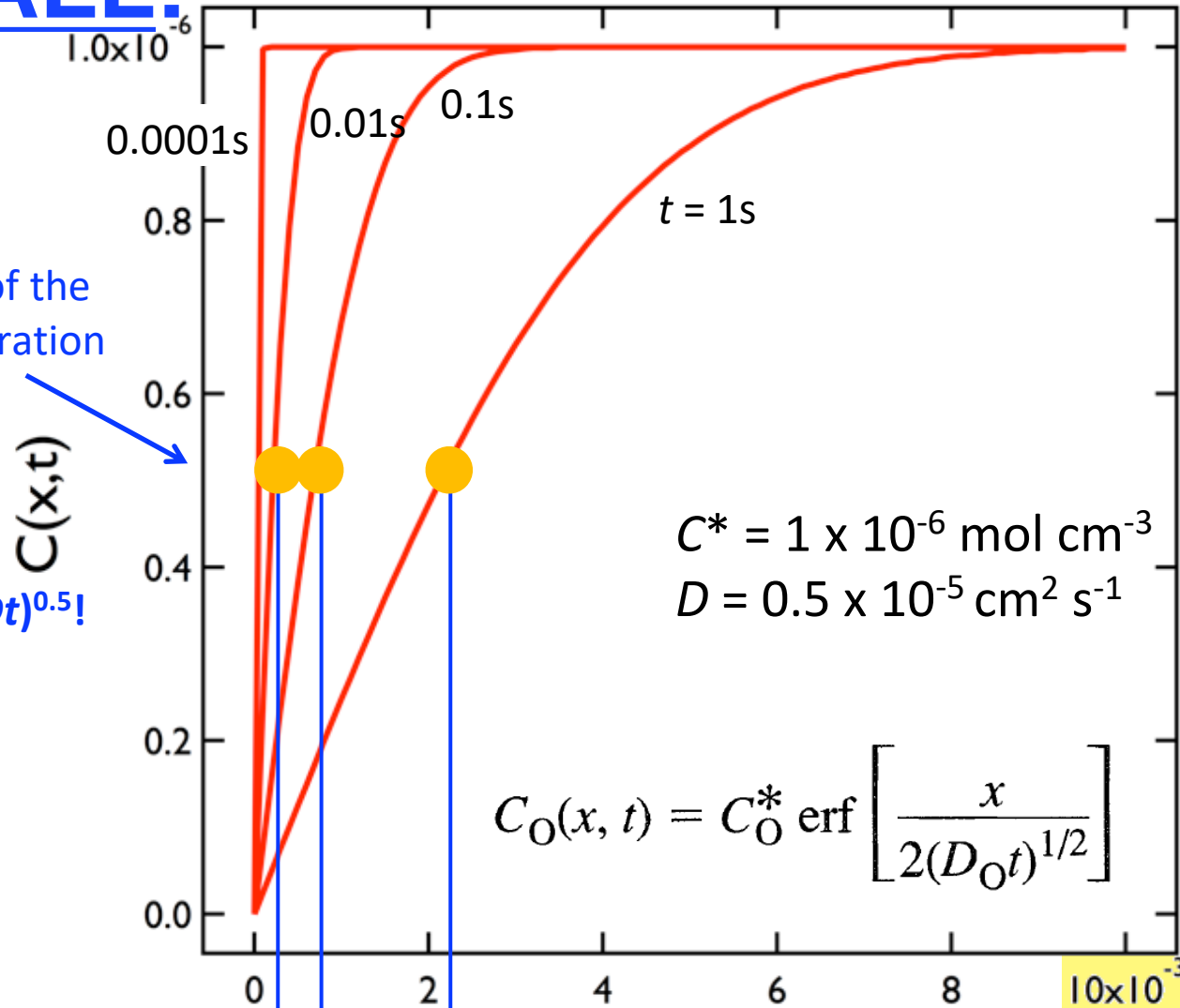$$\overline{\Delta} = \sqrt{(2d)Dt} = \sqrt{\left(\frac{cm^2}{s}\right)s} = cm$$

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

a characteristic "diffusion length"

root mean square (rms) displacement (standard deviation)

Hey, these look completely reasonable for <u>1D diffusion in one direction</u>!

<u>RECALL</u>:

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}

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

0.0001s   0.01s   0.1s $t = 1$s

C(x,t)

1.0x10^{-6}

0.8
0.6
0.4
0.2
0.0

0   2   4   6   8   10x10^{-3}

x, cm

7.1 µm 22 µm

$\sqrt{Dt}$ = 2.2 µm

(100 µm)

… use the geometric area for calculations

RECALL:

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:

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

RECALL:

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

… but we just derived $C_O(x, t)$:

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

… and so we need to evaluate:

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

RECALL:

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

… 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…

RECALL:

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:

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

RECALL:

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

... 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

Cottrell, then at UC Berkeley, invented the *electrostatic precipitator* used to clear smokestacks of charged soot particles…

corona discharge

capture plates

neutral particles

charged particles

> 1 kV
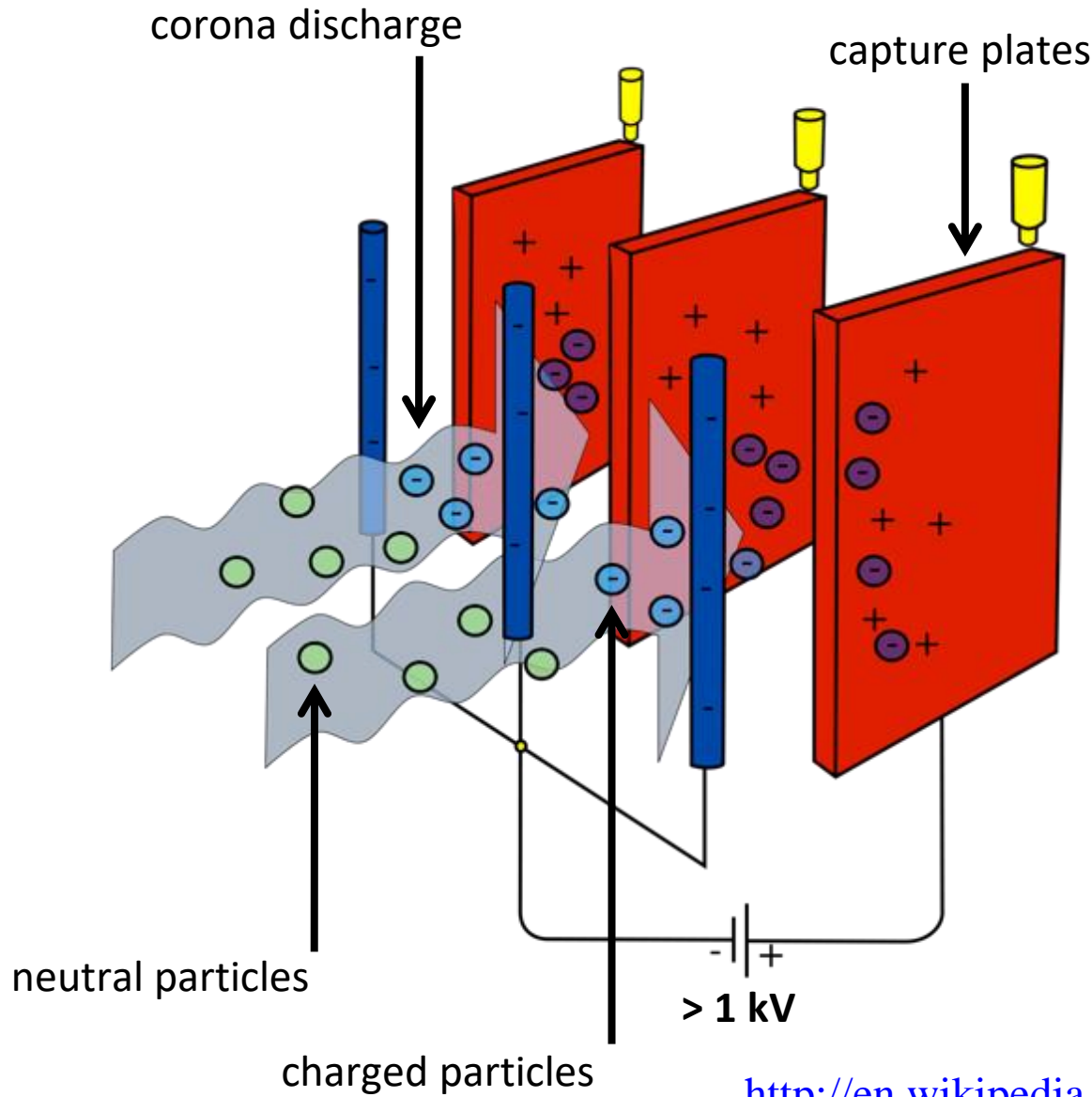
http://en.wikipedia.org/wiki/Electrostatic_precipitator
http://en.wikipedia.org/wiki/Corona_discharge

![Envitech - Industrial Gas Cleaning Systems]

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Wet electrostatic precipitator technology

Posted by Ron Patterson on Fri, Jul 10, 2009 @ 03:10 PM

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In 1824, the German mathematician M. Hohlfeld described the removal of particles from gas streams by electrical forces. However, it was almost a century later when Dr. Frederick G. Cottrell at the University of California, Berkeley commercialized the technology by building the first wet electrostatic precipitator.

A wet electrostatic precipitator uses electrical forces to move particles entrained in a gas stream onto collection surfaces. Electrodes in the wet electrostatic precipitator are held at high voltage which creates a corona discharge. Particles receive an electrical charge as they pass through the corona. The charged particles then follow electric field lines from the charging electrodes to collection surfaces, where they are removed from the gas stream.

Dr. Cottrell applied wet electrostatic precipitator technology to the removal of sulfuric acid mist and lead oxide dust emitted from various acid-making and smelting activities. At the time, vineyards in Northern California were being adversely affected by the lead emissions. Dr. Cottrell's innovative wet electrostatic precipitator solved their problem.
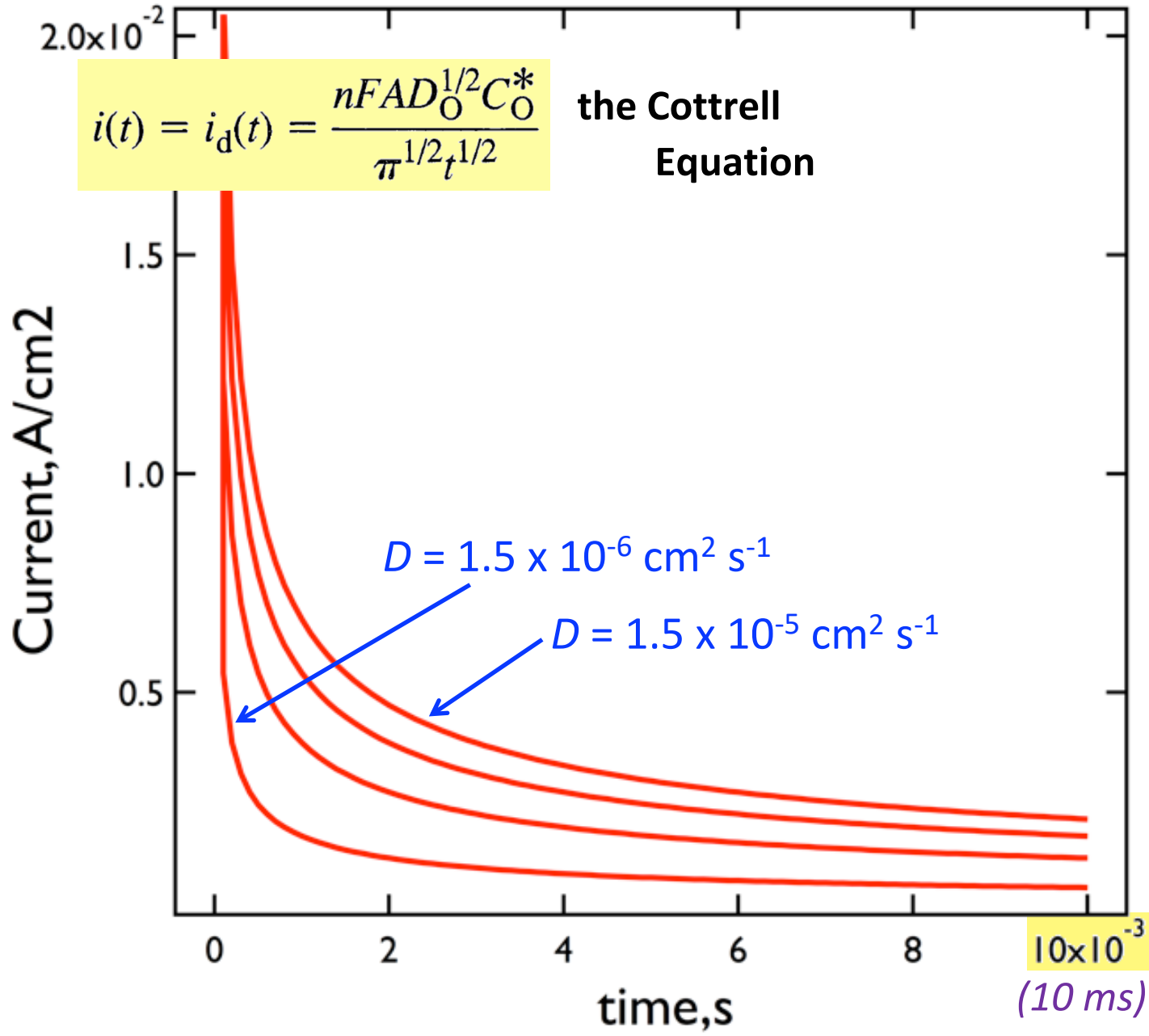
Fast forward to the 2000's. Envitech brought the control of lead and sulfur dioxide to a new level by installing our most advanced wet electrostatic precipitator technology on a secondary lead smelting facility in Southern California. The resulting wet electrostatic precipitator system which removes both sulfur dioxide and lead particles is said to set a new standard in air emission control at lead smelting facilities worldwide.

