Practice Exercises

20.1 anode: \( \text{Mg}(s) \rightarrow \text{Mg}^{2+}(aq) + 2e^- \)
cathode: \( \text{Fe}^{3+}(aq) + 2e^- \rightarrow \text{Fe}(s) \)
cell notation: \( \text{Mg}(s)|\text{Mg}^{2+}(aq)||\text{Fe}^{3+}(aq)||\text{Fe}(s) \)

20.2 anode: \( \text{Al}(s) \rightarrow \text{Al}^{3+}(aq) + 3e^- \)
cathode: \( \text{Ni}^{2+}(aq) + 2e^- \rightarrow \text{Ni}(s) \)
overall: \( 3\text{Ni}^{2+}(aq) + 2\text{Al}(s) \rightarrow 2\text{Al}^{3+}(aq) + 3\text{Ni}(s) \)

20.3 \( E^\circ_{\text{cell}} = E^\circ_{\text{substance reduced}} - E^\circ_{\text{substance oxidized}} \)
2Ag\(^+/\text{(aq)}\) + Cu(s) \( \rightarrow \) 2Ag(s) + Cu\(^2+\text{(aq)}\)
\( E^\circ_{\text{cell}} = E^\circ_{\text{Ag}^+} - E^\circ_{\text{Cu}^2+} \)
\( E^\circ_{\text{cell}} = 0.80 \text{ V} - 0.34 \text{ V} = 0.46 \text{ V} \)

2Ag\(^+/\text{(aq)}\) + Zn(s) \( \rightarrow \) 2Ag(s) + Zn\(^2+\text{(aq)}\)
\( E^\circ_{\text{cell}} = E^\circ_{\text{Ag}^+} - E^\circ_{\text{Zn}^2+} \)
\( E^\circ_{\text{cell}} = 0.80 \text{ V} - (-0.76 \text{ V}) = 1.56 \text{ V} \)
Zinc will have the larger value for \( E^\circ_{\text{cell}} \).

20.4 \( E^\circ_{\text{cell}} = E^\circ_{\text{substance reduced}} - E^\circ_{\text{substance oxidized}} \)
Fe\(^{3+}\text{(aq)}\) + Mg(s) \( \rightarrow \) Mg\(^{2+}\text{(aq)}\) + Fe(s)
\( 1.93 \text{ V} = E^\circ_{\text{Fe}^{2+}} - (-2.37 \text{ V}) \)
\( E^\circ_{\text{Fe}^{2+}} = 1.93 \text{ V} + (-2.37 \text{ V}) = -0.44 \text{ V} \)
This agrees exactly with Table 20.1.

20.5 The half–reaction with the more positive value of \( E^\circ \) (listed higher in Table 20.1) will occur as a reduction.
The half–reaction having the less positive (more negative) value of \( E^\circ \) (listed lower in Table 20.1) will be reversed and occur as an oxidation.
(a) \( I_2(aq) + 2e^- \rightarrow 2I^- (aq) \) oxidation
\( \text{Fe}^{3+}(aq) + e^- \rightarrow \text{Fe}^{2+}(aq) \) reduction
20.6 The half–reaction with the more positive value of $E^\circ$ (listed higher in Table 20.1) will occur as a reduction. The half–reaction having the less positive (more negative) value of $E^\circ$ (listed lower in Table 20.1) will be reversed and occur as an oxidation.

\[
\begin{align*}
\text{Br}_2(aq) + 2e^- &\rightarrow 2\text{Br}^-(aq) \\
\text{SO}_4^{2-}(aq) + 4\text{H}^+(aq) + 2e^- &\rightarrow \text{H}_2\text{SO}_3(aq) + \text{H}_2\text{O} \\
\text{Br}_2(aq) + \text{H}_2\text{SO}_3(aq) + \text{H}_2\text{O} &\rightarrow 2\text{Br}^-(aq) + \text{SO}_4^{2-}(aq) + 4\text{H}^+(aq)
\end{align*}
\]

20.7 Either nickel(II) or iron(III) will be reduced, depending on which way the reaction proceeds. Iron(III) is listed higher than nickel(II) in Table 20.1 (it has a greater reduction potential), so we would expect that the reaction would not be spontaneous in the direction shown.

The spontaneous reaction is:

\[
\text{Ni}(s) + 2\text{Fe}^{3+}(aq) \rightarrow \text{Ni}^{2+}(aq) + 2\text{Fe}^{2+}(aq)
\]

20.8 The half–reaction having the more positive value for $E^\circ$ will occur as a reduction. The other half–reaction should be reversed, so as to appear as an oxidation.

\[
\begin{align*}
\text{NiO}_2(s) + 2\text{H}_2\text{O} + 2e^- &\rightarrow \text{Ni(OH)}_2(s) + 2\text{OH}^-(aq) \\
\text{Fe}(s) + 2\text{OH}^- (aq) &\rightarrow 2e^- + \text{Fe(OH)}_2(s) \\
\text{NiO}_2(s) + \text{Fe}(s) + 2\text{H}_2\text{O} &\rightarrow \text{Ni(OH)}_2(s) + \text{Fe(OH)}_2(s)
\end{align*}
\]

\[
\begin{align*}
E^\circ_{\text{cell}} &= E^\circ_{\text{substance reduced}} - E^\circ_{\text{substance oxidized}} \\
E^\circ_{\text{cell}} &= E^\circ_{\text{NiO}_2} - E^\circ_{\text{Fe}} \\
E^\circ_{\text{cell}} &= 0.49 - (-0.88) = 1.37 \text{ V}
\end{align*}
\]

20.9

\[
\begin{align*}
5\{\text{Cr}(s) \rightarrow \text{Cr}^{3+}(aq) + 3e^-\} &\text{ oxidation} \\
3\{\text{MnO}_4^-(aq) + 8\text{H}^+(aq) + 5e^- \rightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}(l)\} &\text{ reduction} \\
\text{Net reaction} &
\end{align*}
\]

\[
\begin{align*}
5\text{Cr}(s) + 3\text{MnO}_4^-(aq) + 24\text{H}^+(aq) &\rightarrow 3\text{Mn}^{2+}(aq) + 12\text{H}_2\text{O}(l) + 5\text{Cr}^{3+}(aq)
\end{align*}
\]

\[
\begin{align*}
E^\circ_{\text{cell}} &= E^\circ_{\text{substance reduced}} - E^\circ_{\text{substance oxidized}} \\
E^\circ_{\text{cell}} &= E^\circ_{\text{MnO}_4^-} - E^\circ_{\text{Cr}^{3+}} \\
E^\circ_{\text{cell}} &= 1.51 - (-0.74) = 2.25 \text{ V}
\end{align*}
\]

20.10 The half–reaction having the more positive value for $E^\circ$ will occur as a reduction. The other half–reaction should be reversed, so as to appear as an oxidation.

\[
\begin{align*}
3\text{Cu}^{2+}(aq) + 2\text{Cr}(s) &\rightarrow 3\text{Cu}(s) + 2\text{Cr}^{3+}(aq) \\
E^\circ_{\text{cell}} &= E^\circ_{\text{substance reduced}} - E^\circ_{\text{substance oxidized}} \\
E^\circ_{\text{cell}} &= E^\circ_{\text{Cu}^{2+}} - E^\circ_{\text{Cu}^{2+}} \\
E^\circ_{\text{cell}} &= 0.34 - (-0.74) = 1.08 \text{ V}
\end{align*}
\]
20.11 A reaction will occur spontaneously in the forward direction if the value of $E^\circ$ is positive. We therefore evaluate $E^\circ$ for each reaction using:

$$E^\circ_{\text{cell}} = E^\circ_{\text{substance reduced}} - E^\circ_{\text{substance oxidized}}$$

(a) $\text{Br}_2(aq) + 2e^- \rightarrow 2\text{Br}^-(aq)$ reduction

$$E^\circ_{\text{cell}} = E^\circ_{\text{Br}_2} - E^\circ_{\text{I}_2}$$

$E^\circ_{\text{cell}} = 1.07 \text{ V} - (0.54 \text{ V}) = 0.53 \text{ V}$, ∴ spontaneous

(b) $\text{MnO}_4^-(aq) + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}$ reduction

$$E^\circ_{\text{cell}} = E^\circ_{\text{MnO}_4^-} - E^\circ_{\text{Ag}}$$

$E^\circ_{\text{cell}} = 1.51 \text{ V} - (0.80 \text{ V}) = +0.71 \text{ V}$, ∴ spontaneous

20.12 A reaction will occur spontaneously in the forward direction if the value of $E^\circ$ is positive. We therefore evaluate $E^\circ$ for each reaction using:

$$E^\circ_{\text{cell}} = E^\circ_{\text{substance reduced}} - E^\circ_{\text{substance oxidized}}$$

(a) $\text{Br}_2(aq) + 2e^- \rightarrow 2\text{Br}^-(aq)$ reduction

$$E^\circ_{\text{cell}} = E^\circ_{\text{Br}_2} - E^\circ_{\text{HOCl}}$$

$E^\circ_{\text{cell}} = 1.07 \text{ V} - (1.63 \text{ V}) = -0.56 \text{ V}$, ∴ non-spontaneous

(b) $2\text{Cr}^{3+}(aq) + 6e^- \rightarrow 2\text{Cr}(s)$ reduction

$$E^\circ_{\text{cell}} = E^\circ_{\text{Cr}^{3+}} - E^\circ_{\text{Zn}^{2+}}$$

$E^\circ_{\text{cell}} = -0.74 \text{ V} - (-0.76 \text{ V}) = +0.02 \text{ V}$, ∴ spontaneous

20.13 From the equation $\Delta G^\circ = -nFE^\circ_{\text{cell}}$

$$\Delta G^\circ = -30.9 \text{ kJ or } -30,900 \text{ J}$$

$F = 96,500 \text{ C mol}^{-1}$

$E^\circ_{\text{cell}} = 0.107 \text{ V}$

$-30,900 \text{ J} = -n(96,500 \text{ C mol}^{-1})(0.107 \text{ V})$

$n = 2.99$ which rounds to 3

Therefore, 3 moles of electrons are transferred in the reaction.

