

Model Solutions to 3.53 Problem Set 5

Problem 8.3 In solving this problem, the Sand equation (8.2.14) is used.

$$\frac{i\tau^{1/2}}{C_O^*} = \frac{nFA\sqrt{D_O\pi}}{2} = \text{constant} = k \quad (8.2.14)$$

For the known Pb^{2+} solution:

$$k_{\text{Pb}^{2+}} = \frac{273 \text{ mA} \times \sqrt{25.9 \text{ s}}}{1.00 \text{ mM}} = 1.389 \text{ As}^{1/2}/\text{mM} \quad (1)$$

For the known Cd^{2+} solution:

$$k_{\text{Cd}^{2+}} = \frac{136 \text{ mA} \times \sqrt{42.0 \text{ s}}}{0.69 \text{ mM}} = 1.277 \text{ As}^{1/2}/\text{mM} \quad (2)$$

The $E_{\tau/4}$ values are $E_{\tau/4}(\text{Pb}^{2+}) = -0.38 \text{ V vs SCE}$ and $E_{\tau/4}(\text{Cd}^{2+}) = -0.56 \text{ V vs SCE}$. As these differ by approximately 180 mV, it is clear that the Pb^{2+} process finishes before the Cd^{2+} process begins. Thus, for the $\text{Pb}^{2+}/\text{Cd}^{2+}$ mixture,

$$C_{\text{Pb}^{2+}} = \frac{i\sqrt{\tau_1}}{k_{\text{Pb}^{2+}}} = \frac{0.0565 \text{ A} \times \sqrt{7.08 \text{ s}}}{1.389 \text{ As}^{1/2}/\text{mM}} = 0.108 \text{ mM} \quad (3)$$

For Cd^{2+} , the transition occurs at $t = \tau_1 + \tau_2$, when the concentration of Cd^{2+} drops to zero at the electrode surface. For the Cd^{2+} transition time alone, the Sand equation takes the following form.

$$C_{\text{Cd}^{2+}} = \frac{i\sqrt{\tau_1 + \tau_2} - \sqrt{\tau_1}}{k_{\text{Cd}^{2+}}} = \frac{0.0565 \text{ A} \times [\sqrt{7.08 \text{ s} + 7.00 \text{ s}} - \sqrt{7.08 \text{ s}}]}{1.277 \text{ As}^{1/2}/\text{mM}} = 0.0483 \text{ mM} \quad (4)$$

Problem 8.5 Figure 8.4.1 shows an experimental chronopotentiogram with current reversal for the oxidation of diphenylpicrylhydrazyl (DPPH) followed by reaction of the radical cation. From the figure, $t_1 = \tau_1 \approx 15 \text{ s}$ and $\tau_2 \approx 5 \text{ s}$. Since $t_1 = 3\tau_2$ (equation (8.4.9)), the product, DPPH^+ , is stable and undergoes an $n = 1$ reduction ($\text{DPPH}^+ + e \rightleftharpoons \text{DPPH}$) on current reversal with $E_{\tau_1/4} \approx E^o \approx 0.73 \text{ V vs SCE}$. From the figure legend, $C_{\text{DPPH}} = 1.04 \text{ mM}$; $A(\text{Pt electrode}) = 1.2 \text{ cm}^2$; and $i = 100 \mu\text{A}$. Using the Sand equation (8.2.14) with i in mA, τ in s, C_O^* in mM and A in cm^2 , allows one to calculate the diffusion coefficient D_O in cm^2/s .

$$D_O = \left[\frac{0.100 \times \sqrt{15}}{1.04 \times 85.5 \times 1.2} \right]^2 = 1.32 \times 10^{-5} \text{ cm}^2/\text{s} \quad (1)$$

Problem 8.6 From equation (8.7.1), the charge on $C_{inj} = 1 \text{ nF}$ set by a 10 V battery is found.

$$\Delta q = C_{inj} \times V = 10^{-9} \text{ F} \times 10 \text{ V} = 10^{-8} \text{ C} \tag{1}$$

