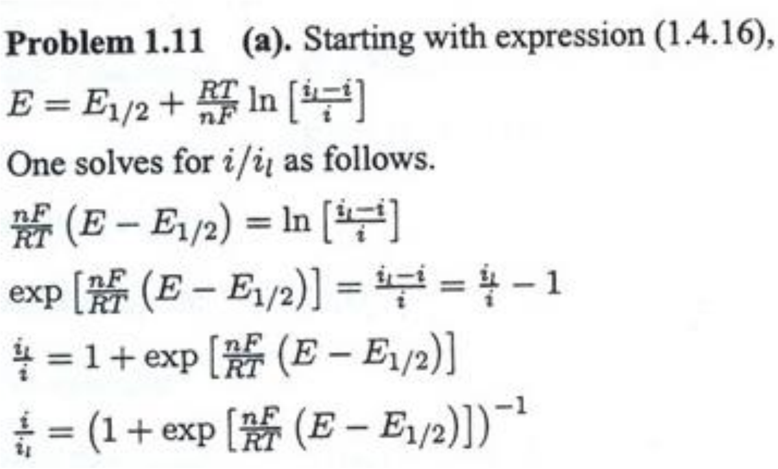
Read Chapter 4, answer the following problems, and indicate with whom you worked: ______________.

(1) Do problems 1.11, 1.12, 2.10, and 4.1 in Bard and Faulkner (B&F).

Answers:



Problem 1.11 **(a).** Starting with expression (1.4.16),

$$E = E_{1/2} + \frac{RT}{nF}\ln\left[\frac{i_l - i}{i}\right]$$

One solves for i/i_l as follows.

$$\frac{nF}{RT}\left(E - E_{1/2}\right) = \ln\left[\frac{i_l - i}{i}\right]$$

$$\exp\left[\frac{nF}{RT}\left(E - E_{1/2}\right)\right] = \frac{i_l - i}{i} = \frac{i_l}{i} - 1$$

$$\frac{i_l}{i} = 1 + \exp\left[\frac{nF}{RT}\left(E - E_{1/2}\right)\right]$$

$$\frac{i}{i_l} = \left(1 + \exp\left[\frac{nF}{RT}\left(E - E_{1/2}\right)\right]\right)^{-1}$$

Problem 1.12a: Starting with expression (1.4.20),

$$E = E^{0\prime} - \frac{RT}{nF}\ln\frac{m_O}{m_R} + \frac{RT}{nF}\ln\left(\frac{i_{l,c} - i}{i - i_{l,a}}\right)$$

Using (1.4.15), $E_{1/2} = E^{0\prime} - \frac{RT}{nF}\ln\frac{m_O}{m_R}$, one gets,

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

One solves for *i* as follows.

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

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

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

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

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

Problem 2.10 Consistent with the comments at the start of Problem 2.2, a sound thermodynamic development of standard potentials (E^0) for half-cell reactions must proceed through free energy calculations, not standard potentials.

(a). First, convert the two standard half-cell potentials into a net reaction by combining the reactions with the H^+/H_2 half-cell reaction.

$$H^+ + e \rightleftharpoons \tfrac{1}{2}H_2(g)$$

Thus,

$$\begin{array}{lll}
Cu^{2+} + 2e \rightleftharpoons Cu & 0.340\ V & = E_r^0 \\
\text{-}2(H^+ + e \rightleftharpoons \tfrac{1}{2}H_2(g)) & \text{-}(0.000\ V) & = E_l^0 \\
\hline
Cu^{2+} + H_2 \rightleftharpoons Cu + 2H^+ & 0.340\ V & = E_{rxn,1}^0
\end{array}$$

$$\Delta G_1^0 = -nFE_{rxn,1}^0 = -2FE_{rxn,1}^0$$

and

$$\begin{array}{lll}
Cu^{2+} + I^- + e \rightleftharpoons CuI & 0.86\ V & = E_r^0 \\
\text{-}(H^+ + e \rightleftharpoons \tfrac{1}{2}H_2(g)) & \text{-}(0.00\ V) & = E_l^0 \\
\hline
Cu^{2+} + I^- + \tfrac{1}{2}H_2 \rightleftharpoons CuI + H^+ & 0.86\ V & = E_{rxn,2}^0
\end{array}$$

