

Read Chapter 5 (at least Sections 5.1, 5.2, 5.3, and 5.8), answer the following problems, fill out the mid-quarter course evaluations, and indicate with whom you worked: _____.

- (1) Do problems 1.4, 2.4 (practice for the first exam), 2.11, 4.3, and 4.4 in Bard and Faulkner (B&F).

Answers:

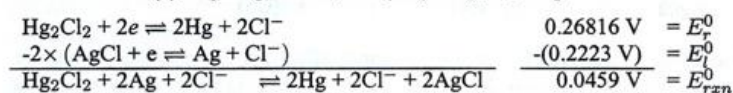
Problem 1.4

- (a) $R_S = \frac{\rho l}{A} = \frac{l}{\sigma A} = \frac{x}{\kappa A} = \frac{3}{(0.013)(0.1)} = \mathbf{2308 \Omega}$, where the first part of the equation was just re-derived from the relation between resistivity, ρ , and resistance, R , while the last expression is what B&F used as equation (1.3.7), although I prefer σ for conductivity.

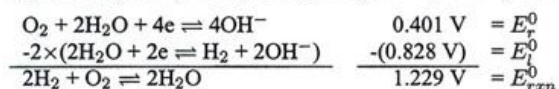
- (b) To be mathematically rigorous, you can calculate the conductivity using equation (2.3.10) – sorry that it is buried in an odd place in my opinion – which for this problem should be $\sigma = F(|z_{K^+}| \mu_{K^+} c_{K^+} + |z_{Cl^-}| \mu_{Cl^-} c_{Cl^-}) = (96485 \text{ C mol}^{-1})((1 \cdot 7.619 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1} \cdot 0.1 \times 10^{-3} \text{ mol cm}^{-3}) + (1 \cdot 7.912 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1} \cdot 0.1 \times 10^{-3} \text{ mol cm}^{-3})) = 0.015 \Omega^{-1} \text{ cm}^{-1} = 15 \text{ mS cm}^{-1}$. Then, for 0.05 cm, $R_U = \frac{l}{\sigma A} = \frac{x}{\kappa A} = \frac{0.05}{(0.015)(0.1)} = \mathbf{33 \Omega}$. For the other distances, the resistance ends up being **67 Ω , 334 Ω , and 667 Ω** , respectively.

- (c) For spherical electrodes, first calculate the radius based on the 0.1 cm² area using $A = 4\pi r^2$, and so $r_0 = \sqrt{\frac{0.1}{4\pi}} = 0.0892 \text{ cm}$. Then use equation (1.3.8), and thus for 0.05 cm, $R_U = \frac{1}{4\pi\kappa r_0} \left(\frac{x}{x+r_0} \right) = \frac{1}{4\pi(0.015)(0.0892)} \left(\frac{0.05}{0.05+0.0892} \right) = 59.5 \left(\frac{0.05}{0.1392} \right) = \mathbf{21 \Omega}$. For the other distances, the resistance ends up being **31 Ω , 51 Ω , and 55 Ω** , respectively.

Problem 2.4 (a). Ag / AgCl / K⁺, Cl⁻(1M) / Hg₂Cl₂ / Hg



(d). Pt / H₂(1 atm) / Na⁺, OH⁻(0.1 M) // Na⁺, OH⁻(0.1 M) / O₂(0.2 atm) / Pt



$$E_r = 0.401 + \frac{0.0591}{4} \log \frac{P_{\text{O}_2}}{[\text{OH}^-]^4} = 0.401 + 0.0148 \log \frac{[0.2]}{[0.1]^4} = 0.450 \text{ V}$$

$$E_l = -0.828 + \frac{0.0591}{2} \log \frac{1}{P_{\text{H}_2}[\text{OH}^-]^2} = -0.828 + 0.0296 \log \frac{1}{[1][0.1]^2} = -0.769 \text{ V}$$

$$E_{rxn} = E_r - E_l = 1.219 \text{ V (spontaneous)}$$

Alternatively, for the reaction as written,

$$E_{rxn} = 1.229 - \frac{0.0591}{4} \log \frac{1}{P_{\text{H}_2}^2 P_{\text{O}_2}} = 1.229 - 0.0148 \log \frac{1}{[1]^2 [0.2]} = 1.219 \text{ V}$$

Note that this cell reaction is the same as that in (c) and that the pressures of the gaseous reactants are also the same. Thus, E_{rxn} must be identical. However, the change in pH in the electrolyte does shift the potentials of the hydrogen and oxygen electrodes to more negative values by 59 mV per unit rise in pH. In practical terms, pH sets the accessible potentials or “solvent window” in aqueous solutions.

$$(b) E_{cell} = E_{cell}^0 - \frac{RT}{2F} \ln \left(\frac{a_{Cu}(a_{Fe^{3+}})^2}{a_{Cu^{2+}}(a_{Fe^{2+}})^2} \right) \approx (E_{red}^0 - E_{ox}^0) - \frac{RT}{2F} \ln \left(\frac{(1)(0.01)^2}{(0.1)(0.1)^2} \right) = (0.340 - 0.771) - \frac{RT}{2F} \ln(0.1) = -0.40142 \text{ V (not spontaneous)}$$

(c) Same answer as in part d, but with different E for each half reaction.

