CHAPTER 17

CORROSION AND DEGRADATION OF MATERIALS

PROBLEM SOLUTIONS

Electrochemical Considerations

17.1 (a) Oxidation is the process by which an atom gives up an electron (or electrons) to become a cation. Reduction is the process by which an atom acquires an extra electron (or electrons) and becomes an anion.

(b) Oxidation occurs at the anode; reduction at the cathode.

17.2 (a) This problem asks that we write possible oxidation and reduction half-reactions for magnesium in various solutions.

(i) In HCl, possible reactions are

$$\mathrm{Mg} \rightarrow \mathrm{Mg}^{2+} + 2e^- \quad \text{(oxidation)}$$

$$2\mathrm{H}^+ + 2e^- \rightarrow \mathrm{H}_2 \quad \text{(reduction)}$$

(ii) In an HCl solution containing dissolved oxygen, possible reactions are

$$\mathrm{Mg} \rightarrow \mathrm{Mg}^{2+} + 2e^- \quad \text{(oxidation)}$$

$$4\mathrm{H}^+ + \mathrm{O}_2 + 4e^- \rightarrow 2\mathrm{H}_2\mathrm{O} \quad \text{(reduction)}$$

(iii) In an HCl solution containing dissolved oxygen and Fe^{2+} ions, possible reactions are

$$\mathrm{Mg} \rightarrow \mathrm{Mg}^{2+} + 2e^- \quad \text{(oxidation)}$$

$$4\mathrm{H}^+ + \mathrm{O}_2 + 4e^- \rightarrow 2\mathrm{H}_2\mathrm{O} \quad \text{(reduction)}$$

$$\mathrm{Fe}^{2+} + 2e^- \rightarrow \mathrm{Fe} \quad \text{(reduction)}$$

(b) The magnesium would probably oxidize most rapidly in the HCl solution containing dissolved oxygen and Fe^{2+} ions because there are two reduction reactions that will consume electrons from the oxidation of magnesium.

17.3 (a) The Faraday constant (represented here as "F") is just the product of the charge per electron and Avogadro's number; that is

$$F = eN_A = (1.602 \text{ x } 10^{-19} \text{ C/electron})(6.023 \text{ x } 10^{23} \text{ electrons/mol})$$

$$= 96{,}488 \text{ C/mol}$$

(b) At 25°C (298 K),

$$\frac{RT}{nF}\ln(x) = \frac{(8.31 \text{ J/mol-K})(298 \text{ K})}{(n)(96{,}500 \text{ C/mol})}(2.303) \log(x)$$

$$= \frac{0.0592}{n} \log(x)$$

This gives units in volts since a volt is a J/C.

17.4 (a) We are asked to compute the voltage of a nonstandard Pb-Sn electrochemical cell. Since tin is lower in the standard emf series (Table 17.1), we will begin by assuming that tin is oxidized and lead is reduced, as

$$\mathrm{Sn} + \mathrm{Pb}^{2+} \rightarrow \mathrm{Sn}^{2+} + \mathrm{Pb}$$

and Equation 17.20 takes the form

$$\Delta V = (V_{\mathrm{Pb}}^{\circ} - V_{\mathrm{Sn}}^{\circ}) - \frac{0.0592}{2} \log \frac{[\mathrm{Sn}^{2+}]}{[\mathrm{Pb}^{2+}]}$$

$$= \left[-0.126 \text{ V} - (-0.136 \text{ V})\right] - \frac{0.0592}{2} \log \left[\frac{0.25}{5 \text{ x } 10^{-2}}\right]$$

$$= -\,0.011 \text{ V}$$

since, from Table 17.1, the standard potentials for Pb and Sn are –0.126 and –0.136, respectively.

(b) Since the ΔV is negative, the spontaneous cell direction is just the reverse of that above, or

$$\mathrm{Sn}^{2+} + \mathrm{Pb} \rightarrow \mathrm{Sn} + \mathrm{Pb}^{2+}$$

17.5 This problem calls for us to determine whether or not a voltage is generated in a Fe/Fe^{2+} concentration cell, and, if so, its magnitude. Let us label the Fe cell having a 0.5 *M* Fe^{2+} solution as cell 1, and the other as cell 2. Furthermore, assume that oxidation occurs within cell 2, wherein $[\text{Fe}_2^{2+}]$ = 2 x 10^{-2} *M*. Hence,

$$\text{Fe}_2 + \text{Fe}_1^{2+} \rightarrow \text{Fe}_2^{2+} + \text{Fe}_1$$

and, employing Equation 17.20 leads to

$$\Delta V = -\frac{0.0592}{2} \log \frac{\left[\text{Fe}_2^{2+}\right]}{\left[\text{Fe}_1^{2+}\right]}$$

$$= -\frac{0.0592}{2} \log \left[\frac{2 \text{ x } 10^{-2}\, M}{0.5\, M}\right] = +0.0414 \text{ V}$$

Therefore, a voltage of 0.0414 V is generated when oxidation occurs in the cell 2, the one having a Fe^{2+} concentration of 2 x 10^{-2} *M*.

