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CHAPTER 16

CORROSION AND DEGRADATION OF MATERIALS

PROBLEM SOLUTIONS

Electrochemical Considerations

16.1 (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.

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

(i) In HCl, possible reactions are

\[ \text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \] (oxidation)

\[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \] (reduction)

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

\[ \text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \] (oxidation)

\[ 4\text{H}^+ + \text{O}_2 + 4e^- \rightarrow 2\text{H}_2\text{O} \] (reduction)

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

\[ \text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \] (oxidation)
\[ 4H^+ + O_2 + 4e^- \rightarrow 2H_2O \]  (reduction)

\[ Fe^{2+} + 2e^- \rightarrow Fe \]  (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.

16.3  (a) The Faraday constant is just the product of the charge per electron and Avogadro's number; that is

\[ F = e \, N_A = (1.602 \times 10^{-19} \text{ C/electron})(6.023 \times 10^{23} \text{ electrons/mol}) \]

\[ = 96,488 \text{ C/mol} \]

(b) At 25°C (298 K),

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

\[ = \frac{0.0592}{n} \log(x) \]

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

16.4  (a) We are asked to compute the voltage of a nonstandard Cd-Fe electrochemical cell. Since iron is lower in the standard emf series (Table 16.1), we will begin by assuming that iron is oxidized and cadmium is reduced, as

\[ Fe + Cd^{2+} \rightarrow Fe^{2+} + Cd \]

and Equation 16.20 takes the form

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


\[
= \left[ -0.403 \text{ V} - (-0.440 \text{ V}) \right] - \frac{0.0592}{2} \log \left[ \frac{0.40}{2 \times 10^{-3}} \right]
\]

\[= -0.031 \text{ V} \]

since, from Table 16.1, the standard potentials for Cd and Fe are –0.403 and –0.440, respectively.

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

\[
\text{Fe}^{2+} + \text{Cd} \rightarrow \text{Fe} + \text{Cd}^{2+}
\]

16.5 This problem calls for us to determine whether or not a voltage is generated in a Zn/Zn\(^{2+}\) concentration cell, and, if so, its magnitude. Let us label the Zn cell having a 1.0 \( M \) Zn\(^{2+}\) solution as cell 1, and the other as cell 2. Furthermore, assume that oxidation occurs within cell 2, wherein [Zn\(^{2+}\)] = 10\(^{-2}\) \( M \). Hence,

\[
\text{Zn}_2 + \text{Zn}^{2+}_1 \rightarrow \text{Zn}^{2+}_2 + \text{Zn}_1
\]

and, employing Equation 16.20 leads to

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

\[= - \frac{0.0592}{2} \log \left[ \frac{10^{-2} \text{ M}}{1.0 \text{ M}} \right] = + 0.0592 \text{ V} \]

Therefore, a voltage of 0.0592 V is generated when oxidation occurs in the cell 2, the one having a Zn\(^{2+}\) concentration of 10\(^{-2}\) \( M \).

16.6 We are asked to calculate the concentration of Pb\(^{2+}\) ions in a copper-lead electrochemical cell. The electrochemical reaction that occurs within this cell is just

\[
\text{Pb} + \text{Cu}^{2+} \rightarrow \text{Pb}^{2+} + \text{Cu}
\]
while $\Delta V = 0.507 \text{ V}$ and $[\text{Cu}^{2+}] = 0.6 \text{ M}$. Thus, Equation 16.20 is written in the form

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

This equation may be rewritten as

$$- \frac{\Delta V - (V_{\text{Cu}}^\circ - V_{\text{Pb}}^\circ)}{0.0296} = \log \frac{[\text{Pb}^{2+}]}{[\text{Cu}^{2+}]}$$

