Read Section 5.9 and Chapter 13, answer the following problems, and indicate with whom you worked:
_____.

(1) Do problems 5.2, 5.16, 2.12, and 2.14 in Bard and Faulkner (B&F).
Answers:

Problem 5.2   The equations for planar and spherical diffusion are similar.

$$i(t) = nFADC^* \left[\frac{1}{\sqrt{\pi Dt}} + \frac{b}{r_0} \right] \tag{1}$$

where $b = 0$ for a planar electrode and $b = 1$ for a spherical electrode. The currents for each are shown in the spreadsheet. Note that for $A = 0.02 \text{ cm}^2 = 4\pi r_0^2$, the radius of the spherical electrode is $r_0 = 0.040$ cm.

n	1
C*	$1.00\text{E-}06$ mol/cm^3
A	0.02 cm^2
D	$1.00\text{E-}05$ cm^2/s
F	96485 C/mol
nFAC*D	$1.93\text{E-}08$ Acm
r_0	0.04 cm

t(s)	$i_{planar}(\mu A)$	$i_{spherical}(\mu A)$
0.1	10.89	11.37
0.5	4.87	5.35
1	3.44	3.93
2	2.43	2.92
3	1.99	2.47
5	1.54	2.02
10	1.09	1.57
20	0.77	1.25
30	0.63	1.11
inf	0.00	0.48
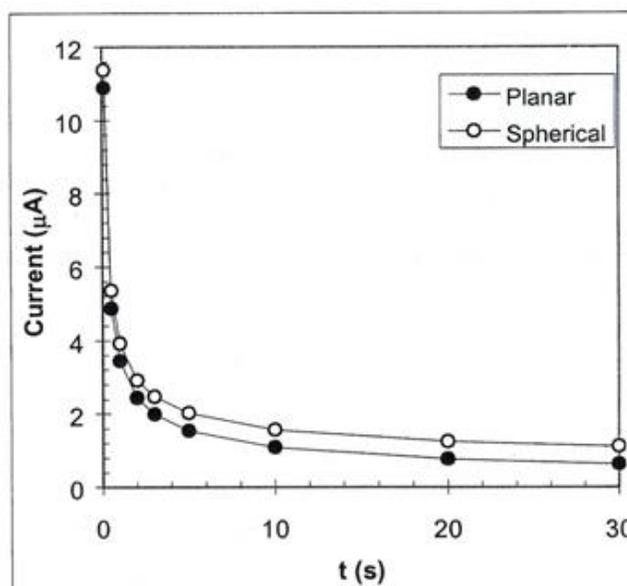
The electrolysis at the spherical electrode exceeds that at the planar electrode by 10% when

$$\frac{i_{spherical}}{i_{planar}} = \frac{\frac{1}{\sqrt{\pi Dt}} + \frac{1}{r_0}}{\frac{1}{\sqrt{\pi Dt}}} > 1.1 \tag{2}$$

$$\frac{1}{r_0} > 0.1 \frac{1}{\sqrt{\pi Dt}}$$

$$10\sqrt{\pi Dt} > r_0$$

$$t > \frac{r_0^2}{10^2 \pi D}$$

For this system, this corresponds to

$$t > \frac{(0.04)^2}{100\pi \times 10^{-5}} = 0.51s \qquad (3)$$

This is consistent with the values shown in the spreadsheet for $t = 0.5$ s.

Cottrell's equation (equation (5.2.11)) is

$$i(t) = \frac{nFAC^*\sqrt{D}}{\sqrt{\pi t}} \qquad (5.2.11)$$

This integrates with respect to t to yield the charge.

$$q(t) = \frac{2nFAC^*\sqrt{Dt}}{\sqrt{\pi}} \qquad (4)$$

For $t = 10$ s and the values listed above, $q(t) = 2.2 \times 10^{-5}$ C. Faraday's Law, $Q/nF = $ moles electrolyzed, yields 2.3×10^{-10} moles. In 10 mL of 1 mM solution, there are 10^{-5} moles of material. In 10 s, the fraction electrolyzed is $2.3 \times 10^{-10}/10^{-5}$ or 0.0023% . Thus, under conditions for normal voltammetric measurements, the bulk concentration of the redox species is not perturbed significantly.