17.6 We are asked to calculate the concentration of Cu^{2+} ions in a copper-cadmium electrochemical cell. The electrochemical reaction that occurs within this cell is just

$$\mathrm{Cd} + \mathrm{Cu}^{2+} \rightarrow \mathrm{Cd}^{2+} + \mathrm{Cu}$$

while $\Delta V = 0.775$ V and $[Cd^{2+}] = 6.5 \times 10^{-2}$ *M*. Thus, Equation 17.20 is written in the form

$$\Delta V = \left(V_{\mathrm{Cu}}^{\circ} - V_{\mathrm{Cd}}^{\circ}\right) - \frac{0.0592}{2} \log \frac{[\mathrm{Cd}^{2+}]}{[\mathrm{Cu}^{2+}]}$$

This equation may be rewritten as

$$-\frac{\Delta V - \left(V_{\mathrm{Cu}}^{\circ} - V_{\mathrm{Cd}}^{\circ}\right)}{0.0296} = \log \frac{[\mathrm{Cd}^{2+}]}{[\mathrm{Cu}^{2+}]}$$

Solving this expression for $[Cu^{2+}]$ gives

$$[\mathrm{Cu}^{2+}] = [\mathrm{Cd}^{2+}] \exp + \left[(2.303) \frac{\Delta V - \left(V_{\mathrm{Cu}}^{\circ} - V_{\mathrm{Pb}}^{\circ}\right)}{0.0296}\right]$$

The standard potentials from Table 17.1 are $V_{\mathrm{Cu}}^{\circ} = +0.340$ V and $V_{\mathrm{Cd}}^{\circ} = -0.403$ V. Therefore,

$$[\mathrm{Cu}^{2+}] = (6.5 \times 10^{-2}\ M) \exp + \left[(2.303)\ \frac{0.775\ \mathrm{V} - \{0.340\ \mathrm{V} - (-0.403\ \mathrm{V})\}}{0.0296}\right]$$

$$= 0.784\ M$$

17.7 This problem asks for us to calculate the temperature for a zinc-lead electrochemical cell when the potential between the Zn and Pb electrodes is +0.568 V. On the basis of their relative positions in the standard emf series (Table 17.1), assume that Zn is oxidized and Pb is reduced. Thus, the electrochemical reaction that occurs within this cell is just

$$\mathrm{Pb}^{2+} + \mathrm{Zn} \rightarrow \mathrm{Pb} + \mathrm{Zn}^{2+}$$

Thus, Equation 17.20 is written in the form

$$\Delta V = \left(V^{\circ}_{\mathrm{Pb}} - V^{\circ}_{\mathrm{Zn}}\right) - \frac{RT}{nF}\ln\frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Pb}^{2+}]}$$

Solving this expression for T gives

$$T = -\frac{nF}{R}\left[\frac{\Delta V - \left(V^{\circ}_{\mathrm{Pb}} - V^{\circ}_{\mathrm{Zn}}\right)}{\ln\dfrac{[\mathrm{Zn}^{2+}]}{[\mathrm{Pb}^{2+}]}}\right]$$

The standard potentials from Table 17.1 are V°_{Zn} = – 0.763 V and V°_{Pb} = – 0.126 V. Therefore,

$$T = -\frac{(2)(96{,}500\ \mathrm{C/mol})}{8.31\ \mathrm{J/mol\text{-}K}}\left[\frac{0.568\ \mathrm{V} - \{-0.126\ \mathrm{V} - (-0.763\ \mathrm{V})\}}{\ln\left(\dfrac{10^{-2}\ M}{10^{-4}\ M}\right)}\right]$$

$$= 348\ \mathrm{K} = 75^{\circ}\mathrm{C}$$

17.8 This problem asks, for several pairs of alloys that are immersed in seawater, to predict whether or not corrosion is possible, and if it is possible, to note which alloy will corrode. In order to make these predictions it is necessary to use the galvanic series, Table 17.2. If both of the alloys in the pair reside within the same set of brackets in this table, then galvanic corrosion is unlikely. However, if the two alloys do not lie within the same set of brackets, then that alloy appearing lower in the table will experience corrosion.

(a) For the aluminum-cast iron couple, corrosion is possible, and aluminum will corrode.

(b) For the Inconel-nickel couple, corrosion is unlikely inasmuch as both alloys appear within the same set of brackets (in both active and passive states).

(c) For the cadmium-zinc couple, corrosion is possible, and zinc will corrode.

(d) For the brass-titanium pair, corrosion is possible, and brass will corrode.

(e) For the low-carbon steel-copper couple, corrosion is possible, and the low-carbon steel will corrode.

17.9 (a) The following metals and alloys may be used to galvanically protect cast iron: aluminum/aluminum alloys, cadmium, zinc, magnesium/magnesium alloys. These metals/alloys appear below cast iron in the galvanic series. Table 17.2.

(b) The following metals/alloys could be used to protect a nickel-steel galvanic couple: aluminum/aluminum alloys, cadmium, zinc, magnesium/magnesium alloys; all these metal/alloys are anodic to steel in the galvanic series.

Corrosion Rates

17.10 This problem is just an exercise in unit conversions. The parameter K in Equation 17.23 must convert the units of W, ρ, A, and t, into the unit scheme for the CPR.

For CPR in mpy (mil/yr)

$$K = \frac{W(\mathrm{mg})(1\ \mathrm{g}/1000\ \mathrm{mg})}{\rho\left(\dfrac{\mathrm{g}}{\mathrm{cm}^3}\right)\left(\dfrac{2.54\ \mathrm{cm}}{\mathrm{in.}}\right)^3\left[A(\mathrm{in.}^2)\right]\left(\dfrac{1\ \mathrm{in.}}{1000\ \mathrm{mil}}\right)[t(\mathrm{h})]\left(\dfrac{1\ \mathrm{day}}{24\ \mathrm{h}}\right)\left(\dfrac{1\ \mathrm{yr}}{365\ \mathrm{days}}\right)}$$

$$= 534.6$$

For CPR in mm/yr

$$K = \frac{W(\mathrm{mg})(1\ \mathrm{g}/1000\ \mathrm{mg})}{\rho\left(\dfrac{\mathrm{g}}{\mathrm{cm}^3}\right)\left(\dfrac{1\ \mathrm{cm}}{10\ \mathrm{mm}}\right)^3\left[A(\mathrm{cm}^2)\right]\left(\dfrac{10\ \mathrm{mm}}{\mathrm{cm}}\right)^2[t(\mathrm{h})]\left(\dfrac{1\ \mathrm{day}}{24\ \mathrm{h}}\right)\left(\dfrac{1\ \mathrm{yr}}{365\ \mathrm{days}}\right)}$$

$$= 87.6$$

17.11 This problem calls for us to compute the time of submersion of a metal plate. In order to solve this problem, we must first rearrange Equation 17.23, as