20.14 $\Delta G^\circ = -n \mathcal{F} E^\circ_{\text{cell}}$

From Practice Exercise 11 (a): $n = 2 \ e^-, E^\circ_{\text{cell}} = 0.53 \text{ V}$

$\Delta G^\circ = -n \mathcal{F} E^\circ_{\text{cell}} = -(2 \ e^-)(96,500 \text{ F})(0.53 \text{ V}) = -102,000 \text{ J} = -102 \text{ kJ}$

From Practice Exercise 11 (b): $n = 5 \ e^-, E^\circ_{\text{cell}} = 0.71 \text{ V}$

$\Delta G^\circ = -n \mathcal{F} E^\circ_{\text{cell}} = -(5 \ e^-)(96,500 \text{ F})(0.71 \text{ V}) = -342,600 \text{ J} = -343 \text{ kJ}$

From Practice Exercise 12 (a): $n = 2 \ e^-, E^\circ_{\text{cell}} = -0.56 \text{ V}$

$\Delta G^\circ = -n \mathcal{F} E^\circ_{\text{cell}} = -(2 \ e^-)(96,500 \text{ F})(-0.56 \text{ V}) = 108,080 \text{ J} = 108 \text{ kJ}$

From Practice Exercise 12 (b): $n = 6 \ e^-, E^\circ_{\text{cell}} = 0.02 \text{ V}$
\[ \Delta G^0 = -n \mathcal{F} E^\circ_{\text{cell}} = -(6 \, e^-)(96,500 \, \text{F})(0.02 \, \text{V}) = 11,600 \, \text{J} = -11.6 \, \text{kJ} \]

20.15 Using Equation 20.7,
\[ E^\circ_{\text{cell}} = \frac{RT}{n \mathcal{F}} \ln K_c \]
\[ -0.46 \, \text{V} = \frac{(8.314 \, \text{J mol}^{-1} \text{K}^{-1})(298 \, \text{K})}{2(96,500 \, \text{C mol}^{-1})} \ln K_c \]
\[ \ln K_c = -35.83 \]
Taking the antilog \((e^x)\) of both sides of the above equation gives
\[ K_c = 2.7 \times 10^{-16} \]
This very small value for the equilibrium constant means that the products of the reaction are not formed spontaneously. The equilibrium lies far to the left, favoring reactants, and we do not expect much product to form.

The reverse reaction will be spontaneous, therefore, the value for \(K_c\) for the spontaneous reaction will be:
\[ \text{Cu(s)} + 2\text{Ag}^+(aq) \rightarrow \text{Cu}^{2+}(aq) + 2\text{Ag(s)} \]
\[ K_c' = \frac{1}{K_c} = \frac{1}{2.7 \times 10^{-16}} = 3.7 \times 10^{15} \]

20.16 \[ \text{Ag}^+(aq) + e^- \rightarrow \text{Ag(s)} \quad E^\circ = 0.80 \, \text{V} \]
\[ \text{AgBr(s)} + e^- \rightarrow \text{Ag(s)} + \text{Br}^- (aq) \quad E^\circ = 0.07 \, \text{V} \]
Equation for the spontaneous reaction:
\[ \text{Ag}^+(aq) + \text{Br}^- (aq) \rightarrow \text{AgBr(s)} \quad E^\circ_{\text{cell}} = 0.73 \, \text{V} \]
\[ K = \left[ \left( \frac{\text{Ag}^+}{\text{Br}^-} \right) \right] \]
\[ \ln K_c = \frac{E^\circ_{\text{cell}} n \mathcal{F}}{RT} = \frac{(0.73 \, \text{V})(1 \, \text{e}^-)(96,500 \, \text{C mol}^{-1})}{(8.314 \, \text{J mol}^{-1} \text{K}^{-1})(298 \, \text{K})} = 28.43 \]
\[ K_c = 2.23 \times 10^{12} \]
\[ K_{sp} \text{ for AgBr is } 5.4 \times 10^{-13} \]
\[ \frac{1}{K_c} = \frac{1}{2.23 \times 10^{12}} = 4.5 \times 10^{-13} \]
The \(K_c\) is the inverse of the \(K_{sp}\). So the cell potential value agrees with \(K_{sp}\) table.

20.17 \[ \text{Cu}^{2+}(aq) + \text{Mg(s)} \rightarrow \text{Cu(s)} + \text{Mg}^{2+}(aq) \quad E^\circ_{\text{cell}} = 0.34 - (-2.37 \, \text{V}) = 2.71 \, \text{V} \]
\[ E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{n \mathcal{F}} \ln \left[ \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]} \right] \]
\[ E_{\text{cell}} = 2.71 \, \text{V} - \frac{(8.314 \, \text{J mol}^{-1} \text{K}^{-1})(298 \, \text{K})}{(2)(96,500 \, \text{C mol}^{-1})} \ln \left[ \frac{2.2 \times 10^{-6}}{0.015} \right] = 2.82 \, \text{V} \]
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20.18 \( E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln \left[ \frac{\text{1}}{[\text{H}^+]^2} \right] \)

\[
0.00 = 0.14 \text{ V} - \frac{\left( 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \right) \left( 298 \text{ K} \right)}{2 \left( 96,500 \text{ C mol}^{-1} \right)} \ln \left[ \frac{\text{1}}{[\text{H}^+]^2} \right]
\]

\[
0.14 \text{ V} = -2.57 \times 10^{-2} \ln[\text{H}^+]
\]

\[
5.45 = -\ln[\text{H}^+] = -2.303 \log[\text{H}^+]
\]

\[
2.37 = -\log[\text{H}^+] = \text{pH}
\]

20.19 \( \text{Zn(s)} \rightarrow \text{Zn}^{2+}(aq) + 2e^- \) oxidation
\( \text{Cu}^{2+}(aq) + 2e^- \rightarrow 2\text{Cu(s)} \) reduction

\( E^\circ = E^\circ_{\text{Cu}^{2+}} - E^\circ_{\text{Zn}^{2+}} \)

\( E^\circ_{\text{cell}} = +0.34 \text{ V} - (-0.76 \text{ V}) = +1.10 \text{ V} \)

The Nernst equation for this cell is:

\[
E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln \left[ \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right]
\]

\[
E_{\text{cell}} = 1.10 \text{ V} - \frac{\left( 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \right) \left( 298 \text{ K} \right)}{2 \left( 96,500 \text{ C mol}^{-1} \right)} \ln \left[ \frac{\text{1}}{0.010} \right]
\]

\[
= 1.10 \text{ V} - 0.01284(4.605) = 1.04 \text{ V}
\]

20.20 \( \text{Cu}^{2+}(aq) + \text{Mg(s)} \rightarrow \text{Cu(s)} + \text{Mg}^{2+}(aq) \) oxidation
\( E^\circ_{\text{cell}} = 0.34 - (-2.37 \text{ V}) = 2.71 \text{ V} \)

\[
E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln \left[ \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]} \right]
\]

\[
2.79 = 2.71 \text{ V} - \frac{\left( 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \right) \left( 298 \text{ K} \right)}{2 \left( 96,500 \text{ C mol}^{-1} \right)} \ln \left[ \frac{[\text{Mg}^{2+}]}{0.015} \right]
\]

\[
0.08 \text{ V} = -0.0128 \ln \left[ \frac{[\text{Mg}^{2+}]}{0.015} \right] \ln \left[ \frac{[\text{Mg}^{2+}]}{0.015} \right]
\]

\[
-6.25 = \ln \left[ \frac{[\text{Mg}^{2+}]}{0.015} \right]
\]

\[
e^{-6.25} = \left[ \frac{[\text{Mg}^{2+}]}{0.015} \right]
\]

\[
[\text{Mg}^{2+}] = 2.95 \times 10^{-5} \text{ M}
\]

20.21 \( \text{Cu(s)} \rightarrow \text{Cu}^{2+}(aq) + 2e^- \) oxidation
\( \text{Ag}^+(aq) + e^- \rightarrow \text{Ag(s)} \) reduction
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\[ E^{\circ}_{cell} = E^{\circ}_{Ag^+} - E^{\circ}_{Cu^{2+}} \]

\[ E^{\circ}_{cell} = +0.80 \text{ V} - (+0.34 \text{ V}) = +0.46 \text{ V} \]

\[ E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln \left[ \frac{[Cu^{2+}]}{[Ag^+]^2} \right] \]

\[ \ln \left[ \frac{[Cu^{2+}]}{[Ag^+]^2} \right] = \frac{(E^{\circ}_{cell} - E_{cell})}{(RT/nF)} \]

\[ = \frac{(0.46 \text{ V} - 0.57 \text{ V})}{0.01284} \]

\[ = -8.5670 \]

\[ \left[ \frac{[Cu^{2+}]}{[Ag^+]^2} \right] = e^{-8.5670} = 1.9 \times 10^{-4} \]

Since the [Ag\(^+\)] = 0.225 \text{ M}, [Cu\(^{2+}\)] = 9.6 \times 10^{-6} \text{ M}

Substituting the second value of 0.82 V into the same expression gives

[Cu\(^{2+}\)] = 3.4 \times 10^{-14} \text{ M}

20.22 We are told that, in this galvanic cell, the chromium electrode is the anode, meaning that oxidation occurs at the chromium electrode.