(e) $E = +0.05916 \text{ V (spontaneous)}$; use the Nernst equation but if you solve this as one total reaction, be sure to not cancel out the concentrations of chlorides because they are not equal. So, $E_{cell} = (E_{red}^0 - E_{ox}^0) - \frac{RT}{1 \cdot F} \ln \left(\frac{a_{Ag(red)} a_{Cl^-(red)} a_{AgCl(ox)}}{a_{Ag(ox)} a_{Cl^-(ox)} a_{AgCl(red)}} \right) \approx (0 - 0) - \frac{RT}{F} \ln \left(\frac{(1)(0.1)(1)}{(1)(1)(1)} \right) = +0.05916 \text{ V}$.

$$(f) E_{cell} = E_{cell}^0 - \frac{RT}{1 \cdot F} \ln \left(\frac{a_{Fe^{2+}} a_{Ce^{4+}}}{a_{Fe^{3+}} a_{Ce^{3+}}} \right) \approx (E_{red}^0 - E_{ox}^0) - \frac{RT}{F} \ln \left(\frac{(0.01)(0.1)}{(0.1)(0.01)} \right) = (0.771 - 1.72) - 0 = -0.994 \text{ V (not spontaneous)}$$

Problem 2.11

(a) $96.5 \text{ C} = 0.001 \text{ mol } e^- = 0.001 \text{ mol Ag (1 mmol of Ag)} = 0.108 \text{ g}$ of Ag, because the molar mass of silver is $107.8682 \text{ g mol}^{-1}$

(b) **Still 0.1 M in each**, because from the balance sheet only Ag^+ will carry the ionic current and thus for each Ag^+ that is generated at the right (+) electrode (due to oxidation of Ag), a Ag^+ is lost at the left (-) electrode (due to reduction to Ag) and Ag^+ migrates from the right electrode to the left electrode. Thus, the net change in $[Ag^+] = 0$.

(c) Now for each redox reaction that occurs (that is per electron at each electrode), one NO_3^- will migrate to the (+) electrode. Notwithstanding, no Ag^+ will be replenished or lost due to migration and so all redox chemistry will result in a loss or gain in the $[Ag^+]$. Because 1 mmol of Ag was deposited, this means 0.04 M of Ag^+ was lost from the left (-) electrode and 0.04 M of Ag^+ was added to the right (+) electrode container. Thus, after electrolysis, **L = 0.06 M, C = 0.1 M, R = 0.14 M**.

(d) Because the Ag^+ increased to 0.121 M, it means 0.021 M was added which equates to 0.525 mmol of Ag^+ . Based on parts a, b, and c, this means that NO_3^- migrated for 52.5% of the current ($t_{NO_3^-} = 0.525$) and so Ag^+ migrated for 47.5% of the current ($t_{Ag^+} = 0.475$).

Problem 4.3 The thickness of the diffusion layer can be estimated from the root-mean-square diffusion length given as equation (4.4.3).

$$\bar{\Delta} = \sqrt{2Dt} \quad (4.4.3)$$

Thus, the minimum distance d between the working electrode surface and the cell wall is

$$d = 5\bar{\Delta} = 5\sqrt{2Dt} = 5\sqrt{2 \times 10^{-5} \text{ cm}^2/\text{s} \times 100 \text{ s}} = 0.2 \text{ cm} \quad (1)$$

