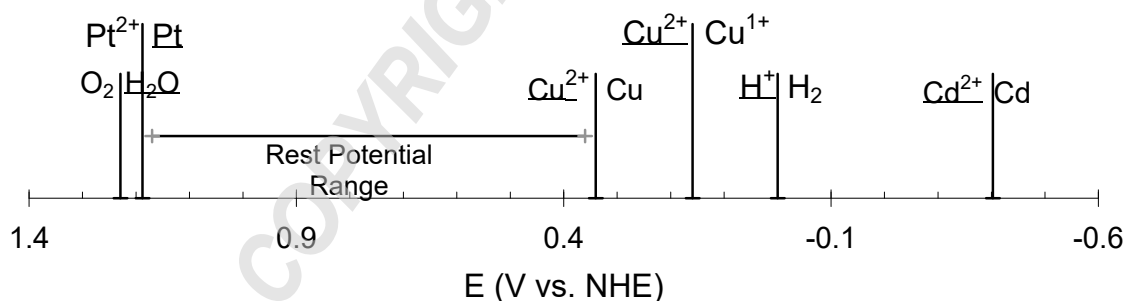


# 1 OVERVIEW OF ELECTRODE PROCESSES

**Problem 1.1**<sup>©</sup> (a). In approaching this kind of problem, it is useful to list all the couples in Table C.1 that are relevant to the system.

| $E^0$ vs. NHE (V) | Reaction                                                                     |
|-------------------|------------------------------------------------------------------------------|
| 1.229             | $\text{O}_2 + 4\text{H}^+ + 4\text{e} \rightleftharpoons \text{H}_2\text{O}$ |
| 1.188             | $\text{Pt}^{2+} + 2\text{e} \rightleftharpoons \text{Pt}$                    |
| 0.340             | $\text{Cu}^{2+} + 2\text{e} \rightleftharpoons \text{Cu}$                    |
| 0.159             | $\text{Cu}^{2+} + \text{e} \rightleftharpoons \text{Cu}^+$                   |
| 0.000             | $2\text{H}^+ + 2\text{e} \rightleftharpoons \text{H}_2$                      |
| -0.4025           | $\text{Cd}^{2+} + 2\text{e} \rightleftharpoons \text{Cd}$                    |

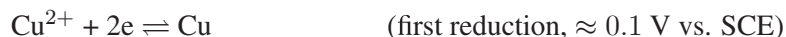
Alternatively, a graphical representation may prove useful. Here, the standard or formal potentials for each redox couple are plotted on a potential axis. The species present in solution are underlined. Note the reduced half of the couple is noted toward more negative potentials. The vertical line indicates the approximate potential range where both halves of the redox couple can exist. For electrode potentials positive of a given line, the oxidized half of the couple is stable at the electrode surface; for electrode potentials negative of the line, the reduced form is stable. Note that for  $n = 1$ , electrode potentials within 118 mV of  $E^0$  require no less than 1% of either the oxidized or reduced halves of the couple as given by  $\log \frac{[\text{O}]}{[\text{R}]} = -n(E - E^0)/0.059$ .



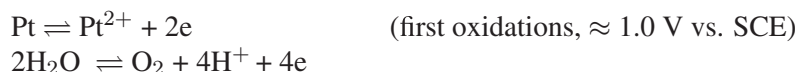
The composition of the system dictates that the rest (zero current) potential be more positive than  $E_{\text{Cu}^{2+}/\text{Cu}}^0$  and more negative than  $E_{\text{O}_2/\text{H}_2\text{O}}^0$  or  $E_{\text{Pt}^{2+}/\text{Pt}}^0$ , i.e., between about 0.34 V and 1.2 V vs. NHE. Graphically, this is apparent because this is the voltage range over which the oxidized ( $\text{Cu}^{2+}$ ) and reduced species (Pt or  $\text{H}_2\text{O}$ ) present in the solution are most adjacent on the graph. This defines a zone of stability set by the oxidized and reduced species. (Note that the cell would not be at equilibrium if oxidized and reduced species of two or more couples were present such that they were on the outer sides of the lines. For example, if the solution contained Cu and  $\text{O}_2$ , there would be a thermodynamic driving force for these species to react spontaneously to form water and  $\text{Cu}^{2+}$ .) In the rest potential range, the potential is not well defined in a thermodynamic sense; the electrode is not well poised, because no couple has both oxidized and reduced forms present. Calculation of the equilibrium potential by the Nernst equation cannot be made.

## Chapter 1 OVERVIEW OF ELECTRODE PROCESSES

Current will flow when the potential is moved negatively from the rest potential to about 0.340 V (or  $0.340 + (-0.2412) = 0.099$  V vs. SCE) so that  $\text{Cu}^{2+}$  is reduced at the electrode surface first.