Solving this expression for $[\text{Pb}^{2+}]$ gives

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

The standard potentials from Table 16.1 are $V_{\text{Cu}}^\circ = +0.340 \text{ V}$ and $V_{\text{Pb}}^\circ = -0.126 \text{ V}$. Therefore,

$$[\text{Pb}^{2+}] = (0.6 \text{ M}) \exp \left[ - \frac{2.303}{0.0296} \frac{0.507 \text{ V} - (0.340 \text{ V} - (-0.126 \text{ V}))}{0.0296} \right] = 2.5 \times 10^{-2} \text{ M}$$

16.7 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 $+0.568 \text{ V}$. On the basis of their relative positions in the standard emf series (Table 16.1), assume that Zn is oxidized and Pb is reduced. Thus, the electrochemical reaction that occurs within this cell is just

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

Thus, Equation 16.20 is written in the form

$$\Delta V = (V_{\text{Pb}}^\circ - V_{\text{Zn}}^\circ) - \frac{RT}{nF} \ln \frac{[\text{Zn}^{2+}]}{[\text{Pb}^{2+}]}$$

Solving this expression for $T$ gives
\[ T = -\frac{nF}{R} \left[ \frac{\Delta V - (V_{\text{Pb}}^\circ - V_{\text{Zn}}^\circ)}{\ln \left( \frac{[\text{Zn}^{2+}]}{[\text{Pb}^{2+}]} \right)} \right] \]

The standard potentials from Table 16.1 are \( V_{\text{Zn}}^\circ = -0.763 \) V and \( V_{\text{Pb}}^\circ = -0.126 \) V. Therefore,

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

\[ = 348 \text{ K} = 75^\circ \text{C} \]

16.8 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 16.2. 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-magnesium couple, corrosion is possible, and magnesium will corrode.

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

(c) For the brass-monel couple, corrosion is unlikely inasmuch as both alloys appear within the same set of brackets.

(d) For the titanium-304 stainless steel pair, the stainless steel will corrode, inasmuch as it is below titanium in both its active and passive states.

(e) For the cast iron-316 stainless steel couple, the cast iron will corrode since it is below stainless steel in both active and passive states.

16.9 The following metals and alloys may be used to galvanically protect 304 stainless steel in the active state: cast iron, iron, steel, aluminum alloys, cadmium, commercially pure aluminum, zinc, magnesium, and magnesium alloys. All of these alloys appear below 304 stainless steel (active state) in the galvanic series. Table 16.2.
Corrosion Rates

16.10 This problem is just an exercise in unit conversions. The parameter \( K \) in Equation 16.23 must convert the units of \( W, \rho, A, \) and \( t \) into the unit scheme for the CPR.

For CPR in mpy (mil/yr)

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

\[= 534.6\]

For CPR in mm/yr

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

\[= 87.6\]

16.11 This problem calls for us to compute the time of submersion of a steel piece. In order to solve this problem, we must first rearrange Equation 16.23, as

\[
t = \frac{KW}{\rho A \text{(CPR)}}
\]

Thus,

\[
t = \frac{(534)(2.6 \times 10^6 \text{ mg})}{(7.9 \text{ g/cm}^3)(10 \text{ in.}^2)(200 \text{ mpy})}
\]

\[= 8.8 \times 10^4 \text{ h} = 10 \text{ yr}\]

16.12 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 16.23 leads to
\[
CPR(\text{mm/yr}) = \frac{KW}{\rho A t}
\]

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

\[= 0.952 \text{ mm/yr}
\]

Also

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

\[= 37.4 \text{ mpy}
\]

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

\[
CPR = \frac{KAi}{n \rho}
\]

in which \(K\) is a constant, \(A\) is the atomic weight, \(n\) is the number of electrons ionized per metal atom, and \(\rho\) 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 16.24 has the units (SI)

\[
r = \frac{i}{nF} = \frac{C}{m^2 \cdot s} \text{ (unitless)}(C/\text{mol}) = \frac{\text{mol}}{m^2 \cdot s}
\]

The units of CPR in Equation 16.23 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 \(\rho\) as

\[
\frac{rA}{\rho} = \frac{(\text{mol/m}^2 \cdot s)(\text{g/mol})}{\text{g/m}^3} = \text{m/s}
\]

