

470

Lecture #13 of 18(?)

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Time-Dependence in Electrochemistry

Chapters 4 and 5

471

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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

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473

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

473

The experiment we will model is a *potential step experiment*... 474
 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:

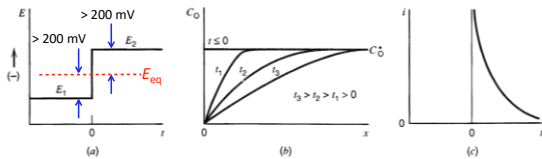


Figure 5.1.2 (a) Waveform for a step experiment in which species O is electroinactive at E_1 , but is reduced at a diffusion-limited rate at E_2 . (b) Concentration profiles for various times into the experiment. (c) Current flow vs. time.

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

474

Does this make sense? 475

RECALL:

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

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

... well, for large x , $\operatorname{erf} = 1$ ($\operatorname{erfc} = 0$) and so $C(x, t) = C^*$... Check!

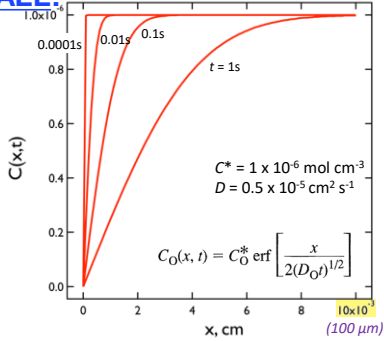
... and for $x = 0$, $\operatorname{erf} = 0$ ($\operatorname{erfc} = 1$) and so $C(x, t) = 0$... Check!

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

475

Hey, these look completely reasonable... and they are not exponential! 476

RECALL:



476

How large is the diffusion layer? Recall the rms displacement... 477

RECALL:

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

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

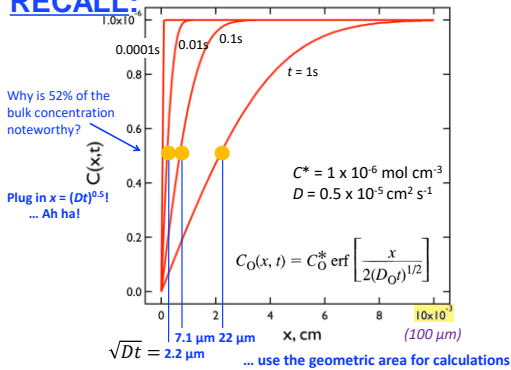
$\bar{\Delta} = \sqrt{(2d)Dt}$, where d is the dimension root mean square (rms) displacement (standard deviation)

... and the "2" is for positive and negative directions

477

Hey, these look completely reasonable for 1D diffusion in one direction! 478

RECALL:



478

OK... that's Step #1... Whoa! That was deep!... The last two steps are not... 479

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 \rightarrow

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

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

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

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... now Step #2...

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 $C_O(x, t)$:

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

... and so we need to evaluate:

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

480

480

... now Step #2...

RECALL:

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

... we use the *Leibniz rule*, to get $d/dx(\operatorname{erf}(x))$ 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...

481

481

OK... that's Steps #1 and 2...

482

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 \rightarrow

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

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

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

482

... and finally, Step #3 using Step #2...

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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.

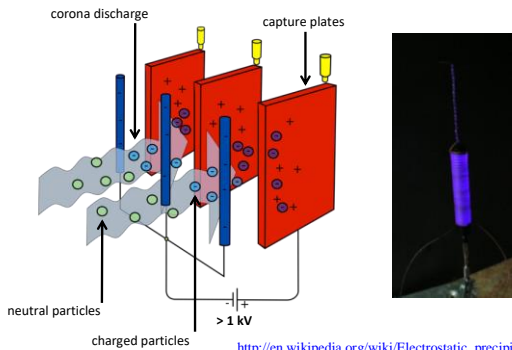
... established Research Corporation for Science Advancement in 1912

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

483

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

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Air Pollution Control Innovations

Wet electrostatic precipitator technology

Dr. Conrad applied wet electrostatic precipitator technology to the removal of sulfur and metal and lead oxide dust emitted from various packaging and printing activities. At the time, vineyards in Northern California were being adversely affected by the dust emissions. Dr. Conrad's innovative wet electrostatic precipitator solved their problem.