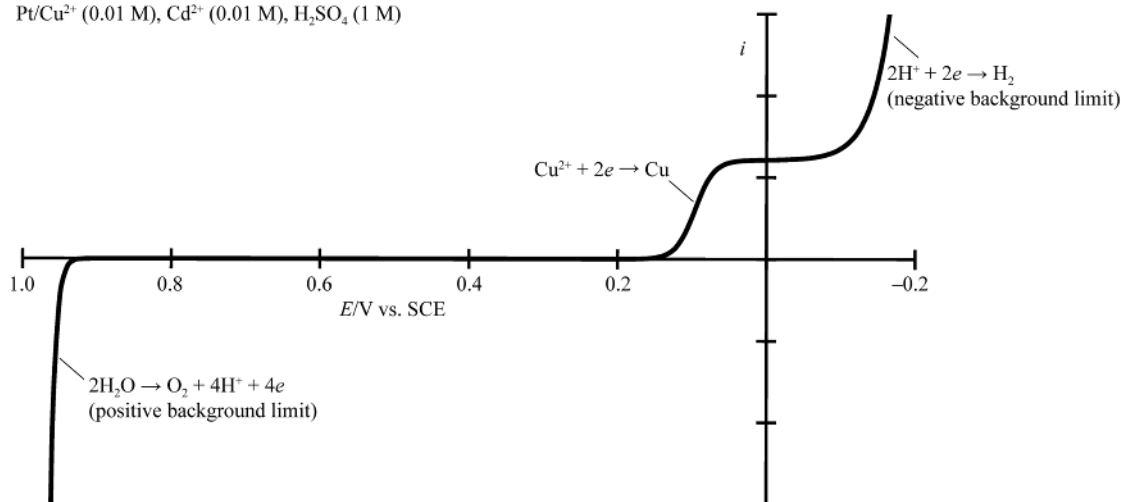


A positive movement from the rest potential first causes significant current flow when platinum and water are oxidized.



Actually, Pt would form a thin oxide film, then it would stabilize, and only the oxygen evolution reaction would occur, with a significant negative (anodic) current flow due to the oxidation of water, which marks the positive background limit. The current-potential curve would look like the following with a transition from a limiting positive (cathodic) current flow due to  $\text{Cu}^{2+}$  reduction to Cu metal that plates onto the Pt UME to a significant cathodic current beginning at -0.1 V vs SCE due to  $\text{H}^+$  (2M in solution) reduction, which marks the negative background limit. Although  $\text{Cd}^{2+}$  is present in the solution, its reduction to Cd cannot be observed, because this reduction occurs at about -0.6 V vs. SCE, far beyond the negative background limit.

Pt/ $\text{Cu}^{2+}$  (0.01 M),  $\text{Cd}^{2+}$  (0.01 M),  $\text{H}_2\text{SO}_4$  (1 M)

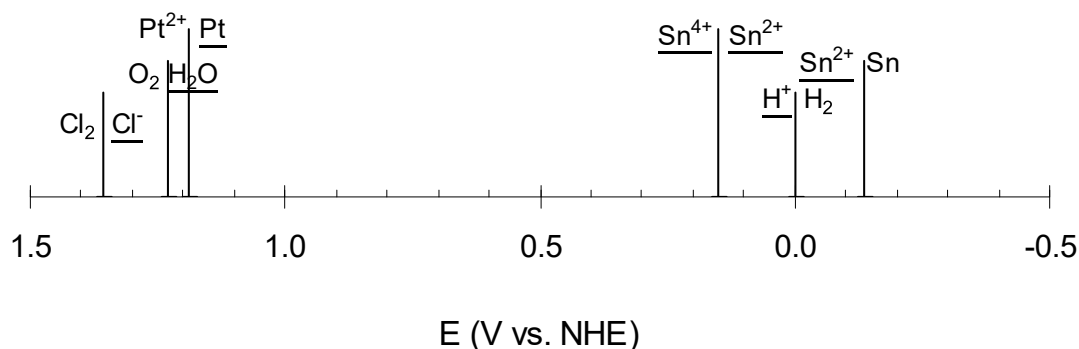


The reader may be puzzled regarding the locations of the background limits, which are less extreme than the related standard potentials. One must remember that a background curve represents just the foot of an enormous wave supported by a highly available electroreactant (in this case,  $\text{H}^+$  or  $\text{H}_2\text{O}$ ). The half-wave potential for that wave might be near the standard potential of the couple, but on the current scale that allows observation of voltammetric features of interest, one never approaches the standard potential before the background current becomes prohibitive. In general, a background limit based on a reversible or quasireversible couple is less extreme than the corresponding standard potential by about 0.1 V.

(b). The couples to be considered from Table C.1 are as follows:

| $E^0$ vs. NHE (V) | Reaction                                                              |
|-------------------|-----------------------------------------------------------------------|
| 1.3583            | $\text{Cl}_{2(g)} + 2e \rightleftharpoons 2\text{Cl}^-$               |
| 1.229             | $\text{O}_2 + 4\text{H}^+ + 4e \rightleftharpoons \text{H}_2\text{O}$ |
| 1.188             | $\text{Pt}^{2+} + 2e \rightleftharpoons \text{Pt}$                    |
| 0.15              | $\text{Sn}^{4+} + 2e \rightleftharpoons \text{Sn}^{2+}$               |
| 0.000             | $2\text{H}^+ + 2e \rightleftharpoons \text{H}_2$                      |
| -0.1375           | $\text{Sn}^{2+} + 2e \rightleftharpoons \text{Sn}$                    |

The graphical representation is as follows.