Problem 5.16   From the caption of Figure 5.8.3, for the forward step, the slope is 9.89×10^{-6} $C/s^{1/2}$ and the intercept is 7.9×10^{-7} C. From equation (5.8.2) for the forward step, the charge is

$$Q(t) = \frac{2nFAC_O^0\sqrt{D_Ot}}{\sqrt{\pi}} + Q_{dl} + nFA\Gamma_O \qquad (5.8.2)$$

From Figure 5.8.1, $n = 1$, $A = 0.018$ cm^2, and $C_O^* = 0.95 \times 10^{-6}$ mol/cm^3. The potential is stepped -260 mV past $E^{0'}$, so that the step is to the mass transport limit. Thus, from $Q(t)$ vs. $\sqrt{t}$,

$$\begin{aligned}
D_O &= \left[\frac{slope\sqrt{\pi}}{2nFAC_O^*}\right]^2 = \left[\frac{(9.89 \times 10^{-6}\ C/\sqrt{s})\sqrt{\pi}}{2 \times 1 \times (96485\ C/mol)\,(0.018\ cm^2)\,(0.95 \times 10^{-6}\ mol/cm^3)}\right]^2 \\
&= 2.82 \times 10^{-5}\ cm^2/s \qquad (1)
\end{aligned}$$

Typical values of diffusion coefficients in solution are of the order of 10^{-5} to 10^{-6} cm^2/s, with diffusion coefficients in most volatile (less viscous) organics faster than those in water. The most common source of error in calculating diffusion coefficients is using units of M instead of mol/cm^3 for the concentration.

A comparison of equations (5.8.2) and (5.8.6) indicates that the slopes for the forward and reverse steps should be equal if the system is characterized by simple mass transport limited oxidation and reduction. The slope reported for the oxidation is about 5% lower than that for the reduction. The intercepts for the reduction and oxidation are, respectively, 7.9×10^{-7} C and 6.6×10^{-7} C.

One possible cause of the differences in slopes and intercept is that the oxidized species DCB adsorbs whereas the reduced species DCB$^{\bullet}$ either does not adsorb or adsorbs less than DCB. If the surface excess for the two forms differ, then this is reflected in the difference in the intercepts for the forward and reverse steps. If the adsorption associated with the forward step is extensive enough, it can disturb the concentration profile sufficiently that the concentration profile of R is disrupted from that expected for a simple mass transport limited reaction.

An alternative reason for the difference in the slopes is that DCB$^{\bullet}$ is being consumed through a chemical reaction so that its concentration is less than that of DCB. Here, the formal potential is sufficiently negative that trace oxygen could react with DCB$^{\bullet}$.

Problem 5.16 (cont'd).

Other explanations that make sense include that the gunk on the surface from the redox chemistry changed the active area and that the bulk concentration is not as well-defined for the revere reaction and so that concentration may change during the measurements.

Problem 2.12   The total charge passed through the cell consists of the two components representing ionic (q_{ion}) and electronic (q_{el}) conduction.

$$q = q_{ion} + q_{el} \tag{1}$$

The q_{ion} component is due to a faradaic process (i.e., reduction of silver) and can be calculated as follows for $q_{ion} = nF \times moles$ where here $n = 1$.

$$q_{ion} = 1 \times 96485 \ C/mol \times \frac{1.12 \ g - 1.00 \ g}{107.87 \ g/mol} = 107.83 \ C \tag{2}$$

The total charge passed is $q = 0.2A \times 600s = 120C$. Thus,

$$q_{el} = 120 \ C - 107.83 \ C = 12.67 \ C \tag{3}$$

and

$$\frac{q_{el}}{q} = \frac{12.67 \ C}{120 \ C} = 0.106 \tag{4}$$

gives the fraction of the current passing through the cell due to electronic conduction.