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Fast forward to the 2010's, Envitech brought the control of lead and sulfur dioxide to a new level by installing our most advanced wet electrostatic precipitator technology at an industrial facility in Southern California. The resulting wet electrostatic precipitator system which removes both sulfur dioxide and lead particles is said to be a new standard in air emission control at steel smelting, various refineries.

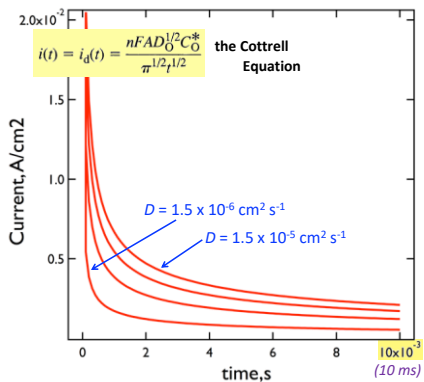
With over thirty years in the industry, we wanted to start sharing the knowledge and expertise that we have gained from solving gas stream air pollution control technologies.

Tags: wet electrostatic precipitators

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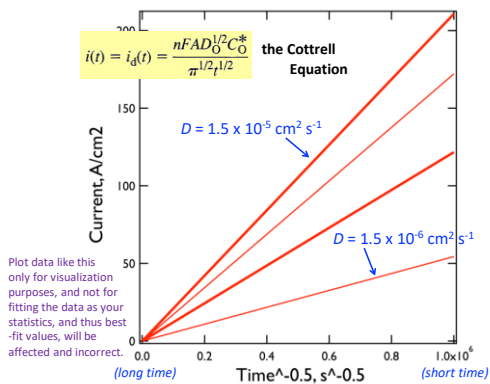
... OK, so what does it predict?



486

486

... OK, so what does it predict?

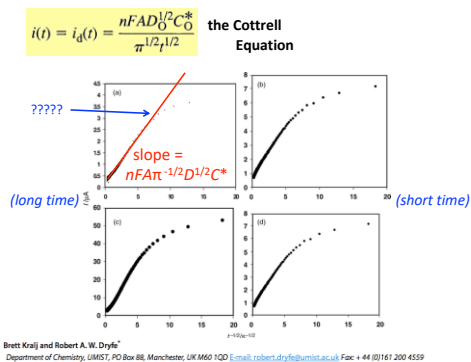


487

487

... OK, so what does it predict?

488



488

... use the Cottrell Equation to measure D , such as in thin films/coatings! 489
... but what are the problems with this approach?

$i(t) = i_d(t) = \frac{nFAD_0^{1/2}C_0^*}{\pi^{1/2}t^{1/2}}$ **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...

$Q_d = \frac{2nFAD_0^{1/2}C_0^*t^{1/2}}{\pi^{1/2}}$ **the integrated Cottrell Equation**

489

$Q_d = \frac{2nFAD_0^{1/2}C_0^*t^{1/2}}{\pi^{1/2}}$ **the integrated Cottrell Equation**

490

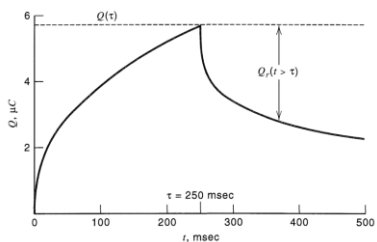


Figure 5.8.2
Chronocoulometric response for a double-step experiment performed on the system of Figure 5.8.1. The reversal step was made to 0.0 V vs. QRE. [Data courtesy of R. S. Glass.]

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

490

... this is called an Anson plot.