With over thirty years in the industry, we wanted to start sharing the knowledge and expertise that we have gained from cleaning gas streams of unwanted contaminants. Look for future postings that examine various aspects of state-of-the-art air pollution control technologies.
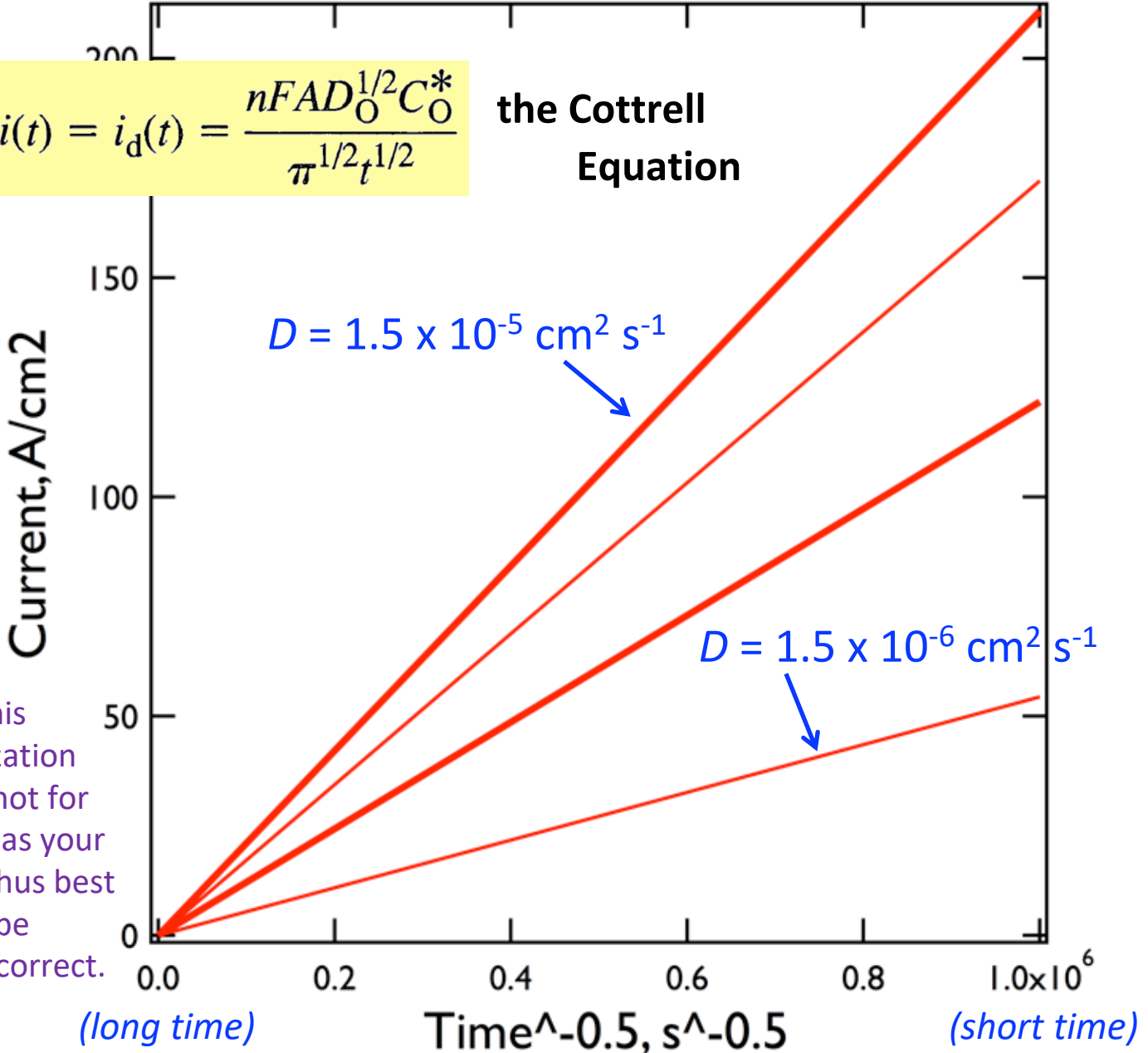
Tags: **wet electrostatic precipitators**

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

the Cottrell Equation

$D = 1.5 \times 10^{-6}$ cm^2 s^{-1}

$D = 1.5 \times 10^{-5}$ cm^2 s^{-1}

Current, A/cm2

time, s

(10 ms)

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

the Cottrell Equation

$D = 1.5 \times 10^{-5}$ cm^2 s^{-1}

$D = 1.5 \times 10^{-6}$ cm^2 s^{-1}

Current, A/cm2

200

150

100

50

0

Plot data like this only for visualization purposes, and not for fitting the data as your statistics, and thus best-fit values, will be affected and incorrect.

0.0   0.2   0.4   0.6   0.8   1.0x10^6

(long time)   Time^-0.5, s^-0.5   (short time)

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

the Cottrell Equation

?????

slope = $nFA\pi^{-1/2}D^{1/2}C^*$

(long time)

(short time)
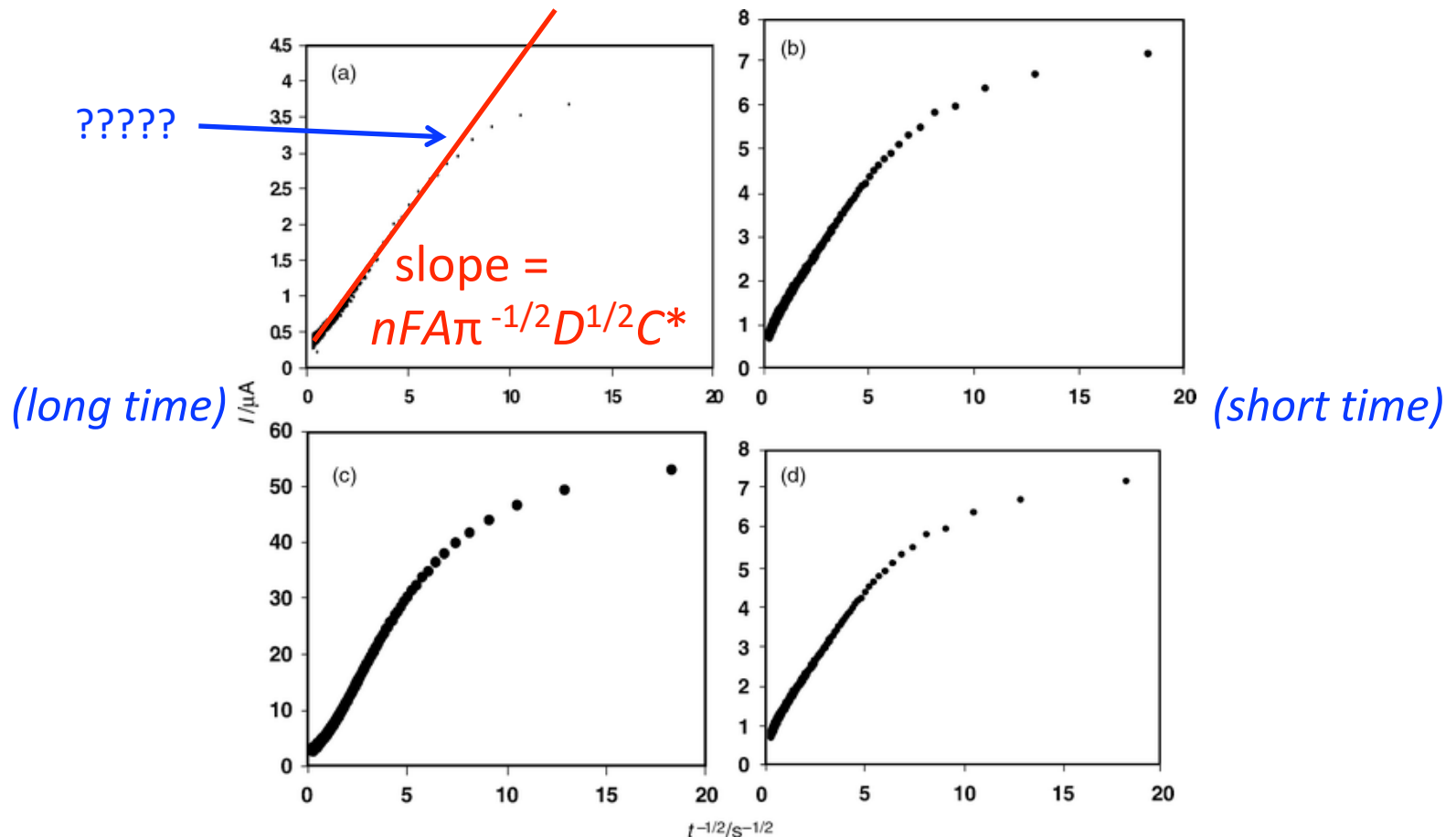
Brett Kralj and Robert A. W. Dryfe[*]

Department of Chemistry, UMIST, PO Box 88, Manchester, UK M60 1QD E-mail: robert.dryfe@umist.ac.uk Fax: + 44 (0)161 200 4559

... **use the Cottrell Equation to measure *D*,** *such as in thin films/coatings*!

... but what are the problems with this approach?

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

the Cottrell Equation

1) Huge initial currents... beware of compliance current!
2) Noise.
3) *RC* time limitations *decrease expected current* at really short times.
4) Roughness factor *increases expected current* at short times.
5) Adsorbed (electrolyzable) gunk *increases expected current* at short times.
6) Convection, "edge effects," and thin pathlengths impose a "long" time limit to these types of experiments.

... Solution: Integrate the Cottrell equation with respect to time...

$$Q_d = \frac{2nFAD_O^{1/2}C_O^*t^{1/2}}{\pi^{1/2}}$$

the *integrated* **Cottrell Equation**

$$Q_d = \frac{2nFAD_O^{1/2}C_O^* t^{1/2}}{\pi^{1/2}}$$

the *integrated* **Cottrell Equation**
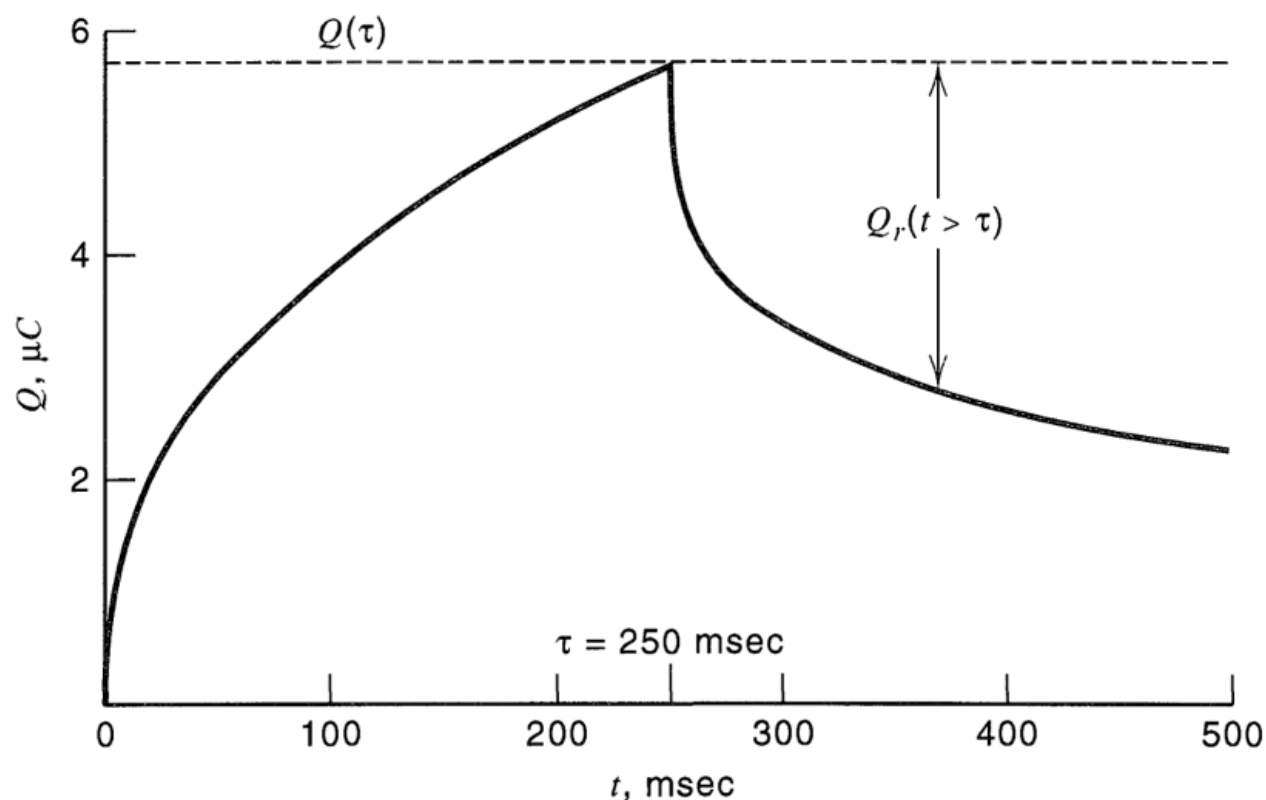
Figure 5.8.2 Chronocoulometric response for a double-step experiment performed on the system of Figure 5.8.1. The reversal step was made to 0.0 V *vs.* QRE. [Data courtesy of R. S. Glass.]
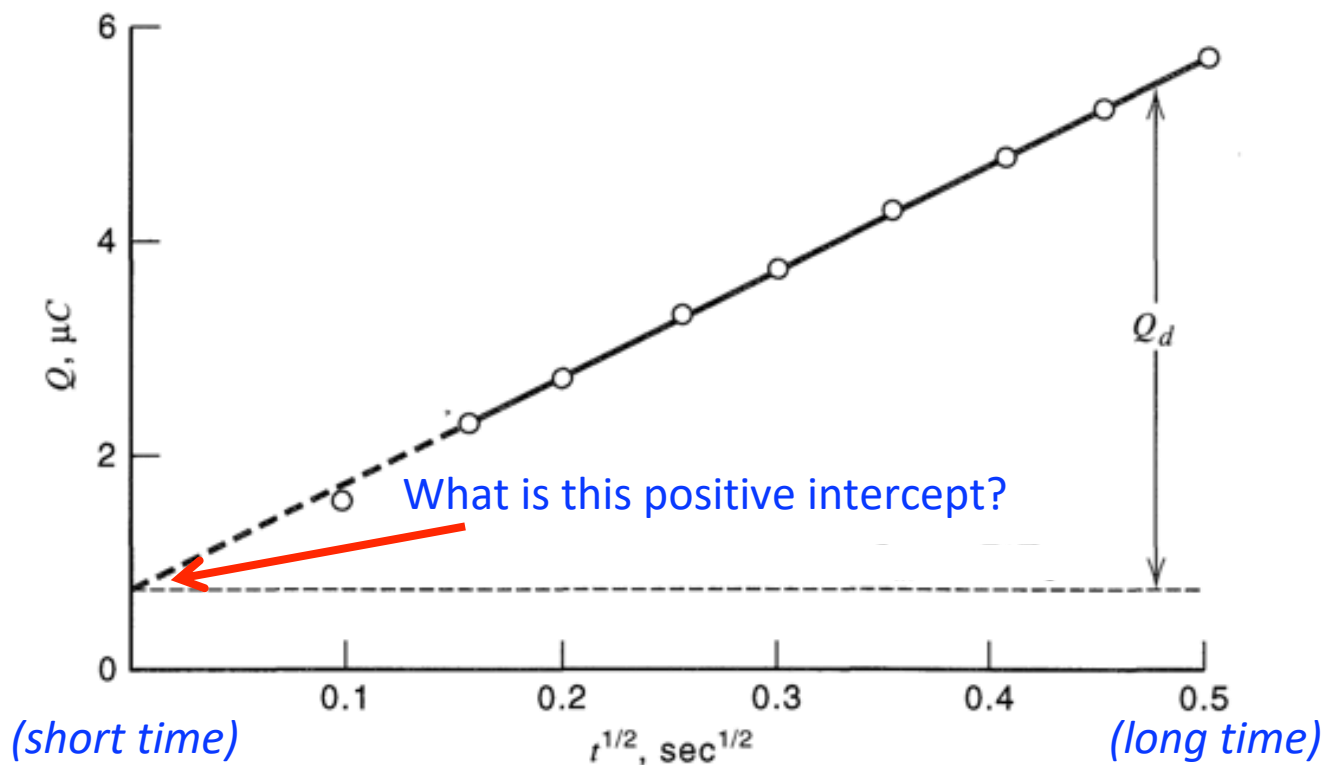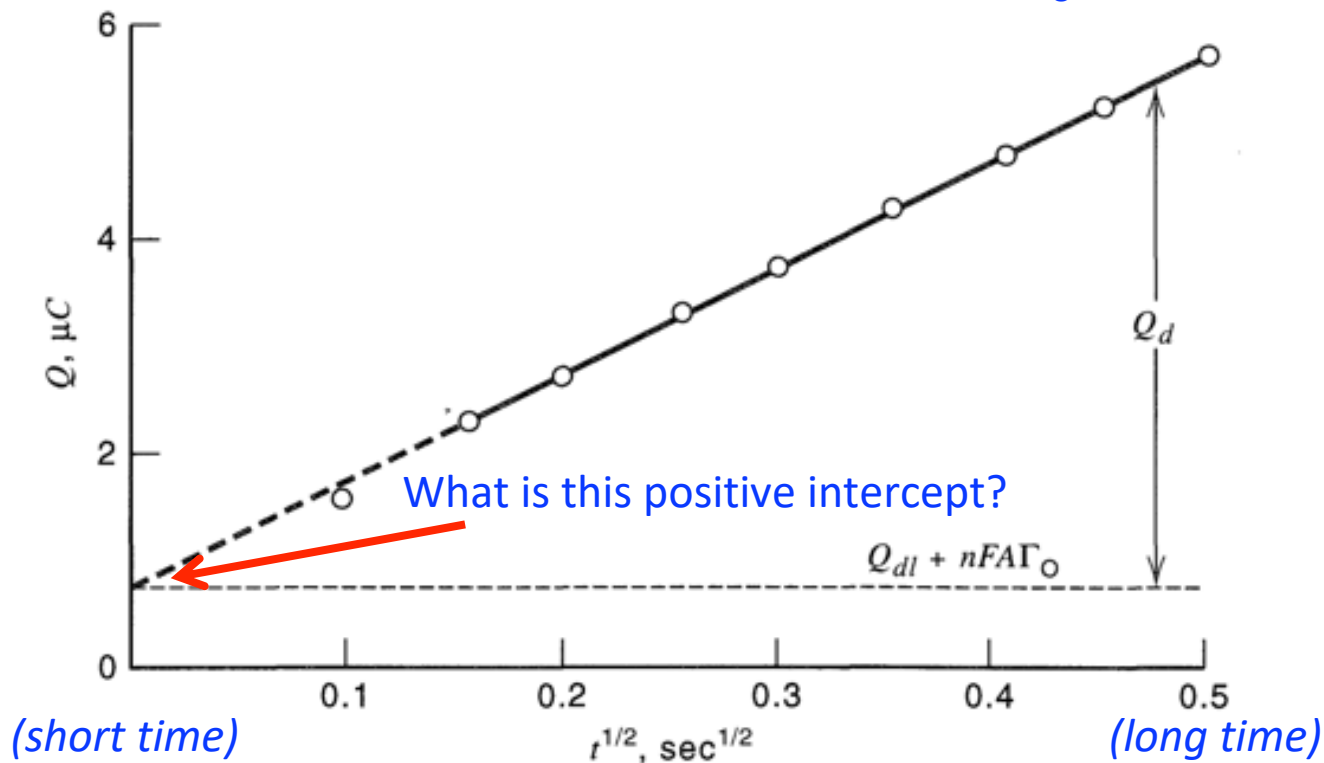
Anson, *Anal. Chem.*, 1966, *38*, 54