Thus, the CPR is proportional to \(r\), and substituting for \(r\) from Equation 16.24 into the above expression leads to
\[ \text{CPR} = K'^r = \frac{K'A_i}{nF\rho} \]

in which \( K' \) and \( K'^r \) are constants which will give the appropriate units for CPR. Also, since \( F \) is also a constant, this expression will take the form

\[ \text{CPR} = \frac{KA_i}{n\rho} \]

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 \( \mu \text{A/cm}^2 \) \((10^{-6} \text{ A/cm}^2)\). It should be noted that the units of \( A \) (in \( \mu \text{A/cm}^2 \)) are amperes or \( \text{C/s} \). Substitution of the units normally used into the former CPR expression above leads to

\[ \text{CPR} = K' \frac{A_i}{nF\rho} \]

\[ = K' \frac{(\text{g/mol})(\text{C/s} \cdot \text{cm}^{-2})}{(\text{unitless})(\text{C/mol})(\text{g/cm}^3)} = \text{cm/s} \]

Since we want the CPR in mpy and \( i \) is given in \( \mu \text{A/cm}^2 \), and realizing that \( K = K'/F \) leads to

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

\[ = 0.129 \]

16.14 We are asked to compute the CPR in mpy for the corrosion of Fe for a corrosion current density of \( 8 \times 10^{-5} \text{ A/cm}^2 \) \((80 \mu \text{A/cm}^2)\). From Problem 16.13, the value of \( K \) in Equation 16.38 is 0.129, and therefore

\[ \text{CPR} = \frac{KA_i}{n\rho} \]

\[ = \frac{(0.129)(55.85 \text{ g/mol})(80 \mu \text{A/cm}^2)}{(2)(7.9 \text{ g/cm}^3)} = 36.5 \text{ mpy} \]
Prediction of Corrosion Rates

16.15 (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.

16.16 (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 16.24 for the dynamic equilibrium state.

16.17 (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 16.25 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 16.24. The two potential expressions are as follows:

For hydrogen reduction

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

And for Ni oxidation

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

Setting \( V_H = V_{Ni} \) and solving for \( \log i (\log i_c) \) leads to
\[
\log i_c = \left( \frac{1}{\beta_{Ni} - \beta_{H}} \right) \left[ V_{(H^+/H_2)} - V_{(Ni/Ni^{2+})} - \beta_{H} \log i_{0H} + \beta_{Ni} \log i_{0Ni} \right]
\]

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

\[= -6.055 \]

Or

\[i_c = 10^{-6.055} = 8.81 \times 10^{-7} \text{ A/cm}^2\]

And from Equation 16.24

\[r = \frac{i_c}{nF} = \frac{8.81 \times 10^{-7} \text{ C/s - cm}^2}{(2)(96,500 \text{ C/mol})} = 4.56 \times 10^{-12} \text{ mol/cm}^2 \cdot \text{s}\]

(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

\[V_c = V_{(H^+/H_2)} + \beta_{H} \log \left( \frac{i_c}{i_{0H}} \right)\]

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

16.18 (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 16.25 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 16.24. 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

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

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

$$= -7.20$$

Or

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

And from Equation 16.24

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

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

$$V_c = V_{(H^+/H_2)} + \beta_H \log \left( \frac{i_c}{I_{0H}} \right)$$

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

16.19 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 16.26. 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

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

16.21 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

16.22 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 16.7.
16.23 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.

16.24 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 16.24.

16.25 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 16.16 are

$$M_{H}^{2+} + 2e^- \rightarrow M \quad v_{M}^o$$

$$M \rightarrow M_{L}^{2+} + 2e^- \quad -v_{M}^o$$

Whereas the overall cell reaction is

$$M_{H}^{2+} + M \rightarrow M + M_{L}^{2+}$$

From Equation 16.19, this yields a cell potential of

$$\Delta V = V_{M}^o - V_{M}^o - \frac{RT}{nF} \ln \left( \frac{[M_{L}^{2+}]}{[M_{H}^{2+}]} \right)$$

$$= - \frac{RT}{nF} \ln \left( \frac{[M_{L}^{2+}]}{[M_{H}^{2+}]} \right)$$

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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 \(\Delta V\). This means that the electrochemical reaction is spontaneous as written, or that oxidation occurs at the electrode having the lower \(M^{2+}\) concentration.

