Model Solutions to 3.53 Problem Set 3

5.5. In answering this question, one can follow the procedure of Section 5.4.4. For

$$M^{+n} + ne \rightleftarrows M(solid) \qquad (1)$$

$$E = E^o_{M^{+n},M(solid)} + \frac{RT}{nF}\ln\frac{C_{M^{+n}}(0,t)}{C_{M(solid)}(0,t)} = E^o_{M^{+n},M(solid)} + \frac{RT}{nF}\ln\frac{C_{M^{+n}}(0,t)}{1} \qquad (2)$$

since $a_M = 1$, and which follows from equation (5.1.5). The following relations also apply

$$i(t) = nFAm_{M^{+n}}\left[C^*_{M^{+n}} - C_{M^{+n}}(0,t)\right] \qquad (3)$$

$$i_d(t) = nFAm_{M^{+n}}C^*_{M^{+n}} \qquad (4)$$

where $m_{M^{+n}}$ is the mass transfer coefficient which replaces $\sqrt{D_{M^{+n}}/\pi t}$ in equation (5.4.65) and $i_d(t)$ follows from equation (5.2.11). Solving equation (3) for $C_{M^{+n}}(0,t)$

$$C_{M^{+n}}(0,t) = C^*_{M^{+n}} - \frac{i(t)}{nFAm_{M^{+n}}} \qquad (5)$$

and equation (4) for $C^*_{M^{+n}}$

$$C^*_{M^{+n}} = \frac{i_d(t)}{nFAm_{M^{+n}}} \qquad (6)$$

allows equation (5) to be written as

$$C_{M^{+n}}(0,t) = \frac{i_d - i(t)}{nFAm_{M^{+n}}} \qquad (7)$$

Substituting this result into equation (2) leads to

$$E = E^o_{M^{+n},M(solid)} + \frac{RT}{nF}\ln\frac{i_d(t) - i(t)}{nFAm_{M^{+n}}}$$
$$= E^o_{M^{+n},M(solid)} - \frac{RT}{nF}\ln nFAm_{M^{+n}} + \frac{RT}{nF}\ln(i_d(t) - i(t)) \qquad (8)$$

From Section 5.4.1(b), when

$$i(t) = \frac{i_d(t)}{2}, \text{ then } E = E_{1/2} \qquad (9)$$

so that equation (8) may be rewritten

$$E_{1/2} = E^{o}_{M^{+n},M_{(solid)}} - \frac{RT}{nF}\ln nFAm_{M^{+n}} + \frac{RT}{nF}\ln\frac{i_d(t)}{2} \quad (10)$$

which shows the relationship between $E_{1/2}$ and $i_d(t)$. From equation (6)

$$\frac{i_d(t)}{2} = nFAm_{M^{+n}}\frac{C^{*}_{M^{+n}}}{2} \quad (11)$$

which, when substituted into equation (10)

$$E_{1/2} = E^{o}_{M^{+n},M_{(solid)}} - \frac{RT}{nF}\ln nFAm_{M^{+n}} + \frac{RT}{nF}\ln nFAm_{M^{+n}} + \frac{RT}{nF}\ln\frac{C^{*}_{M^{+n}}}{2} \quad (12)$$

$$= E^{o}_{M^{+n},M_{(solid)}} + \frac{RT}{nF}\ln\frac{C^{*}_{M^{+n}}}{2}$$

leads to the relationship between $E_{1/2}$ and $C^{*}_{M^{+n}}$.

5.6. The system is analogous to that shown in equation (5.4.70).

$$MX_p^{2-p} + 2e \rightleftharpoons M(Hg) + pX^-$$

(a) Given the conditions outlined after equation (5.4.70), equation (5.4.80) applies.

$$E^{c}_{1/2} = E^{0'}_{M} - \frac{RT}{nF}\ln K_c - \frac{pRT}{nF}\ln C^{*}_{X} + \frac{RT}{nF}\ln\frac{m_A}{m_C}$$

A plot of $E^{c}_{1/2}$ versus $\ln C^{*}_{X}$ yields a slope of $-pRT/nF$. The intercept is equal to $E^{0'}_{M} - \frac{RT}{2F}\ln K_C + \frac{RT}{nF}\ln\frac{m_A}{m_C}$. Linear regression yields $E^{c}_{1/2} = -0.0513\times\ln C^{*}_{X} - 0.566$ with $r = 0.99998$ for the data shown in the problem. Thus, $-p = 2\times 38.92V^{-1}\times -0.0513 = -3.99$. p is 4.