Because both  $\text{Sn}^{4+}$  and  $\text{Sn}^{2+}$  are present, the system is poised and a well-defined thermodynamic equilibrium potential exists. From the Nernst equation (1.3.13), the equilibrium potential is 0.15 V vs. NHE or -0.09 V vs. SCE. Moving negatively from this potential favors  $\text{Sn}^{2+}$  at the electrode and requires reduction of  $\text{Sn}^{4+}$ .

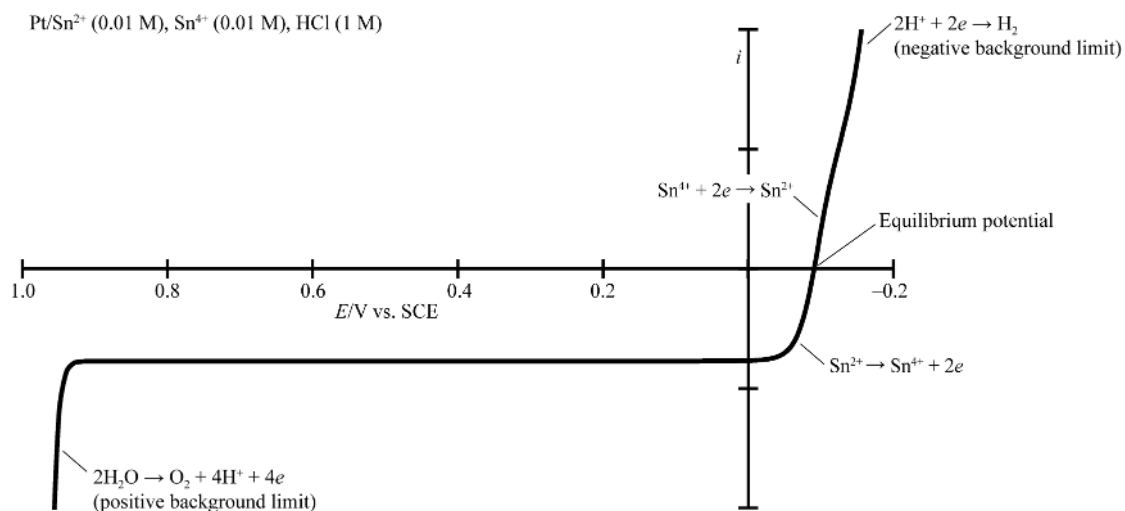


Likewise, a move positive of the rest potential favors  $\text{Sn}^{4+}$  at the electrode and drives oxidation.



The current potential curve resembles the following where the equilibrium potential (-0.09 V vs SCE) for the  $\text{Sn}^{4+}/\text{Sn}^{2+}$  couple is shown because both tin cations are present in the electrochemical cell at the same concentration. Moving negative from this potential for  $\text{Sn}^{4+}/\text{Sn}^{2+}$  and positive from this potential for  $\text{Sn}^{2+}/\text{Sn}^{4+}$  leads to a cathodic and anodic limiting current respectively that are equal but opposite in sign. Moving yet more negative in potential from the cathodic limiting current leads to a significant increase in cathodic current at -0.1 V vs SCE due to proton (1 M) reduction, which corresponds to the negative background limit. The limiting current for reduction of  $\text{Sn}^{4+}$  is not fully resolved from the current rise at this limit. Moving more positive in potential from about +0.9 V from the anodic limiting current leads to a significant excursion of the anodic current due to water oxidation, which corresponds to the positive background limit.

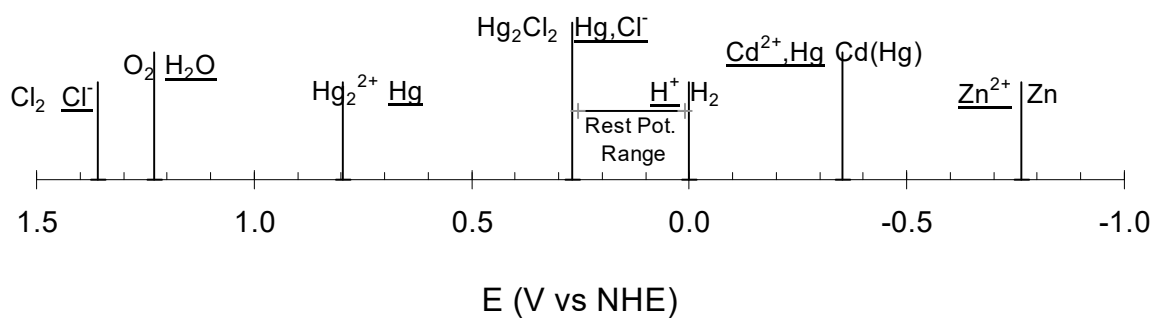
## Chapter 1 OVERVIEW OF ELECTRODE PROCESSES



(c). The couples to be considered from Table C.1 are as follows:

| $E^0$ vs. NHE (V) | Reaction                                                                   |
|-------------------|----------------------------------------------------------------------------|
| 1.3583            | $\text{Cl}_{2(g)} + 2e \rightleftharpoons 2\text{Cl}^-$                    |
| 1.229             | $\text{O}_2 + 4\text{H}^+ + 4e \rightleftharpoons \text{H}_2\text{O}$      |
| 0.7960            | $\text{Hg}_2^{2+} + 2e \rightleftharpoons 2\text{Hg}$                      |
| 0.26816           | $\text{Hg}_2\text{Cl}_2 + 2e \rightleftharpoons 2\text{Hg} + 2\text{Cl}^-$ |
| 0.000             | $2\text{H}^+ + 2e \rightleftharpoons \text{H}_2$                           |
| -0.3515           | $\text{Cd}^{2+} + 2e \rightleftharpoons \text{Cd}(\text{Hg})$              |
| -0.7656           | $\text{Zn}^{2+} + 2e \rightleftharpoons \text{Zn}(\text{Hg})$              |

The graphical representation is shown.