Now in general, we have the equation:

\[ E^{\circ}_{cell} = E^{\circ}_{\text{reduction}} - E^{\circ}_{\text{oxidation}} \]

which becomes, in particular for this case:

\[ E^{\circ}_{cell} = E^{\circ}_{Ni^{2+}} - E^{\circ}_{Cr^{3+}} \]

The net cell reaction is given by the sum of the reduction and the oxidation half-reactions, multiplied in each case so as to eliminate electrons from the result:

\[ 3 \times [Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)] \quad \text{reduction} \]
\[ 2 \times [Cr(s) \rightarrow Cr^{3+}(aq) + 3e^-] \quad \text{oxidation} \]
\[ 3Ni^{2+}(aq) + 2Cr(s) \rightarrow 2Cr^{3+}(aq) + 3Ni(s) \quad \text{net reaction} \]

In this reaction, \( n = 6 \), and the Nernst equation becomes:

\[ E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln \left[ \frac{[Cr^{3+}]^2}{[Ni^{2+}]^3} \right] \]

\[ \ln \left[ \frac{[Cr^{3+}]^2}{[Ni^{2+}]^3} \right] = \frac{(E^{\circ}_{cell} - E_{cell})}{(RT/nF)} \]
\[
\ln \left( \frac{[\text{Cr}^{3+}]}{[\text{Ni}^{2+}]} \right)^2 = \frac{(0.487 \text{ V} - 0.552 \text{ V})}{0.004279}
\]
\[
\ln \left( \frac{[\text{Cr}^{3+}]}{[\text{Ni}^{2+}]} \right)^2 = -15.190
\]
\[
\frac{[\text{Cr}^{3+}]}{[\text{Ni}^{2+}]} = \exp(-15.190) = 2.5 \times 10^{-7}
\]

Substituting \([\text{Ni}^{2+}] = 1.20 \text{ M}\), we solve for \([\text{Cr}^{3+}]\) and get: \([\text{Cr}^{3+}] = 6.6 \times 10^{-4} \text{ M}\).

20.23 \(\text{Fe}^{3+}(aq) + e^- \rightarrow \text{Fe}^{2+}(aq)\) \(E^o = 0.77 \text{ V}\)
2I\(_2\)(s) + e\(^-\) \rightarrow 2I\(^-\)(aq) \(E^o = +0.54 \text{ V}\)
O\(_2\)(g) + 4H\(^+\)(aq) + 4e\(^-\) \rightarrow 2\text{H}_2\text{O} \(E^o = +1.23 \text{ V}\)

The reaction with the least positive reduction potential will be the easiest to oxidize, and its product will be the product at the anode. \(\text{I}_2\) will be produced.

20.24 The cathode is always where reduction occurs. We must consider which species could be candidates for reduction, then choose the species with the highest reduction potential from Table 20.1.

\(\text{Cd}^{2+}(aq) + 2e^- \rightarrow 2\text{Cd}(s)\) \(E^o = -0.40 \text{ V}\)
\(\text{Sn}^{2+}(aq) + 2e^- \rightarrow 2\text{Sn}(s)\) \(E^o = -0.14 \text{ V}\)
\(2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)\) \(E^o = -0.83 \text{ V}\)

Tin(II) has the highest reduction potential, so we would expect it to be reduced in this environment. We expect \(\text{Sn}(s)\) at the cathode.

20.25 The number of Coulombs is: \(4.00 \text{ A} \times 180 \text{ s} = 720 \text{ C}\)
The number of moles is:

\[
\text{mol OH}^- = 720 \text{ C} \times \frac{1 \text{ F}}{96,500 \text{ C}} \times \frac{1 \text{ mol OH}^-}{1 \text{ F}} = 7.46 \times 10^{-3} \text{ mol OH}^-
\]

20.26 The number of moles of \(\text{Au}\) to be deposited is: \(3.00 \text{ g Au} \div 197 \text{ g/mol} = 0.0152 \text{ mol Au}\). The number of Coulombs (\(A \times s\)) is:

\[
\text{Coulombs} = 0.0152 \text{ mol Au} \times \frac{3 \text{ F}}{1 \text{ mol Au}} \times \frac{96,500 \text{ C}}{1 \text{ F}} = 4.40 \times 10^3 \text{ C}
\]
The number of minutes is:

\[
\text{min} = \frac{4.40 \times 10^3 \text{ A} \cdot \text{s}}{10.0 \text{ A}} \times \frac{1 \text{ min}}{60 \text{ s}} = 7.33 \text{ min}
\]

20.27 As in Practice Exercise 26 above, the number of Coulombs is \(4.40 \times 10^3 \text{ C}\). This corresponds to a current of:

\[
A = \frac{4.40 \times 10^3 \text{ A} \cdot \text{s}}{20.0 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} = 3.67 \text{ A}
\]
20.28 The number of Coulombs is:

\[ 0.100 \, \text{A} \times 1.25 \, \text{hr}(3600 \, \text{s/hr}) = 450 \, \text{C} \]

The number of moles of copper ions produced is:

\[ \text{mol Cu}^{2+} = \frac{450 \, \text{C} \times 1 \, \text{mol e}^{-}}{96,500 \, \text{C} \times 2 \, \text{mol e}^{-}} = 0.00233 \, \text{mol Cu}^{2+} \]

Therefore, the increase in concentration is:

\[ M = \frac{0.00233 \, \text{mol Cu}^{2+}}{0.125 \, \text{L}} = 0.0187 \, \text{M} \]

Review Questions

20.1 A galvanic cell is one in which a spontaneous redox reaction occurs, producing electricity. A half–cell is one of either the cathode or the anode, together with the accompanying electrolyte.

20.2 The salt bridge connects two half–cells, and allows for electrical neutrality to be maintained by a flow of appropriate ions.

20.3 These must be kept separate, because otherwise Ag⁺ ions would be reduced directly by Cu metal, and no external current would be produced.

20.4 The anode is the electrode at which oxidation takes place, and the cathode is the electrode at which reduction takes place. The charges of the electrodes in a galvanic cell are opposite to those in the electrolysis cell; the cathode is positive and the anode is negative.

20.5 In both the galvanic and the electrolysis cells, the electrons move away from the anode and toward the cathode.

20.6 The anions move away from the cathode toward the anode, and the cations move away from the anode toward the cathode.

20.7 Aluminum metal constitutes the anode: \( \text{Al(s)} \rightarrow \text{Al}^{3+}(aq) + 3e^- \)

The cathode is tin metal: \( \text{Sn}^{2+}(aq) + 2e^- \rightarrow \text{Sn(s)} \)

20.8 A cell potential is a standard potential only if the temperature is 25 °C, the pressure is 1 atm, and all ions have a concentration of 1 M.

20.9 The cell potential for the anode half–reaction is subtracted from the cell potential for the cathode half–cell:

\[ E^\circ_{\text{cell}} = E^\circ_{\text{reduction}} - E^\circ_{\text{oxidation}} \]

20.10 The standard hydrogen electrode is diagramed in Figure 20.5 of the text. It consists of a platinum wire in contact with a solution having \([\text{H}^+]\) equal to 1 M, and hydrogen gas at a pressure of 1 atm is placed over the system. The half–cell potential is 0 V.

20.11 A positive reduction potential indicates that the substance is more easily reduced than the hydrogen ion. Conversely, a negative reduction potential indicates that the substance comprising the half–cell is less easily reduced than the hydrogen ion.

20.12 The difference between the reduction potentials for hydrogen and copper is a constant that is independent of the choice for the reference potential. In other words, the reduction half–cell potential for copper is to be 0.34 units higher for copper than for hydrogen, regardless of the chosen point of reference. If \( E^\circ \) for copper is taken to be 0 V, then \( E^\circ \) for hydrogen must be \(-0.34 \, \text{V} \).
20.13 The negative terminal of the voltmeter must be connected to the anode in order to obtain correct readings of the voltage that is generated by the cell.

20.14 The metals are placed into the activity series based on their values of standard reduction potentials.

20.15 The silver will be reduced, according to the standard reduction potentials.

The net cell reaction is:

$$\text{Fe(s)} + 3\text{Ag}^+(aq) \rightarrow \text{Fe}^{3+}(aq) + 3\text{Ag(s)}$$

20.16

The net cell reaction is:

$$2\text{Fe}^{2+}(aq) + \text{Br}_2(aq) \rightarrow 2\text{Fe}^{3+}(aq) + 2\text{Br}^-(aq)$$

20.17 \[ \Delta G^o = -nF E^o_{\text{cell}} \]

20.18 \[ E^o_{\text{cell}} = \frac{0.0592}{n} \log K_c \]
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20.19 The Nernst equation:
\[ E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln Q \]
\[ R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \]
\[ T = 25 ^\circ \text{C} = 298 \text{ K} \]
\[ F = 96,494 \text{ C mol}^{-1} \]
\[ \frac{RT}{F} = 0.02567 \text{ J C}^{-1} \]
\[ E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln Q \]
If the system is at equilibrium, \( Q = K_c \).
And \( E_{\text{cell}} = 0 \)
\[ 0 = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln K_c \]
\[ E_{\text{cell}}^\circ = \frac{RT}{nF} \ln K_c \]

20.20 We begin by separating the reaction into its two half–reactions, in order to obtain the value of \( n \).
\[ \text{Pb(s)} + \text{SO}_4^{2–}(aq) \rightarrow \text{PbSO}_4(s) + 2e^- \]
\[ \text{PbO}_2(s) + 4\text{H}^+(aq) + \text{SO}_4^{2–}(aq) + 2e^- \rightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O} \]
Thus, \( n \) is equal to 2, and the equation that we are to use is:
\[ E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log Q \]
\[ E_{\text{cell}} = 2.05 \text{ V} - \frac{0.0592}{2} \log \left( \frac{1}{[\text{H}^+]^4[\text{SO}_4^{2–}]^2} \right) \]

20.21 A concentration cell consists of two almost identical half–cells, the two half–cells are composed of the same substances, but have difference concentrations of the solute species.
\[ E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln \left( \frac{[\text{ion}]_{\text{dilute}}}{[\text{ion}]_{\text{conc}}} \right) \]
\[ E_{\text{cell}}^0 = 0 \text{ because the standard cell potential is the reduction potential of the substance being reduce less the reduction potential of the substance being oxidized, and the two are equal to each other because they are the same substance.} \]

20.22 Pb(s) + SO_4^{2–}(aq) \rightarrow PbSO_4(s) + 2e^- \quad \text{anode}
PbO_2(s) + 4H^+(aq) + SO_4^{2–}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O \quad \text{cathode}
Connecting six cells in series produces 12 volts.