Problem 2.14   **(a).** Type 2, common anion. From equation (2.3.40),

$$E_j = -\frac{RT}{F} \ln \frac{\Lambda_{NaCl}}{\Lambda_{HCl}} \tag{1}$$

From equation (2.3.14) and using Table 2.3.2,

$$
\begin{aligned}
\Lambda_{NaCl} &= \lambda_{Na^+} + \lambda_{Cl^-} = 50.11 + 76.34 = 126.45 \\
\Lambda_{HCl} &= \lambda_{H^+} + \lambda_{Cl^-} = 349.82 + 76.34 = 426.16
\end{aligned}
\tag{2}
$$

Substitution leads to $E_j = 31.2$ mV. The junction is dominated by the very mobile H^+, which tends to place a positive net charge in the right hand phase.

(c). Type 3. From the Hendersen equation (2.3.39), $E_j = 46.2$ mV. The junction is dominated by mobile OH^- which deposits a net negative charge on the left- hand phase. The situation is analogous to (b), but OH^- is not as mobile as H^+, hence E_j is lower here than in (b).

(b) HCl (0.1 M) / NaCl (0.01 M) is a Type 3 liquid junction because both the cation and the anion will diffuse. Thus, $E_j =$

$$\frac{\left\{\frac{|z_{H^+}|\mu_{H^+}}{z_{H^+}}\left(c_{H^+}^\beta - c_{H^+}^\alpha\right)\right\}+\left\{\frac{|z_{Cl^-}|\mu_{Cl^-}}{z_{Cl^-}}\left(c_{Cl^-}^\beta - c_{Cl^-}^\alpha\right)\right\}+\left\{\frac{|z_{Na^+}|\mu_{Na^+}}{z_{Na^+}}\left(c_{Na^+}^\beta - c_{Na^+}^\alpha\right)\right\}}{\left\{|z_{H^+}|\mu_{H^+}\left(c_{H^+}^\beta - c_{H^+}^\alpha\right)\right\}+\left\{|z_{Cl^-}|\mu_{Cl^-}\left(c_{Cl^-}^\beta - c_{Cl^-}^\alpha\right)\right\}+\left\{|z_{Na^+}|\mu_{Na^+}\left(c_{Na^+}^\beta - c_{Na^+}^\alpha\right)\right\}}\frac{RT}{F}\ln\left(\frac{\left\{|z_{H^+}|\mu_{H^+}c_{H^+}^\alpha\right\}+\left\{|z_{Cl^-}|\mu_{Cl^-}c_{Cl^-}^\alpha\right\}+\left\{|z_{Na^+}|\mu_{Na^+}c_{Na^+}^\alpha\right\}}{\left\{|z_{H^+}|\mu_{H^+}c_{H^+}^\beta\right\}+\left\{|z_{Cl^-}|\mu_{Cl^-}c_{Cl^-}^\beta\right\}+\left\{|z_{Na^+}|\mu_{Na^+}c_{Na^+}^\beta\right\}}\right)$$

$$E_j = \frac{\left\{\frac{(1)(3.625\cdot10^{-3})}{1}(0-0.1)\right\}+\left\{\frac{(1)(7.912\cdot10^{-4})}{-1}(0.01-0.1)\right\}+\left\{\frac{(1)(5.193\cdot10^{-4})}{1}(0.01-0)\right\}}{\{(1)(3.625\cdot10^{-3})(0-0.1)\}+\{(1)(7.912\cdot10^{-4})(0.01-0.1)\}+\{(1)(5.193\cdot10^{-4})(0.01-0)\}}\cdot$$
$$0.05916\log\left(\frac{\{(1)(3.625\cdot10^{-3})(0.1)\}+\{(1)(7.912\cdot10^{-4})(0.1)\}+\{(1)(5.193\cdot10^{-4})(0)\}}{\{(1)(3.625\cdot10^{-3})(0)\}+\{(1)(7.912\cdot10^{-4})(0.01)\}+\{(1)(5.193\cdot10^{-4})(0.01)\}}\right)$$

$$E_j = \frac{-(3.625\cdot10^{-4})+(7.1208\cdot10^{-5})+(5.193\cdot10^{-6})}{-(3.625\cdot10^{-4})-(7.1208\cdot10^{-5})+(5.193\cdot10^{-6})}\cdot 0.05916\log\left(\frac{(3.625\cdot10^{-4})+(7.912\cdot10^{-5})+(0)}{(0)+(7.912\cdot10^{-6})+(5.193\cdot10^{-6})}\right)$$

$$E_j = \frac{-2.86099\cdot10^{-4}}{-4.28515\cdot10^{-4}}\cdot 0.05916\log\left(\frac{4.4162\cdot10^{-4}}{1.3105\cdot10^{-5}}\right) = 0.060338 \approx \mathbf{60\ mV}$$