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**Corrosion Prevention**

16.26 (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.

---

16.27 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**

16.28 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 16.33 (or Equation 16.32). For magnesium, oxidation occurs by the reaction

\[
Mg + \frac{1}{2}O_2 \rightarrow MgO
\]

and therefore, from Equation 16.32

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\[
P - B \text{ ratio } = \frac{A_{\text{MgO}} \rho_{\text{Mg}}}{A_{\text{Mg}} \rho_{\text{MgO}}}
\]

\[
= \frac{(40.31 \text{ g/mol})(1.74 \text{ g/cm}^3)}{(24.31 \text{ g/mol})(3.58 \text{ g/cm}^3)} = 0.81
\]

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

\[
2V + \frac{5}{2} \text{O}_2 \rightarrow V_2\text{O}_5
\]

and the P-B ratio is (Equation 16.33)

\[
P - B \text{ ratio } = \frac{A_{V_2\text{O}_5} \rho_V}{(2)A_V \rho_{V_2\text{O}_5}}
\]

\[
= \frac{(181.88 \text{ g/mol})(6.11 \text{ g/cm}^3)}{(2)(50.94 \text{ g/mol})(3.36 \text{ g/cm}^3)} = 3.25
\]

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,

\[
P - B \text{ ratio } = \frac{A_{\text{ZnO}} \rho_{\text{Zn}}}{A_{\text{Zn}} \rho_{\text{ZnO}}}
\]

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

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

16.29 Silver does not oxidize appreciably at room temperature and in air even though, according to Table 16.3, 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.

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16.30 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 16.34, 16.35, and 16.36, 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 16.34

\[ W^2 = K_1 t + K_2 \]

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 16.34 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 \( W = \sqrt{13.73} = 3.70 \text{ mg/cm}^2 \).

16.31 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 16.35, 16.34, and 16.36, 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 16.34

\[ W^2 = K_1 t + K_2 \]

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

\[
\begin{align*}
(6.16)^2 &= 37.95 = 100K_1 + K_2 \\
(8.59)^2 &= 73.79 = 250K_1 + K_2 \\
(12.72)^2 &= 161.8 = 1000K_1 + K_2
\end{align*}
\]

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 16.35, \( W = K_3 t \). The three equations are thus

\[
\begin{align*}
6.16 &= 100K_3 \\
8.59 &= 250K_3 \\
12.72 &= 1000K_3
\end{align*}
\]

And the three \( K_3 \) values may be computed (one for each equation) which are \( 6.16 \times 10^{-2} \), \( 3.44 \times 10^{-2} \), and \( 1.272 \times 10^{-2} \). 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 16.36. One way this may be accomplished is to use an equation solver. In some instances it is desirable to express Equation 16.36 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

\[ t2 = 250; \quad W2 = 8.59 \]

\[ t3 = 1000; \quad W3 = 12.72 \]

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 16.36 for W at a time of 5000 min

\[ W = K_4 \log (K_5 t + K_6) \]

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

\[ = 17.75 \text{ mg/cm}^2 \]

16.32 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 16.35, 16.34, and 16.36, 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 16.35

\[ W = K_3 t \]

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

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

**DESIGN PROBLEMS**

16.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.

16.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 16.4.

(b) Barrels to contain benzene. Poly(ethylene terephthalate) (PET) would be suited for this application, since it is resistant to degradation by benzene (Table 16.4), and is less expensive than the other two materials listed in Table 16.4 (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 16.4 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 16.8 and 16.9). 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 16.4).

(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).

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