When Δq is distributed over $C_{inj} = 1 \text{ nF}$ and $C_d = 1 \text{ }\mu\text{F}$, the charge is conserved such that

$$\Delta q = q_{inj} + q_d = 10^{-8} \text{ C} \tag{2}$$

Also, the voltage drop across the two capacitors must be equal. Thus,

$$\frac{q_{inj}}{C_{inj}} = \frac{q_d}{C_d} = \frac{q_{inj}}{10^{-9} \text{ F}} = \frac{q_d}{10^{-6} \text{ F}} \tag{3}$$

Solution of two equations in two unknowns yields $q_d = 9.99 \times 10^{-9} \text{ C}$ and $q_{inj} = 9.99 \times 10^{-12} \text{ C}$. Thus, all of the charge is delivered from C_{inj} to C_d .

The total capacitance in the Figure 8.9.1 circuit is found as follows.

$$\frac{1}{C_T} = \frac{1}{C_{inj}} + \frac{1}{C_d} = 10^9 + 10^6 \approx 10^9 \text{ F}^{-1} \tag{4}$$

$$C_T \approx 10^{-9} \text{ F} \tag{5}$$

The time constant $\tau = R_\Omega C_T \approx 100 \text{ }\Omega \times 10^{-9} \text{ F} \approx 10^{-7} \text{ s}$. From equation (1.2.6), the current for charging C_d drops to 5% of its initial value at $t = 3\tau$ and 1% of its initial value at $t = 5\tau$. Thus, C_d is 95% charged in $\approx 3 \times 10^{-7} \text{ s}$ or > 99% charged in $\approx 5 \times 10^{-7} \text{ s}$.

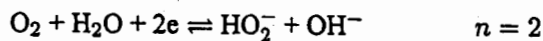
Problem 9.3 This problem is based on the data in Figure (9.3.8). From the Figure legend,

$$f = 2500 \text{ rpm} = 2500 \text{ rev/min} \times 1 \text{ min}/60 \text{ s} = 41.67 \text{ rev/s}$$

$$\omega = 2\pi f = 2\pi \times 41.67 \text{ s}^{-1} = 262/\text{s} \quad \omega^{1/2} = 16.2 \text{ s}^{-1/2}$$

$$\text{Au electrode, } A = 0.196 \text{ cm}^2$$

$$C_{O_2}^* = 1.00 \text{ mM (saturated)} = 1.0 \times 10^{-3} \text{ mol/cm}^3$$



(a). The D_{O_2} in 0.1 M NaOH is found from the $i - E$ curve in Figure (9.3.8a), where $i_{l,c} \approx 6.5 \times 10^{-4} \text{ A}$. From equation (9.3.22),

$$\begin{aligned} D_{O_2}^{2/3} &= \frac{i_{l,c}}{0.62nFA\omega^{1/2}\nu^{-1/6}C_{O_2}^*} \tag{1} \\ &= \frac{(6.5 \times 10^{-4} \text{ A}) (0.01 \text{ cm}^2/\text{s})^{1/6}}{(0.62) (2) (96485 \text{ C/mol}) (0.196 \text{ cm}^2) (16.2 \text{ s}^{-1/2}) (10^{-6} \text{ mol/cm}^3)} \end{aligned}$$

$$D_{O_2} = \left[7.94 \times 10^{-4} \frac{\text{cm}^4/3}{\text{s}^{2/3}} \right]^{3/2} = 2.2 \times 10^{-5} \text{ cm}^2/\text{s} \tag{2}$$

(b). The Koutecky-Levich equation (9.3.39) shows that a graph of $1/i_{i,c}$ versus $\omega^{-1/2}$ leads to an intercept of $1/i_K$. From Figure 9.3.8, the intercept at 0.75 V is $i^{-1} = i_K^{-1} \approx 1.2 \text{ mA}^{-1}$. This yields $i_K = 8.3 \times 10^{-4} \text{ A}$. From equation (9.3.38),

$$\begin{aligned} k_f(E) &= \frac{i_K}{nFAC_{O_2}^*} & (3) \\ &= \frac{8.3 \times 10^{-4} \text{ A}}{(2)(96485 \text{ C/mol})(0.196 \text{ cm}^2)(10^{-6} \text{ mol/cm}^3)} \\ &= 2.2 \times 10^{-2} \text{ cm/s at } 0.75 \text{ V} \end{aligned}$$