(b) From equation (5.4.72), $K_C = C_{MX4}/C_M C_X^4$ is the formation constant for the reaction $M^{2+} + 4X^- \rightleftharpoons MX_4$. The stability constant is the same as K_C. From equation (5.4.82), one can solve for K_C as follows,

$$K_C = \exp\left\{-\frac{nF}{RT}(E^{C}_{1/2} - E^{M}_{1/2}) - p\ln C^{*}_{X}\right\}$$

Because the diffusion coefficients are equal for the complex ion and the metal atom, $m_A = m_C$. An Excel spreadsheet can be set up as shown below.

n	2
p	4
F/RT(V^{-1})	38.92
$E_{1/2,M}$(V)	0.081

$E_{1/2,C}$(V)	$nF(E_{1/2,C}-E_{1/2,M})/RT$	C_X^*	$\ln(C_X^*)$	$p\ln(C_X^*)$	K_C
-0.448	-41.17736	0.10	-2.30259	-9.21034	7.64012E+21
-0.531	-47.63808	0.50	-0.69315	-2.77259	7.81763E+21
-0.566	-50.36248	1.00	0	0	7.44984E+21

An average of the last column leads to a stability constant of 7.6×10^{21}. Alternatively, from equation (5.4.82), a plot of $-nF(E_{1/2}^C - E_{1/2}^M)/RT$ versus $\ln C_X^*$ leads to a slope of p and an intercept of $\ln K_C$. A linear regression of the data given leads to p = 3.993 = 4 and $\ln K_C$ = 50.38 (with r = 0.99998) or $K_C = 7.58 \times 10^{21} = 7.6 \times 10^{21}$, which agrees with the previous result.

5.7 (a). The reversible reaction under consideration is

$$\mathrm{O} + p\mathrm{H}^+ + ne \rightleftarrows \mathrm{R}$$

The Nernst equation for this reaction follows from equation (5.1.5) and can is written as

$$E = E^o_{O,R} + \frac{RT}{nF}\ln\left[\frac{C_O(0,t)C^p_{H^+}(0,t)}{C_R(0,t)}\right] \tag{1}$$

Proceeding as in Sections 5.5.3 and 5.5.4, the following equations can be written

$$i(t) = nFAm_O\left[C_O^* - C_O(0,t)\right] \tag{2}$$

$$i_d(t) = nFAm_O C_O^* \tag{3}$$

$$i(t) = nFAm_{H^+}\left[C_{H^+}^* - C_{H^+}(0,t)\right] \tag{4}$$

$$i(t) = nFAm_R\left[C_R(0,t) - C_R^*\right] = nFAm_R C_R(0,t) \tag{5}$$

The equality in the rightmost expression of equation (5) arises because species R is initially absent. Solving equations (2), (4), and (5), for $C_O(0,t)$, $C_{H^+}(0,t)$, and $C_R(0,t)$, respectively leads to

$$C_O(0,t) = \frac{i_d(t) - i(t)}{nFAm_O} \tag{6}$$

$$C_{H^+}(0,t) = C_{H^+}^* - \frac{i(t)}{nFAm_{H^+}} \cong C_{H^+}^* \quad (\text{if } C_{H^+}^* >> i(t)/nFAm_{H^+}) \tag{7}$$

$$C_R(0,t) = \frac{i(t)}{nFAm_R} \tag{8}$$

Substituting equations (6)-(8) into equation (1) leads to

$$E = E^o_{O,R} + \frac{RT}{nF}\ln\frac{m_R}{m_O} + \frac{pRT}{nF}\ln C_{H^+}^* + \ln\left[\frac{i_d(t) - i(t)}{i(t)}\right] \tag{9}$$

which is the equation for the steady-state voltammogram of the reaction.