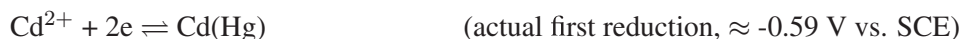
As in (a), the system is unpoised and the rest potential is not well defined, but exists between  $E_{\text{H}^+/\text{H}_2}^0 = 0.0$  V vs. NHE and  $E_{\text{Hg}_2\text{Cl}_2/\text{Hg}}^0$  at 0.26816 V vs. NHE; that is, between -0.2412 V and 0.02696 V vs. SCE. The first oxidation occurs when the potential is drawn to more positive values than  $\approx -0.1$  V vs. SCE, where the following reaction begins.



The chart and diagram predict that the first reduction will be the evolution of hydrogen.



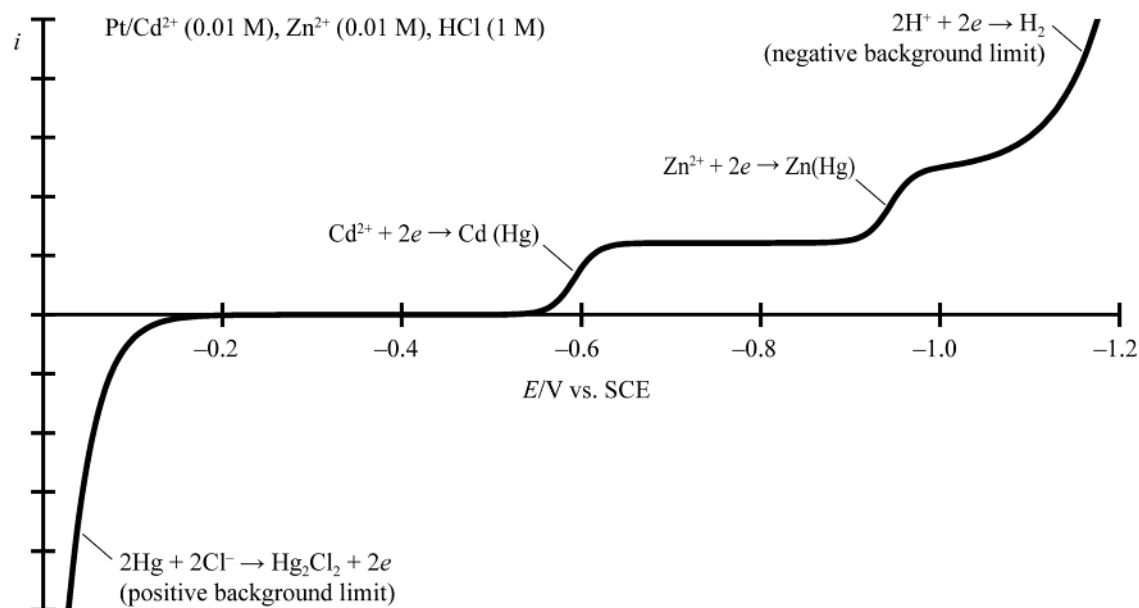
However, this reaction is extremely slow on mercury (i.e., it has a high overpotential; see Section 1.1.7(c) and Chapters 1 and 3) and does not occur at an appreciable rate until far more negative potentials are reached. Thus, the first reduction of significance is the deposition of cadmium into the mercury to form the amalgam.



This is an example of kinetics superseding thermodynamic expectation during dynamic perturbation of an electrochemical system. The overpotential of hydrogen on mercury significantly widens the range of accessible potentials (i.e., the “potential window”) in water, and is one reason mercury was long-favored for electrochemical analysis and thermodynamic evaluations despite its toxicity. The reduction waves for  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  can both be observed at a mercury electrode.

The reduction of  $\text{Cd}^{2+}$  will lead to a limiting current at  $-0.59 \text{ V vs SCE}$ , followed by a limiting current of similar height for the reduction of  $\text{Zn}^{2+}$  at about  $-1.0 \text{ V vs. SCE}$ . Finally, the reduction of  $\text{H}^+$  begins at approximately  $-1.1 \text{ V vs. SCE}$  with a cathodic current that appears infinite on the current scale due to the  $\text{H}^+$  concentration of  $1 \text{ M}$ .

The current-potential curve resembles the following where the anodic current due to the oxidation of  $\text{Hg}$  at  $0.0 \text{ V vs SCE}$  appears practically infinite on the current scale. This oxidation defines the anodic background limit.