$$\Delta G_2^0 = -nFE_{rxn,2}^0 = -1FE_{rxn,2}^0$$

Then, note that subtracting the second reaction from the first yields

$$CuI + \tfrac{1}{2}H_2 \rightleftharpoons Cu + I^- + H^+$$

This has a standard free energy of

$$\Delta G^0 = \Delta G_1^0 - \Delta G_2^0 = -F\left(2E_{rxn,1}^0 - E_{rxn,2}^0\right) \tag{1}$$

This is a single electron transfer reaction, so the emf for this reaction is

$$E_{rxn}^0 = -\frac{\Delta G^0}{1F} = 2E_{rxn.1}^0 - E_{rxn,2}^0 = -0.18\ V \tag{2}$$

Finally, the standard potential for the half reaction is found as

$$\begin{array}{lll}
CuI + e \rightleftharpoons Cu + I^- & & = E_r^0 \\
\text{-}(H^+ + e \rightleftharpoons \tfrac{1}{2}H_2(g)) & \text{-}(0.00\ V) & = E_l^0 \\
\hline
CuI + \tfrac{1}{2}H_2 \rightleftharpoons Cu + I^- + H^+ & \text{-}0.18\ V & = E_{rxn,3}^0
\end{array}$$

which is satisfied for the standard potential of the half reaction, $E_r^0 = E_{rxn,3}^0 + E_l^0 = -0.18$ V.

Generalized Form: The above processes can be generalized and simplified because the reference half reaction of H^+/H_2 and $-F$ cancel out. For the addition or subtraction of the standard potentials (E_1^0 and E_2^0) of two half reactions to yield the standard potential (E_3^0) of a third half reaction,

$$E_3^0 = \frac{n_1E_1^0 \pm n_2E_2^0}{n_3} \tag{3}$$

where the reactions have n_1, n_2, and n_3 electrons, respectively. Note that in all the previous problems in this Chapter, the special case applies where reactions are combined to yield a net equation with no explicit electrons. Then, $n_1 = n_2 = n_3$, and equation (3) reduces to $E_3^0 = E_1^0 \pm E_2^0$.

(b) This example is done using the generalized expression, equation (3). The half reactions are combined by subtraction of Rxn2 from Rxn1. Note, that the calculations yield a half reaction (i.e., there are explicit electrons in the final reaction) and the generalized form is required.

$$\begin{array}{ll} O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O & E_1^0 = 1.229\text{ V} \\ \underline{-(H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O)} & \underline{E_2^0 = -(1.763\text{ V})} \\ O_2 + 2H^+ + 2e \rightleftharpoons H_2O_2 & E_3^0 \end{array}$$

where

$$E_3^0 = \frac{4E_1^0 - 2E_2^0}{2} = \frac{4 \times 1.229 - 2 \times 1.763}{2} = 0.695\ V \tag{4}$$

Problem 4.1 The only ionic species in solution are Na^+ and OH^-, both present at 0.10 M. Using equation (4.2.10), the transference number for Na^+ is

$$t_{Na^+} = \frac{|z_{Na^+}|C_{Na^+}\lambda_{Na^+}}{|z_{Na^+}|C_{Na^+}\lambda_{Na^+} + |z_{OH^-}|C_{OH^-}\lambda_{OH^-}} \tag{1}$$