20.23 PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2–}(aq) \quad \text{cathode}
PbSO_4(s) + 2H_2O \rightarrow 2e^- + PbO_2(s) + 4H^+(aq) + SO_4^{2–}(aq) \quad \text{anode}

20.24 This is diagramed in Figure 20.11. The float inside the hydrometer sinks to a level that is inversely proportional to the density of the liquid that is drawn into it. This works because the concentration of the sulfuric acid (and hence the state of charge of the battery) is proportional to the concentration of sulfuric acid in the battery.

20.25 The anodic reaction is: Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-
Chapter 20

Several reactions take place at the cathode; one of the important ones is:
\[ 2\text{MnO}_2(s) + 2\text{NH}_4^+(aq) + 2e^- \rightarrow \text{Mn}_2\text{O}_3(s) + 2\text{NH}_3(aq) + \text{H}_2\text{O} \]

20.26 \[ \text{Zn}(s) + 2\text{OH}^-(aq) \rightarrow \text{ZnO}(s) + \text{H}_2\text{O} + 2e^- \] anode
\[ 2\text{MnO}_2(s) + \text{H}_2\text{O} + 2e^- \rightarrow \text{Mn}_2\text{O}_3(s) + 2\text{OH}^-(aq) \] cathode

20.27 \[ \text{Cd}(s) + 2\text{OH}^-(aq) \rightarrow \text{Cd(OH)}_2(s) + 2e^- \] anode
\[ 2e^- + \text{NiO}_2(s) + 2\text{H}_2\text{O} \rightarrow \text{Ni(OH)}_2(s) + 2\text{OH}^-(aq) \] cathode

The overall cell reaction on discharge of the battery is:
\[ \text{Cd}(s) + \text{NiO}_2(s) + 2\text{H}_2\text{O} \rightarrow \text{Cd(OH)}_2(s) + \text{Ni(OH)}_2(s) \]

On charging the battery, the reactions are reversed.

20.28 The hydrogen is held in a metal alloy, Mg_2Ni, which has the ability to absorb and hold substantial amounts of hydrogen. The electrolyte is KOH.

20.29 \[ \text{MH}(s) + \text{OH}^-(aq) \rightarrow \text{M}(s) + \text{H}_2\text{O} + e^- \] anode
\[ \text{NiO(OH)}(s) + \text{H}_2\text{O} + e^- \rightarrow \text{Ni(OH)}_2(s) + \text{OH}^-(aq) \] cathode
\[ \text{MH} + \text{NiO(OH)}(s) \rightarrow \text{M}(s) + \text{Ni(OH)}_2(s) \] overall reaction

The reactions are reversed upon charging.

20.30 Lithium has the most negative reduction potential of any metal, so it is very easy to oxidize making it an excellent material for an anode, and it is a very lightweight metal. The major problem with lithium in a cell is that it reacts vigorously with water. Also, lithium batteries often have a large negative \( \Delta H \).

20.31 In a typical primary lithium cell, the electrodes are lithium as the anode and manganese(IV) oxide as the cathode.
\[ \text{Li} \rightarrow \text{Li}^+ + e^- \] anode
\[ \text{MnO}_2 + \text{Li}^+ + e^- \rightarrow \text{LiMnO}_2 \] cathode
\[ \text{Li} + \text{MnO}_2 \rightarrow \text{LiMnO}_2 \] net cell reaction

20.32 The electrode materials in a typical lithium ion cell are graphite and cobalt oxide. When the cell is charged, Li^+ ions leave LiCoO_2 and travel through the electrolyte to the graphite. When the cell discharges, the Li^+ ions move back through the electrolyte to the cobalt oxide while electrons move through the external circuit to keep the charge in balance.

20.33 \[ \text{O}_2(g) + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-(aq) \] cathode
\[ \text{H}_2(g) + 2\text{OH}^-(aq) \rightarrow 2\text{H}_2\text{O} + 2e^- \] anode
\[ 2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O} \] net cell reaction

20.34 Fuel cells are more efficient thermodynamically, and more of the energy of the reaction can be made available for useful work provided that the supply of reactants is maintained. The only product formed by the cell is water.

20.35 In an electrolytic cell, the cathode is negative, and the anode is positive. The opposite is true of a galvanic cell. An inert electrode is an electrode which does not chemically react in the measurement of electrochemical data.

20.36 The flow of electrons in the external circuit must be accompanied by the electrolysis reaction. Otherwise the electrodes would accumulate charge, and the system would cease to function.

20.37 In solid NaCl, the ions are held in place and cannot move about. In molten NaCl, the crystal lattice of the solid has been destroyed; the ions are free to move, and consequently to conduct current by migrating either to the anode or to the cathode.
Anode: \[ 2\text{Cl}^- \rightarrow \text{Cl}_2(g) + 2e^- \]
Chapter 20

20.41 The deposition of 0.10 mol of Cr from a Cr

20.42 The Ag

Cathode: $\text{Na}^+(l) + e^- \rightarrow \text{Na}(l)$

Net: $2\text{Na}^+(l) + 2\text{Cl}^-(l) \rightarrow 2\text{Na}(l) + \text{Cl}_2(g)$

$20.43 \text{oxidation: } 2\text{H}_2\text{O} \rightarrow 4\text{H}^+(aq) + 4e^- + \text{O}_2(g)$

$20.44 \text{reduction: } 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$

20.39 It is reduction that occurs at the cathode, and near it, the pH increases due to the formation of OH$^-(aq)$. At the anode, where the oxidation of water occurs, the pH decreases due to the production of H$^+(aq)$. See the equations given in the answer to Review Question 20.38. The overall change in pH is 0 since the amount of H$^+$ formed and the amount of OH$^-$ formed are equal. K$_2$SO$_4$ serves as charge carriers to balance the charge that occurs upon electrolysis of the K$_2$SO$_4$ solution.

20.40 One Faraday (F) is equivalent to one mole of electrons. Also, one Faraday is equal to 96,500 Coulombs, and a Coulomb is equivalent to an Ampere-second:

$1 \, \text{F} = 96,500 \, \text{C}$ and $1 \, \text{C} = 1 \, \text{A-s}$

20.41 The deposition of 0.10 mol of Cr from a Cr$^{3+}$ solution will take longer than the deposition of 0.10 mol Cu from a Cu$^{2+}$ solution because the Cr$^{3+}$ requires 1.5 times as many electrons for deposition than Cu$^{2+}$. This is due to the difference in charges on the two ions.

20.42 The Ag$^+$ solution will give more metal deposited since it is in the +1 state while the Cu$^{2+}$ solution will give half as much since the copper is in the +2 state.

20.43 Copper has a larger atomic mass than iron; therefore, the copper will deposit a greater mass of metal. Both metals are in the same +2 state.

20.44 Electroplating is a procedure by which a metal is deposited on another conducting surface.

20.45 $\text{Al}_2\text{O}_3(s)$ is dissolved in molten cryolite, Na$_3$AlF$_6$. The liquid mixture is electrolyzed to drive the following reaction: $2\text{Al}_2\text{O}_3(l) \rightarrow 4\text{Al}(l) + 3\text{O}_2(g)$

The two half-reactions are:

$\text{anode: } 2\text{O}^{2-} \rightarrow \text{O}_2(g) + 4e^-$

$\text{cathode: } \text{Al}^{3+}(l) + 3e^- \rightarrow \text{Al}(l)$

Overall cell reaction $6\text{O}^{2-} + 4\text{Al}^{3+} \rightarrow 3\text{O}_2(g) + 4\text{Al}(l)$
20.46 The oxygen that is formed slowly decomposes the anode.

20.47 Sodium is obtained from electrolysis of molten NaCl using the Downs cell. Some of the uses of sodium are to make tetraethyl lead, for sodium vapor lamps, and as a coolant in nuclear reactors.

\[
\begin{align*}
\text{Na}^+ + e^- & \rightarrow \text{Na}(l) & \text{cathode} \\
\text{Cl}^- & \rightarrow 1/2\text{Cl}_2(g) + e^- & \text{anode} \\
\text{NaCl}(l) & \rightarrow \text{Na}(l) + 1/2\text{Cl}_2(g) & \text{net reaction}
\end{align*}
\]

20.48 This is shown in a photo and a diagram (Figure 20.24) of the text. Impure copper is the anode, which dissolves during the process. Pure copper is deposited at the cathode. Anode sludge contains precious metals, whose value makes the process cost effective.

Typical reactions occurring at the anode are:
- \(\text{Cu}(s) \rightarrow \text{Cu}^{2+}(aq) + 2e^-\)
- \(\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^-\)
- \(\text{Fe}(s) \rightarrow \text{Fe}^{2+}(aq) + 2e^-\)

The reaction that occurs at the cathode is:
- \(\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s)\)

20.49 One of the various methods arise diagramed in Figure 20.25 of the text. The physical apparatus influences the products that are obtained. The cathode reaction is the same in stirred and unstirred cells:

\[
\begin{align*}
2\text{H}_2\text{O} + 2e^- & \rightarrow \text{H}_2(g) + 2\text{OH}^-\text{(aq)} \\
\text{Cl}^-\text{(aq)} & \rightarrow \text{Cl}_2(g) + 2e^-
\end{align*}
\]

The unstirred anode reaction is:
- \(2\text{Cl}^-\text{(aq)} \rightarrow \text{Cl}_2(g) + 2e^-\)

The net reaction is:
\[
2\text{NaCl}(aq) + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH}(aq) + \text{Cl}_2(g) + \text{H}_2(g)
\]

In a stirred cell, the \(\text{Cl}_2(g)\) that is produced reacts with the \(\text{OH}^-\text{(aq)}\) present forming \(\text{Cl}^-\text{(aq)}, \text{OCl}^-\text{(aq)}\) and water. The anode reaction in the stirred cell is therefore,

\[
\begin{align*}
\text{Cl}^-\text{(aq)} + 2\text{OH}^-\text{(aq)} & \rightarrow \text{OCl}^-\text{(aq)} + \text{H}_2\text{O} + 2e^- \\
\text{NaCl}(aq) + \text{H}_2\text{O} & \rightarrow \text{NaOCl}(aq) + \text{H}_2(g)
\end{align*}
\]