Problem 4.4

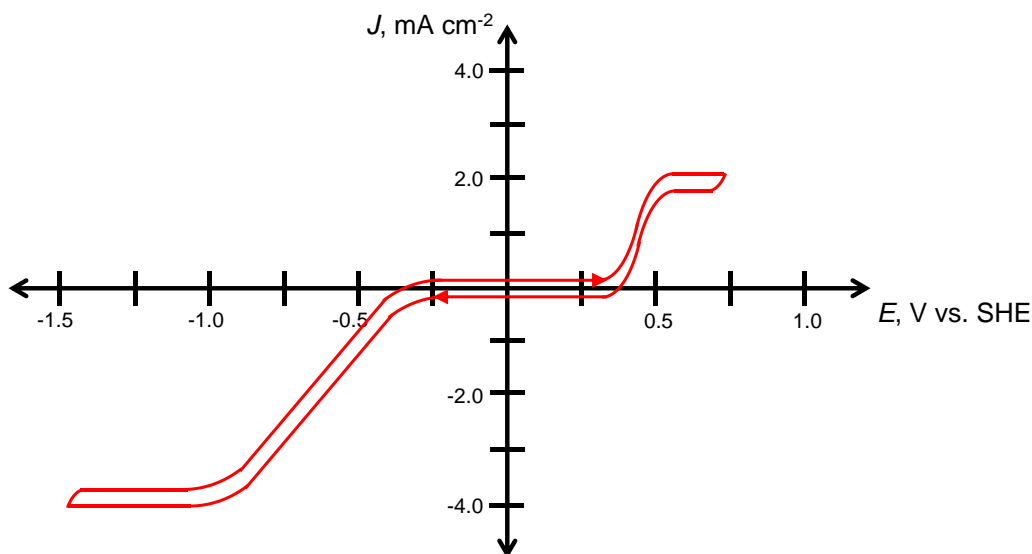
(a) Given that $\mu = \frac{|z|FD}{RT}$, and so $D = \frac{RT\mu}{|z|F}$, $D_{H^+} = \frac{RT(3.625 \cdot 10^{-3})}{F} = \frac{RT(3.625 \cdot 10^{-3})}{F} = 9.31 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, and so $D_{I^-} = 2.05 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $D_{Li^+} = 1.03 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

(b) By diving some entries in Table 2.3.2, one can immediately see that the equation that relates λ_0 to μ is $\mu = \frac{\lambda_0}{F}$, and so $D = \frac{RT\lambda_0}{|z|F^2}$.

(2) Answer the following based on the $J-E$ curve below, which was measured using a 3-electrode setup at a scan rate of 100 mV s^{-1} and using an aqueous electrolyte at room temperature.

- Over approximately what potential range do Faradaic reactions occur? Answer: $\sim[-\infty, -0.25] \text{ V}$ and $\sim[0.3, \infty] \text{ V}$
- Over approximately what potential range do non-Faradaic reactions occur? Answer: **The entire domain of potentials**, because the non-Faradaic charging is always present even though we only easily see the non-Faradaic charging over the domain $\sim(-0.25, 0.3)$, where only non-Faradaic charging is present.
- What is the approximate double-layer capacitance and what does that tell you about the roughness factor of the electrode? Answer: Take the current in the flat region around the potential axis (i.e. $J = 0$) and use $C = J/v = 0.2/0.1 = 2 \text{ mF cm}^{-2}$ if you assume that all current goes to charging and none to uncompensated resistance which is a fair assumption; based on the ideal capacitance of $10 - 20 \mu\text{F cm}^{-2}$, this electrode has a **roughness factor ≈ 100** .
- If I told you that the cathodic reaction was a one-electron-transfer process, approximately how many electrons were transferred during the anodic reaction? Answer: **2**, because the slope of the sloping region of the $J-E$ curve is about twice as large for the anodic reaction; see equation (1.4.16) and use your Excel sheet from the last HW to see how the curve changes as the number of electrons changes.
- If I told you that the initial concentration of both species (reduced form of one molecule and oxidized form of other molecule) was the same, what can you tell me about the diffusion coefficient of the molecule being reduced in relation to the diffusion coefficient of the molecule being oxidized? Answer: D_O , which is for the molecule by reduced, **is 4 times as large**, because the unsigned limiting current is twice as large but it also involves half the number of electrons; see equation (1.4.9).
- If I told you there was 1 M H^+ present in the electrolyte, what can you tell me about the rate of catalysis for evolving H_2 versus the rate of catalysis for the cathodic reaction? Answer: **It is much slower** because little current is passed until you get to $\sim 300 \text{ mV}$ passed the standard reduction potential for H_2 evolution; said another way, **the overpotential required for H_2 evolution is large**.

- g. If I told you that the diffusion coefficient for the oxidized and reduced versions of the molecule that were participating in the cathodic reaction was the same, what does its $E_{1/2}$ stand for? Answer: E^0 (**formal potential**), because we assume that δ is set by the small amount of stirring and is the same for both R and O.
- h. If I told you that the cathodic current was perfectly linear on this plot, and not sigmoidal, what is likely the cause of this slope and how would the slope change if I added more supporting electrolyte? Answer: **Ohmic iR drop** due to uncompensated resistance between the WE and RE; **linear slope would become steeper (larger)**, because the electrolyte would become more conductive.
- i. On the same y-axis scale, what would the J - E curve look like if I removed all the supporting electrolyte and just used deionized water? (Assume the solution resistance is 18.2 MOhm and that the electrode area is 10 mm².) Answer: **It would be perfectly flat with a y-value of seemingly zero (i.e. without double-layer charging)**, because the RC time constant would be $18.2 \times 10^6 \text{ Ohm} \times 0.002 \text{ F cm}^{-2} \times 0.1 \text{ cm}^2 = 3,640 \text{ s}$ and a full sweep in one direction only takes $\sim 22 \text{ sec}$ (100 mV s^{-1} over $\sim 2.2 \text{ V}$). *Of note is that deionized water has a resistivity of $\sim 18.2 - 18.3 \text{ MOhm cm}$, but the resistance is a little less well defined and surely more challenging to measure and/or approximate.*