$$t = \frac{KW}{\rho A\,(\mathrm{CPR})}$$

Thus, using values for the various parameters given in the problem statement

$$t = \frac{(87.6)\left(7.6 \text{ x } 10^6 \text{ mg}\right)}{\left(4.5 \text{ g/cm}^3\right)\left(800 \text{ in.}^2\right)(4 \text{ mm/yr})}$$

$$= 4.62 \text{ x } 10^4 \text{ h} = 5.27 \text{ yr}$$

17.12 This problem asks for us to calculate the CPR in both mpy and mm/yr for a thick steel sheet of area 100 in.^{2} which experiences a weight loss of 485 g after one year. Employment of Equation 17.23 leads to

$$\text{CPR(mm/yr)} = \frac{KW}{\rho A t}$$

$$= \frac{(87.6)(485\ \text{g})(10^3\ \text{mg/g})}{(7.9\ \text{g/cm}^3)(100\ \text{in.}^2)(2.54\ \text{cm/in.})^2(24\ \text{h/day})(365\ \text{day/yr})(1\ \text{yr})}$$

$$= 0.952\ \text{mm/yr}$$

Also

$$\text{CPR(mpy)} = \frac{(534)(485\ \text{g})(10^3\ \text{mg/g})}{(7.9\ \text{g/cm}^3)(100\ \text{in.}^2)(24\ \text{h/day})(365\ \text{day/yr})(1\ \text{yr})}$$

$$= 37.4\ \text{mpy}$$

17.13 (a) We are to demonstrate that the CPR is related to the corrosion current density, *i*, in A/cm^2 through the expression

$$\mathrm{CPR} = \frac{KAi}{n\rho}$$

in which *K* is a constant, *A* is the atomic weight, *n* is the number of electrons ionized per metal atom, and ρ is the density of the metal. Possibly the best way to make this demonstration is by using a unit dimensional analysis. The corrosion rate, *r*, in Equation 17.24 has the units (SI)

$$r = \frac{i}{nF} = \frac{\mathrm{C/m^2\text{-}s}}{\mathrm{(unitless)(C/mol)}} = \frac{\mathrm{mol}}{\mathrm{m^2\text{-}s}}$$

The units of CPR in Equation 17.23 are length/time, or in the SI scheme, m/s. In order to convert the above expression to the units of m/s it is necessary to multiply *r* by the atomic weight *A* and divide by the density ρ as

$$\frac{rA}{\rho} = \frac{\mathrm{(mol/m^2\text{-}s)(g/mol)}}{\mathrm{g/m^3}} = \mathrm{m/s}$$

Thus, the CPR is proportional to *r*, and substituting for *r* from Equation 17.24 into the above expression leads to

$$\mathrm{CPR} = K''r = \frac{K'Ai}{nF\rho}$$

in which *K'* and *K''* are constants which will give the appropriate units for CPR. Also, since *F* (i.e., Faraday’s constant) is also a constant, this expression will take the form

$$\mathrm{CPR} = \frac{KAi}{n\rho}$$

in which $K = K'/F$.

(b) Now we will calculate the value of *K* in order to give the CPR in mpy for *i* in μA/cm^2 (10^{-6} A/cm^2). It should be noted that the units of A (in μA/cm^2) are amperes or C/s. Substitution of the units normally used into the former CPR expression above leads to

$$\mathrm{CPR} = K'\frac{Ai}{nF\rho}$$

$$= K' \, \frac{(\mathrm{g/mol})(\mathrm{C/s\text{-}cm^2})}{(\mathrm{unitless})(\mathrm{C/mol})(\mathrm{g/cm^3})} = \mathrm{cm/s}$$

Since we want the CPR in mpy and i is given in μA/cm^2, and realizing that $K = K'/F$ leads to

$$K = \left(\frac{1}{96{,}500 \ \mathrm{C/mol}}\right)\left(\frac{10^{-6}\ \mathrm{C}}{\mu\mathrm{C}}\right)\left(\frac{1 \ \mathrm{in.}}{2.54 \ \mathrm{cm}}\right)\left(\frac{10^3 \ \mathrm{mil}}{\mathrm{in.}}\right)\left(\frac{3.1536 \ \times 10^7 \ \mathrm{s}}{\mathrm{yr}}\right)$$

$$= 0.129$$

17.14 We are asked to compute the CPR in mpy for the corrosion of Fe for a corrosion current density of 8 x 10^{-5} A/cm^2 (80 μA/cm^2). From Problem 17.13, the value of K in Equation 17.38 is 0.129, and therefore

$$\mathrm{CPR} = \frac{KAi}{n\rho}$$

$$= \frac{(0.129)(55.85\ \mathrm{g/mol})(80\ \mu\mathrm{A/cm^2})}{(2)(7.9\ \mathrm{g/cm^3})} = 36.5\ \mathrm{mpy}$$

Prediction of Corrosion Rates

17.15 (a) Activation polarization is the condition wherein a reaction rate is controlled by one step in a series of steps that takes place at the slowest rate. For corrosion, activation polarization is possible for both oxidation and reduction reactions. Concentration polarization occurs when a reaction rate is limited by diffusion in a solution. For corrosion, concentration polarization is possible only for reduction reactions.

(b) Activation polarization is rate controlling when the reaction rate is low and/or the concentration of active species in the liquid solution is high.

(c) Concentration polarization is rate controlling when the reaction rate is high and/or the concentration of active species in the liquid solution is low.

17.16 (a) The phenomenon of dynamic equilibrium is the state wherein oxidation and reduction reactions are occurring at the same rate such that there is no net observable reaction.

(b) The exchange current density is just the current density which is related to both the rates of oxidation and reduction (which are equal) according to Equation 17.26 for the dynamic equilibrium state.