Figure 5.8.1 Linear plot of chronocoulometric response at a planar platinum disk. System is 0.95 mM 1,4-dicyanobenzene (DCB) in benzonitrile containing 0.1 M tetra-n-butylammonium fluoborate. Initial potential: 0.0 V vs. Pt QRE. Step potential: -1.892 V vs. Pt QRE. $T = 25°C$, $A = 0.018$ cm^2. $E^{0'}$ for DCB $+ e \rightleftarrows$ DCB$^{\cdot-}$ is -1.63 V vs. QRE. The actual chronocoulometric trace is the part of Figure 5.8.2 corresponding to $t < 250$ ms. [Data courtesy of R. S. Glass.]

Anson, *Anal. Chem.*, 1966, *38*, 54

$$Q = \frac{2nFAD_O^{1/2}C_O^{*}t^{1/2}}{\pi^{1/2}} + Q_{dl} + nFA\Gamma_O \qquad (5.8.2)$$

with Γ_O, the surface excess of O (mol cm^{-2})

Q_d

What is this positive intercept?

$Q_{dl} + nFA\Gamma_O$

(short time) $t^{1/2}$, sec$^{1/2}$ *(long time)*

Figure 5.8.1   Linear plot of chronocoulometric response at a planar platinum disk. System is 0.95 mM 1,4-dicyanobenzene (DCB) in benzonitrile containing 0.1 M tetra-*n*-butylammonium fluoborate. Initial potential: 0.0 V *vs.* Pt QRE. Step potential: -1.892 V *vs.* Pt QRE. $T = 25°C$, $A = 0.018$ cm^2. $E^{0'}$ for DCB $+ e \rightleftarrows$ DCB$\cdot^-$ is -1.63 V *vs.* QRE. The actual chronocoulometric trace is the part of Figure 5.8.2 corresponding to $t < 250$ ms. [Data courtesy of R. S. Glass.]

Anson, *Anal. Chem.*, 1966, *38*, 54

Preface

Tribute to Fred Anson and list of publications

Fred Anson
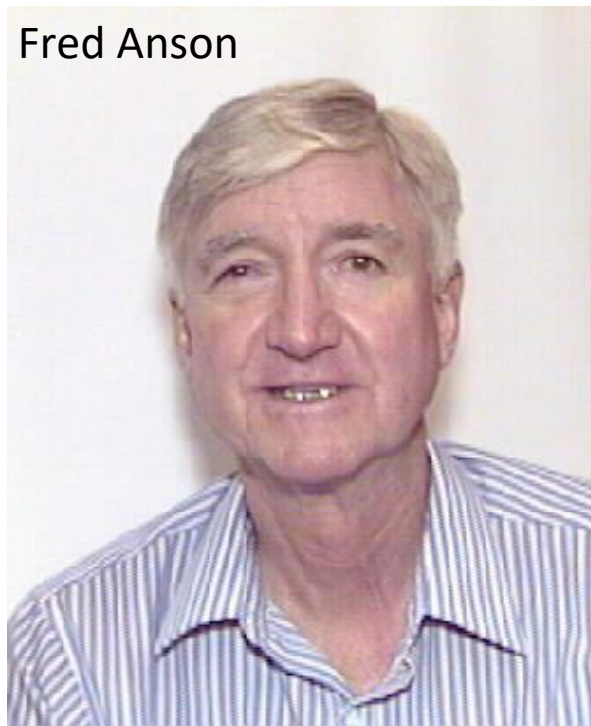
Fred's scientific accomplishments in over 300 publications cover the gamut of inorganic, analytical, and physical electrochemistry. He started out in his Ph.D. work with J.J. Lingane and in his early work at Caltech looking at various reactions at Pt electrodes and in coulometry and coulometric titrations. In his early days at Caltech, he had a number of papers dealing with the 'rediscovered' technique of chronopotentiometry. This led, in a classical example of serendipity, to the discovery of what is now termed thin-layer electrochemistry. His interest in surface processes at electrodes led, somewhat later, to the discovery of chronocoulometry. His pioneering contributions to this area eventually led to the naming of the 'Anson plot' of Q vs. $t^{1/2}$ after him. While primarily an experimentalist, he has contributed to a theoretical understanding of inner and outer sphere reactions and double layer effects at electrodes. A major theme to be found in Fred's publications is an interest in the electron transfer kinetics and mechanisms of

Anson, *Anal. Chem.*, 1966, *38*, 54

… one data set, from "one" experiment…
… **where either plot allows you to calculate *D*!**

experiment	observable	governing equation
Chronoamperometry (or differentiate CC)	meas *I(t)* *(or use dQ(t)/dt)*	$i_d(t) = \dfrac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}}$
Chronocoulometry (or integrate CA)	meas *Q(t)* *(or use I(t) area)*	$Q = \dfrac{2nFAD_O^{1/2}C_O^*t^{1/2}}{\pi^{1/2}}$

… how else can one calculate *D*? …

… how about not using electrochemistry, **<u>but NMR instead</u>**… What?

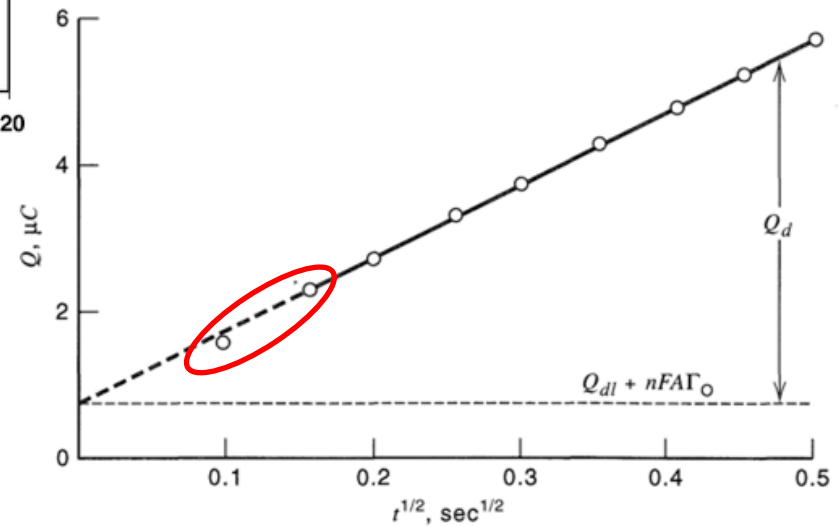… Yes! **Pulsed-Field Gradient (PFG) NMR!**

… so, <u>without</u> diffusion…
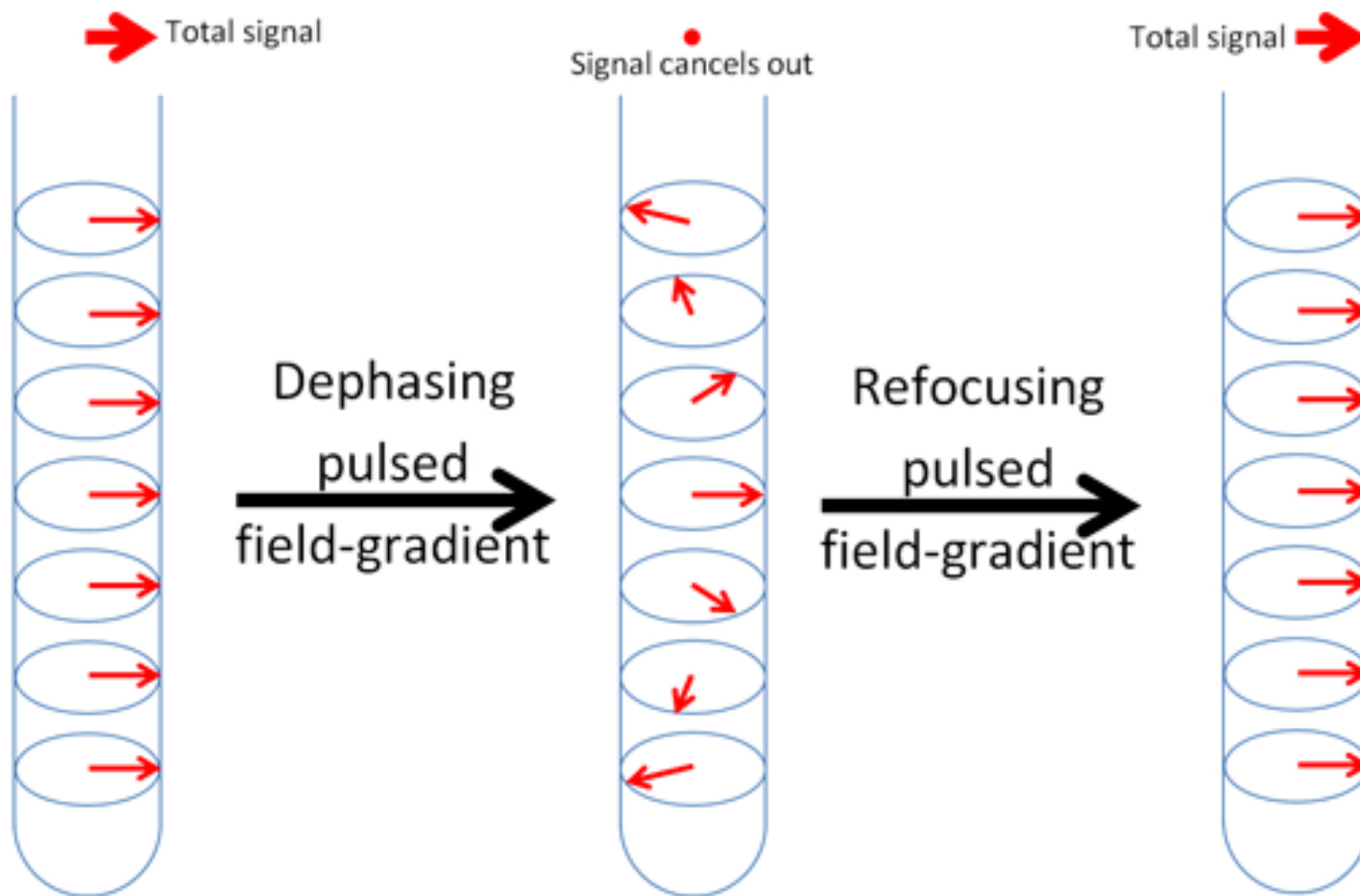
http://chem.ch.huji.ac.il/nmr/techniques/other/diff/diff.html
http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3003887/

… how else can one calculate *D*? …

… how about not using electrochemistry, <u>**but NMR instead**</u>… What?