Problem 9.4 (a). The first reduction step is characterized by the first current step for both the ring and the disk. Both waves yield $E_{1/2} \sim 0.1 \text{ V}$, as the potential at half the plateau current. The ring current is shown for $i_D = 0$, such that equation (9.4.8) applies.

$$\begin{aligned} \frac{i_R}{i_D} &= \beta^{2/3} = \left[\left(\frac{r_3}{r_1} \right)^3 - \left(\frac{r_2}{r_1} \right)^3 \right]^{2/3} & (9.4.8) \\ &\cong \frac{1100 \mu\text{A}}{300 \mu\text{A}} = 3.67 \end{aligned}$$

Or, $\beta = 7.02$.

To determine the diffusion coefficient for Cu^{2+} , the Levich equation for the mass transport limited current is used.

$$i_{D,\text{lim}} = 0.62nFAC^*D^{2/3}\nu^{-1/6}\omega^{1/2} \quad (9.3.22)$$

Data provided in the correct units are $i_{\text{disk}} = 3 \times 10^{-4} \text{ A}$, $n = 1$, $A = 0.962 \text{ cm}^2$, $C_O^* = 5 \times 10^{-6} \text{ mol/cm}^3$, and $\omega = 201 \text{ s}^{-1}$. The kinematic viscosity, the ratio of viscosity to density, is provided in the caption, $\nu = 0.011 \text{ cm}^2/\text{s}$. Rearranging the above equation yields

$$\begin{aligned} D &= \left[\frac{i_{\text{disk}} \times \nu^{-1/6}}{0.62nFAC^*\omega^{1/2}} \right]^{3/2} & (1) \\ &= \left[\frac{3 \times 10^{-4} \text{ A} \times (0.011 \text{ cm}^2/\text{s})^{1/6}}{0.62 \times 1 \times 96485 \text{ C/mol} \times 0.0962 \text{ cm}^2 \times 5 \times 10^{-6} \text{ mol/cm}^3 \sqrt{201 \text{ s}^{-1}}} \right]^{3/2} \\ &= 6.48 \times 10^{-6} \text{ cm}^2/\text{s} \end{aligned}$$

(b). If $E_D = -0.1 \text{ V}$, the disk is on the mass transport limited plateau for reduction of Cu^{2+} , so the system is set up for a shielding experiment because Cu^{2+} will be reduced at both electrodes. Because $i_D = i_{D,\text{lim}}$, equation (9.4.20) applies.

$$i_{R,\text{lim}} = i_{R,\text{lim}}^0 (1 - N\beta^{-2/3}) \quad (9.4.20)$$

From the figure, $i_{R,\text{lim}}^0 = \beta^{2/3}i_{D,\text{lim}} = 1100 \mu\text{A}$ as the value recorded when $i_D = 0$. It is given that $N = 0.53$. From part (a), $\beta^{2/3} = 3.67$. Then, $i_{R,\text{lim}} = i_{R,\text{lim}}^0 (1 - N\beta^{-2/3}) = 1100 \mu\text{A} (1 - 0.53/3.67) = 940 \mu\text{A}$.

(c). If $E_R = +0.4 \text{ V}$ and $E_D = -0.10 \text{ V}$, then the experiment is a collection experiment with mass transport limited current at both electrodes. From the collection efficiency (equation (9.4.15)), $-i_R = N \times i_D = -0.53 \times 300 \mu\text{A} = -160 \mu\text{A}$.

(d). The second wave arises from the reduction $\text{Cu}^+ + e \rightleftharpoons \text{Cu}^0$. The wave shape and height is similar to that for the one electron reduction of Cu^{2+} . There are two differences. First, the mass transport limited currents exhibit higher noise than the rest of the curves. This is likely due to the deposition of copper metal on the electrode surface that may increase surface roughness and disrupt the diffusion boundary layer.