17.17 (a) This portion of the problem asks that we compute the rate of oxidation for Ni given that both the oxidation and reduction reactions are controlled by activation polarization, and also given the polarization data for both nickel oxidation and hydrogen reduction. The first thing necessary is to establish relationships of the form of Equation 17.25 for the potentials of both oxidation and reduction reactions. Next we will set these expressions equal to one another, and then solve for the value of *i* which is really the corrosion current density, i_c. Finally, the corrosion rate may be calculated using Equation 17.24. The two potential expressions are as follows:

For hydrogen reduction

$$V_{\mathrm{H}} = V_{(\mathrm{H}^+/\mathrm{H}_2)} + \beta_{\mathrm{H}} \log\left(\frac{i}{i_{0_{\mathrm{H}}}}\right)$$

And for Ni oxidation

$$V_{\mathrm{Ni}} = V_{(\mathrm{Ni}/\mathrm{Ni}^{2+})} + \beta_{\mathrm{Ni}} \log\left(\frac{i}{i_{0_{\mathrm{Ni}}}}\right)$$

Setting $V_{\mathrm{H}} = V_{\mathbf{Ni}}$ and solving for log *i* (log i_c) leads to

$$\log i_c = \left(\frac{1}{\beta_{\mathrm{Ni}} - \beta_{\mathrm{H}}}\right)\left[V_{(\mathrm{H}^+/\mathrm{H}_2)} - V_{(\mathrm{Ni}/\mathrm{Ni}^{2+})} - \beta_{\mathrm{H}} \log i_{0_{\mathrm{H}}} + \beta_{\mathrm{Ni}} \log i_{0_{\mathrm{Ni}}}\right]$$

And, incorporating values for the various parameters provided in the problem statement leads to

$$\log i_c = \left[\frac{1}{0.12 - (-0.10)}\right]\Big[0 - (-0.25) - (-0.10)\left\{\log\left(6 \text{ x } 10^{-7}\right)\right\} + (0.12)\left\{\log\left(10^{-8}\right)\right\}\Big]$$

$$= -6.055$$

Or

$$i_c = 10^{-6.055} = 8.81 \text{ x } 10^{-7} \text{ A/cm}^2$$

And from Equation 17.24

$$r = \frac{i_c}{nF}$$

$$= \frac{8.81 \ \text{x} \ 10^{-7} \ \text{C/s-cm}^2}{(2)(96{,}500 \ \text{C/mol})} = 4.56 \ \text{x} \ 10^{-12} \ \text{mol/cm}^2\text{-s}$$

(b) Now it becomes necessary to compute the value of the corrosion potential, V_c. This is possible by using either of the above equations for V_{H} or V_{Ni} and substituting for i the value determined above for i_c. Thus

$$V_c = V_{(\text{H}^+/\text{H}_2)} + \beta_{\text{H}} \log \left(\frac{i_c}{i_{0_{\text{H}}}} \right)$$

$$= 0 + (-0.10 \ \text{V}) \log \left(\frac{8.81 \ \text{x} \ 10^{-7} \ \text{A/cm}^2}{6 \ \text{x} \ 10^{-7} \ \text{A/cm}^2} \right) = -0.0167 \ \text{V}$$

17.18 (a) This portion of the problem asks that we compute the rate of oxidation for a divalent metal M given that both the oxidation and reduction reactions are controlled by activation polarization, and also given the polarization data for both M oxidation and hydrogen reduction. The first thing necessary is to establish relationships of the form of Equation 17.25 for the potentials of both oxidation and reduction reactions. Next we will set these expressions equal to one another, and then solve for the value of *i* which is really the corrosion current density, i_c. Finally, the corrosion rate may be calculated using Equation 17.24. The two potential expressions are as follows:

For hydrogen reduction

$$V_H = V_{(H^+/H_2)} + \beta_H \log\left(\frac{i}{i_{0_H}}\right)$$

And for M oxidation

$$V_M = V_{(M/M^{2+})} + \beta_M \log\left(\frac{i}{i_{0_M}}\right)$$

Setting $V_H = V_M$ and solving for log *i* (log i_c) leads to

$$\log i_c = \left(\frac{1}{\beta_M - \beta_H}\right)\left[V_{(H^+/H_2)} - V_{(M/M^{2+})} - \beta_H \log i_{0_H} + \beta_M \log i_{0_M}\right]$$

And, incorporating values for the various parameters provided in the problem statement leads to

$$\log i_c = \left[\frac{1}{0.10 - (-0.15)}\right]\left[0 - (-0.90) - (-0.15)\left\{\log\left(10^{-10}\right)\right\} + (0.10)\left\{\log\left(10^{-12}\right)\right\}\right]$$

$$= -7.20$$

Or

$$i_c = 10^{-7.20} = 6.31 \text{ x } 10^{-8} \text{ A/cm}^2$$

And from Equation 17.24

$$r = \frac{i_c}{nF}$$

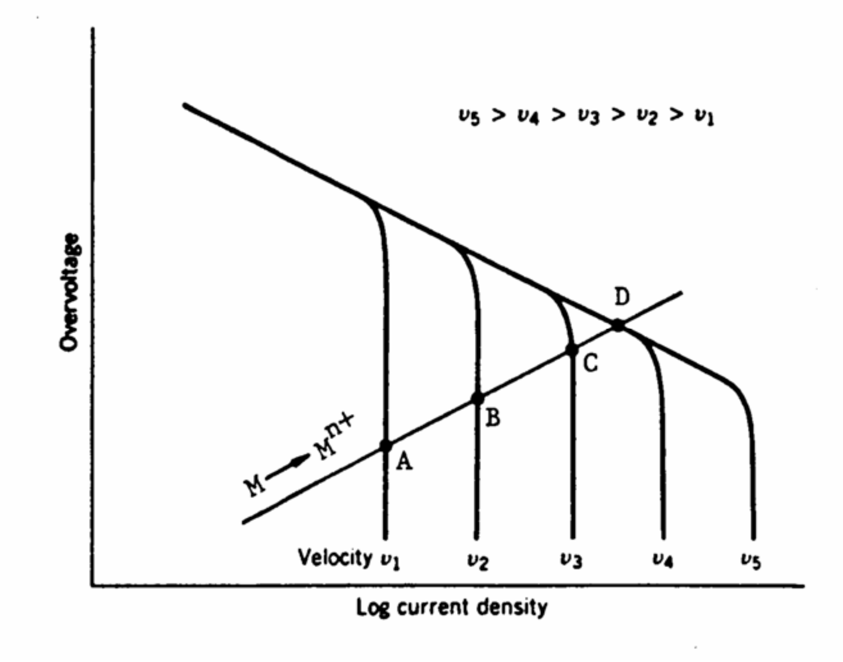
$$= \frac{6.31 \text{ x } 10^{-8} \text{ C/s-cm}^2}{(2)(96{,}500 \text{ C/mol})} = 3.27 \text{ x } 10^{-13} \text{ mol/cm}^2\text{ - s}$$