… Yes! **Pulsed-Field Gradient (PFG) NMR!**

… and, <u>with</u> diffusion…

http://chem.ch.huji.ac.il/nmr/techniques/other/diff/diff.html
http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3003887/
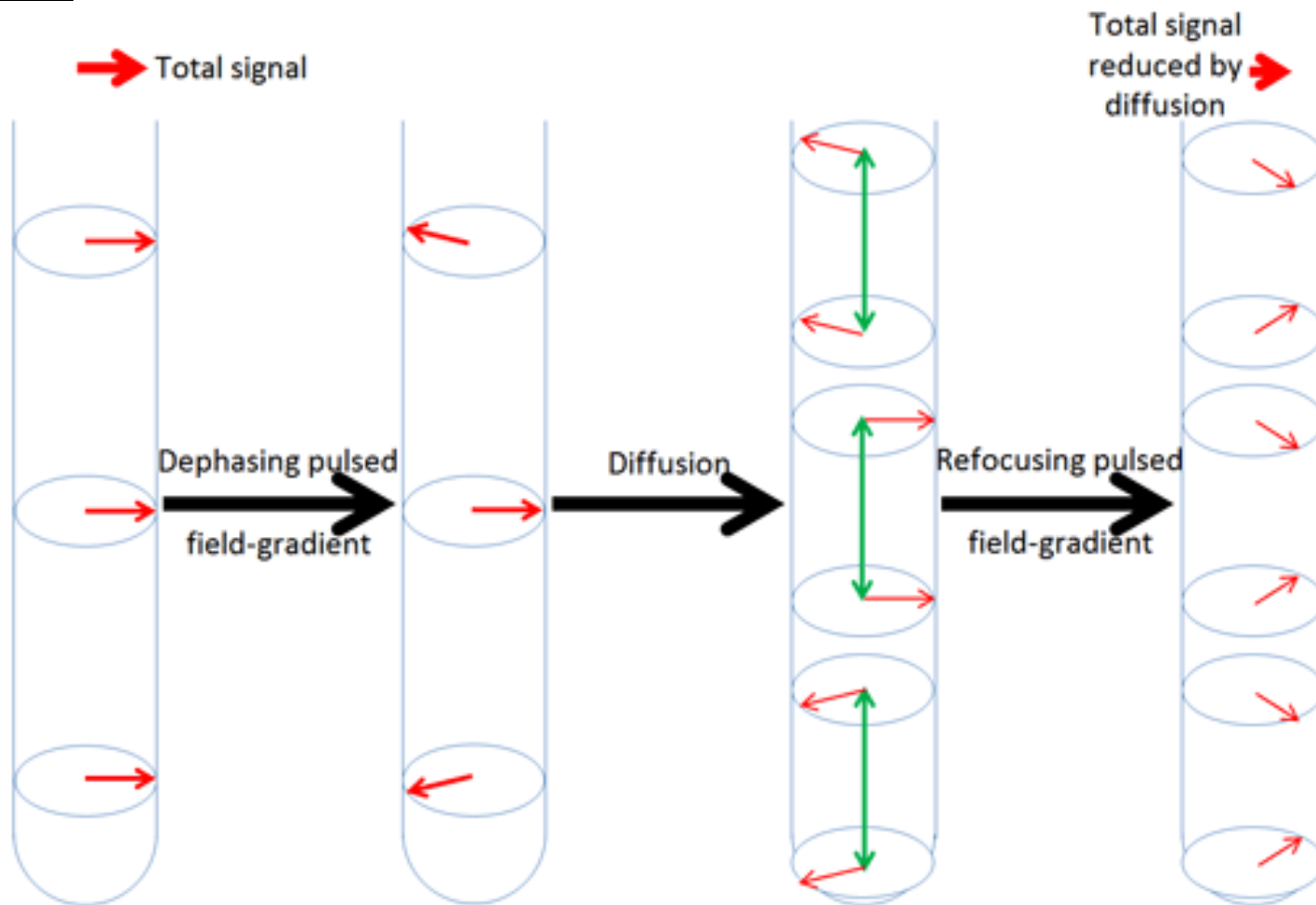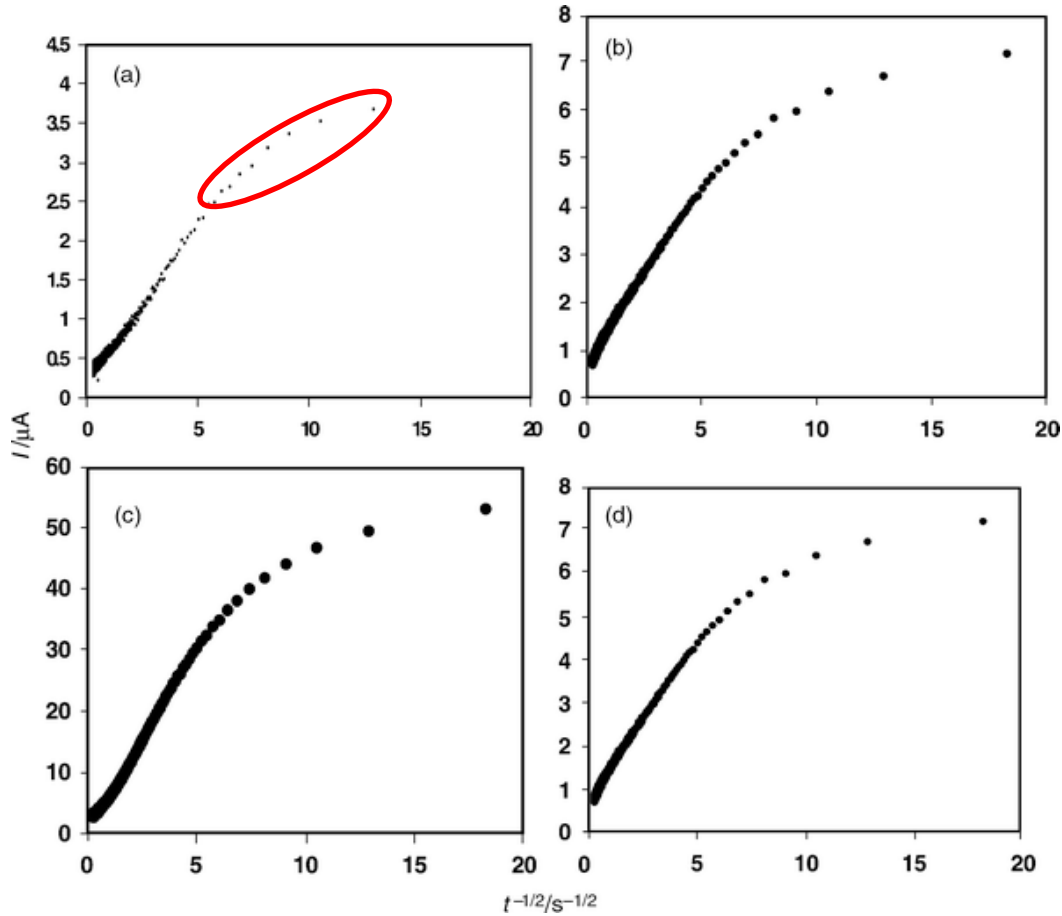
Short times... check!

we have equations for the "signal" and the "noise," so…
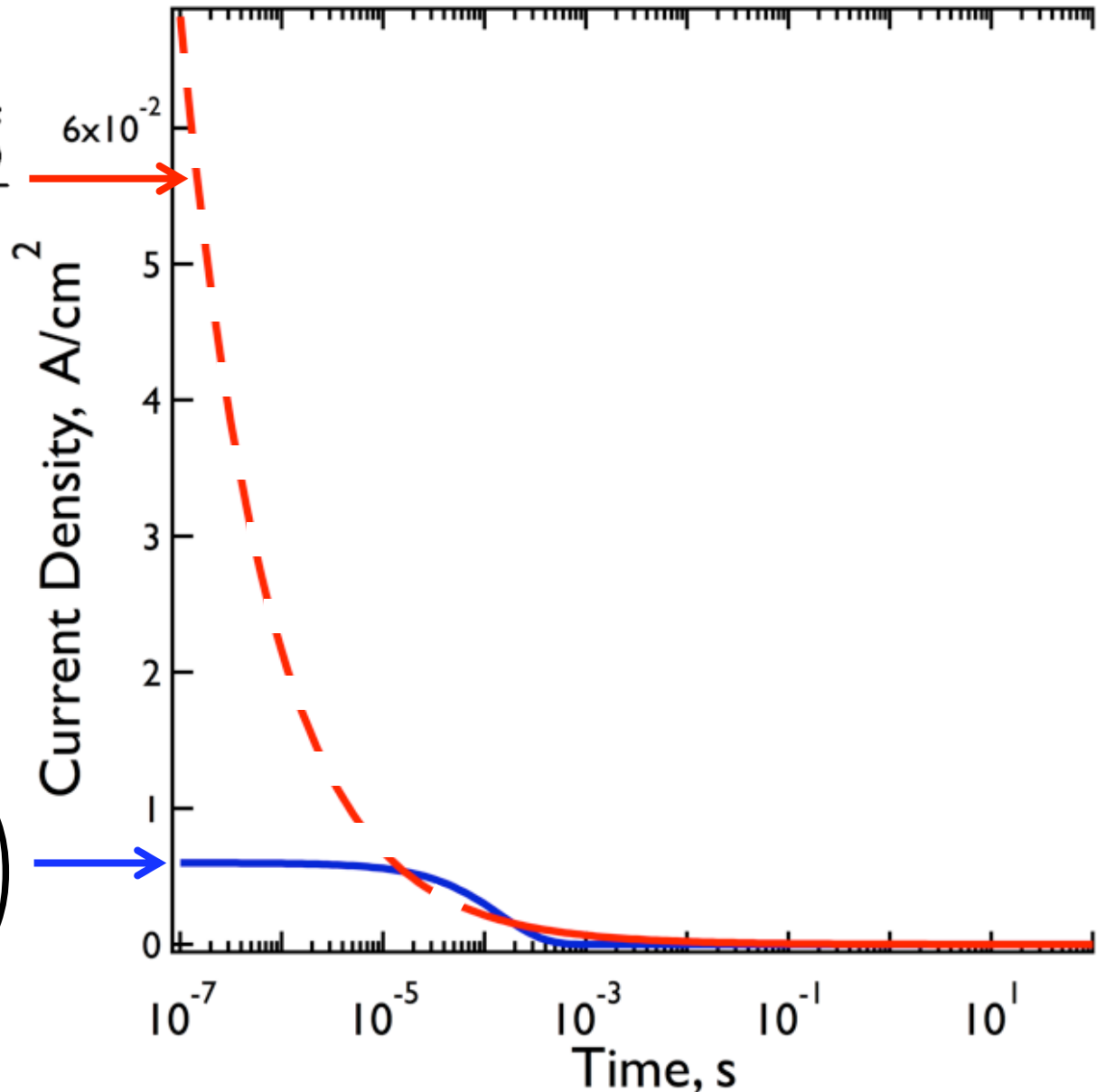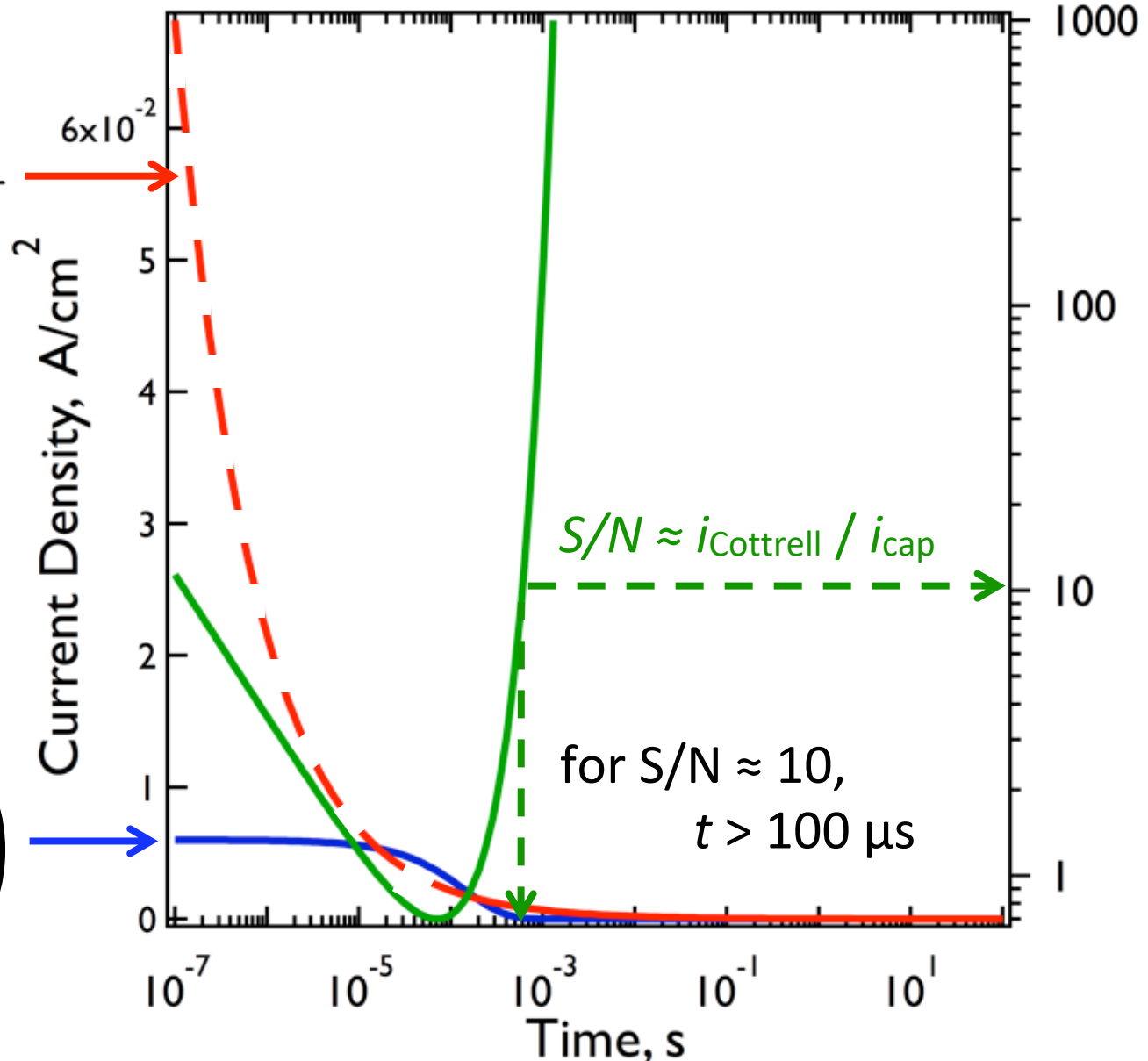we can calculate the signal-to-noise ratio for a potential step experiment

signal

$$i_{\mathrm{d}}(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}}$$

noise

$$i = \frac{E}{R}exp\left(\frac{-t}{RC}\right)$$

… here we assume
$E = 0.6$ V, $R = 100\ \Omega$

we have equations for the "signal" and the "noise," so...
we can calculate the signal-to-noise ratio for a potential step experiment

signal

$$i_{\mathrm{d}}(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}}$$

noise

$$i = \frac{E}{R}exp\left(\frac{-t}{RC}\right)$$

... here we assume
$E = 0.6$ V, $R = 100$ Ω

$S/N \approx i_{\text{Cottrell}} / i_{\text{cap}}$

for S/N ≈ 10,
$t > 100$ μs

… the *RC* time constant of the cell imposes a lower limit on the **(UPDATED)** 500 accessible time window (~100 μs) for a potential step experiment…

… but what is the origin of the long time limit?