Review Problems

20.50 (a) anode: \(\text{Cd}(s) \rightarrow \text{Cd}^{2+}(aq) + 2e^-\)
- cathode: \(\text{Au}^{3+}(aq) + 3e^- \rightarrow \text{Au}(s)\)
- cell: \(3\text{Cd}(s) + 2\text{Au}^{3+}(aq) \rightarrow 3\text{Cd}^{2+}(aq) + 2\text{Au}(s)\)

(b) anode: \(\text{Fe}(s) \rightarrow \text{Fe}^{2+}(aq) + 2e^-\)
- cathode: \(\text{Br}_2(aq) + 2e^- \rightarrow 2\text{Br}^-(aq)\)
- cell: \(\text{Fe}(s) + \text{Br}_2(aq) \rightarrow \text{Fe}^{2+}(aq) + 2\text{Br}^-(aq)\)

(c) anode: \(\text{Cr}(s) \rightarrow \text{Cr}^{3+}(aq) + 3e^-\)
- cathode: \(\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s)\)
- cell: \(2\text{Cr}(s) + 3\text{Cu}^{2+}(aq) \rightarrow 2\text{Cr}^{3+}(aq) + 3\text{Cu}(s)\)

20.51 (a) anode: \(\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^-\)
- cathode: \(\text{Cr}^{3+}(aq) + 3e^- \rightarrow \text{Cr}(s)\)
cell: \[ 3\text{Zn}(s) + 2\text{Cr}^{3+}(aq) \rightarrow 3\text{Zn}^{2+}(aq) + 2\text{Cr}(s) \]

(b) anode: \[ \text{Pb}(s) + \text{HSO}_4^-(aq) \rightarrow \text{PbSO}_4(s) + \text{H}^+(aq) + 2e^- \]
cathode: \[ \text{PbO}_2(s) + \text{HSO}_4^-(aq) + 3\text{H}^+(aq) + 2e^- \rightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O} \]
cell: \[ \text{Pb}(s) + \text{PbO}_2(s) + 2\text{HSO}_4^-(aq) + 2\text{H}^+(aq) \rightarrow 2\text{PbSO}_4(s) + 2\text{H}_2\text{O} \]

(c) anode: \[ \text{Mg}(s) \rightarrow \text{Mg}^{2+}(aq) + 2e^- \]
cathode: \[ \text{Sn}^{2+}(aq) + 2e^- \rightarrow \text{Sn}(s) \]
cell: \[ \text{Mg}(s) + \text{Sn}^{2+}(aq) \rightarrow \text{Mg}^{2+}(aq) + \text{Sn}(s) \]

20.52 (a) \[ \text{Pt}(s)|\text{Fe}^{2+}(aq),\text{Fe}^{3+}(aq)\|\text{NO}_3^-(aq), \text{H}^+(aq)|\text{NO}(g)|\text{Pt}(s) \]
(b) \[ \text{Pt}(s)|\text{Br}_2(aq),\text{Br}^-(aq)\|\text{Cl}^-(aq),\text{Cl}_2(g)|\text{Pt}(s) \]
(c) \[ \text{Ag}(s)|\text{Ag}^+(aq)\|\text{Au}^{3+}(aq)|\text{Au}(s) \]

20.53 (a) \[ \text{Fe}(s)|\text{Fe}^{2+}(aq)\|\text{Cd}^{2+}(aq)|\text{Cd}(s) \]
(b) \[ \text{Ag}(s)|\text{Ag}^+(aq)\|\text{Ni}^{2+}(aq),\text{H}^+(aq)\|\text{NiO}_2(s)|\text{Pt}(s) \]
(c) \[ \text{Mg}(s)|\text{Mg}^{2+}(aq)\|\text{Cd}^{2+}(aq)|\text{Cd}(s) \]

20.54 (a) \[ \text{Sn}(s) \]
(b) \[ \text{Br}^-(aq) \]
(c) \[ \text{Zn}(s) \]
(d) \[ \Gamma^{(aq)} \]

20.55 a) \[ \text{MnO}_4^-(aq) \]
(b) \[ \text{Au}^{3+}(aq) \]
(c) \[ \text{PbO}_2(s) \]
(d) \[ \text{HOCl}(aq) \]

20.56 (a) \[ E^0_{\text{cell}} = 0.96 \text{ V} - (0.77) \text{ V} = 0.19 \text{ V} \]
(b) \[ E^0_{\text{cell}} = 1.07 \text{ V} - (1.36) \text{ V} = -0.29 \text{ V} \]
(c) \[ E^0_{\text{cell}} = 1.42 \text{ V} - (0.80) \text{ V} = 0.62 \text{ V} \]

20.57 (a) \[ E^0_{\text{cell}} = -0.40 \text{ V} - (-0.44) \text{ V} = 0.04 \text{ V} \]
(b) The data for this question is not available in the textbook.
(c) \[ E^0_{\text{cell}} = -0.40 \text{ V} - (-2.37) \text{ V} = 1.97 \text{ V} \]

20.58 The reactions are spontaneous if the overall cell potential is positive.
\[ E^0_{\text{cell}} = E^0_{\text{substance reduced}} - E^0_{\text{substance oxidized}} \]

(a) \[ E^0_{\text{cell}} = 1.42 \text{ V} - (0.54) \text{ V} = 0.88 \text{ V} \] spontaneous

(b) \[ E^0_{\text{cell}} = 1.07 \text{ V} - (0.17) \text{ V} = 0.90 \text{ V} \] spontaneous

(c) \[ E^0_{\text{cell}} = -0.74 \text{ V} - (-2.76) \text{ V} = 2.02 \text{ V} \] spontaneous

20.59 A reaction is spontaneous if its net cell potential is positive:
\[ E^0_{\text{cell}} = E^0_{\text{substance reduced}} - E^0_{\text{substance oxidized}} \]

(a) \[ E^0_{\text{cell}} = 1.07 \text{ V} - (1.36) \text{ V} = -0.29 \text{ V} \] not spontaneous

(b) \[ E^0_{\text{cell}} = -0.44 \text{ V} - (-0.96) \text{ V} = -1.40 \text{ V} \] not spontaneous

(c) \[ E^0_{\text{cell}} = -0.25 \text{ V} - (-0.44) \text{ V} = +0.19 \text{ V} \] spontaneous

20.60 The half–cell with the more positive \( E^0_{\text{cell}} \) will appear as a reduction, and the other half–reaction is reversed, to appear as an oxidation:
\[ \text{BrO}_3^- (aq) + 6\text{H}^+(aq) + 6e^- \rightarrow \text{Br}^-(aq) + 3\text{H}_2\text{O} \] reduction
The two half–reactions are:

\[
\text{SO}_4^{2-} + 2e^- + 4H^+ \rightarrow H_2SO_3 + H_2O
\]

\[
2\Gamma (aq) \rightarrow I_2 + 2e^-
\]

Since the overall cell potential is negative, we conclude that the reaction is not spontaneous in the direction written.

The two half–reactions are:

\[
S_2O_5^{2-} + 2e^- \rightarrow 2SO_4^{2-}
\]

\[
\text{Ni(OH)}_2 + 2OH^- \rightarrow \text{NiO}_2 + 2H_2O + 2e^-
\]

Since the overall cell potential is positive, we conclude that the reaction is spontaneous in the direction written.

First, separate the overall reaction into its two half–reactions:

\[
2Br^- (aq) \rightarrow Br_2 (aq) + 2e^-
\]
I_2(s) + 2e^- → 2I^-(aq) \quad \text{reduction}

E^{\circ}_{\text{cell}} = E^{\circ}_{\text{reduction}} - E^{\circ}_{\text{oxidation}} = 0.54 \text{ V} - (1.07 \text{ V}) = -0.53 \text{ V}

The value of n is 2: \[ \Delta G^\circ = -n \mathcal{F} E^{\circ}_{\text{cell}} = -(2)(96,500 \text{ C})(-0.53 \text{ J/C}) = 1.0 \times 10^5 \text{ J} = 1.0 \times 10^2 \text{ kJ} \]

20.7 Using the equation \[ \Delta G^\circ = -n \mathcal{F} E^{\circ}_{\text{cell}} \], we have \[ \Delta G^\circ = -n(96,500 \text{ C/mol e}^-)(1.69 \text{ V}) \] for which we need n.

Upon writing the two half–reactions, i.e.,

\[
\begin{align*}
\text{MnO}_4^- (aq) + 8H^+ (aq) + 5e^- &\rightarrow \text{Mn}^{2+} (aq) + 4H_2O \quad \text{reduction} \\
\text{HCHO}_2(l) &\rightarrow \text{CO}_2(g) + 2H^+ (aq) + 2e^- \quad \text{oxidation}
\end{align*}
\]

we see that we need to multiply the reduction half–reaction by 2 and the oxidation reaction by 5 in order to balance the equation:

\[
\begin{align*}
2\text{MnO}_4^- (aq) + 16H^+ (aq) + 10e^- &\rightarrow 2\text{Mn}^{2+} (aq) + 8H_2O \quad \text{reduction} \\
5\text{HCHO}_2(l) &\rightarrow 5\text{CO}_2(g) + 10H^+ (aq) + 10e^- \quad \text{oxidation}
\end{align*}
\]

The net reaction has n = 10. So, \[ \Delta G^\circ = -(10 \text{ mol e}^-)(96,500 \text{ C/mol e}^-)(1.69 \text{ V}) = -1.63 \times 10^3 \text{ kJ} \].