491

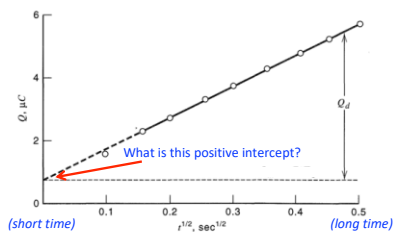


Figure 5.8.1 Linear plot of chronocoulometric response at a planar platinum disk. System is 0.95 mM 1,4-dicyanobenzene (DCB) in benzonitrile containing 0.1 M tetra-*n*-butylammonium fluoborate. Initial potential: 0.0 V vs. Pt QRE. Step potential: -1.892 V vs. Pt QRE. $T = 25^\circ\text{C}$, $A = 0.018$ cm². E^0 for DCB + e \rightleftharpoons DCB⁻ 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

491

... this is called an Anson plot.

492

$$Q = \frac{2nFAD_0^{1/2}C_0^*t^{1/2}}{\pi^{1/2}} + Q_{dl} + nFAT_0 \quad (5.8.2)$$

with T_0 , the surface excess of O (mol cm⁻²)

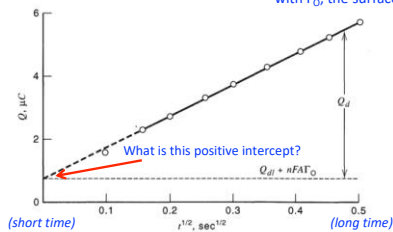


Figure 5.8.1 Linear plot of chronocoulometric response at a planar platinum disk. System is 0.95 mM 1,4-dicyanobenzene (DCB) in benzonitrile containing 0.1 M tetra-*n*-butylammonium fluoborate. Initial potential: 0.0 V vs. Pt QRE. Step potential: -1.892 V vs. Pt QRE. $T = 25^\circ\text{C}$, $A = 0.018$ cm². E^0 for DCB + e \rightleftharpoons DCB⁻ 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

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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

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

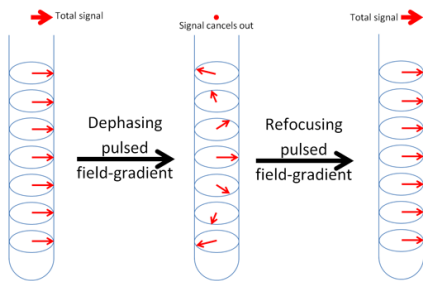
494

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

494

... how else can one calculate D ? ...
 ... how about not using electrochemistry, **but NMR instead**... What?
 ... Yes! Pulsed-Field Gradient (PFG) NMR!
 ... so, **without diffusion**...

495

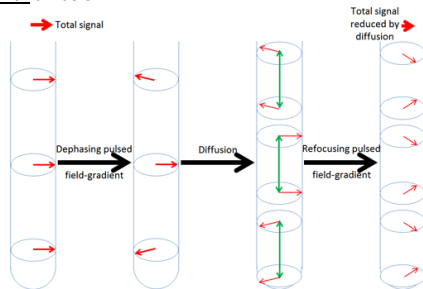


<http://chem.ch.huji.ac.il/nmr/techniques/other/diff/diff.html>
<http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3003887/>

495

... how else can one calculate D ? ...
 ... how about not using electrochemistry, **but NMR instead**... What?
 ... Yes! Pulsed-Field Gradient (PFG) NMR!
 ... and, **with diffusion**...