(b). When $i(t) = i_d(t)/2$, the last natural logarithm term of equation (9) is zero and equation (9) can then be recast as

$$E_{1/2} = E^o_{O,R} + \frac{RT}{nF}\ln\frac{m_R}{m_O} + \frac{pRT}{nF}\ln C^*_{H^+} \tag{10}$$

Then

$$\frac{dE_{1/2}}{d\ln C^*_{H^+}} = \frac{pRT}{nF} \tag{11}$$

or, at 25 °C,

$$\frac{dE_{1/2}}{d\log C^*_{H^+}} = 2.303\frac{p}{n}\frac{8.31441 Jmol^{-1}K^{-1} \times 298.15K}{96485 Cmol^{-1}} = 0.0592\frac{p}{n} \tag{12}$$

which has units of volts. If $\log C^*_{H^+} \approx -\text{pH}$, then

$$\frac{dE_{1/2}}{dpH} = -0.0592\frac{p}{n} \tag{13}$$

Experimentally, a plot of $E_{1/2}$ as a function of pH will be linear with a slope of -0.0592*p/n* (units of volts) **from which *p* can be determined.**

5.13. The electrochemical **reaction under consideration** is

$$I_3^- + 2e \rightleftarrows 3I^- \tag{1}$$

with only species I^- present initially. The key to deriving the shape of the sampled-current voltammogram that would be recorded at a stationary Pt microelectrode can be found in Section 5.4.3 where

$$i(t) = nFAm_R\left[C_R(0,t) - C^*_R\right] \tag{2}$$

When solved for $C_R(0,t)$, this becomes

$$C_R(0,t) = C^*_R + \frac{i(t)}{nFAm_R} \tag{3}$$

where $m_R = (D_R/\pi t)^{1/2}$, as defined on page 185. Equation (3) can be written in terms of the diffusion limited current which follows from equation (1.4.17).

$$-\frac{i_d(t)}{C^*_R} = nFAm_R \tag{4}$$

This allows one to write

$$C_R(0,t) = C_R^*\left(\frac{i_d(t) - i(t)}{i_d(t)}\right) \tag{5}$$

The flux condition at the electrode surface is equivalent to equation (5.4.27), written as

$$3D_O^{1/2}C_O(0,t) + D_R^{1/2}C_R(0,t) = D_R^{1/2}C_R^* \tag{6}$$

where the factor of three accounts for the fact that the flux of I^- is three times the flux of I_3^-. Equation (6) leads to the following expression for $C_O(0,t)$ after substitution of equation (5).

$$C_O(0,t) = \frac{C_R^*}{3}\left(\frac{D_R}{D_O}\right)^{1/2}\left[\frac{i(t)}{i_d(t)}\right] \tag{7}$$

The Nernst equation (5.4.1) is written as

$$E = E^{o'} + \frac{RT}{2F}\ln\left(\frac{C_O(0,t)}{C_R^3(0,t)}\right) \tag{8}$$

for reaction (1). Substituting for $C_O(0,t)$ and $C_R(0,t)$ from equations (5) and (7) respectively leads to

$$E = E^{o'} + \frac{RT}{4F}\ln\frac{D_R}{D_O} - \frac{RT}{F}\ln C_R^* - \frac{RT}{2F}\ln 3 + \frac{RT}{2F}\ln\left\{\frac{i(t)i_d^2(t)}{\left[i_d(t) - i(t)\right]^3}\right\} \tag{9}$$

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after some algebra. When $i(t) = i_d(t)/2, E = E_{1/2}$, and equation (9) reduces to

$$E_{1/2} = E^{o'} + \frac{RT}{4F}\ln\frac{D_R}{D_O} - \frac{RT}{F}\ln C_R^* + \frac{RT}{2F}\ln\left(\frac{4}{3}\right) \tag{10}$$

Thus, $E_{1/2}$ depends on the bulk concentration of species R or I^-. Equations (9) and (10) are to be compared to equations (5.4.21) and (5.4.22) for the simpler O + ne ⇄ R case. One can immediately see that a plot of E *vs* log [(i_d-i)/i)] based on equations (9) and (10) would not be linear with a slope of 59.1/n mV at 25 °C. Moreover, $E_{1/2}$ for the simpler reaction does not depend on concentration.