20.68 (a) \[ E^{\circ}_{\text{cell}} = E^{\circ}_{\text{reduction}} - E^{\circ}_{\text{oxidation}} = 2.01 \text{ V} - (1.47 \text{ V}) = 0.54 \text{ V} \]

(b) Since n = 10, \[ \Delta G^\circ = -n \mathcal{F} E^{\circ}_{\text{cell}} = -(10)(96,500 \text{ C})(0.54 \text{ J/C}) = -5.2 \times 10^5 \text{ J} \]

(c) \[ E^{\circ}_{\text{cell}} = \frac{RT}{n\mathcal{F}} \ln K_c \]

\[
0.54 \text{ V} = \frac{(8.314 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})}{10(96,500 \text{ C mol}^{-1})} \ln K_c
\]

\[
\ln K_c = 210.3
\]

Taking the exponential of both sides of this equation:

\[
K_c = 2.1 \times 10^{21}
\]

20.69 Ni^{2+} is reduced by two electrons and Co is oxidized by two electrons.

\[ E^{\circ}_{\text{cell}} = E^{\circ}_{\text{reduction}} - E^{\circ}_{\text{oxidation}} = -0.25 - (-0.28) = +0.03 \text{ V} \]

\[
E^{\circ}_{\text{cell}} = \frac{0.0592}{n} \log K_c
\]

\[
+0.03 = (0.0592/2) \times \log K_c
\]

log K_c = 1 and K_c = 10^1 = 10

20.70 Sn is oxidized by two electrons and Ag is reduced by two electrons:

\[
E^{\circ}_{\text{cell}} = \frac{0.0592}{n} \log K_c
\]

\[
-0.015 \text{ V} = (0.0592 \text{ V}/2) \times \log K_c
\]

log K_c = -0.51

K_c = \text{antilog}(-0.51) = 0.31

20.71 First, separate the overall reaction into two half–reactions:

\[
\begin{align*}
2\text{H}_2\text{O} &\rightarrow 4\text{H}^+ + 4e^- + \text{O}_2 \quad \text{oxidation} \\
2 \times (\text{Cl}_2 + 2e^- &\rightarrow 2\text{Cl}^-) \quad \text{reduction}
\end{align*}
\]

\[
E^{\circ}_{\text{cell}} = E^{\circ}_{\text{reduction}} - E^{\circ}_{\text{oxidation}} = 1.36 - (1.23) = 0.13 \text{ V} \]
Chapter 20

20.72 This reaction involves the oxidation of Ag by two electrons and the reduction of Ni by two electrons. The concentration of the hydrogen ion is derived from the pH of the solution: $[H^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-2) = 1 \times 10^{-2} \text{ M}

\[ E_{\text{cell}} = 2.48 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \left( \frac{[\text{Ag}^+]^2 [\text{Ni}^{2+}]}{[\text{H}^+]^4} \right) \]

\[ = 2.48 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \left( \frac{3.0 \times 10^{-2}^2 [3.0 \times 10^{-2}]}{1.0 \times 10^{-2}^4} \right) \]

\[ E_{\text{cell}} = 2.48 \text{ V} - 0.101 \text{ V} = 2.38 \text{ V} \]

20.73 The following half-reactions indicate that the value of n is 30:

\[
5\text{Cr}_2\text{O}_7^{2-} + 70\text{H}^+ + 30\text{e}^- \rightarrow 10\text{Cr}^{3+} + 35\text{H}_2\text{O} \\
3\text{I}_2 + 18\text{H}_2\text{O} \rightarrow 6\text{IO}_3^- + 36\text{H}^+ + 30\text{e}^- 
\]

\[ E_{\text{cell}} = 0.135 \text{ V} - \frac{0.0592 \text{ V}}{30} \log \left( \frac{[\text{IO}_3^-]^6 [\text{Cr}^{3+}]^{10}}{[\text{H}^+]^{34} [\text{Cr}_2\text{O}_7^{2-}]^5} \right) \]

\[ = 0.135 \text{ V} - \frac{0.0592 \text{ V}}{30} \log \left( \frac{0.00010^6 [0.0010]^{10}}{[0.10]^{34} [0.010]^5} \right) \]

\[ = 0.135 \text{ V} - \frac{0.0592 \text{ V}}{30} \log 1.0 \times 10^{-10} \]

\[ = 0.155 \text{ V} \]

20.74 $E_{\text{cell}} = E^0_{\text{cell}} - \frac{RT}{nF} \ln \left( \frac{[\text{Mg}^{2+}]}{[\text{Cd}^{2+}]} \right)$

\[ E_{\text{cell}} = 1.97 - \left( \frac{8.314 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})}{2(96,500 \text{ C mol}^{-1})} \right) \ln \left( \frac{1.00}{[\text{Cd}^{2+}]} \right) \]

\[ 1.54 \text{ V} = 1.97 \text{ V} - 0.01284 \ln \left( \frac{1}{[\text{Cd}^{2+}]} \right) \]

\[ \ln (1/[\text{Cd}^{2+}]) = 33.489 \]

Taking $(e^x)$ of both sides:

\[ 1/[\text{Cd}^{2+}] = 3.50 \times 10^{14} \]

\[ [\text{Cd}^{2+}] = 2.86 \times 10^{-15} \text{ M} \]

20.75 Since the copper half-cell is the cathode; this is the half-cell in which reduction takes place. The silver half-cell is therefore the anode, where oxidation of silver occurs. The standard cell potential is:
\[ E_{\text{cell}}^o = E_{\text{reduction}}^o - E_{\text{oxidation}}^o = 0.3419 \text{ V} - 0.2223 \text{ V} = 0.1196 \text{ V} \]. The overall cell reaction is:
\[ \text{Cu}^{2+}(aq) + 2\text{Ag}(s) + 2\text{Cl}^-(aq) \rightarrow \text{Cu}(s) + 2\text{AgCl}(s) \], and the Nernst equation becomes:
\[ E_{\text{cell}} = E_{\text{cell}}^o - \frac{0.0592 \text{ V}}{2} \log \left( \frac{[\text{Cu}^{2+}]}{[\text{Cl}^-]^2} \right) \]

If we use the values given in the exercise, we arrive at:
\[ 0.0895 \text{ V} = 0.1196 \text{ V} - 0.0296 \text{ V} \times \log(1/[\text{Cl}^-]^2) \], which rearranges to give:
\[ \log(1/[\text{Cl}^-]^2) = 1.017 \]
\[ [\text{Cl}^-] = 0.310 \text{ M} \]

20.76 In the iron half–cell, we are initially given:
\[ 0.0500 \text{ L} \times 0.100 \text{ mol/L} = 5.00 \times 10^{-3} \text{ mol Fe}^{2+}(aq) \]

The precipitation of Fe(OH)\(_2\)(s) consumes some of the added hydroxide ion, as well as some of the iron ion: \[ \text{Fe}^{3+}(aq) + 2\text{OH}^- (aq) \rightarrow \text{Fe(OH)}_2(s) \]. The number of moles of OH\(^-\) that have been added to the iron half–cell is:
\[ 0.500 \text{ mol/L} \times 0.0500 \text{ L} = 2.50 \times 10^{-2} \text{ mol OH}^- \]

The stoichiometry of the precipitation reaction requires that the following number of moles of OH\(^-\) be consumed on precipitation of \( 5.00 \times 10^{-3} \text{ mol of Fe(OH)}_2(s) \):
\[ 5.00 \times 10^{-3} \text{ mol Fe(OH)}_2 \times (2 \text{ mol OH}^-/\text{mol Fe(OH)}_2) = 1.00 \times 10^{-2} \text{ mol OH}^- \]

The number of moles of OH\(^-\) that are unprecipitated in the iron half–cell is:
\[ 2.50 \times 10^{-2} \text{ mol} - 1.00 \times 10^{-2} \text{ mol} = 1.50 \times 10^{-2} \text{ mol OH}^- \]

Since the resulting volume is 50.0 mL + 50.0 mL, the concentration of hydroxide ion in the iron half–cell becomes, upon precipitation of the Fe(OH)\(_2\):
\[ [\text{OH}^-] = 1.50 \times 10^{-2} \text{ mol/0.100 L} = 0.150 \text{ M OH}^- \]

The standard cell potential is:
\[ E_{\text{cell}}^o = E_{\text{reduction}}^o - E_{\text{oxidation}}^o = 0.3419 \text{ V} - (-0.447 \text{ V}) = 0.7889 \text{ V} \]

The Nernst equation is:
\[ E_{\text{cell}} = E_{\text{cell}}^o - \frac{RT}{nF} \ln \left( \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right) \]
\[ 1.175 = 0.7889 - \frac{8.314 \text{ J mol}^{-1} \text{K}^{-1})(298 \text{ K})}{2(96,500 \text{ C mol}^{-1})} \ln \left( \frac{[\text{Fe}^{2+}]}{[1.00]} \right) \]
\[ 1.175 = 0.7889 - 0.01284 \ln \left( \frac{[\text{Fe}^{2+}]}{[1.00]} \right) \]
\[ \ln[\text{Fe}^{2+}] = -30.08 \]
\[ [\text{Fe}^{2+}] = 8.66 \times 10^{-14} \text{ M} \]

20.77 The half–cell reactions and the overall cell reaction are:
\[ \text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s) \quad E_{\text{red}}^o = +0.3419 \text{ V} \]
\[ \text{H}_2(g) \rightarrow 2\text{H}^+(aq) + 2e^- \quad E_{\text{ox}}^o = 0.0000 \text{ V} \]
\[ \text{Cu}^{2+}(aq) + \text{H}_2(g) \rightarrow \text{Cu}(s) + 2\text{H}^+(aq) \]

(a) The standard cell potential is:
The Nernst equation for this system is:

$$E_{\text{cell}} = E_{\text{o}} - \frac{0.0592 \text{ V}}{2} \log \left( \frac{\left[ H^+ \right]^2}{\left[ Cu^{2+} \right]} \right)$$

which becomes, under the circumstances defined in the problem:

$$E_{\text{cell}} = E_{\text{o}} - \frac{0.0592 \text{ V}}{2} \log \left[ H^+ \right]^2$$

Rearranging the last equation gives:

$$\frac{(2)(E_{\text{cell}} - E_{\text{o}})}{0.0592 \text{ V}} = - \log \left[ H^+ \right]^2$$

which becomes the desired relationship:

$$\frac{(E_{\text{cell}} - E_{\text{o}})}{0.0592 \text{ V}} = - \log \left[ H^+ \right] = \text{pH}$$