The negative background limit in this case is not due to a reversible or quasireversible couple, but, rather, the highly irreversible discharge of  $\text{H}_2$  on a mercury electrode. It occurs at potentials about  $1 \text{ V}$  more extreme than  $E^0$  for the couple because the kinetics have to be activated through a large overpotential.

## Chapter 1 OVERVIEW OF ELECTRODE PROCESSES

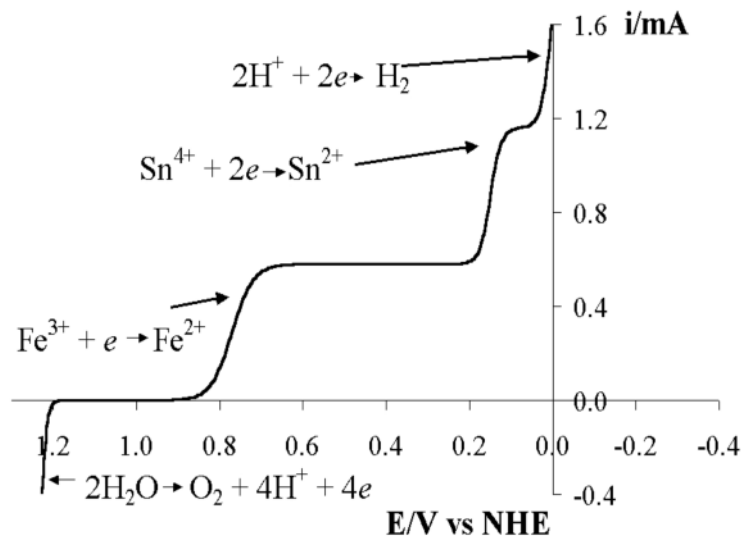
**Problem 1.3**<sup>©</sup> The important reactions are



(a). From (1.3.10) and  $n = 1$ ,  $i_l = nFAm_O C_O^* = 580 \mu\text{A}$ .

(b). Because the concentration of stannic ion is half that of ferric ion but  $n = 2$ , and the mass transfer coefficients of the two ions are the same, the limiting current for the reduction of  $\text{Sn}^{4+}$  is also  $580 \mu\text{A}$ . The halfwave potential,  $E_{1/2}$ , for the ferric reduction is near  $E^0 = 0.77 \text{ V vs. NHE}$ , whereas that for the reduction of stannic ion is near  $0.15 \text{ V vs. NHE}$ .

The  $i - E$  curve is as follows.



**Problem 1.5**<sup>©</sup> The discussion for this problem is found in Section 1.6.4a. From equation (1.6.17),

$$i = -\frac{\Delta E}{R_u} \exp \left[ -\frac{t}{R_u C_d A} \right] \quad (1.6.17)$$

Area  $A$  is introduced where  $C_d$  is expressed as capacitance per area ( $\mu\text{F cm}^{-2}$ ). The cell time constant  $\tau = R_u C_d A$ .

$$i = -\frac{\Delta E}{R_u} \exp \left[ -\frac{t}{\tau} \right]$$

For potential stepped from  $E_1$  to  $E_2$  in the nonfaradaic region,  $\Delta E = E_2 - E_1$ , the capacitor is charged. The initial current, when  $t = 0$ , is the maximum current,  $= -\Delta E/R_u$ . The current decays to  $0.05i(t=0)$  at time  $i(t_{5\%})$  when

$$\begin{aligned} \frac{i(t_{5\%})}{i(t=0)} &= 0.05 = \exp \left[ -\frac{t_{5\%}}{\tau} \right] \\ -\ln(0.05) &= 3.0 = \frac{t_{5\%}}{\tau} \end{aligned}$$

The current decays to 5 % of the initial current when  $t_{5\%} = 3.0\tau$ . At this time, double-layer charging is 95 % complete.

For  $C_d = 20 \mu\text{F cm}^{-2}$  and  $A = 0.1 \text{ cm}^2$ ,  $\tau = R_u C_d A$  and  $t_{5\%} = 3.0\tau$  are found for  $R_u$  of 1, 10, and 100  $\Omega$ .

| $R_s (\Omega)$ | $\tau (\mu\text{s})$ | $3\tau (\mu\text{s})$ |
|----------------|----------------------|-----------------------|
| 1              | 2                    | 6                     |
| 10             | 20                   | 60                    |
| 100            | 200                  | 600                   |

=====

**Problem 1.7**<sup>©</sup> From equation (1.6.23),

$$i = \nu C_d \left[ 1 - \exp \left( -\frac{t}{R_u C_d} \right) \right] \quad (1.6.23)$$

