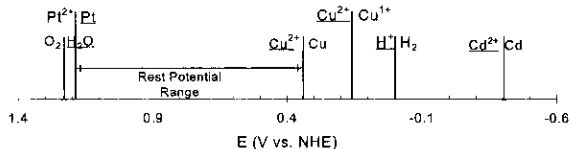


1 INTRODUCTION AND OVERVIEW OF ELECTRODE PROCESSES

Problem 1.1 (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	$O_2 + 4H^+ + 4e \rightleftharpoons H_2O$
1.188	$Pt^{2+} + 2e \rightleftharpoons Pt$
0.340	$Cu^{2+} + 2e \rightleftharpoons Cu$
0.159	$Cu^{2+} + e \rightleftharpoons Cu^+$
0.000	$2H^+ + 2e \rightleftharpoons H_2$
-0.4025	$Cd^{2+} + 2e \rightleftharpoons Cd$

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 $\log \frac{[O]}{[R]} = -n(E - E^0)/0.059$.

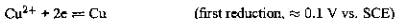


The composition of the system dictates that the rest (zero current) potential be more positive than $E_{Cu^{2+}/Cu}^0$ and more negative than E_{O_2/H_2O}^0 or $E_{Pt^{2+}/Pt}^0$, i.e., between about 0.34 V and 1.2 V vs. NHE. Graphically, this is apparent because this is the voltage range over which the oxidized (Cu^{2+}) and reduced species (Pt or H_2O) 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 O_2 , there would be a thermodynamic driving force for these species to react spontaneously to form water and Cu^{2+} .) Here, 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

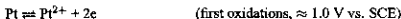
Chapter 1 INTRODUCTION AND OVERVIEW OF ELECTRODE PROCESSES

equilibrium potential by the Nernst equation cannot be made.

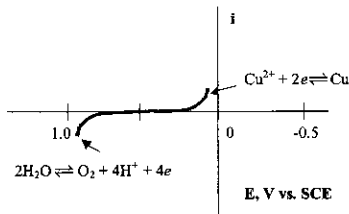
Current will flow when the potential is moved negatively from the rest potential 0.340 V (or 0.340 + (-0.2412) = 0.099 V vs. SCE) so that Cu^{2+} is reduced at the electrode surface first.



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. The current-potential curve would look like the following.

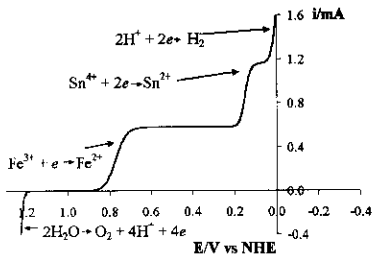


Problem 1.3 The important reactions are



(a). From (1.4.9) and $n = 1$, $i_l = nFAm_0C_0^2 = 580 \mu\text{A}$.

(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 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 V vs. SCE . The $i - E$ curve is as follows:



Problem 1.5 From equation (1.2.10),

$$q = EC_d A \left[1 - \exp\left(\frac{-t}{R_s C_d A}\right) \right] \quad (1)$$

Area appears because C_d is expressed as capacitance per unit area. The time constant τ is $R_s C_d A$.

$$q = \frac{E\tau}{R_s} \left[1 - \exp\left(\frac{-t}{\tau}\right) \right] \quad (2)$$

At complete charging ($t \rightarrow \infty$), $q_{\infty} = E\tau/R_s$. At 95% of q_{∞} , time $t_{95\%}$ is set by

$$0.95 \frac{E\tau}{R_s} = \frac{E\tau}{R_s} \left[1 - \exp\left(\frac{-t_{95\%}}{\tau}\right) \right] \quad (3)$$

This expression is rearranged to $t_{95\%} = 3\tau$ at 95% completeness. For the specified conditions,

R_s/Ω	1	10	100
$\tau/\mu s$	2	20	200
$3\tau/\mu s$	6	60	600

Problem 1.7 (a). From equations (1.4.9) and (1.4.17) for the limiting currents, $\frac{i_{l,s}}{-i_{l,a}} = \frac{nFAm_{\infty}C_s^*}{nFAm_{\infty}C_R^*} = \frac{4.00\mu A}{2.00\mu A} = 1.67$ or $\frac{m_{\infty}}{m_R} = 1.67 \frac{C_s^*}{C_R^*} = 0.833$. From equation (1.4.15), $E_{1/2} = E^{0'} - \frac{RT}{nF} \ln \frac{m_{\infty}}{m_R} = -0.498$ V vs. NHE.

Problem 1.9 The relationships linking current and concentration in the steady-state treatment of mass transfer are equations (1.4.6) and (1.4.7).

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

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

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),

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

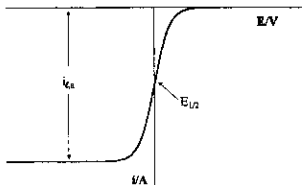
Substitution of (6) and (7) into (5) gives

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

Note that this result is the special case of (1.4.20) 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:



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

$$E = E_{1/2} + \frac{RT}{nF} \ln \left[\frac{i_0 - i}{i} \right]$$

One solves for i/i_0 as follows.

$$\frac{nF}{RT} (E - E_{1/2}) = \ln \left[\frac{i_0 - i}{i} \right]$$

$$\exp \left[\frac{nF}{RT} (E - E_{1/2}) \right] = \frac{i_0 - i}{i} = \frac{i_0}{i} - 1$$

$$\frac{i_0}{i} = 1 + \exp \left[\frac{nF}{RT} (E - E_{1/2}) \right]$$

$$\frac{i}{i_0} = \left(1 + \exp \left[\frac{nF}{RT} (E - E_{1/2}) \right] \right)^{-1}$$