(b) The equation derived in the answer to part (a) of this question is conveniently rearranged to give:

$$E_{\text{cell}} = (0.0592 \text{ V})(\text{pH}) + E_{\text{o}} = (0.0592 \text{ V})(5.15) + 0.3419 \text{ V} = 0.647 \text{ V}$$

(c) The equation that was derived in the answer to part (a) of this question may be used directly:

$$\text{pH} = \frac{(E_{\text{cell}} - E_{\text{o}})}{0.0592 \text{ V}} = \frac{(0.645 \text{ V} - 0.3419 \text{ V})}{0.0592 \text{ V}} = 5.12$$

20.78  

$$E^o = E_{\text{o}} = \frac{RT}{nF} \ln \left( \frac{[Ag^+]_{\text{dilute}}}{[Ag^+]_{\text{conc}}} \right)$$

$$E^o = 0 - \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{(1 \text{ mol})(9.65 \times 10^4 \text{ C mol}^{-1})} \ln \left( \frac{0.015}{0.50} \right) = 0.090 \text{ V}$$

$$E^o = \frac{RT}{nF} \ln \left( \frac{[Ag^+]_{\text{dilute}}}{[Ag^+]_{\text{conc}}} \right)$$

$$E^o = 0 - \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1)(348 \text{ K})}{(1 \text{ mol})(9.65 \times 10^4 \text{ C mol}^{-1})} \ln \left( \frac{0.015}{0.50} \right) = 0.105 \text{ V}$$

20.79 At 25 °C (298 K)
Chapter 20

\[
E^\circ = E^\circ_{\text{cell}} = \frac{RT}{n \mathcal{F}} \ln \left[ \frac{\left[ \text{Cu}^{2+} \right]_{\text{dilute}}}{\left[ \text{Cu}^{2+} \right]_{\text{conc}}} \right]
\]

\[
E^\circ = 0 - \frac{\left( 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \right) (298 \text{ K})}{(1 \text{ mol})(9.65 \times 10^4 \text{ C mol}^{-1})} \ln \left[ \frac{0.015}{0.50} \right]
\]

\[E^\circ = 0.090 \text{ V}\]

At 75 °C (348 K)

\[
E^\circ = 0 - \frac{\left( 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \right) (348 \text{ K})}{(1 \text{ mol})(9.65 \times 10^4 \text{ C mol}^{-1})} \ln \left[ \frac{0.015}{0.50} \right]
\]

\[E^\circ = 0.10 \text{ V}\]

20.80 (a) \(\text{Fe}^{2+}(aq) + 2e^- \rightarrow \text{Fe(s)}\)

\[0.20 \text{ mol Fe}^{2+} \times 2 \text{ mol e}^-/\text{mol Fe}^{2+} = 0.40 \text{ mol e}^-\]

(b) \(\text{Cl}^-(aq) \rightarrow 1/2\text{Cl}_2(g) + e^-\)

\[0.70 \text{ mol Cl}^- \times 1 \text{ mol e}^-/\text{mol Cl}^- = 0.70 \text{ mol e}^-\]

(c) \(\text{Cr}^{3+}(aq) + 3e^- \rightarrow \text{Cr(s)}\)

\[1.50 \text{ mol Cr}^{3+} \times 3 \text{ mol e}^-/\text{mol Cr}^{3+} = 4.50 \text{ mol e}^-\]

(d) \(\text{Mn}^{2+}(aq) + 4\text{H}_2\text{O(l)} \rightarrow \text{MnO}_4^-(aq) + 8\text{H}^+(aq) + 5e^-\)

\[1.0 \times 10^{-2} \text{ mol Mn}^{2+} \times 5 \text{ mol e}^-/\text{mol Mn}^{2+} = 5.0 \times 10^{-2} \text{ mol e}^-\]

20.81 (a) \(\text{Mg}^{2+}(aq) + 2e^- \rightarrow \text{Mg(s)}\)

\[\text{mol e}^- = \left( 5.00 \text{ g Mg} \right) \left( \frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}} \right) \left( \frac{2 \text{ mol e}^-}{1 \text{ mol Mg}} \right) = 0.411 \text{ mol e}^-\]

(b) \(\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu(s)}\)

\[\text{mol e}^- = \left( 41.0 \text{ g Cu} \right) \left( \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \right) \left( \frac{2 \text{ mol e}^-}{1 \text{ mol Cu}} \right) = 1.29 \text{ mol e}^-\]

20.82 \(\text{Fe(s)} + 2\text{OH}^-(aq) \rightarrow \text{Fe(OH)}_2(s) + 2e^-\)

The number of Coulombs is: \(12.0 \text{ min} \times 60 \text{ s/min} \times 8.00 \text{ C/s} = 5.76 \times 10^3 \text{ C}\). The number of grams of \(\text{Fe(OH)}_2\) is:

\[
g \text{Fe(OH)}_2 = \left( 5.76 \times 10^3 \text{ C} \right) \left( \frac{1 \text{ mol e}^-}{96500 \text{ C}} \right) \left( \frac{1 \text{ mol Fe(OH)}_2}{2 \text{ mol e}^-} \right) \left( \frac{89.86 \text{ g Fe(OH)}_2}{1 \text{ mol Fe(OH)}_2} \right)
\]

\[= 2.68 \text{ g Fe(OH)}_2\]

20.83 \(2\text{Cl}^-(l) \rightarrow \text{Cl}_2(g) + 2e^-\)

The number of Coulombs is: \(4.25 \text{ A} \times 35.0 \text{ min} \times 60 \text{ s/min} = 8.92 \times 10^3 \text{ C}\)

The number of grams of \(\text{Cl}_2\) that will be produced is:

\[
g \text{Cl}_2 = \left( 8.92 \times 10^3 \text{ C} \right) \left( \frac{1 \text{ mol e}^-}{96500 \text{ C}} \right) \left( \frac{1 \text{ mol Cl}_2}{2 \text{ mol e}^-} \right) \left( \frac{70.91 \text{ g Cl}_2}{1 \text{ mol Cl}_2} \right) = 3.28 \text{ g Cl}_2\]

20.84 \(\text{Cr}^{3+}(aq) + 3e^- \rightarrow \text{Cr(s)}\)

The number of Coulombs that will be required is:
Coulombs = \( (75.0 \text{ g Cr}) \left( \frac{1 \text{ mol Cr}}{52.00 \text{ g Cr}} \right) \left( \frac{3 \text{ mol e}^-}{1 \text{ mol Cr}} \right) \left( \frac{96,500 \text{ C}}{1 \text{ mol e}^-} \right) = 4.18 \times 10^5 \text{ C} \)

The time that will be required is:

\[ \text{hr} = \left( \frac{4.18 \times 10^5 \text{ C}}{2.25 \text{ C}} \right) \left( \frac{1 \text{ hr}}{3600 \text{ s}} \right) = 51.5 \text{ hr} \]

20.85 The number of Coulombs that will be required is:

\[ \text{Coulombs} = \left( 35.0 \text{ g Pb} \right) \left( \frac{1 \text{ mol Pb}}{207.2 \text{ g Pb}} \right) \left( \frac{2 \text{ mol e}^-}{1 \text{ mol Pb}} \right) \left( \frac{96,500 \text{ C}}{1 \text{ mol e}^-} \right) = 3.26 \times 10^4 \text{ C} \]

The time that will be required is:

\[ \text{hr} = \left( \frac{3.26 \times 10^4 \text{ C}}{1.50 \text{ C}} \right) \left( \frac{1 \text{ hr}}{3600 \text{ s}} \right) = 6.04 \text{ hr} \]

20.86 \( \text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}(l) \)

The number of Coulombs that will be required is:

\[ \text{Coulombs} = \left( 60.0 \text{ g Mg} \right) \left( \frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}} \right) \left( \frac{2 \text{ mol e}^-}{1 \text{ mol Mg}} \right) \left( \frac{96,500 \text{ C}}{1 \text{ mol e}^-} \right) = 4.76 \times 10^5 \text{ C} \]

The number of amperes is: \( 4.76 \times 10^5 \text{ C} \div 8.64 \times 10^4 \text{ s} = 5.50 \times 10^4 \text{ A} \)

(Note: There are \( 8.64 \times 10^4 \text{ s} \) in 24.0 hr.)

20.87 \( \text{Al}^{3+} + 3e^- \rightarrow \text{Al}(s) \)

The number of Coulombs that are required is:

\[ \text{Coulombs} = \left( 409 \times 10^3 \text{ g Al} \right) \left( \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \right) \left( \frac{3 \text{ mol e}^-}{1 \text{ mol Al}} \right) \left( \frac{96,500 \text{ C}}{1 \text{ mol e}^-} \right) = 4.39 \times 10^9 \text{ C} \]

The number of amperes is: \( 4.39 \times 10^9 \text{ C} \div 7200 \text{ s} = 6.64 \times 10^4 \text{ A} \)

(Note: There are \( 8.64 \times 10^4 \text{ s} \) in 24.0 hr.)