The transient term decays in a few time constants. Here, it is negligible after 10  $\mu\text{s}$  (which corresponds to  $5\tau$  in Problem 1.5 at  $R_s = 1 \Omega$ ) to 2 ms (at  $R_s = 100 \Omega$ ). At steady state,

$$i = \nu C_d A$$

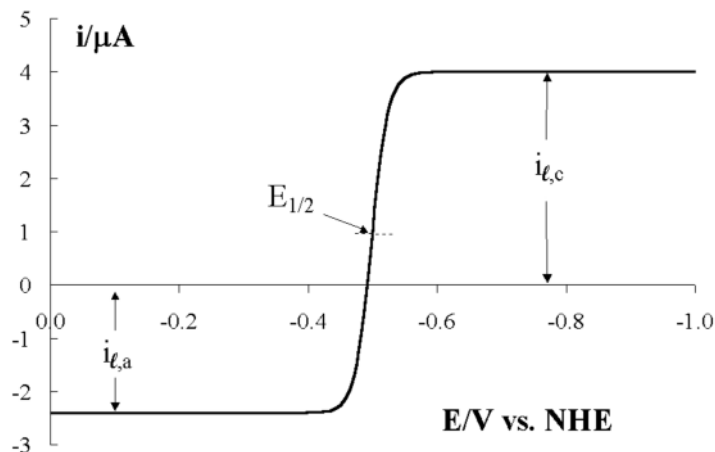
$A$  appears as  $C_d$  is expressed here in capacitance per unit area. Currents are independent of  $R_u$ .

| $\nu (\text{V s}^{-1})$ | 0.02 | 1 | 20 |
|-------------------------|------|---|----|
| $i (\mu\text{A})$       | 0.04 | 2 | 40 |

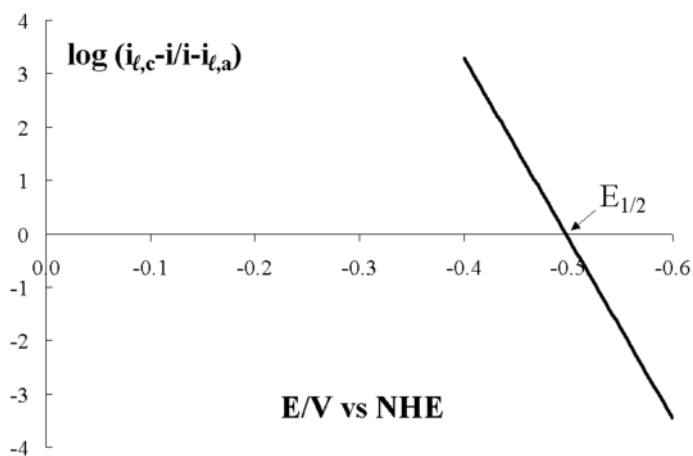
## Chapter 1 OVERVIEW OF ELECTRODE PROCESSES

**Problem 1.8<sup>©</sup>** (a). From equations (1.3.10) and (1.3.18) for the limiting currents,  $\frac{i_{l,c}}{-i_{l,a}} = \frac{nFAm_O C_O^*}{nFAm_R C_R^*} = \frac{4.00\mu A}{2.40\mu A} = 1.67$  or  $\frac{m_O}{m_R} = 1.67 \frac{C_R^*}{C_O^*} = 0.833$ . From equation (1.3.16),  $E_{1/2} = E^{0'} - \frac{RT}{nF} \ln \frac{m_O}{m_R} = -0.498$  V vs. NHE.

(b). The wave has both cathodic and anodic parts, because both  $A^{3+}$  and  $A^+$  are present in the bulk. The potential where the current is midway between the plateaus is  $E_{1/2}$ . The potential where  $i = 0$  is the equilibrium value calculable from the Nernst equation. The  $i - E$  curve is shown.



(c). From (1.3.21), the plot is  $\log [(i_{l,c} - i) / (i - i_{l,a})]$  vs. NHE. The crossing of the abscissa is  $E_{1/2}$ , and the slope magnitude is  $nF/(2.303RT) = n38.92$  V<sup>-1</sup> at 25 °C. The plot is shown.



**Problem 1.10<sup>©</sup>** The relationships linking current and concentration in the steady-state treatment of mass transfer are equations (1.3.7) and (1.3.8).

$$i = nFAm_O[C_O^* - C_O(x=0)] \quad (1)$$

$$i = nFAm_R[C_R(x=0) - C_R^*] \quad (2)$$

Because  $C_O^* = 0$ , the first of these is

$$i = -nFAm_OC_O(x=0) \quad (3)$$

Because  $O$  does not exist in the bulk, no cathodic current can flow. All current goes to oxidize  $R$ . The limiting rate of oxidation is found when  $C_R(x=0) = 0$ , hence the limiting current is

$$i_{l,a} = -nFAm_RC_R^* \quad (4)$$

The system is reversible, hence,

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{C_O(x=0)}{C_R(x=0)} \quad (5)$$

From equation (3),

$$C_O(x=0) = \frac{-i}{nFAm_O} \quad (6)$$

From equations (2) and (4),

$$C_R(x=0) = \frac{i - i_{l,a}}{nFAm_R} \quad (7)$$

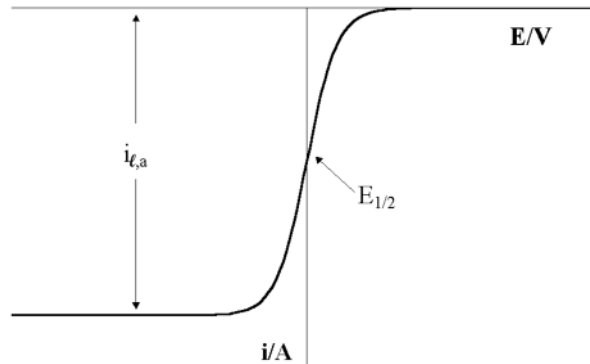
Substitution of (6) and (7) into (5) gives

$$E = E^{0'} + \frac{RT}{nF} \ln \left[ \frac{m_R}{m_O} \right] + \frac{RT}{nF} \ln \left[ \frac{-i}{i - i_{l,a}} \right] \quad (8)$$