(d) NaNO$_3$ (0.1 M) / NaOH (0.1 M) is a Type 2 liquid junction because only the anion will diffuse.

Thus, $E_j = \frac{RT}{F}\ln\left(\frac{|z_{NO_3^-}|\mu_{NO_3^-}c_{NO_3^-}^\alpha}{|z_{OH^-}|\mu_{OH^-}c_{OH^-}^\beta}\right) = 0.05916\log\left(\frac{(1)(7.404\cdot10^{-4})(0.1)}{(1)(2.05\cdot10^{-3})(0.1)}\right) = -0.026166 \approx \mathbf{26\ mV}$

Thus, it means that in all cases the right-hand side is positive with-respect-to the left-hand side based on the typical convention.

(2) What is the iR_u drop for a disk UME immersed in *deionized water* when it reaches steady-state mass-transport-limited current? (Assume that the resistivity of deionized water is ~18.3 MOhm cm – which it is for laboratory deionized water – and that the redox species are not charged, participate in one-electron-transfer reactions, have a diffusion coefficient of 10^{-5} cm^2 s^{-1}, and are present at 1 µM.)

Answer: The conductivity of deionized water is the inverse of the resistivity and so $\kappa = 5.46$ x 10^{-8} S cm^{-1}. Then, $i_l = 4nFDC^*r_0 = 4(1)(96485)(10^{-5})(10^{-6}$ x $10^{-3})r_0$, and $R_u = (4\pi\kappa r_0)^{-1} = (4(3.14159265)(5.46$ x $10^{-8})r_0)^{-1}$. Thus, $i_l R_u = \frac{4(1)(96485)(10^{-14})r_0}{4(3.14159265)(5.46\cdot10^{-8})r_0} = \frac{(96485)(10^{-6})}{(3.14159265)(5.46)} = $
5.6 mV. Wow, that is small! I should have asked this problem using a Luggin capillary and then the usual resistance–resistivity equation could have been used and l and r_0 would have cancelled out; next year!

(3) A Cottrell plot (i versus $t^{-1/2}$) for data measured at a disk UME ($r_0 = 1$ µm) exhibits a slope of 0.022944 $^{nC}/_{\sqrt{s}}$ and a y-intercept of 2.31564 nA.
   a. Determine the value of the diffusion coefficient.

Answer: The slope is $m = \frac{nFA\sqrt{D}C^*}{\sqrt{\pi}}$, and so $nFC^* = \frac{m\sqrt{\pi}}{A\sqrt{D}} = \frac{m\sqrt{\pi}}{\pi r_0^2 \sqrt{D}} = \frac{m}{\sqrt{\pi}r_0^2\sqrt{D}}$. Because the

y-intercept is $b = 4nFDC^*r_0$, $b = 4Dr_0\frac{m}{\sqrt{\pi}r_0^2\sqrt{D}} = \frac{4\sqrt{D}m}{\sqrt{\pi}r_0}$, and so $\sqrt{D} = \frac{b\sqrt{\pi}r_0}{4m}$ and thus

$D = \frac{b^2\pi r_0^2}{16m^2} = \frac{(2.31564)^2\pi(10^{-4})^2}{16(0.022944)^2} = \frac{(2.31564)^2\pi(10^{-4})^2}{16(0.022944)^2} = \mathbf{2\cdot 10^{-5}\ cm^2\ s^{-1}}$.

b. If the concentration of redox-active species is 1 mM, how many electrons are transferred per redox event?