- (3) Answer the following for a 3-electrode measurement of a cell that originally contains both the oxidized (O) and reduced (R) versions of a molecule, and where $D_O = D_R$.
- a. What equation does equation 1.4.20 reduce to when $I = 0$, and what is its name? Answer: Plug in for D_O and D_R , use a single δ value, and use the full equations for $I_{i,a}$ and $I_{i,c}$, and then you get **the Nernst equation, which you know so I will not write it here**.
- b. What is the expression for the current that flows in the cell when the applied potential equals the formal potential? Answer: $I = (I_{i,a} + I_{i,c})/2$, where one could have also plugged

in the equations for the limiting currents to obtain a more detailed, but entirely equivalent, answer. If you'd like, plug this into equation (1.4.20) to verify it is correct.

(4) In Hernandez-Pagan, Vargas-Barbosa, Wang, Zhao, Smotkin, and Mallouk, *Energy & Environmental Science*, 2012, 5, 7582 (see class website), the authors show balance sheets for several scenarios that incorporate ion-selective membranes (i.e. Figure 5 and Figure 7). With this in mind, answer the following.

- Based on the balance sheets shown in Figure 5, explain why there is no diffusive component. **Answer: Because only H⁺ and OH⁻ are being reduced and oxidized and the migration term supplies the required mass to maintain the overall mass balance.**
- All four of the balance sheets are missing counter-ions, which should have resulted in migration opposite of the direction shown. Why were counter-ions not included in the balance sheets? **Answer: Because an ion-selective membrane was used which prevented the counter-ions from diffusing from one side to the other.**
- Quantitatively, how would the balance sheet in Figure 5a change if the electrolyte was at pH = 3 (with HCl) and 1 M KCl was present? *Either draw a new balance sheet or explain this in words and numbers.*
 - What would the value of t_{H^+} be if the pH = 7 (e.g. deionized water), but still with 1 M KCl?

Answers: The conductivity would be based on H⁺, Cl⁻, and K⁺. The conductivity of K⁺ and Cl⁻ would dominate. The migration of K⁺ and H⁺ would be the only species that could transport through the membrane. The denominator would be $|z_{H^+}|\mu_{H^+}c_{H^+} + |z_{Cl^-}|\mu_{Cl^-}c_{Cl^-} + |z_{K^+}|\mu_{K^+}c_{K^+} = (1 \cdot 3.625 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1} \cdot 0.001 \times 10^{-3} \text{ mol cm}^{-3}) + (1 \cdot 0 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1} \cdot 1.001 \times 10^{-3} \text{ mol cm}^{-3}) + (1 \cdot 7.619 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1} \cdot 1 \times 10^{-3} \text{ mol cm}^{-3}) = (3.625 \times 10^{-9}) + (0) + (7.619 \times 10^{-7}) = 7.65525 \times 10^{-7}$. Then to get the transference number for each, simply divide the portion of the denominator for each species by this total value. Thus, **$t_{K^+} = 0.995$ and by subtraction, $t_{H^+} = 0.005$, and so the migration component for each of these in the balance sheet would be this fraction times 4. Then, the diffusive component of protons would be 4×0.995 to make up for the lack of proton migration.** *If one mistakenly and incorrectly included chloride in the denominator of the transference number equation, then the denominator would have been 15.575162×10^{-7} , and thus, $t_{H^+} = 0.0023$, $t_{Cl^-} = 0.51$, and $t_{K^+} = 0.49$. The chloride term should have been omitted because in 5a there is clearly something preventing the anions for migrating across the entire cell.*

(i) At pH = 7, t_{H^+} would be tiny! Thus, within error, $t_{K^+} = 1$. Quantitatively, though, $|z_{H^+}|\mu_{H^+}c_{H^+} + |z_{Cl^-}|\mu_{Cl^-}c_{Cl^-} + |z_{K^+}|\mu_{K^+}c_{K^+} = (1 \cdot 3.625 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1} \cdot 10^{-7} \times 10^{-3} \text{ mol cm}^{-3}) + (1 \cdot 0 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1} \cdot 1 \times 10^{-3} \text{ mol cm}^{-3}) + (1 \cdot 7.619 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1} \cdot 1 \times 10^{-3} \text{ mol cm}^{-3}) = (3.625 \times 10^{-13}) + (0) + (7.619 \times 10^{-7}) = 7.619003625 \times 10^{-7}$. Thus, **$t_{H^+} = 4.758 \times 10^{-7}$.**