Note that this result is the special case of (1.3.21) for  $i_{l,c} = 0$ . When  $i = i_{l,a}/2$ , the last term in (8) is zero and  $E = E_{1/2}$ .

$$E_{1/2} = E^{0'} + \frac{RT}{nF} \ln \frac{m_R}{m_O} \quad (9)$$

The  $i - E$  curve, plotted from equation (8), resembles the following:



## Chapter 1 OVERVIEW OF ELECTRODE PROCESSES

**Problem 1.12<sup>©</sup>** (a). Starting with expression (1.3.17),

$$E = E_{1/2} + \frac{RT}{nF} \ln \left[ \frac{i_l - i}{i} \right] \quad (1.3.17)$$

One solves for  $i/i_l$  as follows.

$$\begin{aligned} \frac{nF}{RT} (E - E_{1/2}) &= \ln \left[ \frac{i_l - i}{i} \right] \\ \exp \left[ \frac{nF}{RT} (E - E_{1/2}) \right] &= \frac{i_l - i}{i} = \frac{i_l}{i} - 1 \\ \frac{i_l}{i} &= 1 + \exp \left[ \frac{nF}{RT} (E - E_{1/2}) \right] \\ \frac{i}{i_l} &= \left( 1 + \exp \left[ \frac{nF}{RT} (E - E_{1/2}) \right] \right)^{-1} \end{aligned} \quad (1.11.1)$$

(b). The limiting current, from expression (1.3.10), is

$$i_l = nFAm_O C_O^* \quad (1.3.10)$$

Here,  $i_l = 96.5 \mu\text{A}$  for  $A = 0.10 \text{ cm}^2$ ,  $m_O = 10^{-3} \text{ cm/s}$ , and  $C_O^* = 10 \text{ mM}$ .

From Appendix C,  $E^0 = 0.10 \text{ V}$  vs. NHE. Note that because  $m_O = m_R = 10^{-3} \text{ cm/s}$ , then  $E_{1/2} = E^0$ , which follows from equation (1.3.16). To calculate the  $i - E$  curve, an Excel spreadsheet follows on page 11.

## Calculation of Reversible Current-Potential Curves

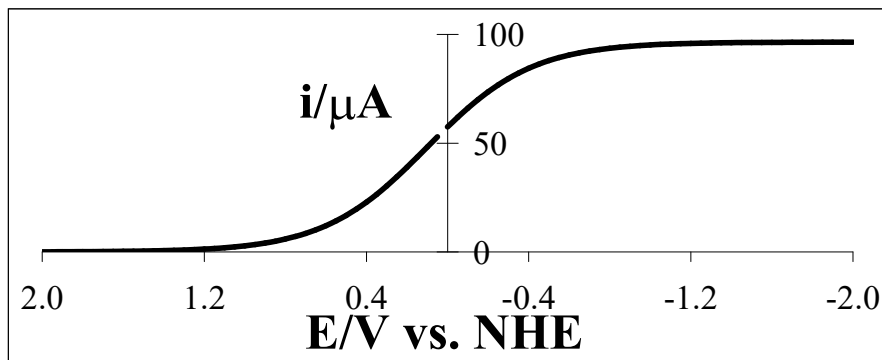
Based on equation (1.3.17)

Calculation of Reversible Current-Potential Curves

Based on B&amp;F eq. 1.4.16

$F(C)$  96485  
 $F/RT(V^{-1})$  38.9218  
 $A(cm^2)$  0.1

$n$  1  
 $E_o(V)$  0.1  
 $E_{1/2}(V)$  0.1  
 $CO(M)$  1.00E-02  
 $CR(M)$  0  
 $mO(cm/s)$  1.00E-03  
 $mR(cm/s)$  1.00E-03  
 $i_{lim,c}(A)$  9.65E-05  
 $i_{lim,a}(A)$  0.00E+00