Answer: One can use either the slope or y-intercept formula. Using the latter, $n =$
$\frac{b}{4FDC^*r_0} = \frac{2.31564}{4(96485)(2\cdot 10^{-5})(10^{-3}\cdot 10^{-3})(10^{-4})} = \frac{2.31564}{4(96485)(2\cdot 10^{-5})(10^{-3}\cdot 10^{-3})(10^{-4})} = \mathbf{3}$.

c. What would the value of the slope be for the corresponding Anson plot (q versus $t^{1/2}$) at early, non-steady-state times?

Answer: Two times larger, $m = \mathbf{0.045888}\ ^{nC}/_{\sqrt{s}}$.

(4) A dialysis bag is filled with 100 mM dianionic protein with sodium counterions and immersed in an aqueous electrolyte containing 1 mM NaCl. Assuming the concentration of NaCl in the electrolyte remains the same and the protein is too large to diffuse out of the bag, answer the following questions when the system is at equilibrium.
  a. What is the concentration of Cl^- in the bag?

Answer: From the lecture notes, $c_{Cl^-}^m = \frac{c_{R^-}^m}{2}\left(\sqrt{1 + 4\left(\frac{c_{Cl^-}^s}{c_{R^-}^m}\right)^2} - 1\right) =$

$\frac{2c_{Protein}^m}{2}\left(\sqrt{1 + 4\left(\frac{c_{Cl^-}^s}{2c_{Protein}^m}\right)^2} - 1\right) = \frac{0.2}{2}\left(\sqrt{1 + 4\left(\frac{0.001}{0.2}\right)^2} - 1\right) = 4.9999\cdot 10^{-6}\ M = \mathbf{5\ \mu M}$

b. What is the Donnan potential? Calculate this using the $[Na^+]$, and verify your answer by then calculating the Donnan potential using the $[Cl^-]$.

Answer: $E_{Donnan} = -\frac{RT}{zF}\ln\frac{a_{Na^+}^s}{a_{Na^+}^m} = -\frac{0.05916}{(+1)}\log\frac{10^{-3}}{0.200005} = -0.05916\log(0.005) =$
$0.136 = \mathbf{136\ mV}$, as outside versus inside
  Then, $E_{Donnan} = -\frac{RT}{zF}\ln\frac{a_{Cl^-}^s}{a_{Cl^-}^m} = -\frac{0.05916}{(-1)}\log\frac{10^{-3}}{5\cdot 10^{-6}} = 0.05916\log(200) = 0.136 =$
$\mathbf{136\ mV}$, as outside versus inside = verified!

(5) A three-electrode measurement is performed using a Pt disk WE, SCE (containing saturated MCl) RE, and a Pt mesh CE, all immersed in an aqueous electrolyte consisting of x mM MCl, 10 μM ferrocene (Fc), and 10 μM ferrocenium (Fc^+). You measure the reduction potential of Fc^+ and

notice that the value is not that expected based on the E^0 from the CRC. Given the following information, what is likely the cause of this discrepancy, <u>and</u> is the discrepancy a more accurate value for the Fc^+ reduction potential?

a. Measured with a voltmeter; the discrepancy is larger when $x = 100$ mM, versus when $x = 1$ mM.

    <u>Answer</u>: **Activity**, where the activity coefficient is farther from one (i.e. smaller) when a larger salt concentration is present and is also farther from one for Fc^+ versus Fc; the actual values are more accurate, so **yes**.

b. Measured with a voltmeter; the discrepancy is larger when $M = Na^+$, versus when $M = K^+$.

    <u>Answer</u>: **Liquid-junction potential** due to the larger difference in transference numbers for Na^+ versus Cl^- in comparison to K^+ versus Cl^-; the CRC/Nernst values are more accurate, so **no**.

c. Measured by performing a CV; the discrepancy is larger when $x = 1$ mM, versus when $x = 100$ mM.

    <u>Answer</u>: iR_u **drop** due to an increased R_u from a smaller conductivity of the electrolyte; the CRC/Nernst values are more accurate, so **no**.

d. Measured by performing a CV; the discrepancy is larger when the WE is not a UME, versus when the WE is a UME.

    <u>Answer</u>: iR_u **drop** due to an increased i from the increased geometric area of the electrode; the CRC/Nernst values are more accurate, so **no**.