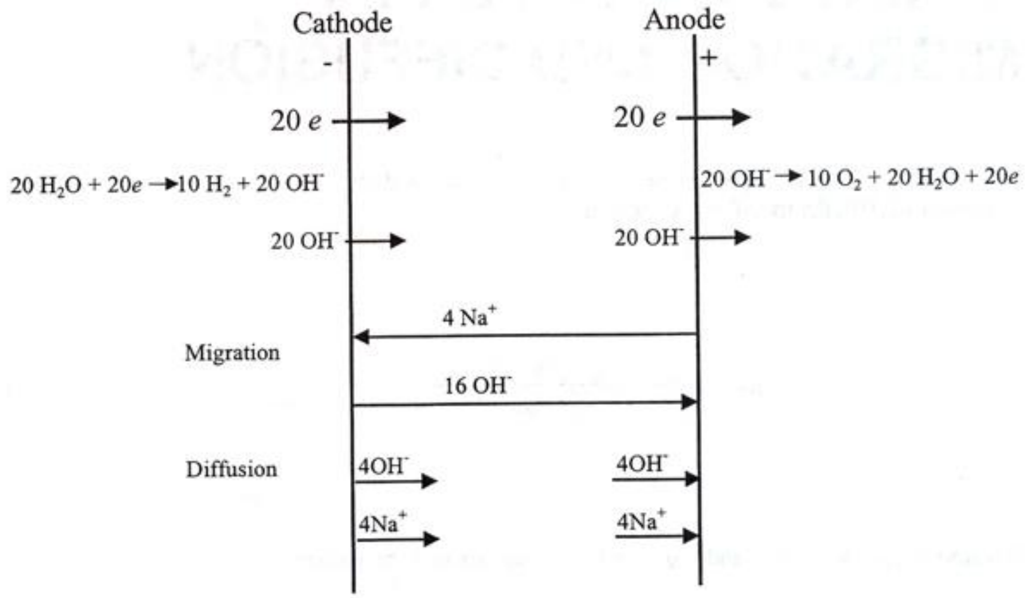
Because $|z_{Na^+}| = |z_{OH^-}|$ and $C_{Na^+} = C_{OH^-}$, this expression reduces to

$$t_{Na^+} = \frac{\lambda_{o,Na^+}}{\lambda_{o,Na^+} + \lambda_{o,OH^-}} = \frac{50.11}{50.11 + 198} = 0.20 \tag{2}$$

where λ_0 has been substituted for λ. From equation (2.3.6),

$$t_{OH^-} = 1 - t_{Na^+} = 0.80 \tag{3}$$

For 20 e passed externally, 20 e are injected at the cathode and 20 e are withdrawn at the anode. Thus, 20 OH^- are created at the cathode and 20 OH^- are removed at the anode. These changes are shown in the balance sheet below.



In the bulk solution, charge is transported only by migration, a fraction 0.80 being carried by OH^- moving to the anode and a fraction 0.20 carried by Na^+ moving to the cathode. Thus, 16 OH^- and 4 Na^+ migrate through the bulk and through diffusion layers, as shown in the balance sheet. This result could also be obtained via equation (4.3.3) by considering current flow at either electrode.

At the anode 20 OH^- are consumed, 16 of which are supplied by migration. The remaining 4 must diffuse to the electrode. No Na^+ is consumed or generated, yet 4 Na^+ exit by migration. At steady state, they must be replaced by diffusion to maintain a constant concentration distribution. Likewise, the cathode generates 20 OH^- and no Na^+, while 16 OH^- leave and 4 Na^+ arrive by migration. Thus, 4 OH^- and 4 Na^+ must diffuse outward per 20 e at steady state. The fluxes from diffusion complete the balance sheet.

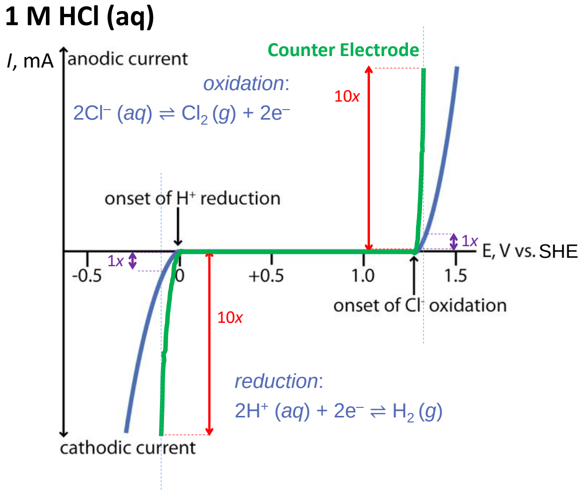
(2) Given a 1 cm^2 perfectly flat and atomically smooth electrode, a second electrode with a roughness factor of 10, and a third electrode made of the same material as the first electrode but with ten times the geometric surface area, answer the following. *Choose any electrolyte condition you wish, but state the condition you chose.*