| E/V   | I/A       | I/ $\mu A$ | E/V  | I/A       | I/ $\mu A$ |
|-------|-----------|------------|------|-----------|------------|
| -2.00 | 9.646E-05 | 96.46      | 0.05 | 5.292E-05 | 52.92      |
| -1.95 | 9.645E-05 | 96.45      | 0.10 | 4.824E-05 | 48.24      |
| -1.90 | 9.644E-05 | 96.44      | 0.15 | 4.356E-05 | 43.56      |
| -1.85 | 9.644E-05 | 96.44      | 0.20 | 3.897E-05 | 38.97      |
| -1.80 | 9.643E-05 | 96.43      | 0.25 | 3.455E-05 | 34.55      |
| -1.75 | 9.641E-05 | 96.41      | 0.30 | 3.036E-05 | 30.36      |
| -1.70 | 9.640E-05 | 96.40      | 0.35 | 2.646E-05 | 26.46      |
| -1.65 | 9.638E-05 | 96.38      | 0.40 | 2.289E-05 | 22.89      |
| -1.60 | 9.636E-05 | 96.36      | 0.45 | 1.967E-05 | 19.67      |
| -1.55 | 9.633E-05 | 96.33      | 0.50 | 1.680E-05 | 16.80      |
| -1.50 | 9.629E-05 | 96.29      | 0.55 | 1.427E-05 | 14.27      |
| -1.45 | 9.625E-05 | 96.25      | 0.60 | 1.206E-05 | 12.06      |
| -1.40 | 9.620E-05 | 96.20      | 0.65 | 1.015E-05 | 10.15      |
| -1.35 | 9.614E-05 | 96.14      | 0.70 | 8.514E-06 | 8.51       |
| -1.30 | 9.607E-05 | 96.07      | 0.75 | 7.119E-06 | 7.12       |
| -1.25 | 9.598E-05 | 95.98      | 0.80 | 5.938E-06 | 5.94       |
| -1.20 | 9.588E-05 | 95.88      | 0.85 | 4.942E-06 | 4.94       |
| -1.15 | 9.575E-05 | 95.75      | 0.90 | 4.105E-06 | 4.10       |
| -1.10 | 9.559E-05 | 95.59      | 0.95 | 3.405E-06 | 3.40       |
| -1.05 | 9.540E-05 | 95.40      | 1.00 | 2.820E-06 | 2.82       |
| -1.00 | 9.517E-05 | 95.17      | 1.05 | 2.333E-06 | 2.33       |
| -0.95 | 9.489E-05 | 94.89      | 1.10 | 1.929E-06 | 1.93       |
| -0.90 | 9.456E-05 | 94.56      | 1.15 | 1.594E-06 | 1.59       |
| -0.85 | 9.415E-05 | 94.15      | 1.20 | 1.316E-06 | 1.32       |
| -0.80 | 9.366E-05 | 93.66      | 1.25 | 1.086E-06 | 1.09       |
| -0.75 | 9.308E-05 | 93.08      | 1.30 | 8.953E-07 | 0.90       |
| -0.70 | 9.238E-05 | 92.38      | 1.35 | 7.382E-07 | 0.74       |
| -0.65 | 9.154E-05 | 91.54      | 1.40 | 6.085E-07 | 0.61       |
| -0.60 | 9.055E-05 | 90.55      | 1.45 | 5.014E-07 | 0.50       |
| -0.55 | 8.937E-05 | 89.37      | 1.50 | 4.131E-07 | 0.41       |
| -0.50 | 8.797E-05 | 87.97      | 1.55 | 3.403E-07 | 0.34       |
| -0.45 | 8.633E-05 | 86.33      | 1.60 | 2.803E-07 | 0.28       |
| -0.40 | 8.443E-05 | 84.43      | 1.65 | 2.309E-07 | 0.23       |
| -0.35 | 8.222E-05 | 82.22      | 1.70 | 1.901E-07 | 0.19       |
| -0.30 | 7.969E-05 | 79.69      | 1.75 | 1.566E-07 | 0.16       |
| -0.25 | 7.681E-05 | 76.81      | 1.80 | 1.289E-07 | 0.13       |
| -0.20 | 7.359E-05 | 73.59      | 1.85 | 1.061E-07 | 0.11       |
| -0.15 | 7.002E-05 | 70.02      | 1.90 | 8.738E-08 | 0.09       |
| -0.10 | 6.613E-05 | 66.13      | 1.95 | 7.194E-08 | 0.07       |
| -0.05 | 6.194E-05 | 61.94      | 2.00 | 5.923E-08 | 0.06       |
| 0.00  | 5.751E-05 | 57.51      |      |           |            |

## Chapter 1 OVERVIEW OF ELECTRODE PROCESSES

**Problem 1.13<sup>©</sup>** (a). Combining equations (1.3.21) and (1.3.16) yields

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

This equation can be rewritten as

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

Or, upon solving for  $i$ ,

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

(c). The equilibrium potential can be calculated from the Nernst equation, as follows.

$$E_{eq} = 0.10 \text{ V} + 0.05915 \log(10 \text{ mM}/5 \text{ mM}) = 0.12 \text{ V}$$

Substitution of  $i = 0.48 \text{ mA/cm}^2$  in equation (1.3.21) yields

$$E = 0.10 \text{ V} + 0.05915 \log \left[ \frac{0.965 - 0.48}{0.48 - (-0.482)} \right] = 0.082 \text{ V}$$

From equation (1.2.1),

$$\begin{aligned} \eta_{mt} &= E - E_{eq} \\ \eta_{mt} &= 0.082 \text{ V} - 0.12 \text{ V} = -0.038 \text{ V} \end{aligned} \tag{1.2.1}$$

(d). The diffusion limiting cathodic current is  $0.000965 \text{ A/cm}^2 \times 0.1 \text{ cm}^2 = 9.65 \times 10^{-5} \text{ A}$ . From equation (1.3.29), for a cathodic process,

$$R_{mt} = \frac{RT}{nF i_{l,c}} \tag{1.3.29}$$

$$R_{mt} = (RT/F) (n i_{l,c})^{-1} = 0.0257 \text{ V} / 9.65 \times 10^{-5} \text{ A} = 266 \Omega.$$