signal

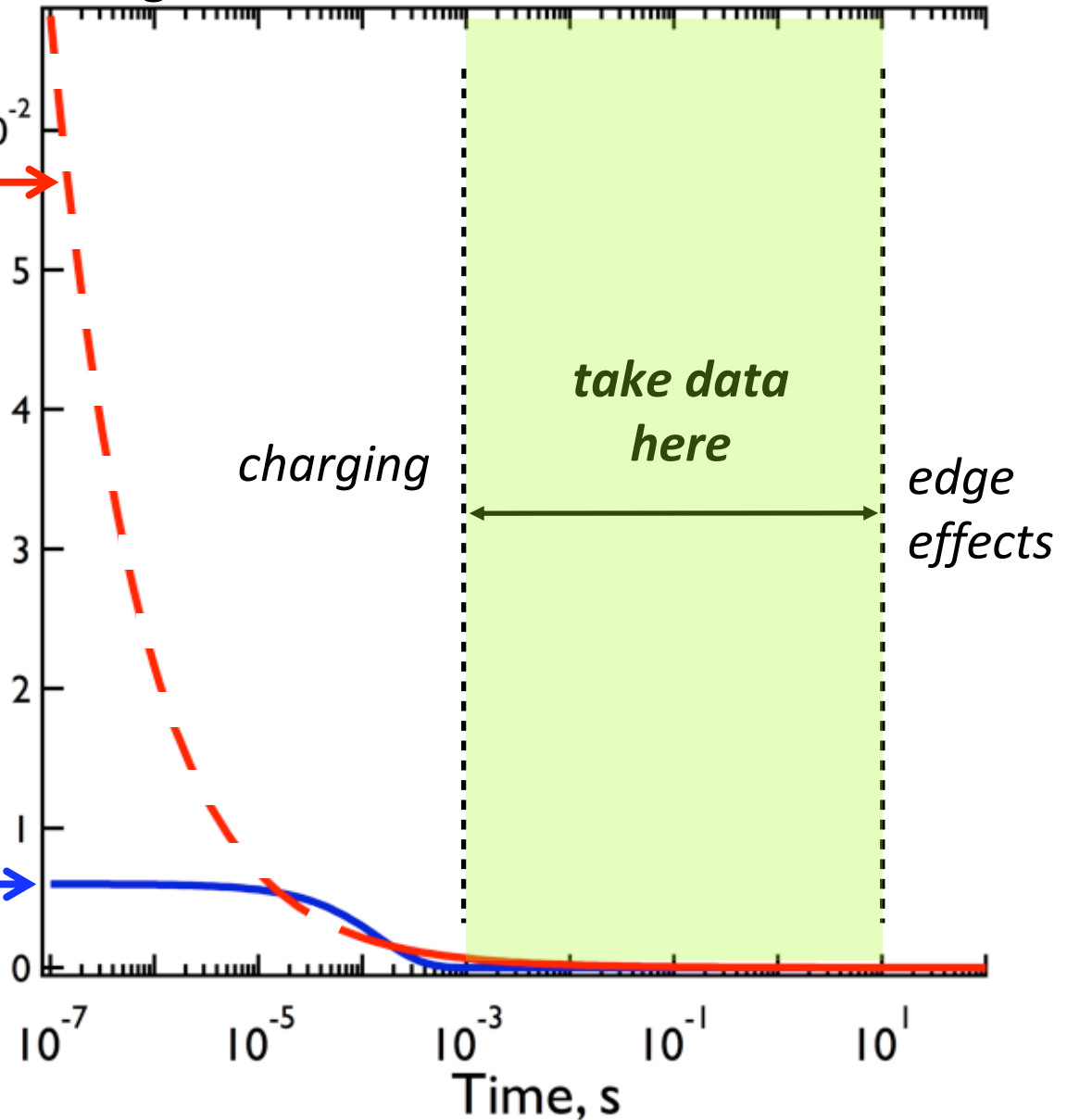$$i_d(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}}$$

noise

$$i = \frac{E}{R}exp\left(\frac{-t}{RC}\right)$$

… here we assume
$E = 0.6$ V, $R = 100$ Ω

charging

take data here

edge effects
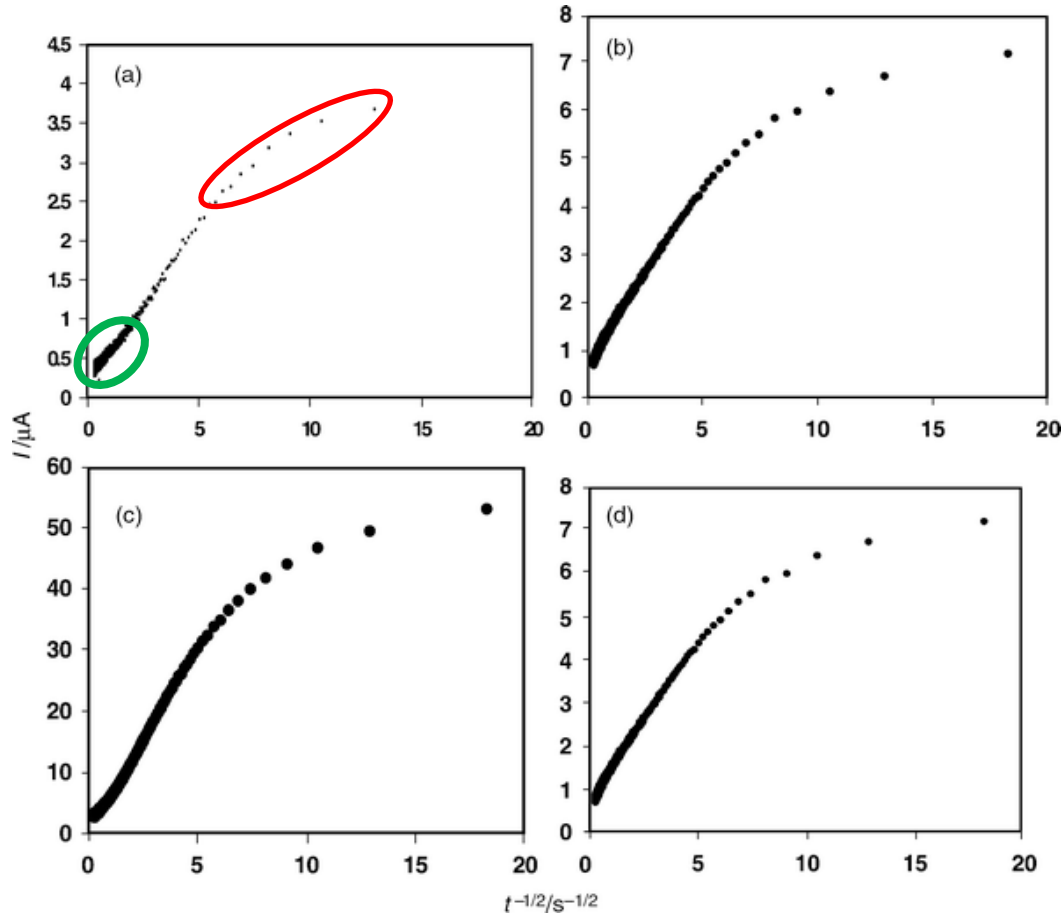
Short times… check!

Long times…
… what is this due to again?
… let's see…
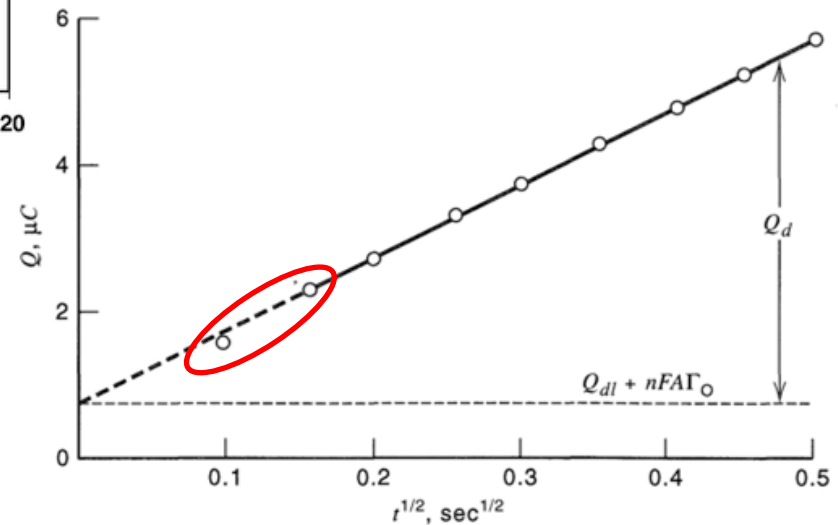
A typical electrode used in a laboratory electrochemistry experiment has an area of 0.05 cm² to 1 cm².

a.

- 3 mm dia. gold disk
- Pt counter electrode
- polyolefin electrode body

BASi Stationary Voltammetry Electrodes Get Prices

MF-2011	Silver Electrode (AGE) (1.6 mm dia.)
MF-2012	Glassy Carbon Electrode (GCE) (3.0 mm dia.)
MF-2070	Glassy Carbon Electrode (pkg. of 3)
MF-2013	Platinum Electrode (PTE) (1.6 mm dia.)
MF-2071	Platinum Electrode (pkg. of 3)
MF-2014	Gold Electrode (AUE) (1.6 mm dia.)
MF-2072	Gold Electrode (pkg. of 3)
MF-2073	GCE, PTE, AUE (pkg. one each)
MF-2010	Electrode Body for 3.0 mm ID Carbon Paste Electrode (CPE): purchase carbo
MF-2015	Small Electrode Body (3 mm OD) for 1.6 mm ID Carbon Paste Electrode (MC paste separately
CF-1010	Carbon Paste (CPO) (1 g): paste of uniform graphite particles mixed with a p aqueous media)
MF-2016	Nickel Electrode (NIE) (3.0 mm dia.)
MF-2018	Palladium Electrode (PDE) (3.0 mm dia.)
Inquire	Custom Voltammetry Electrodes: with other electrode materials

0.75 cm

7.5 cm

6 mm
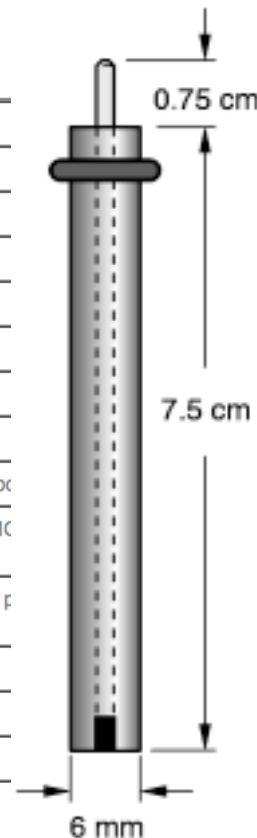
$A = \pi(0.15)^2 = 0.0706 \text{ cm}^2 \approx 7 \text{ mm}^2$

The Cottrell Equation can be used to describe the behavior during a potential step experiment as long as the *thickness of the Nernst diffusion layer is small relative to the electrode dimension* (and, of course, the boundary layer / stagnant layer)…

… So, how long is that, based on S/N ≈ 10:1?

t (s)	$\sqrt{Dt}$	$\dfrac{\sqrt{Dt}}{r_0}$
0.1	0.0007 cm	0.005
1	0.0022 cm	0.015
10	0.0071 cm	0.047
100	0.022 cm (220 μm)	0.15

$D = 0.5 \times 10^{-5}$ cm^2/s
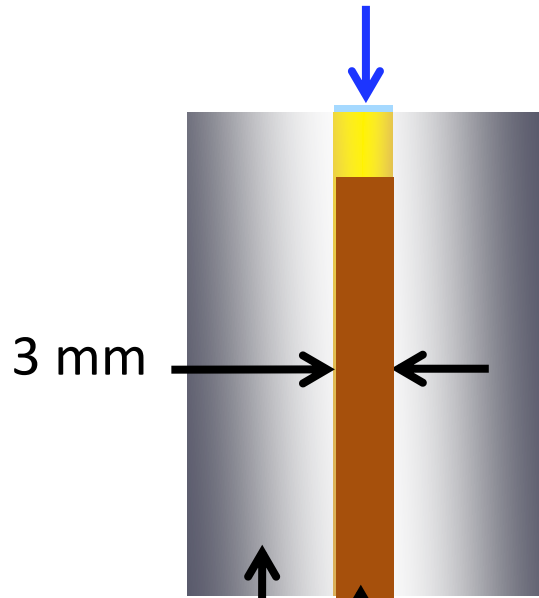*(lower bound for typical value)*

$r_0 = 0.15$ cm
(value from previous slide)

Answer: < ~10 s

When the diffusion layer approaches the dimensions of the electrode diameter, radial diffusion to the edges of the electrode cause the flux to be larger than predicted by the Cottrell Equation, *and non-uniform*.
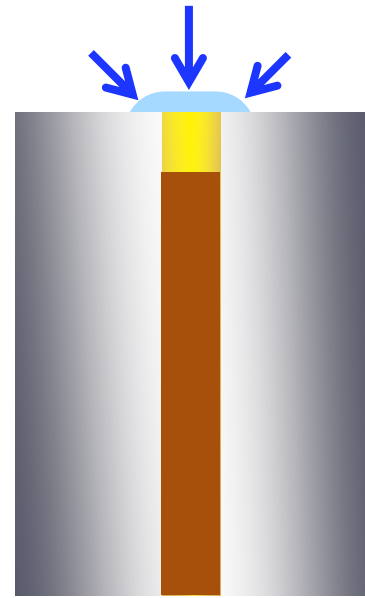

$t \approx 0.1 - 1$ s

linear diffusion

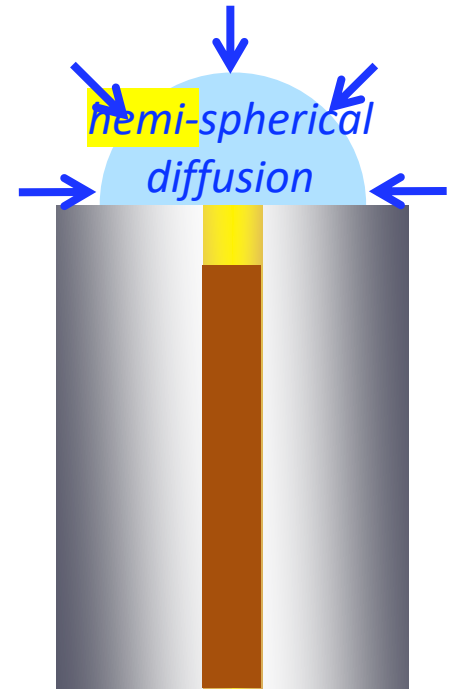$t \approx 1 - 100$ s

mixed diffusion

$t > {\sim}100$ s

hemi-spherical diffusion

3 mm

insulator

Au tip on metal rod

How is current affected, relative to the Cottrell prediction?

… so in a potential step experiment…

1. current changes continuously with time.

2. radial diffusion (AKA "edge effects") limits the data acquisition time window to ~1 – 10 s.

3. charging imposes a lower limit of 0.1 – 0.5 μs on this data acquisition time window.

4. theoretically, maximum current densities are > 60 mA cm^{-2} initially, but just 100 μA cm^{-2} at S/N ≈ 10.

… but, why do we care?