496

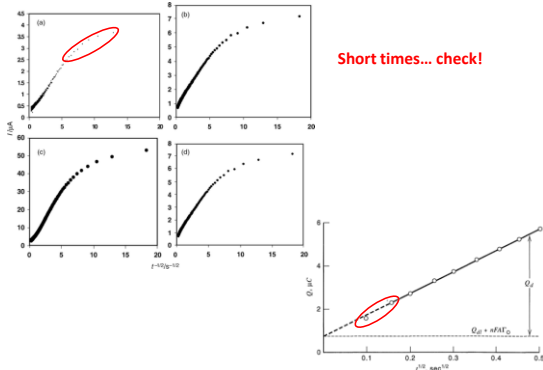


<http://chem.ch.huji.ac.il/nmr/techniques/other/diff/diff.html>
<http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3003887/>

496

So, where is the non-ideal data in a Cottrell and Anson plot?

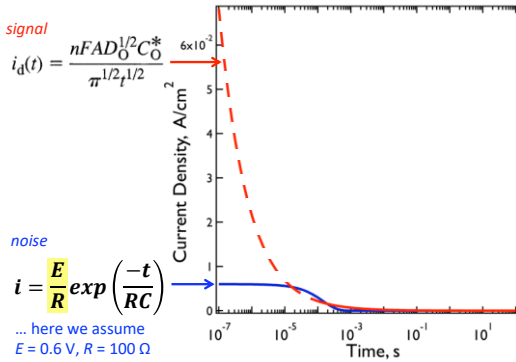
497



Short times... check!

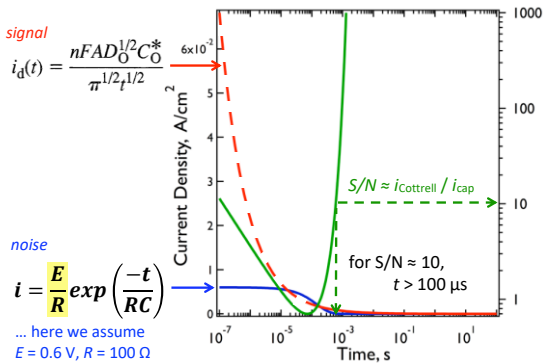
497

we have equations for the "signal" and the "noise," so... (UPDATED) 498
we can calculate the signal-to-noise ratio for a potential step experiment

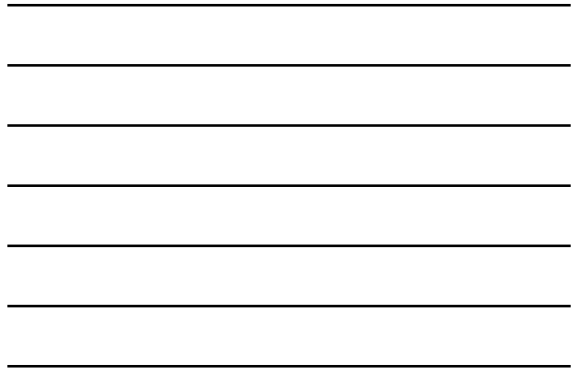


498

we have equations for the "signal" and the "noise," so... (UPDATED) 499
we can calculate the signal-to-noise ratio for a potential step experiment



499



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 $S/N \approx 10:1$?

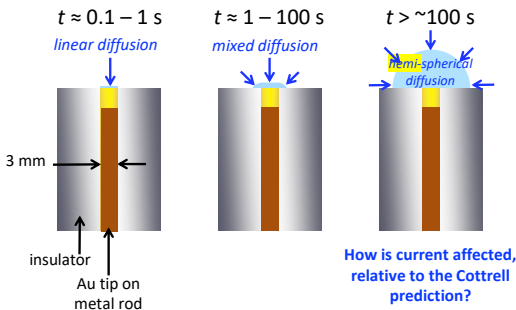
t (s)	\sqrt{Dt}	$\frac{\sqrt{Dt}}{r_0}$
0.1	0.0007 cm	0.005
1	0.0022 cm	0.015
10	0.0071 cm	0.047
100	0.022 cm (220 μm)	0.15

$D = 0.5 \times 10^{-5} \text{ cm}^2/\text{s}$
(lower bound for typical value)
 $r_0 = 0.15 \text{ cm}$
(value from previous slide)

Answer: $< \sim 10 \text{ s}$

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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*.