(b) Now it becomes necessary to compute the value of the corrosion potential, V_c. This is possible by using either of the above equations for V_{H} or V_{M} and substituting for i the value determined above for i_c. Thus

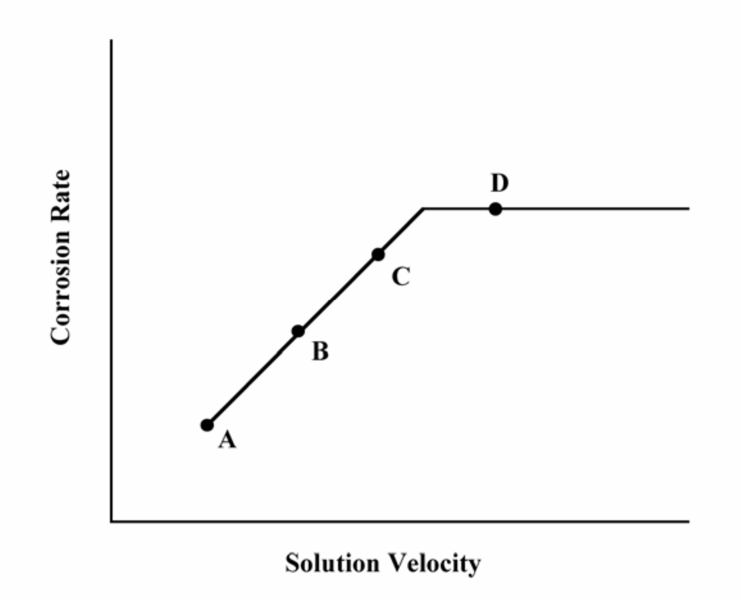
$$V_c = \mathrm{V}_{(\mathrm{H}^+/\mathrm{H}_2)} + \beta_{\mathrm{H}} \log\left(\frac{i_c}{i_{0_{\mathrm{H}}}}\right)$$

$$= 0 + (-0.15 \text{ V}) \log\left(\frac{6.31 \text{ x } 10^{-8} \text{ A/cm}^2}{10^{-10} \text{ A/cm}^2}\right) = -0.420 \text{ V}$$

17.19 This problem asks that we make a schematic plot of corrosion rate versus solution velocity. The reduction reaction is controlled by combined activation-concentration polarization for which the overvoltage versus logarithm current density is shown in Figure 17.26. The oxidation of the metal is controlled by activation polarization, such that the electrode kinetic behavior for the combined reactions would appear schematically as shown below.



Thus, the plot of corrosion rate versus solution velocity would be as



The corrosion rate initially increases with increasing solution velocity (for velocities v_1, v_2, and v_3), corresponding to intersections in the concentration polarization regions for the reduction reaction. However, for the higher solution velocities (v_4 and v_5), the metal oxidation line intersects the reduction reaction curve in the linear activation polarization region, and, thus, the reaction becomes independent of solution velocity.

Passivity

17.20 Passivity is the loss of chemical reactivity, under particular environmental conditions, of normally active metals and alloys. Stainless steels and aluminum alloys often passivate.

17.21 The chromium in stainless steels causes a very thin and highly adherent surface coating to form over the surface of the alloy, which protects it from further corrosion. For plain carbon steels, rust, instead of this adherent coating, forms.

Forms of Corrosion

17.22 For each of the forms of corrosion, the conditions under which it occurs, and measures that may be taken to prevent or control it are outlined in Section 17.7.

17.23 Cold-worked metals are more susceptible to corrosion than noncold-worked metals because of the increased dislocation density for the latter. The region in the vicinity of a dislocation that intersects the surface is at a higher energy state, and, therefore, is more readily attacked by a corrosive solution.

17.24 For a small anode-to-cathode area ratio, the corrosion rate will be higher than for a large ratio. The reason for this is that for some given current flow associated with the corrosion reaction, for a small area ratio the current density at the anode will be greater than for a large ratio. The corrosion rate is proportional to the current density (i) according to Equation 17.24.

17.25 For a concentration cell, corrosion occurs at that region having the lower concentration. In order to explain this phenomenon let us consider an electrochemical cell consisting of two divalent metal M electrodes each of which is immersed in a solution containing a different concentration of its M^{2+} ion; let us designate the low and high concentrations of M^{2+} as $[M_L^{2+}]$ and $[M_H^{2+}]$, respectively. Now assuming that reduction and oxidation reactions occur in the high- and low-concentration solutions, respectively, let us determine the cell potential in terms of the two $[M^{2+}]$'s; if this potential is positive then we have chosen the solutions in which the reduction and oxidation reactions appropriately.