Why do we care? One reason…

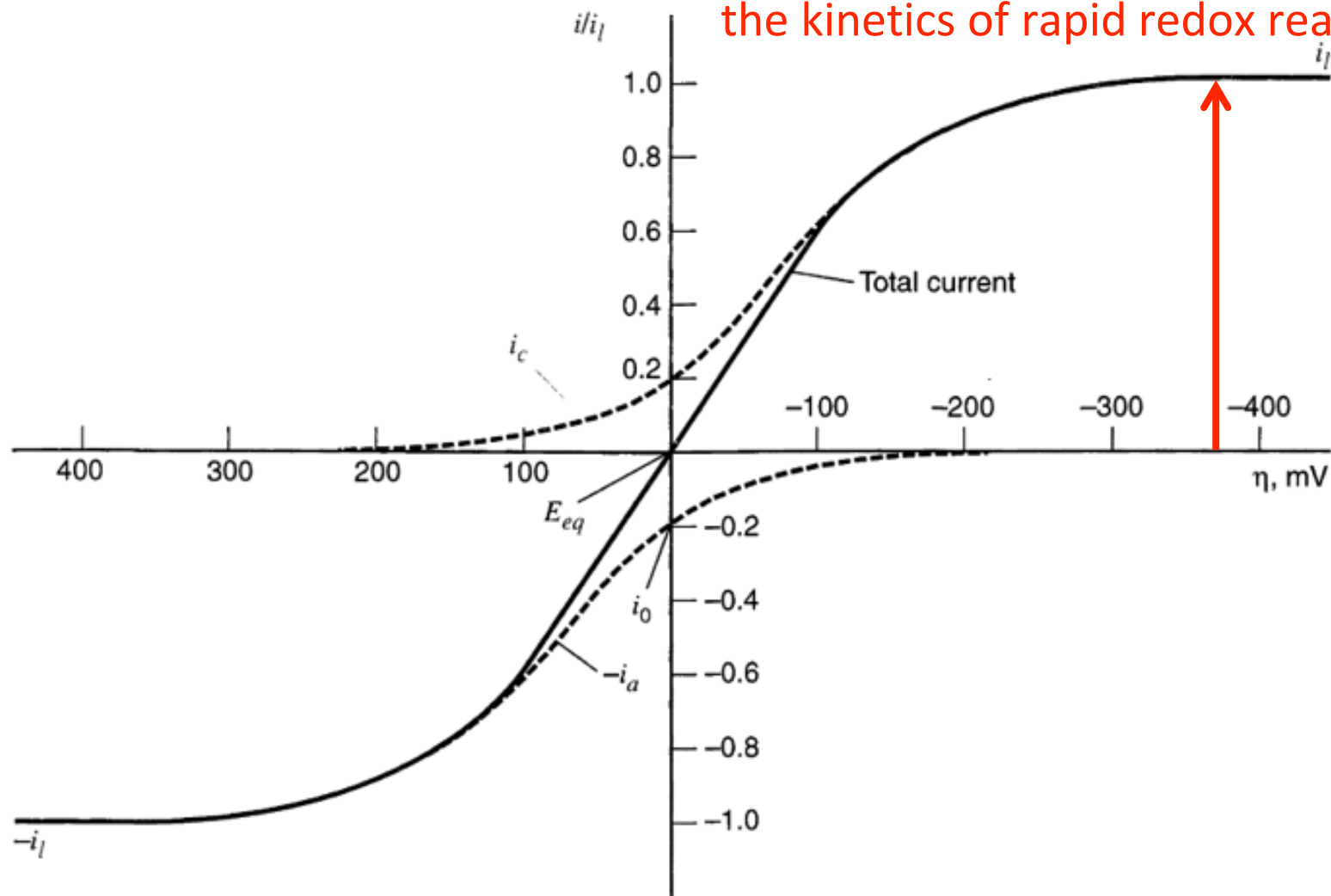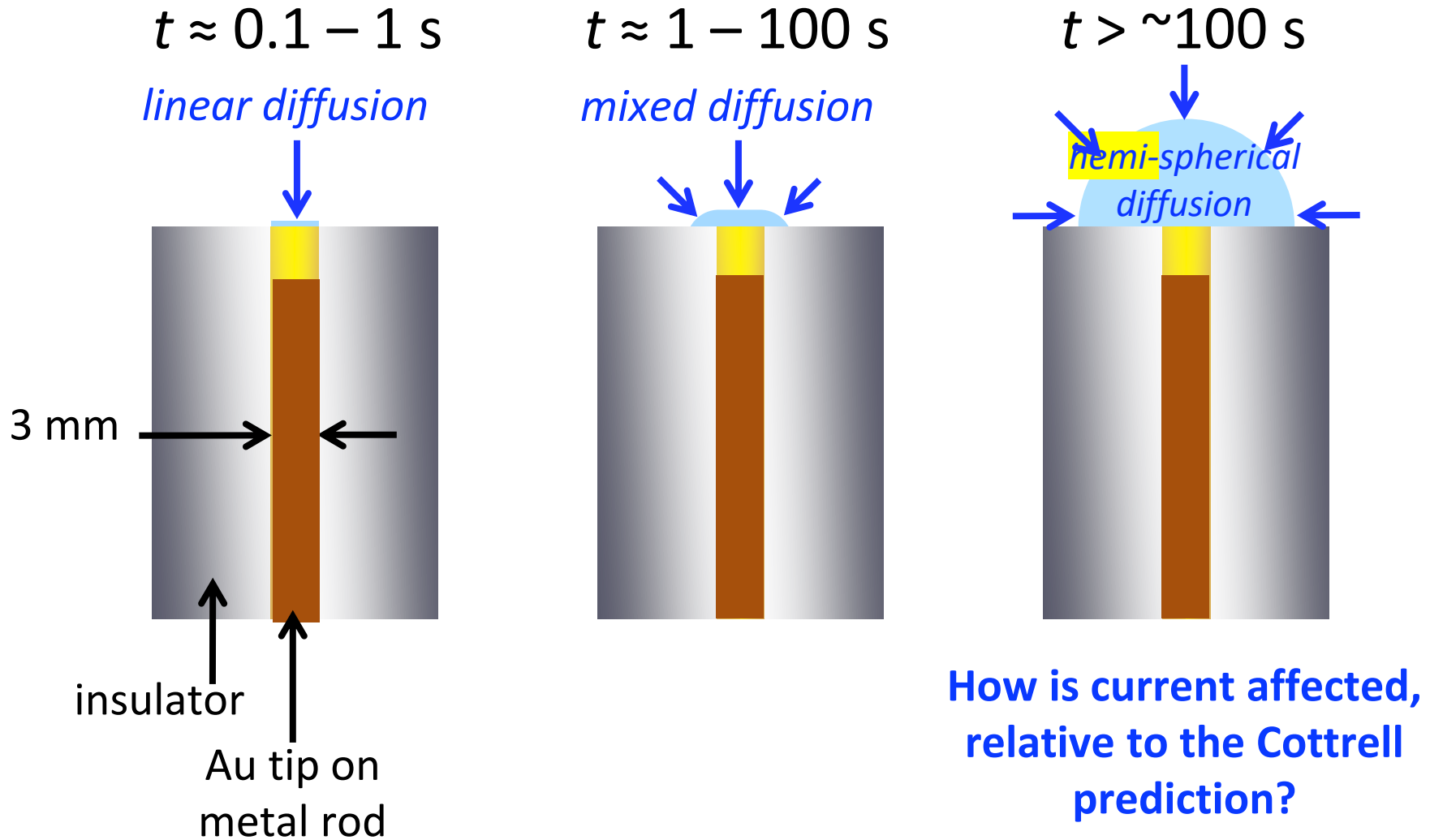we need to push this up in order to perform meaningful measurements of the kinetics of rapid redox reactions

Figure 3.4.1 Current-overpotential curves for the system $O + e \rightleftarrows R$ with $\alpha = 0.5$, $T = 298$ K, $i_{l,c} = -i_{l,a} = i_l$ and $i_0/i_l = 0.2$. The dashed lines show the component currents i_c and i_a.

… but deleterious edge effects also suggest an opportunity:

What if instead of avoiding radial diffusion, we exploit it?... Wait, what?

$t \approx 0.1 - 1$ s

linear diffusion

$t \approx 1 - 100$ s

mixed diffusion

$t > \sim 100$ s

hemi-spherical diffusion

3 mm

insulator

Au tip on metal rod

How is current affected, relative to the Cottrell prediction?

Let's design an experiment in which we intentionally operate in this
radial diffusion limit the "entire" time!

… well we actually start in the linear regime, and then switch over quickly…

side view   top view

10 nm – 50 μm

insulator

Au, C, Pt on metal rod
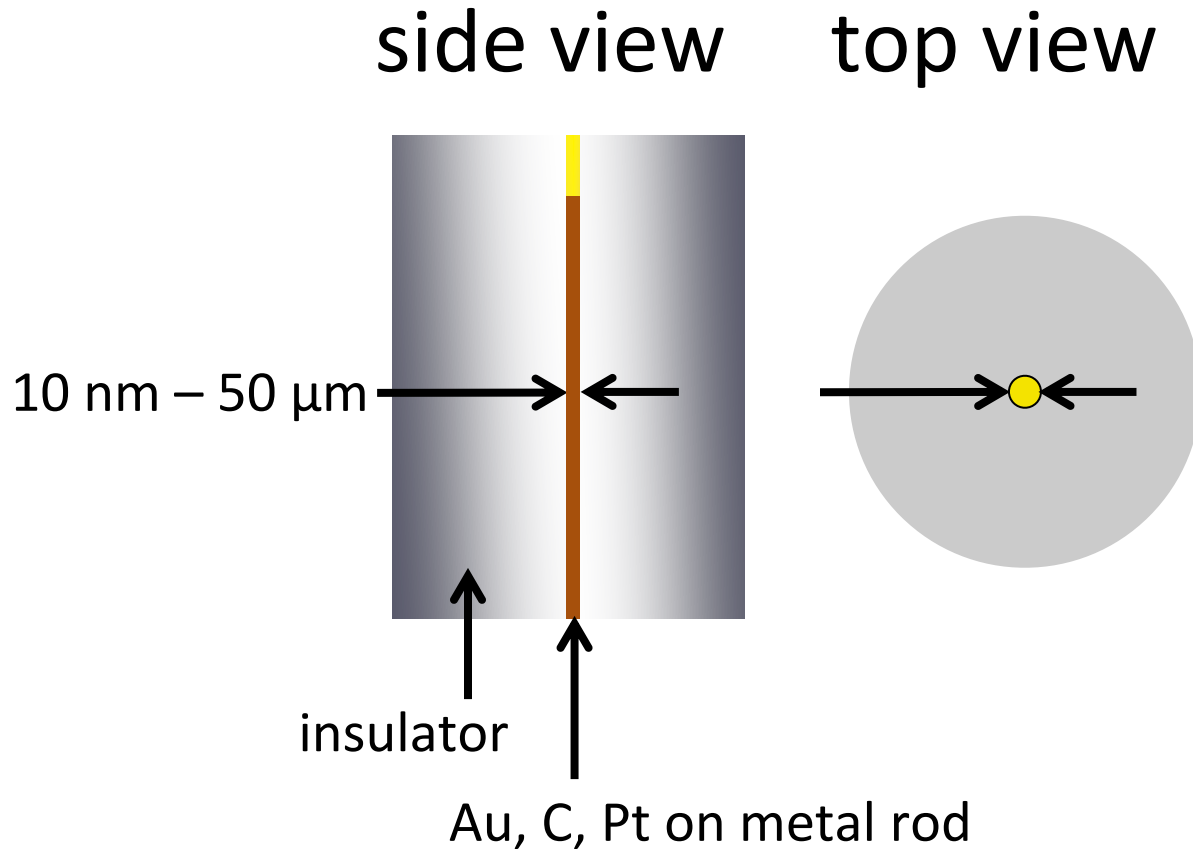
… called "ultramicroelectrodes" or "UMEs"

Recall that for linear diffusion from a plane, *current changes continuously with time…*
… this means:

$$\frac{\partial C(x,t)}{\partial t} = \boxed{0} = D\left(\frac{\partial^2 C(x,t)}{\partial x^2}\right) \text{ has no solution}$$
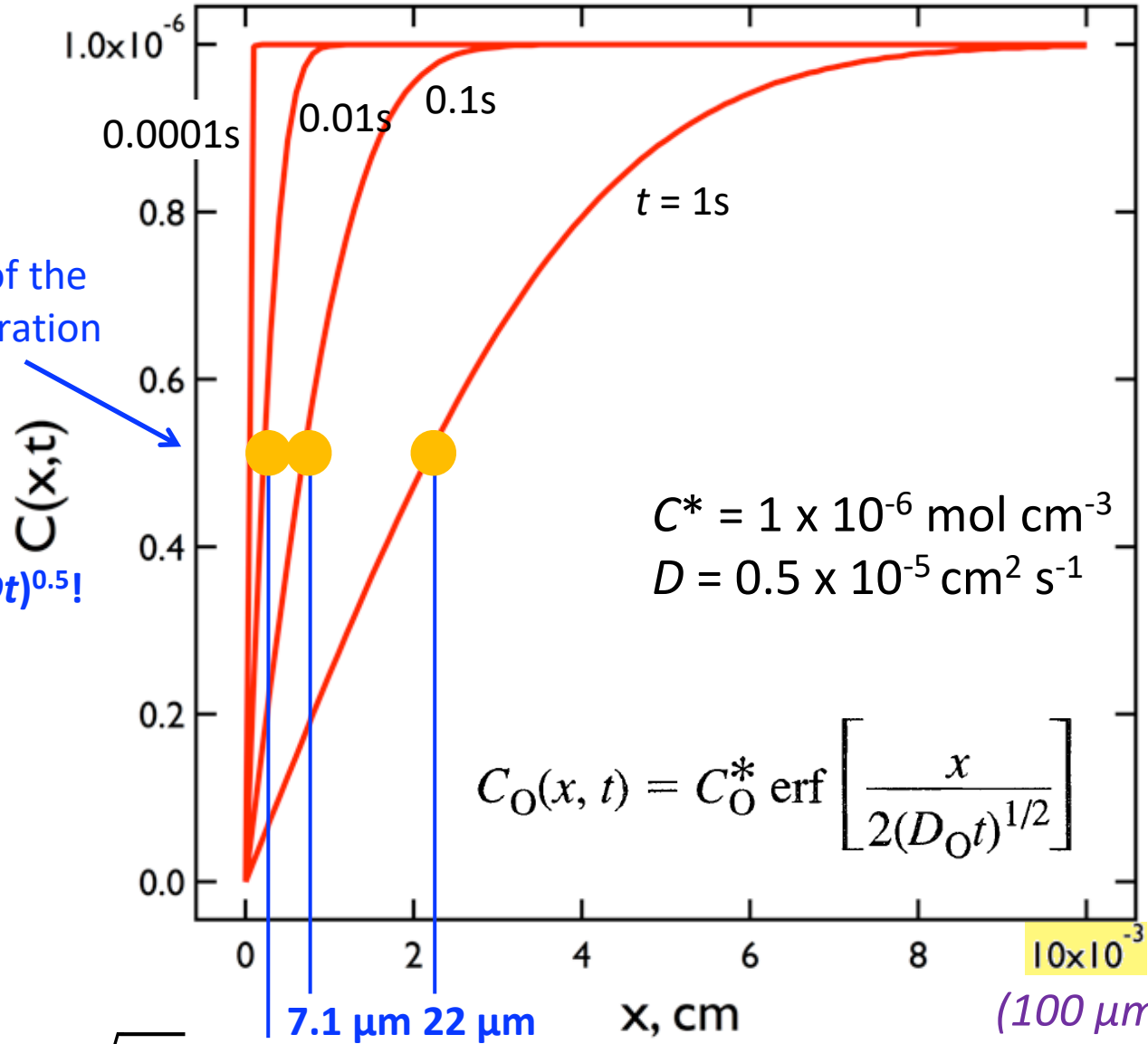
… but recall from Section 1.4.2 that the Nernst diffusion layer (δ) ends up reaching a steady-state distance due to natural convection that sets the boundary layer / stagnant layer…

… anyway, this doesn't help us simplify our experiment…

Why is 52% of the bulk concentration noteworthy?

Plug in $x = (Dt)^{0.5}$!
    … Ah ha!