Second, the waves rise more sharply for the second wave. Again, this is because reduction product is insoluble. Consider equation (9.3.34), which describes the relationship between E and i for both the oxidized and reduced species soluble.

$$E = E_{1/2} + \frac{RT}{nF} \ln \left[\frac{i_{l,c} - i}{i - i_{l,a}} \right] \tag{9.9.34}$$

This is rearranged to yield

$$i = \frac{i_{l,c} + i_{l,a} \exp \left[\frac{nF}{RT} (E - E_{1/2}) \right]}{1 + \exp \left[\frac{nF}{RT} (E - E_{1/2}) \right]} \tag{2}$$

This is the equation that describes the relationship between the current and potential for the first wave. For the second wave, the appropriate equation is found by considering the development in the text on page 33, Section 1.4(c). For $\text{Cu}^+ + e \rightleftharpoons \text{Cu}^0$, the Nernst equation is

$$E = E^{0'} + \frac{RT}{nF} \ln C_{\text{Cu}^+}(y = 0) \tag{3}$$

The concentration of Cu^+ is defined by equation 9.3.31a.

$$C_{\text{Cu}^+}(y = 0) = C^* \left[1 - \frac{i}{i_{l,c}} \right] \tag{4}$$

Substitution into equation (3) yields the Nernst equation.

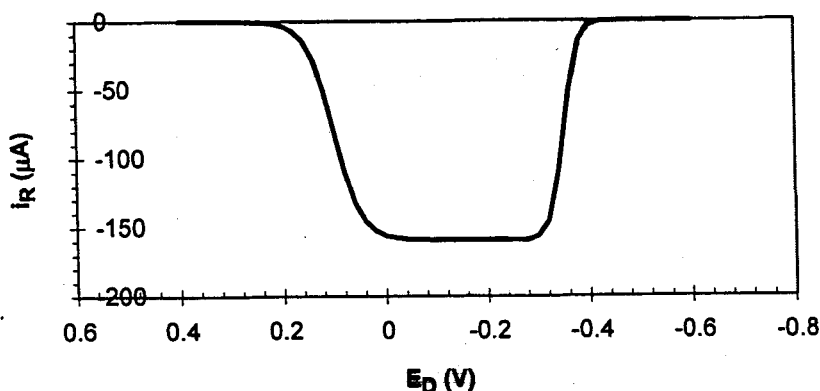
$$E = E^{0'} + \frac{RT}{nF} \ln C^* + \frac{RT}{nF} \ln \left[1 - \frac{i}{i_{l,c}} \right] \tag{5}$$

This is rearranged to the current expression as

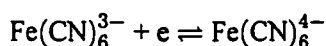
$$\frac{i}{i_{l,c}} = 1 - \frac{\exp \left[\frac{nF}{RT} (E - E^{0'}) \right]}{C^*} \tag{6}$$

Compare the functional forms for equations (2) and (6). For a change in E , the expression for the case where both the oxidized and reduced species are present is damped relative to the form where the product is insoluble. This explains the sharper rise in the second waves.

(e). For the ring at +0.4 V and the disk scanned from 0.4 to -0.6 V, the system will be configured for a collection experiment. The collection efficiency defines the current at the ring relative to that at the disk; $N = -i_R/i_D$, provided the product at the disk is soluble. As the potential is scanned negatively at the disk, Cu^{2+} is first reduced to yield Cu^+ . The disk current increases and limits at 300 μA . The Cu^+ is collected at the ring and a current -53% of the disk value is generated at the ring; here, $N = 0.53$. On the limiting plateau, the ring current is 180 μA . As the disk potential shifts further negative into the second reduction wave, the disk current increases as the Cu^+ is reduced to copper metal. The copper metal plates on the electrode surface and is not swept across the ring and the ring current diminishes. As the electrolysis to copper metal at the disk approaches mass transport limited at about -0.4 V, there is no Cu^+ reaching the ring, and the current decays to zero at the ring.