504

... 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 $\sim 1 - 10 \text{ s}$.
3. charging imposes a lower limit of $0.1 - 0.5 \mu\text{s}$ on this data acquisition time window.
4. **theoretically**, maximum current densities are $> 60 \text{ mA cm}^{-2}$ initially, but just $100 \mu\text{A cm}^{-2}$ at $S/N \approx 10$.

... but, why do we care?

505

Why do we care? One reason...

506

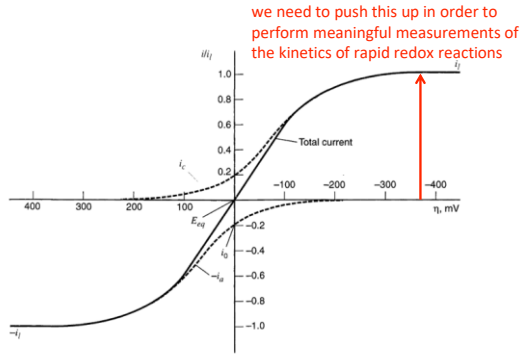
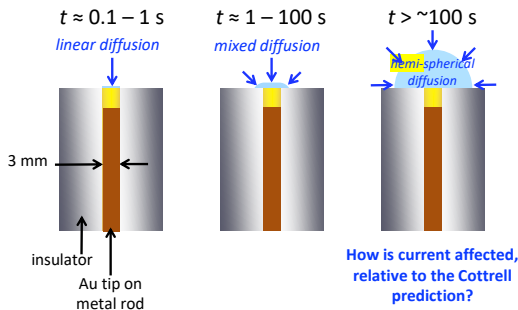


Figure 3.4.1 Current-overpotential curves for the system $O + e \rightleftharpoons R$ with $\alpha = 0.5$, $T = 298$ K, $i_{L,c} = -i_{L,a} = i_L$ and $i_0/i_L = 0.2$. The dashed lines show the component currents i_c and i_a .

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... but deleterious edge effects also suggest an opportunity: (UPDATED) 507

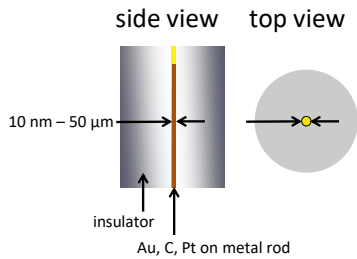
What if instead of avoiding radial diffusion, we exploit it?... Wait, what?



507

Let's design an experiment in which we intentionally operate in this radial diffusion limit the "entire" time! (UPDATED) 508

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



... called "ultramicroelectrodes" or "UMEs"

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Recall that for linear diffusion from a plane, *current changes continuously with time...* 509
 ... this means:

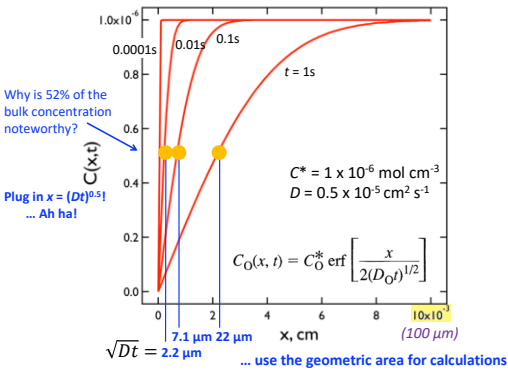
$$\frac{\partial C(x, t)}{\partial t} = 0 = D \left(\frac{\partial^2 C(x, t)}{\partial x^2} \right) \text{ has no solution}$$

... 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...