C(x,t)

1.0×10^{-6}

0.0001s   0.01s   0.1s

$t = 1s$

0.8

0.6

0.4

0.2

0.0

$C^* = 1 \times 10^{-6}$ 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   2   4   6   8 10×10^{-3}

7.1 μm 22 μm   x, cm   (100 μm)

$\sqrt{Dt} = 2.2$ μm

… use the geometric area for calculations

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

the Cottrell Equation

$D = 1.5 \times 10^{-6}$ cm^2 s^{-1}

$D = 1.5 \times 10^{-5}$ cm^2 s^{-1}

Current, A/cm2

time, s

10×10^{-3}

(10 ms)
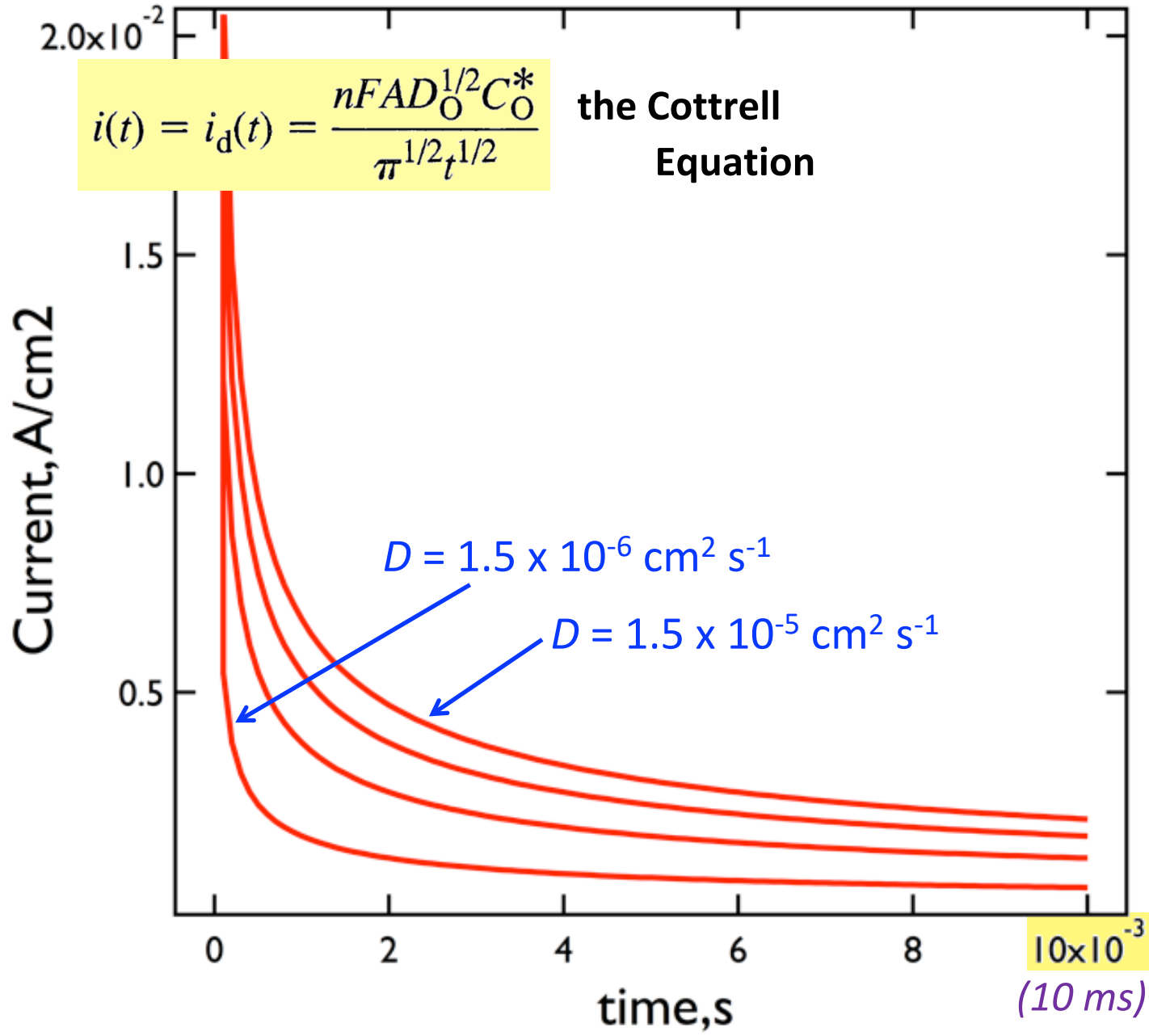
... but the same is <u>not true</u> for purely spherical diffusion:

$$\frac{\partial C(r,t)}{\partial t} = 0 = D\left(\frac{\partial^2 C(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial C(r,t)}{\partial r}\right)$$

... which has solutions:

$$C(r,t) = B + \frac{A}{r}$$

... so, for a spherical diffusion field:

$$\frac{\partial^2 C(r,t)}{\partial r^2} = \frac{2A}{r^3} \qquad \frac{\partial C(r,t)}{\partial t} = \frac{-A}{r^2}$$

and so...

$$\frac{\partial C(r,t)}{\partial t} = 0 = D\left(\frac{2A}{r^3} + \frac{2}{r}\left(\frac{-A}{r^2}\right)\right)$$

1. semi-infinite boundary condition…

$$C(r, t) = B + \frac{A}{r}$$

$$\lim_{r \to \infty} C(r, t) = C^* = B + 0$$

$$B = C^*$$

2. electrode surface (edge/circumference) boundary condition…

$$C(r_0, t) = 0 \qquad 0 = C^* + \frac{A}{r_0}$$

$$A = -C^* r_0$$

… so Fick's 2nd Law predicts that the steady-state concentration gradient is:

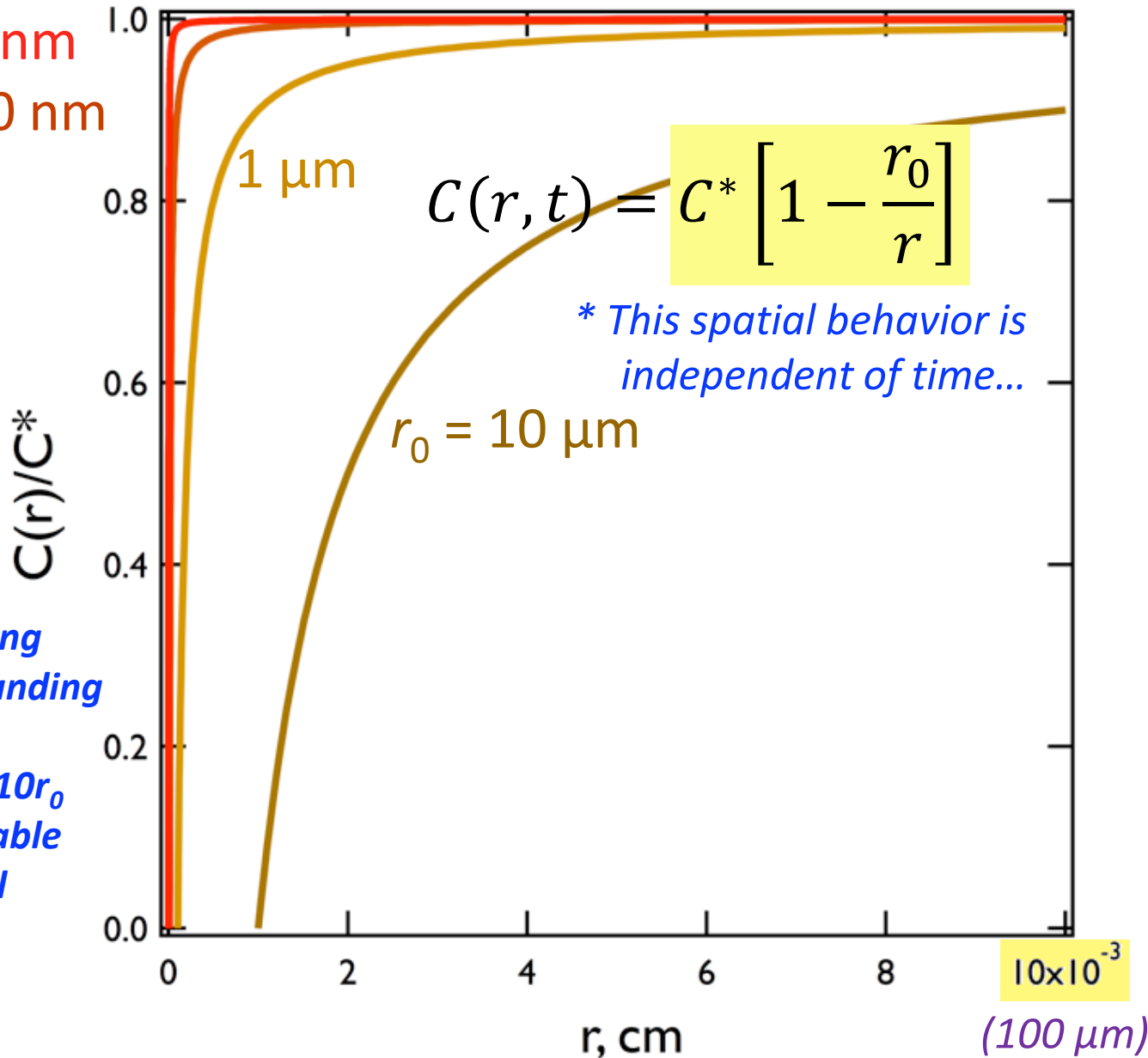$$C(r, t) = C^* - \frac{C^* r_0}{r} = C^* \left[1 - \frac{r_0}{r} \right]$$

… notice that here we can reach a *time-independent* condition!

… What?

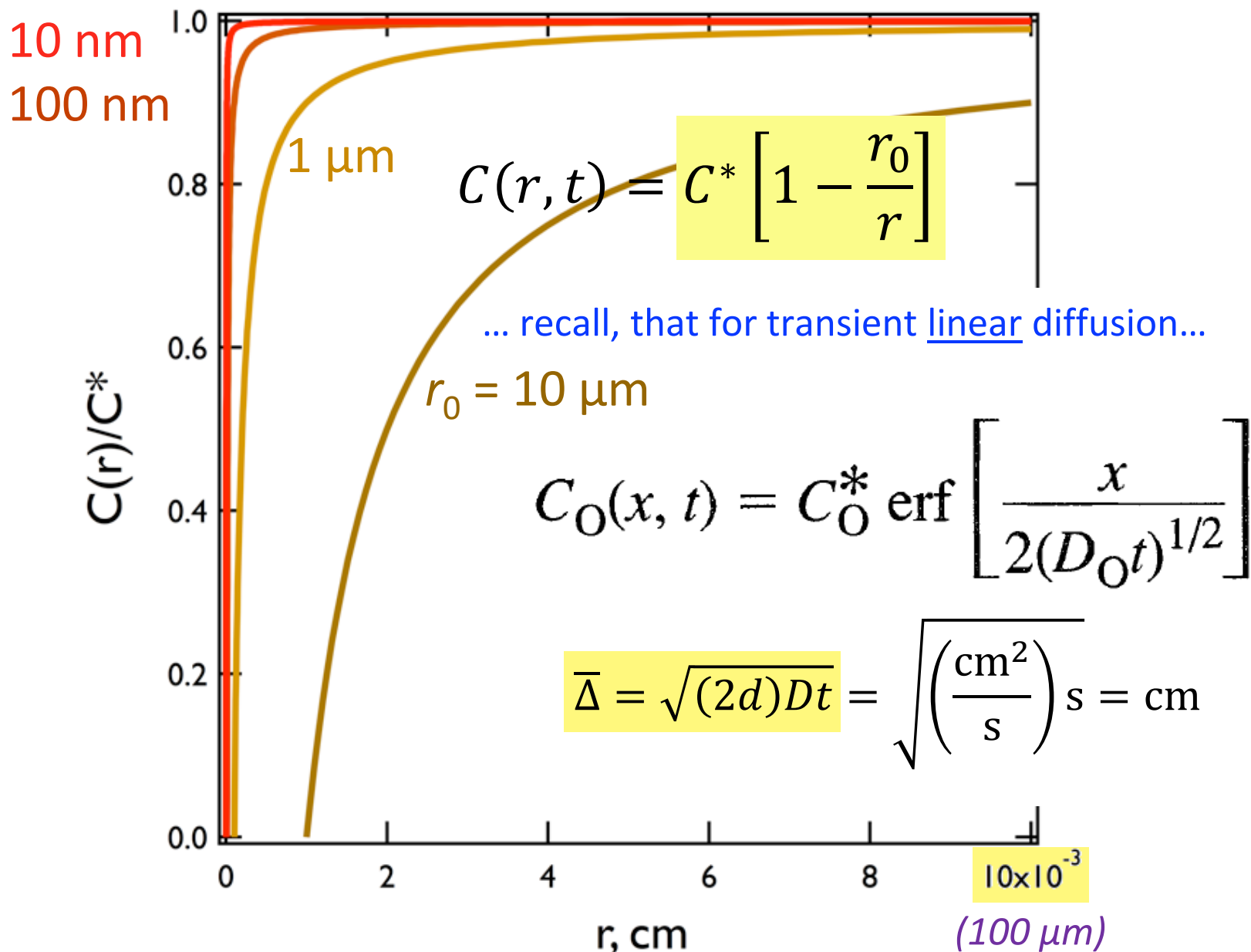... the diffusion layer "thickness" is **$2r_0$**, no matter how small r_0 is!

... at this distance, the concentration is 50% of the bulk... **Plug it in! ... Ah ha!**
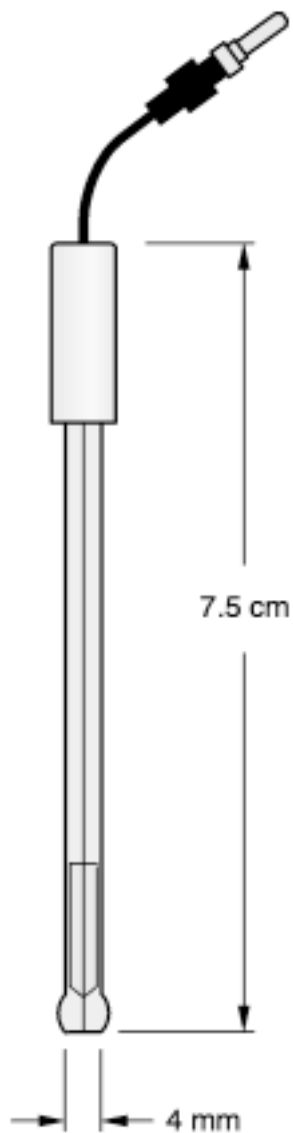
10 nm

100 nm

1 μm

$$C(r,t) = C^* \left[1 - \frac{r_0}{r} \right]$$

* This spatial behavior is independent of time...

r_0 = 10 μm

... the insulating shroud surrounding the electrode should be > ~$10r_0$ to observe stable hemispherical diffusion

C(r)/C*

r, cm

10×10^{-3}

(100 μm)

... the diffusion layer "thickness" is **$2r_0$**, no matter how small r_0 is!

10 nm

100 nm

1 μm

$$C(r,t) = C^* \left[1 - \frac{r_0}{r} \right]$$

... recall, that for transient <u>linear</u> diffusion...

r_0 = 10 μm

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

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

C(r)/C*

r, cm

10×10^{-3}

(100 μm)

Ordering Information [Get Prices]

MF-2005	10 µm diameter Platinum Microelectrode
MF-2006	10 µm diameter Gold Microelectrode
MF-2007	11 µm (±2 µm) diameter Carbon Fiber Microelectrode
MF-2150	100 µm diameter Platinum Microelectrode

Custom fabrication is available, e.g., 33 µm carbon, 25 µm silver, 25 µm gold, etc. Please Contact BASi to discuss your requirements.