Thus, the two half-reactions in the form of Equations 17.16 are

$$M_H^{2+} + 2e^- \rightarrow M \qquad V_M^\circ$$

$$M \rightarrow M_L^{2+} + 2e^- \qquad -V_M^\circ$$

Whereas the overall cell reaction is

$$M_H^{2+} + M \rightarrow M + M_L^{2+}$$

From Equation 17.19, this yields a cell potential of

$$\Delta V = V_M^\circ - V_M^\circ - \frac{RT}{nF}\ln\left(\frac{[M_L^{2+}]}{[M_H^{2+}]}\right)$$

$$= -\frac{RT}{nF}\ln\left(\frac{[M_L^{2+}]}{[M_H^{2+}]}\right)$$

Inasmuch as $[M_L^{2+}] < [M_H^{2+}]$ then the natural logarithm of the $[M^{2+}]$ ratio is negative, which yields a positive value for ΔV. This means that the electrochemical reaction is spontaneous as written, or that oxidation occurs at the electrode having the lower M^{2+} concentration.

Corrosion Prevention

17.26 (a) Inhibitors are substances that, when added to a corrosive environment in relatively low concentrations, decrease the environment's corrosiveness.

(b) Possible mechanisms that account for the effectiveness of inhibitors are: (1) elimination of a chemically active species in the solution; (2) attachment of inhibitor molecules to the corroding surface so as to interfere with either the oxidation or reduction reaction; and (3) the formation of a very thin and protective coating on the corroding surface.

17.27 Descriptions of the two techniques used for galvanic protection are as follows:

(1) A sacrificial anode is electrically coupled to the metal piece to be protected, which anode is also situated in the corrosion environment. The sacrificial anode is a metal or alloy that is chemically more reactive in the particular environment. It (the anode) preferentially oxidizes, and, upon giving up electrons to the other metal, protects it from electrochemical corrosion.

(2) An impressed current from an external dc power source provides excess electrons to the metallic structure to be protected.

Oxidation

17.28 With this problem we are given, for three metals, their densities, oxide chemical formulas, and oxide densities, and are asked to compute the Pilling-Bedworth ratios, and then to specify whether or not the oxide scales that form will be protective. The general form of the equation used to calculate this ratio is Equation 17.32 (or Equation 17.33). For magnesium, oxidation occurs by the reaction

$$\mathrm{Mg} + \frac{1}{2}\mathrm{O}_2 \rightarrow \mathrm{MgO}$$

and therefore, from Equation 17.32

$$\mathrm{P-B\ ratio} = \frac{A_{\mathrm{MgO}}\,\rho_{\mathrm{Mg}}}{A_{\mathrm{Mg}}\,\rho_{\mathrm{MgO}}}$$

$$= \frac{(40.31\ \mathrm{g/mol})(1.74\ \mathrm{g/cm^3})}{(24.31\ \mathrm{g/mol})(3.58\ \mathrm{g/cm^3})} = 0.81$$

Thus, this would probably be a nonprotective oxide film since the P-B ratio is less than unity; to be protective, this ratio should be between one and two.

The oxidation reaction for V is just

$$2\mathrm{V} + \frac{5}{2}\mathrm{O}_2 \rightarrow \mathrm{V_2O_5}$$

and the P-B ratio is (Equation 17.33)

$$\mathrm{P-B\ ratio} = \frac{A_{\mathrm{V_2O_5}}\,\rho_{\mathrm{V}}}{(2)A_{\mathrm{V}}\,\rho_{\mathrm{V_2O_5}}}$$

$$= \frac{(181.88\ \mathrm{g/mol})(6.11\ \mathrm{g/cm^3})}{(2)(50.94\ \mathrm{g/mol})(3.36\ \mathrm{g/cm^3})} = 3.25$$

Hence, the film would be nonprotective since the ratio does not lie between one and two.

Now for Zn, the reaction for its oxidation is analogous to that for Mg above. Therefore,

$$\text{P} - \text{B ratio} \;=\; \frac{A_{\text{ZnO}}\,\rho_{\text{Zn}}}{A_{\text{Zn}}\,\rho_{\text{ZnO}}}$$

$$=\; \frac{(81.39\ \text{g/mol})(7.13\ \text{g/cm}^3)}{(65.39\ \text{g/mol})(5.61\ \text{g/cm}^3)} \;=\; 1.58$$

Thus, the ZnO film would probably be protective since the ratio is between one and two.

17.29 Silver does not oxidize appreciably at room temperature and in air even though, according to Table 17.3, the oxide coating should be nonprotective. The reason for this is that the oxidation of silver in air is not thermodynamically favorable; therefore, the lack of a reaction is independent of whether or not a protective scale forms.

17.30 For this problem we are given weight gain-time data for the oxidation of Ni at an elevated temperature.

(a) We are first asked to determine whether the oxidation kinetics obey a parabolic, linear, or logarithmic rate expression, which expressions are represented by Equations 17.34, 17.35, and 17.36, respectively. One way to make this determination is by trial and error. Let us assume that the parabolic relationship is valid; that is from Equation 17.34

$$W^2 = K_1 t + K_2$$

which means that we may establish three simultaneous equations using the three sets of given W and t values, then using two combinations of two pairs of equations, solve for K_1 and K_2; if K_1 and K_2 have the same values for both solutions, then the kinetics are parabolic. If the values are not identical then the other kinetic relationships need to be explored. Thus, the three equations are

$$(0.527)^2 = 0.278 = 10K_1 + K_2$$
$$(0.857)^2 = 0.734 = 30K_1 + K_2$$
$$(1.526)^2 = 2.329 = 100K_1 + K_2$$

From the first two equations $K_1 = 0.0228$ and $K_2 = 0.050$; these same two values are obtained using the last two equations. Hence, the oxidation rate law is parabolic.

(b) Since a parabolic relationship is valid, this portion of the problem calls for us to determine W after a total time of 600 min. Again, using Equation 17.34 and the values of K_1 and K_2

$$W^2 = K_1 t + K_2$$

$$= (0.0228)(600 \text{ min}) + 0.05 = 13.37$$

Or $W = \sqrt{13.73} = 3.70 \text{ mg/cm}^2$.