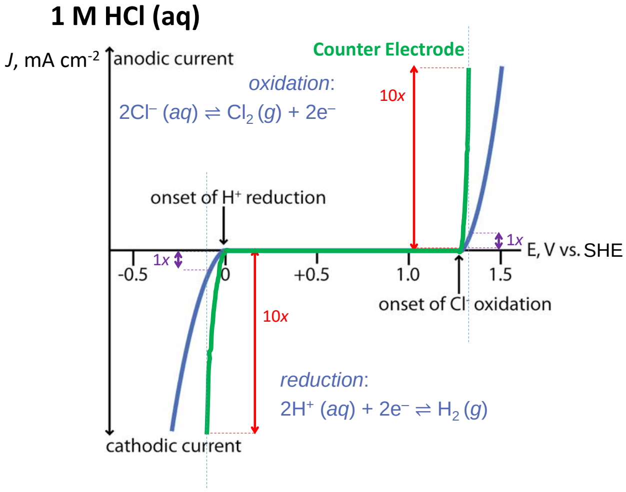
a. On one set of axes, plot a non-hysteretic *I*–*E* curve for each electrode when it is the WE in a three-electrode set-up.
b. On one set of axes, plot a non-hysteretic *J*–*E* curve for each electrode when it is the WE in a three-electrode set-up.

Answers:

(a) The *I*–*E* curves for each as WE are on the next page; **the first electrode's response would be the curve depicted in blue, while the second and third electrodes' response would be the curve depicted in green.**

(b) The *J*–*E* curves for each as WE are on the next page where the plots look the same as we only divided by the geometric area; **the first and third electrodes' response would be the curve depicted in blue, while the second electrode's response would be the curve depicted in green.**





(3) In Trotochaud, Ranney, Williams, and Boettcher, *Journal of the American Chemical Society*, 2012, *134*, 17253 (see class website), the authors plot of their J–E curves with more complex abscissa axes (e.g. Figure 3 and Figure 6). With this in mind, answer the following.

a. Why is iR_u subtracted from the values of the potential?
b. How would the plots have changed if iR_u had not been subtracted from the potentials? Show this graphically and/or describe it in words.
c. Explain the difference(s) between the top and bottom abscissa axes and why it was useful to show both.
d. The data in the inset of Figure 6 can be obtained by integrating I–t curves with respect to time. However, the data can also be obtained using the J–E curves shown in the main part of the figure, and the scan rate. Explain how the data in the figure inset was calculated from the data in the main part of the figure.

Answers:

(a) **To correct the E_{app} so that the plot is the potential felt by the WE versus the RE and not that which was applied by the potentiostat. The potential felt by the WE (vs. RE) is what really matters, not what was applied.**

(b) **The potential for each current point would have been shifted farther from the *x*-intercepts. That is, the J–E plot would be stretched out both on the top (anodic current) and on the bottom (cathodic current).** That is, subtracting iR_u tightens up the curve (i.e. makes it skinnier).

(c) **The bottom axis is the typical potential applied (and corrected by iR_u), while the top axis is the overpotential (corrected by iR_u), which is the potential beyond the thermodynamic equilibrium potential. The bottom axis includes a reference electrode so we know the potential values on a meaningful scale. The top axis shows the potential beyond the thermodynamic potential, which is wasted as heat but allows the reaction to proceed more quickly; i.e. overpotential speed up kinetics.**

(d) **Either the abscissa axis was converted into units of time by dividing by the scan rate, and then the new *J–t* curve was integrated over the range of the redox peak (resulting in units of (mA cm^{-2})(s) = mC cm^{-2}), or the *J–E* curve was first integrated over the range of the redox peak (resulting in units of (mA cm^{-2})(V) = mA V cm^{-2}) and then the resulting data was divided by the scan rate (resulting in units of (mA V cm^{-2}) / (V s^{-1}) = mC cm^{-2}).**