7.5 cm

4 mm

E / V vs Ag|AgCl

A

E / V vs Ag|AgCl

B
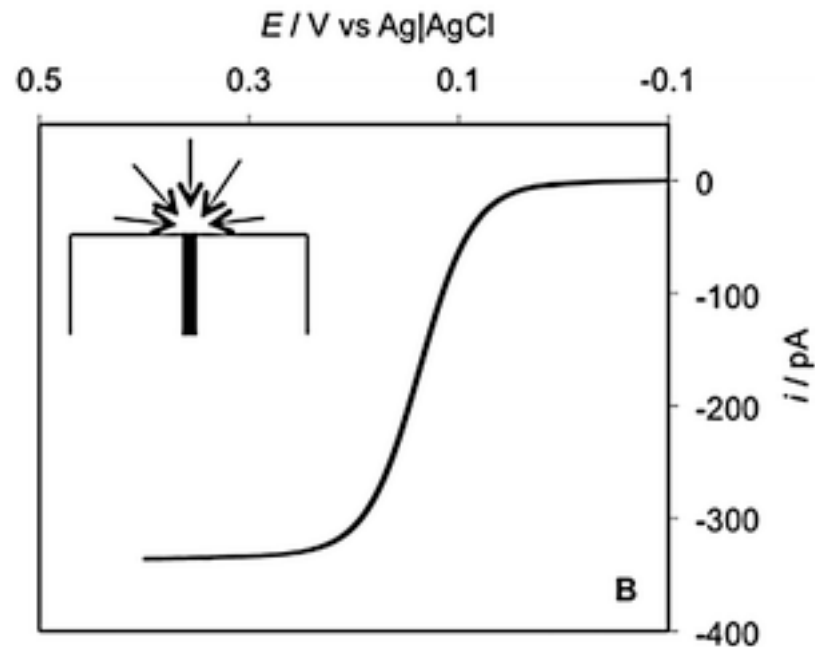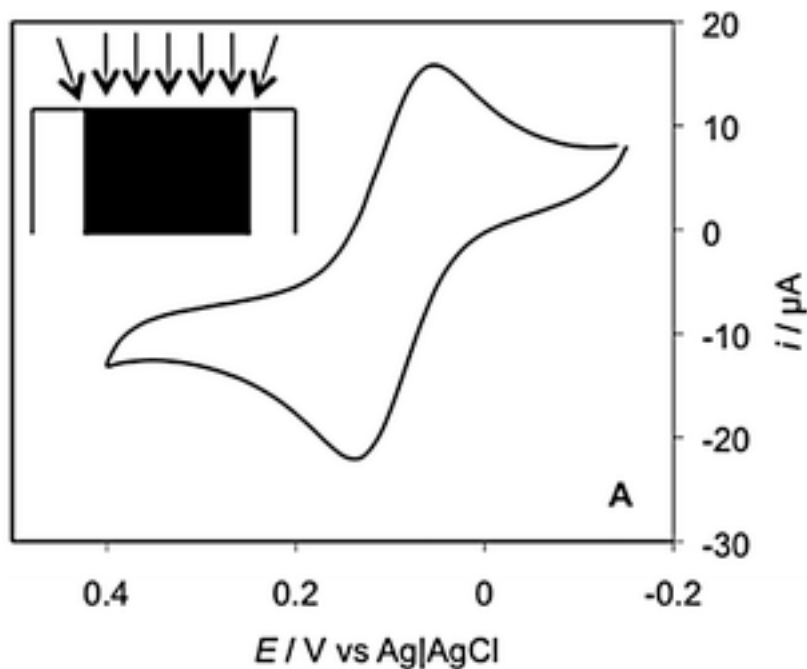
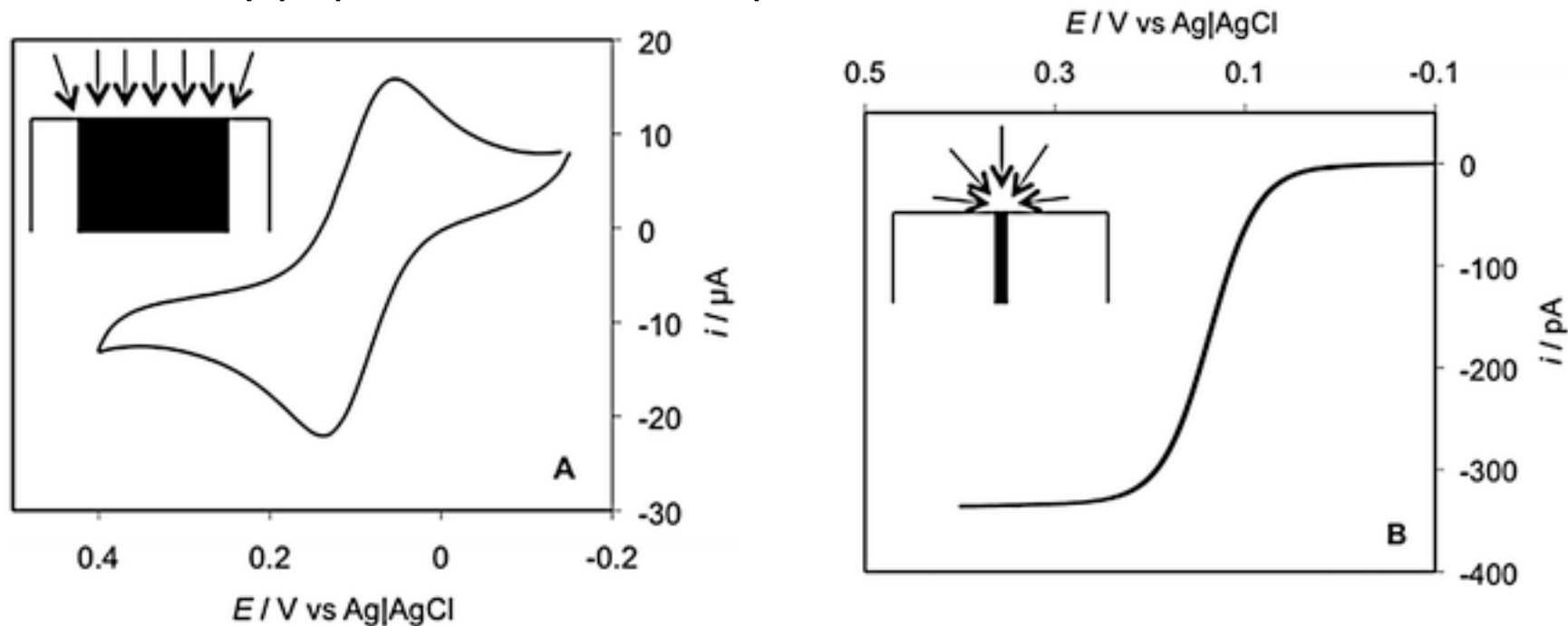**… steady-state is "often" reached at each applied potential at a UME during a sweep**

… Let's quantify it… steady-state occurs when $v \ll RTD/(nFr_0^2)$

… v (mV s^{-1}) $\ll$ 26 mV x (D/r_0^2)… for a *BASi* UME with $r_0 = 5\ \mu m$…

… 26 mV x $((0.5 \times 10^{-5}\ cm^2\ s^{-1}) / (0.5 \times 10^{-3}\ cm)^2)$ = 26 mV x $(20\ s^{-1})$

… $v \ll 0.5$ V s^{-1}… Wow, you can still scan quite fast!

Walsh, Lovelock, & Licence, *Chem. Soc. Rev.*, 2010, *39*, 4185

(1) Change sign of currents, because B&F indicates that positive current is cathodic
    … this is likely because electrons are the charge carrier of current
    … but physicists disagree; also, ions can be + or − so no need to focus on e⁻

(2) Mirror image the plot through the origin so that the axes look like math axes

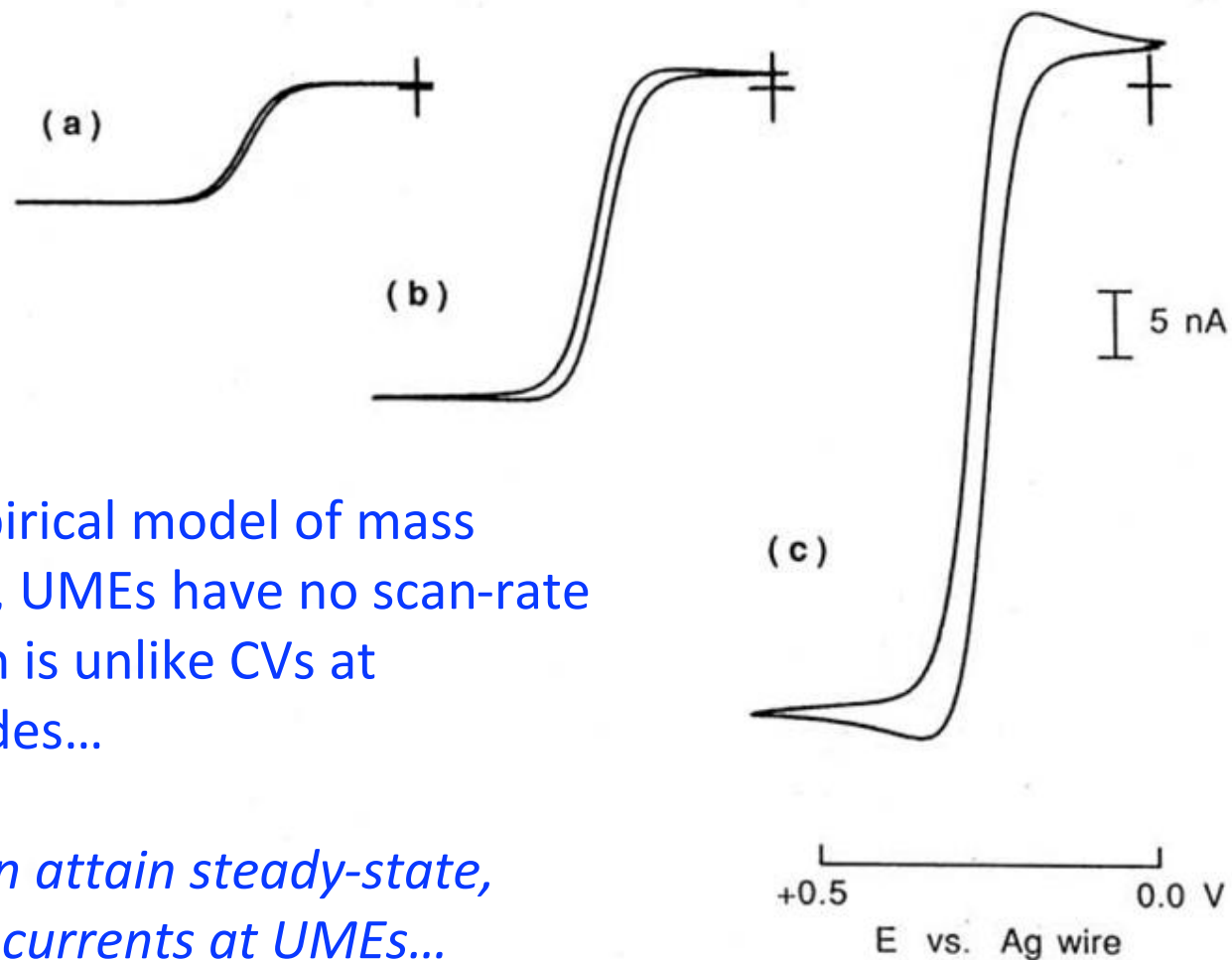Walsh, Lovelock, & Licence, *Chem. Soc. Rev.*, 2010, *39*, 4185
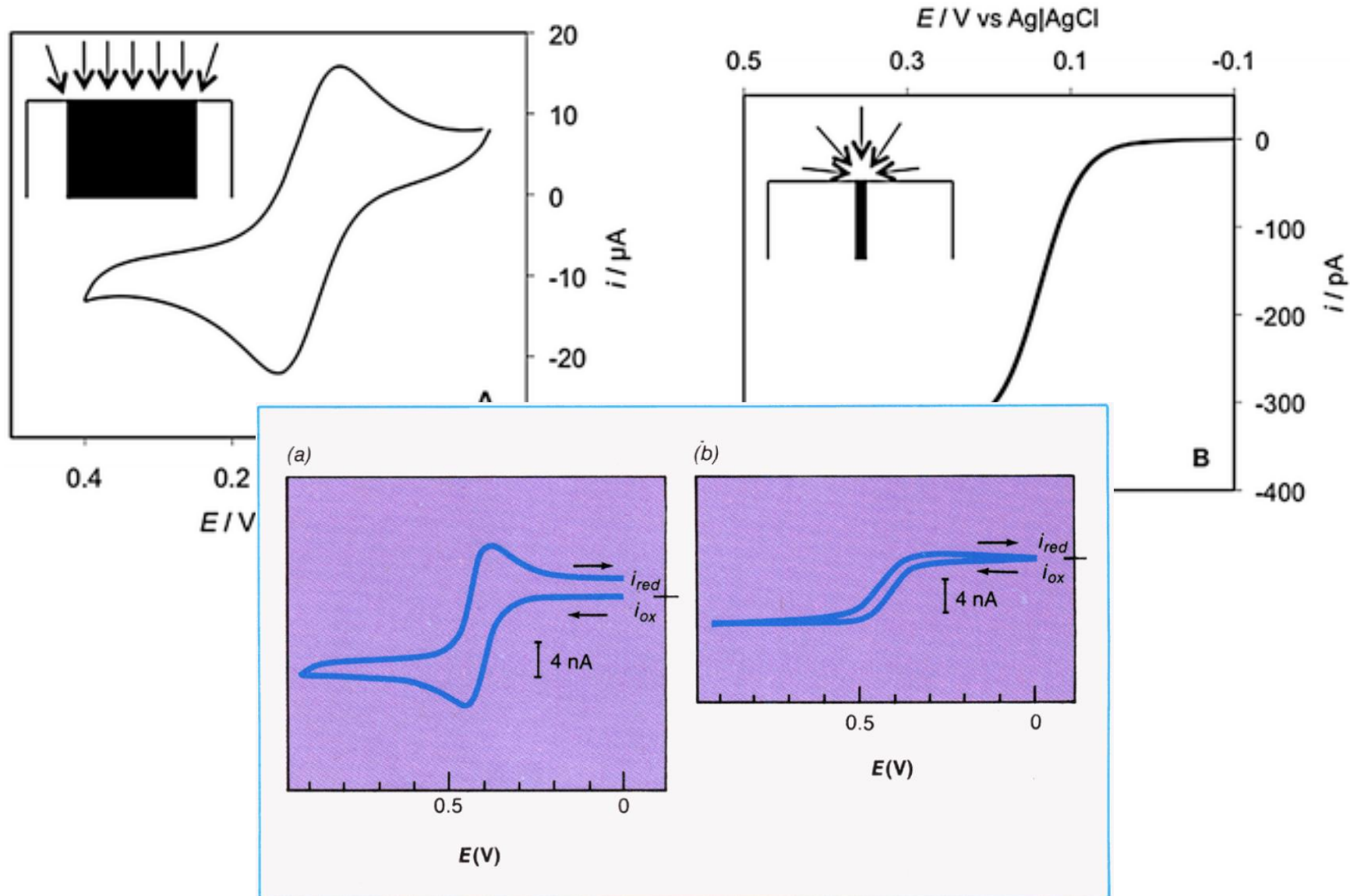
Figure 1. Cyclic voltammogram of ferrocene (1.0 mM) in acetonitrile with 0.1 M tetra-n-butylammonium perchlorate at a gold microdisk electrode ($r = 6.5\ \mu m$). (a) 10 V s^{-1} scan rate. (b) 0.1 V s^{-1} scan rate

Wightman, *Anal. Chem.*, 1981, *53*, 1125A

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Connecticut College, New London, CT 06320

(BRIEFLY)

… akin to the semi-empirical model of mass transfer (Section 1.4.2), UMEs have no scan-rate dependence to I_l, which is unlike CVs at traditional disk electrodes…
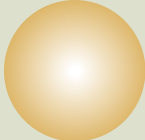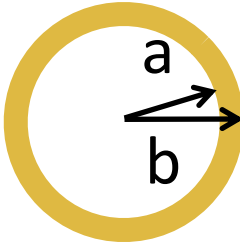
… this is because we can attain steady-state, mass-transport-limited currents at UMEs…

… without stirring at all!

Figure 3. Cyclic voltammograms of 1 mM ferrocene in 0.1 M TBAPF$_6$/CH$_3$CN solutions obtained with (a) 10; (b) 25; (c) 50 µm-diameter Pt disks. The scan rate in 50 mV/s.

Ching, Dudek, & Tabet, *J. Chem. Educ.*, 1994, *71*, 602

and the diffusion-limited current pre-factor depends on **electrode geometry**...

$$i_l = "x"nFDC^*r_0$$ ... but not scan rate!

electrode geometry	"x"	
sphere	4π	
hemisphere	2π	
disk	**4**	
ring	$\dfrac{\pi^2(b+a)}{r_0 \ln\left[16 \left. (b+a) \middle/ (b-a) \right.\right]}$	

... disk and ring–disk electrodes are real things that we will cover later