17.31 For this problem we are given weight gain-time data for the oxidation of some metal at an elevated temperature.

(a) We are first asked to determine whether the oxidation kinetics obey a linear, parabolic, or logarithmic rate expression, which expressions are described by Equations 17.35, 17.34, and 17.36, respectively. One way to make this determination is by trial and error. Let us assume that the rate expression is parabolic, that is from Equation 17.34

$$W^2 = K_1 t + K_2$$

which means that we may establish three simultaneous equations using the three sets of given W and t values, then using two combinations of two pairs of equations, solve for K_1 and K_2; if K_1 and K_2 have the same values for both solutions, then the rate law is parabolic. If the values are not the same then the other kinetic relationships need to be explored. Thus, the three equations are

$$(6.16)^2 = 37.95 = 100K_1 + K_2$$

$$(8.59)^2 = 73.79 = 250K_1 + K_2$$

$$(12.72)^2 = 161.8 = 1000K_1 + K_2$$

From the first two equations $K_1 = 0.238$ and $K_2 = 14.2$; while from the second and third equations $K_1 = 0.117$ and $K_2 = 44.5$. Thus, a parabolic rate expression is not obeyed by this reaction.

Let us now investigate linear kinetics in the same manner, using Equation 17.35, $W = K_3 t$. The three equations are thus

$$6.16 = 100K_3$$

$$8.59 = 250K_3$$

$$12.72 = 1000K_3$$

And the three K_3 values may be computed (one for each equation) which are 6.16×10^{-2}, 3.44×10^{-2}, and 1.272×10^{-2}. Since these K_3 values are all different, a linear rate law is not a possibility, and, by process of elimination, a logarithmic expression is obeyed.

(b) In order to determine the value of W after 5000 min, it is first necessary that we solve for the K_4, K_5, and K_6 constants of Equation 17.36. One way this may be accomplished is to use an equation solver In some instances it is desirable to express Equation 17.36 in exponential form, as

$$K_5 + K_6 = 10^{W/K_4}$$

For some solvers, using the above expression, the following instructions can be used:

```
K5 *t1 + K6 = 10^(W1/K4)
K5 *t2 + K6 = 10^(W2/K4)
K5 *t3 + K6 = 10^(W3/K4)

t1 = 100;       W1 = 6.16
t2 = 250;       W2 = 8.59
t3 = 1000;      W3 = 12.72
```

The resulting solutions—i.e., values for the *K* parameters—are

$K_4 = 7.305$
$K_5 = 0.0535$
$K_6 = 1.622$

Now solving Equation 17.36 for *W* at a time of 5000 min

$$W = K_4 \log\left(K_5 t + K_6\right)$$

$$= 7.305 \log\left[(0.0535)(5000 \text{ min}) + 1.622\right]$$

$$= 17.75 \text{ mg/cm}^2$$

17.32 For this problem we are given weight gain-time data for the oxidation of some metal at an elevated temperature.

(a) We are first asked to determine whether the oxidation kinetics obey a linear, parabolic, or logarithmic rate expression, which expressions are described by Equations 17.35, 17.34, and 17.36, respectively. One way to make this determination is by trial and error. Let us assume that the rate expression is linear, that is from Equation 17.35

$$W = K_3 t$$

which means that we may establish three simultaneous equations using the three sets of given W and t values, then solve for K_3 for each; if K_3 is the same for all three cases, then the rate law is linear. If the values are not the same then the other kinetic relationships need to be explored. Thus, the three equations are

$$1.54 = 10K_3$$

$$23.24 = 150K_3$$

$$95.37 = 620K_3$$

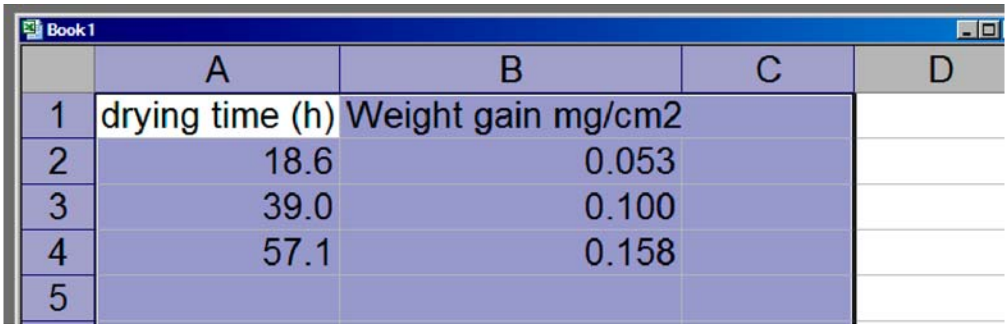
In all three instances the value of K_3 is about equal to 0.154, which means the oxidation rate obeys a linear expression.

(b) Now we are to calculate W after a time of 1200 min; thus

$$W = K_3 t = (0.154)(1200 \text{ min}) = 184.80 \text{ mg/cm}^2$$

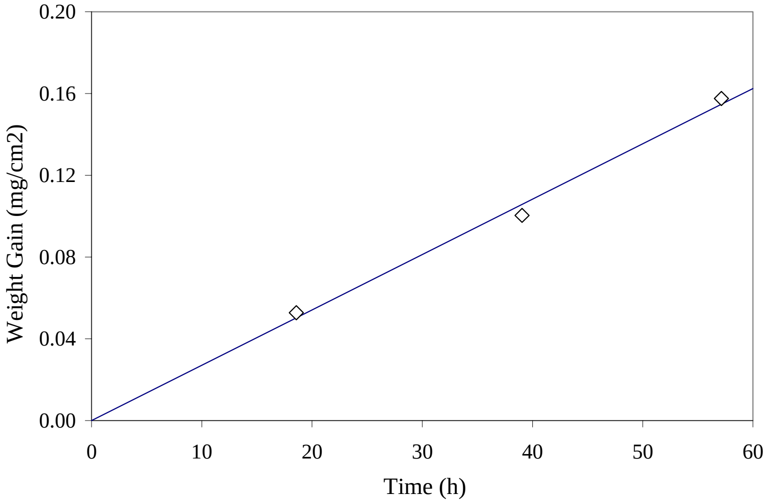
Bond Rupture

17.33 One way to solve this problem is to use the Excel spreadsheet software. We can begin by plotting the data provided in the problem statement. This will at least tell us whether or not the oxidation kinetics are linear. The data may be entered in the spreadsheet as follows:



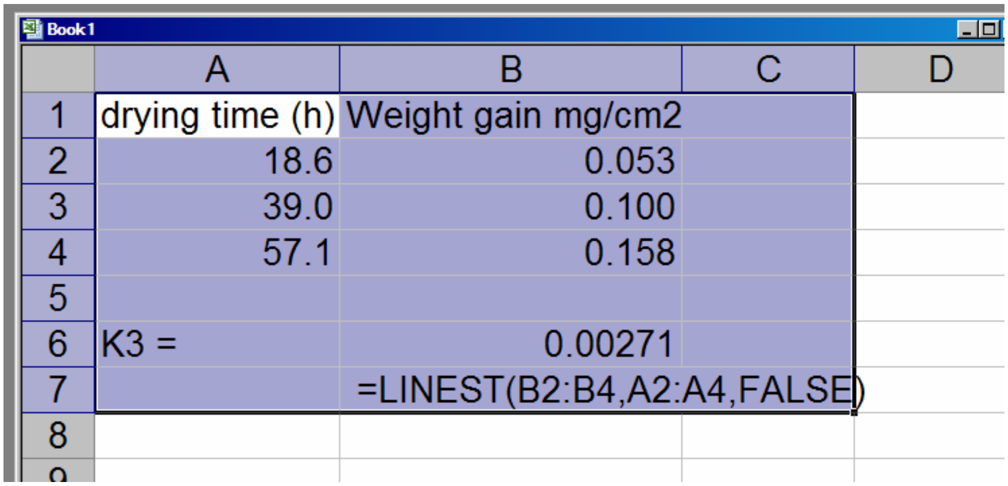
	A	B	C	D
1	drying time (h)	Weight gain mg/cm2		
2	18.6	0.053		
3	39.0	0.100		
4	57.1	0.158		
5				

And, when these data is plotted, the following graph results:



From this plot it is obvious that the oxidation kinetics do indeed obey a linear relationship.

It next becomes necessary to solve for the constant K_3 of Equation 17.35. This is possible using the function LINEST(*known_y's*,*known_x's*,*const*) in Excel. Additional entries are made in the worksheet as follows:



	A	B	C	D
1	drying time (h)	Weight gain mg/cm2		
2	18.6	0.053		
3	39.0	0.100		
4	57.1	0.158		
5				
6	K3 =	0.00271		
7		=LINEST(B2:B4,A2:A4,FALSE)		
8				

Here values for *known_y's* are in cells B2, B3, and B4 which is abbreviated in Excel as B2:B4. The values for *known_x's* are in cells A2, A3, and A4 which is abbreviated as A2:A4. The value of *const* determines whether or not the linear equation will be fit with a *y*-intercept as shown below.

	y-intercept	no y-intercept
Equation Form	y = mx + b	y = mx
Value of *const*	*const* = TRUE	*const* = FALSE

Since Equation 17.35 has no *y*-intercept, we enter the equation

= LINEST(B2:B4,A2:A4,FALSE)

into cell B6 which gives us the result that the slope K_3 = 0.00271 mg/cm^2-h.

(b) The time to reach W = 0.120 mg/cm^2 is calculated by rearranging Equation 17.35 to give

$$t = \frac{W}{K_3} = \frac{0.120 \text{ mg/cm}^2}{0.00271 \text{ mg/cm}^2 \text{ - h}} = 44.3 \text{ h}$$

DESIGN PROBLEMS

17.D1 Possible methods that may be used to reduce corrosion of the heat exchanger by the brine solution are as follows:

(1) Reduce the temperature of the brine; normally, the rate of a corrosion reaction increases with increasing temperature.

(2) Change the composition of the brine; the corrosion rate is often quite dependent on the composition of the corrosion environment.

(3) Remove as much dissolved oxygen as possible. Under some circumstances, the dissolved oxygen may form bubbles, which can lead to erosion-corrosion damage.

(4) Minimize the number of bends and/or changes in pipe contours in order to minimize erosion-corrosion.

(5) Add inhibitors.

(6) Avoid connections between different metal alloys.

17.D2 This question asks that we suggest appropriate materials, and if necessary, recommend corrosion prevention measures that should be taken for several specific applications. These are as follows:

(a) Laboratory bottles to contain relatively dilute solutions of nitric acid. Probably the best material for this application would be polytetrafluoroethylene (PTFE). The reasons for this are: (1) it is flexible and will not easily break if dropped; and (2) PTFE is resistant to this type of acid, as noted in Table 17.4.

(b) Barrels to contain benzene. Poly(ethylene terephthalate) (PET) would be suited for this application, since it is resistant to degradation by benzene (Table 17.4), and is less expensive than the other two materials listed in Table 17.4 (see Appendix C).

(c) Pipe to transport hot alkaline (basic) solutions. The best material for this application would probably be a nickel alloy (Section 13.3). Polymeric materials listed in Table 17.4 would not be suitable inasmuch as the solutions are hot.

(d) Underground tanks to store large quantities of high-purity water. The outside of the tanks should probably be some type of low-carbon steel that is cathodically protected (Sections 17.8 and 17.9). Inside the steel shell should be coated with an inert polymeric material; polytetrafluoroethylene or some other fluorocarbon would probably be the material of choice (Table 17.4).

(e) Architectural trim for high-rise buildings. The most likely candidate for this application would probably be an aluminum alloy. Aluminum and its alloys are relatively corrosion resistant in normal atmospheres (Section 16.8), retain their lustrous appearance, and are relatively inexpensive (Appendix C).

17.D3 Each student or group of students is to submit their own report on a corrosion problem investigation that was conducted.