Problem 9.5 This problem is based on Figure 9.10.2, which features RRDE voltammograms for the reduction



The data provided are as follows.

$$f = 48.6 \text{ rev/s}$$

$$\omega = 2\pi f = 2\pi(48.6 \text{ s}^{-1}) = 305 \text{ s}^{-1} \quad \omega^{1/2} = 17.5 \text{ s}^{-1/2}$$

$$C^* = 5.0 \text{ mM} = 5 \times 10^{-6} \text{ mol/cm}^3$$

$$r_2 = 0.188 \text{ cm} = \text{inner radius} \quad r_3 = 0.325 \text{ cm} = \text{outer radius}$$

$$r_3^3 - r_2^3 = (0.325 \text{ cm})^3 - (0.188 \text{ cm})^3 = 2.77 \times 10^{-2} \text{ cm}^3$$

$$\pi (r_3^3 - r_2^3)^{2/3} = 0.287 \text{ cm}^2$$

$$\nu = 0.01 \text{ cm}^2/\text{s} \quad \nu^{-1/6} = 2.15 \text{ cm}^{-2/6}/\text{s}^{-1/6}$$

(a). From Figure 9.10.2,

	i_D (μA)	$i_{R,l}$ (μA)
Curve (1)	0	≈ 1380
Curve (2)	302	≈ 1200

From equation (9.4.19),

$$\begin{aligned} N &= - \left(\frac{i_{R,l} - i_{R,l}^0}{i_D} \right) \\ &= - \left(\frac{1200 \mu\text{A} - 1380 \mu\text{A}}{302 \mu\text{A}} \right) = 0.60 \end{aligned} \quad (9.4.19)$$

From equation (9.4.5),

$$\begin{aligned} D_O^{2/3} &= \frac{i_{R,l,c}}{0.62nF\pi (r_3^3 - r_2^3)^{2/3} \omega^{1/2} \nu^{-1/6} C_O^*} \\ &= \frac{1.38 \times 10^{-3} \text{ A}}{0.62 \times 1 \times \frac{96485 \text{ C}}{\text{mol}} \times 0.287 \text{ cm}^2 \times 17.5 \text{ s}^{-1/2} \times \frac{2.15 \text{ cm}^{-2/6}}{\text{s}^{-1/6}} \times \frac{5 \times 10^{-6} \text{ mol}}{\text{cm}^3}} \\ &= 4.27 \times 10^{-4} \text{ cm}^{4/3}/\text{s}^{2/3} \end{aligned} \quad (1)$$

Or,

$$D_O = \left(4.27 \times 10^{-4} \text{ cm}^{4/3} / \text{s}^{2/3}\right)^{3/2} = 8.8 \times 10^{-6} \text{ cm}^2 / \text{s} \quad (2)$$

(b). From equation (9.3.22),

$$\begin{aligned} \frac{i_{l,c}}{\omega^{1/2}} &= 0.62nFAD_O^{2/3}v^{-1/6}C_O^* \\ &= \frac{302 \mu\text{A}}{17.5 \text{ s}^{-1/2}} = 17.3 \mu\text{A s}^{1/2} \end{aligned} \quad (3)$$

(c). Values for $i_{D,l,c}$ and $i_{R,l,c}$ at 5000 rpm are found through the proportionality of equation (9.3.22) between i_l and $\omega^{1/2}$. Data from Figure 9.10.2 are used.

$$f = 5000 \text{ rev/min} = 5000 \text{ rev/min} \times 1 \text{ min} / 60 \text{ s} = 83.3 \text{ rev/s}$$

$$\omega = 2\pi f = 2\pi \times (83.3 \text{ rev/s}) = 523.6 \text{ s}^{-1} \quad \omega^{1/2} = 22.9 \text{ s}^{-1/2}$$

$$i_{D,l,c} = 302 \mu\text{A} \times \left(\frac{22.9 \text{ s}^{-1/2}}{17.5 \text{ s}^{-1/2}}\right) = 395 \mu\text{A} \quad (4)$$

$$i_{R,l,c}(i_D = 0) = 1380 \mu\text{A} \times \left(\frac{22.9 / \text{s}^{1/2}}{17.5 / \text{s}^{1/2}}\right) = 1.81 \text{ mA} \quad (5)$$

$$i_{R,l,c}(i_D = i_{D,l,c}) = 1200 \mu\text{A} \times \left(\frac{22.9 / \text{s}^{1/2}}{17.5 / \text{s}^{1/2}}\right) = 1.57 \text{ mA} \quad (6)$$