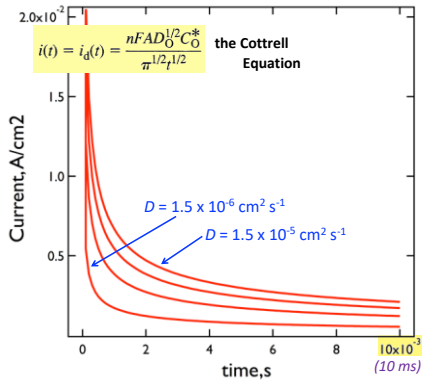
509

... the linear diffusion layer grows with time (indefinitely)... 510



510

... and thus linear-diffusion-controlled currents decay with time ("indefinitely")... 511



511

... but the same is not true for purely spherical diffusion:

512

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

... which has solutions:

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

... so, for a spherical diffusion field:

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

and so...

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

512

1. semi-infinite boundary condition...

$$C(r,t) = B + \frac{A}{r} \quad 513$$

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

$$B = C^*$$

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

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

$$A = -C^* r_0$$

... 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!

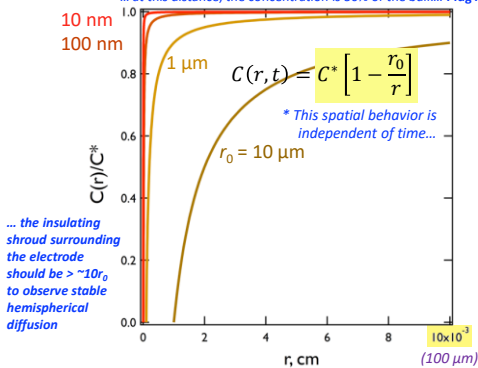
... What?

513

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

514

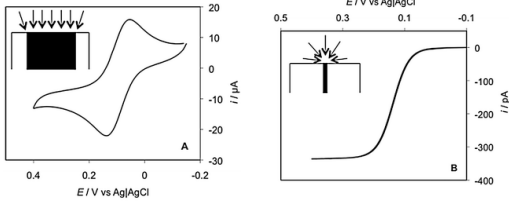
... at this distance, the concentration is 50% of the bulk... Plug it in! ... Ah ha!



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

514

... and back by popular demand: "Steps to convert TX to IUPAC" ..(BRIEFLY) 518



- (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

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... and back by popular demand: "Steps to convert TX to IUPAC" ..(BRIEFLY) 519

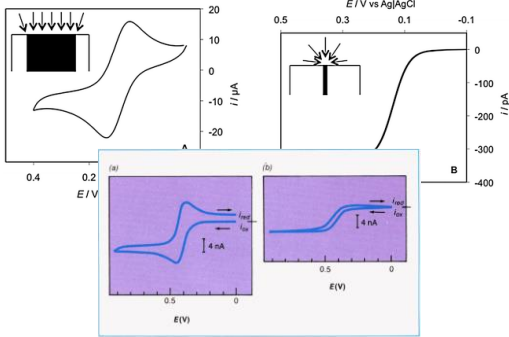


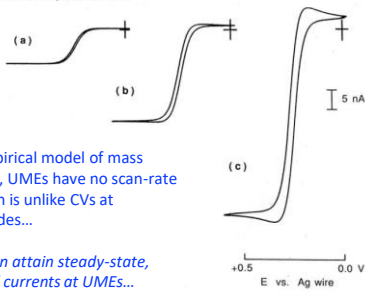
Figure 1. Cyclic voltammogram of ferrocene (1.0 mM) in acetonitrile with 0.1 M tetrabutylammonium perchlorate at a grid microdisk electrode ($r = 6.5 \mu\text{m}$). (a) 10 V s^{-1} scan rate. (b) 0.1 V s^{-1} scan rate

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

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Stanton Ching, Ray Dudek, and Elie Tabet
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_p , 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 TBAPF₆/CH₃CN solutions obtained with (a) 10; (b) 25; (c) 50 μm -diameter Pt disks. The scan rate is 50 mV/s.

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

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and the diffusion-limited current pre-factor depends on *electrode geometry*... 521

$$i_l = "x" n F D C^* r_0 \dots \text{but not scan rate!}$$

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

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

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