20.88 The electrolysis of NaCl solution results in the reduction of water, together with the formation of hydroxide ion: \( 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^- (\text{aq}) \). The number of Coulombs is: 2.00 A \times 20.0 \text{ min} \times 60 \text{ s/min} = 2.40 \times 10^3 \text{ C}. The number of moles of \( \text{OH}^- \) is:

\[ \text{mol OH}^- = \left( 2.40 \times 10^3 \text{ C} \right) \left( \frac{1 \text{ mol e}^-}{96,500 \text{ C}} \right) \left( \frac{2 \text{ mol OH}^-}{2 \text{ mol e}^-} \right) = 0.0249 \text{ mol OH}^- \]

\[ [\text{OH}^-] = 0.0249 \text{ mol/0.250 L} = 0.0996 \text{ M} \]

20.89 The electrolysis of NaCl solution results in the reduction of water, together with the formation of hydroxide ion: \( 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^- (\text{aq}) \). The number of seconds is: 25.0 \text{ min} \times 60 \text{ s/min} = 1.50 \times 10^3 \text{ s}. The number of moles of \( \text{OH}^- \) is:

\[ \text{mol OH}^- = \left( 1.50 \times 10^3 \text{ s} \right) \left( \frac{1.45 \text{ C}}{\text{s}} \right) \left( \frac{1 \text{ mol e}^-}{96,500 \text{ C}} \right) \left( \frac{2 \text{ mol OH}^-}{2 \text{ mol e}^-} \right) = 2.25 \times 10^{-3} \text{ mol OH}^- \]

\[ [\text{OH}^-] = \left( \frac{2.25 \times 10^{-2} \text{ mol OH}^-}{0.100 \text{ L}} \right) = 0.225 \text{ M} \]

\( 2 \text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \)
\[ (2.25 \times 10^{-2} \text{ mol OH}^-) \left( \frac{1 \text{ mol Cl}_2}{2 \text{ mol OH}^-} \right) = 1.125 \times 10^{-2} \text{ mol Cl}_2 \]

Assuming Cl\(_2\) and OH\(^-\) react to make OCl\(^-\)

\[
\begin{bmatrix}
\text{OCl}^-
\end{bmatrix} = \frac{1.125 \times 10^{-2} \text{ mol}}{0.100 \text{ L}} = 0.122 \text{ M}
\]

20.90 Possible cathode reactions:

- \( \text{Al}^{3+} + 3e^- \quad \text{Al(s)} \quad E^o = -1.66 \text{ V} \)
- \( 2\text{H}_2\text{O} + 2e^- \quad \text{H}_2\text{O}(g) + 2\text{OH}^- (aq) \quad E^o = -0.83 \text{ V} \)

Possible anode reactions:

- \( \text{S}_2\text{O}_8^{2-} + 2e^- \quad 2\text{SO}_4^{2-} \quad E^o = +2.05 \text{ V} \)
- \( \text{O}_2 + 4\text{H}^+ + 4e^- \quad 2\text{H}_2\text{O} \quad E^o = +1.23 \text{ V} \)

Cathode reaction: \( 2\text{H}_2\text{O} + 2e^- \quad \text{H}_2(g) + 2\text{OH}^- (aq) \quad E^o = -0.83 \text{ V} \)

Anode reactions: \( 2\text{H}_2\text{O} \quad \text{O}_2 + 4\text{H}^+ + 4e^- \quad E^o = -1.23 \text{ V} \)

Net cell reaction: \( 2\text{H}_2\text{O} \quad 2\text{H}_2(g) + \text{O}_2(g) \quad E^o = -2.06 \text{ V} \)

20.91 Possible cathode reactions:

- \( \text{Cd}^{2+} + 2e^- \quad \text{Cd(s)} \quad E^o = -0.40 \text{ V} \)
- \( 2\text{H}_2\text{O} + 2e^- \quad \text{H}_2(g) + 2\text{OH}^- (aq) \quad E^o = -0.83 \text{ V} \)

Possible anode reactions:

- \( \text{O}_2 + 4\text{H}^+ + 4e^- \quad 2\text{H}_2\text{O} \quad E^o = +1.23 \text{ V} \)
- \( \text{I}_2(s) + 2e^- \quad 2\text{I}^- \quad E^o = +0.54 \text{ V} \)

Cathode reaction: \( \text{Cd}^{2+} + 2e^- \quad \text{Cd(s)} \quad E^o = -0.40 \text{ V} \)

Anode reaction: \( 2\text{I}^- \quad \text{I}_2(s) + 2e^- \quad E^o = -0.54 \text{ V} \)

Net reaction: \( \text{Cd}^{2+} + 2\text{I}^- \quad \text{I}_2(s) + \text{Cd(s)} \quad E^o = -0.94 \text{ V} \)

20.92 The answers to the previous Review Problems guide us here:

Possible cathode reactions:

- \( \text{K}^+ + e^- \quad \text{K(s)} \quad E^o = -2.92 \text{ V} \)
- \( \text{Cu}^{2+} + 2e^- \quad \text{Cu(s)} \quad E^o = +0.34 \text{ V} \)
- \( 2\text{H}_2\text{O} + 2e^- \quad \text{H}_2(g) + 2\text{OH}^- (aq) \quad E^o = -0.83 \text{ V} \)

Cathode reaction: \( \text{Cu}^{2+} + 2e^- \quad \text{Cu(s)} \)

Possible anode reactions:

- \( 2\text{SO}_4^{2-} \quad \text{S}_2\text{O}_8^{2-} + 2e^- \quad E^o = -2.01 \text{ V} \)
- \( 2\text{Br}^- \quad \text{Br}_2 + 2e^- \quad E^o = -1.07 \text{ V} \)
- \( 2\text{H}_2\text{O} \quad \text{O}_2(g) + 4\text{H}^+ (aq) + 4e^- \quad E^o = -1.23 \text{ V} \)

Anode reaction: \( 2\text{Br}^- \quad \text{Br}_2 + 2e^- \)
Overall reaction:  \( \text{Cu}^{2+} + 2\text{Br}^{-} \rightarrow \text{Br}_2 + \text{Cu(s)} \)

20.93 At the cathode, where reduction occurs, we expect \( \text{Cu(s)} \). At the anode, where oxidation occurs, we expect \( \text{I}_2(aq) \).
The net cell reaction would be \( \text{Cu}^{2+}(aq) + 2\text{I}^{-}(aq) \rightarrow \text{Cu(s)} + \text{I}_2(aq) \)

20.94 In aqueous solution the following reduction of water can occur:
\[ 2\text{H}_2\text{O}(l) + 2e^{-} \rightarrow \text{H}_2(g) + 2\text{OH}^{-}(aq) \quad E^o = -0.83 \text{ V} \]
Reactions that are less positive than this cannot occur at the cathode.
Therefore, \( \text{Al}^{3+}, \text{Mg}^{2+}, \text{Na}^+, \text{Ca}^{2+}, \text{K}^+, \text{and Li}^+ \) would not be reduced at the cathode.

20.95 In aqueous solution the following oxidation of water can occur:
\[ 2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4e^{-} \quad E(\text{oxidation}) = -1.23 \text{ V} \]
Reactions that are more negative than this cannot occur at the anode.
Therefore, \( \text{Cl}^-, \text{Au}, \text{Br}^-, \text{Pb}^{2+}, \text{Mn}^{2+}, \text{Cl}_2, \text{PbSO}_4, \text{SO}_4^{2-}, \text{and F}^- \) would not be oxidized at the anode.

**Additional Exercises**

20.96 \( \Delta G^o = -n \mathcal{F} E^o_{\text{cell}} \)
\( E^o_{\text{cell}} = 1.34 \text{ V} = 1.34 \text{ J/C} \), and \( n = 2 \)
\( \Delta G^o = -(2)(96,500 \text{ C})(1.34 \text{ J/C}) = -2.59 \times 10^5 \text{ J per mol of HgO} \)

The maximum amount of work that can be derived from this cell, on using 1.00 g of HgO, is thus:
\[
J = \left( 1.00 \text{ g HgO} \right) \left( \frac{1 \text{ mol HgO}}{216.6 \text{ g HgO}} \right) \left( \frac{2.59 \times 10^5 \text{ J}}{1 \text{ mol HgO}} \right) = 1.20 \times 10^3 \text{ J}
\]

Now, since 1 watt = 1 J s\(^{-1}\), then 2 \( \times 10^{-3} \text{ watt} = 2 \times 10^{-3} \text{ J s}^{-1} \), and the time required for this process is:
\[
\text{hr} = \left( 1.20 \times 10^3 \text{ J} \right) \left( \frac{1 \text{ s}}{2 \times 10^{-3} \text{ J}} \right) \left( \frac{1 \text{ min}}{60 \text{ s}} \right) \left( \frac{1 \text{ hr}}{60 \text{ min}} \right) = 167 \text{ hr}
\]

20.97 The initial numbers of moles of \( \text{Ag}^+ \) and \( \text{Zn}^{2+} \) are: 1.00 mol/L \( \times \) 0.100 L = 0.100 mol. The number of Coulombs (A \( \times \) s) that have been employed is: 0.10 C/s \( \times \) 15.00 hr \( \times \) 3600 s/hr = 5.4 \( \times \) 10\(^3\) C. The number of moles of electrons is: 5.4 \( \times \) 10\(^3\) C \( / \) 96,500 C/mol = 5.6 \( \times \) 10\(^{-2}\) mol electrons.

For \( \text{Ag}^+ \), there is 1 mol per mole of electrons, and for \( \text{Zn}^{2+} \), there are two moles of electrons per mol of \( \text{Zn} \). This means that the number of moles of the two ions that have been consumed or formed is given by:
\[
5.6 \times 10^{-2} \text{ mol } \text{e}^- \times 1 \text{ mol } \text{Ag}^+/1 \text{ mol } \text{e}^- = 5.6 \times 10^{-2} \text{ mol } \text{Ag}^+ \text{ reacted.}
\]
\[
5.6 \times 10^{-2} \text{ mol } \text{e}^- \times 1 \text{ mol } \text{Zn}^{2+}/2 \text{ mol } \text{e}^- = 2.8 \times 10^{-2} \text{ mol } \text{Zn}^{2+} \text{ formed}
\]

The number of moles of \( \text{Ag}^+ \) that remain is: 0.100 – 0.056 = 0.044 mol of \( \text{Ag}^+ \)
The final concentration of silver ion is: \([\text{Ag}^+] = 0.044 \text{ mol/0.100 L} = 0.44 \text{ M} \)
The number of moles of \( \text{Zn}^{2+} \) that are present is: 0.100 + 0.028 = 0.128 mol \( \text{Zn}^{2+} \)
The final concentration of zinc ion is: \[ [\text{Zn}^{2+}] = 0.128 \text{ mol/0.100 L} = 1.28 M \]

The standard cell potential should be: \[ E_{\text{cell}}^0 = E_{\text{reduction}}^0 - E_{\text{oxidation}}^0 = 0.80 - (-0.76) = 1.56 \text{ V} \]

We now apply the Nernst equation:

\[
E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0592 \text{ V}}{2} \log \left( \frac{1.28}{(0.44)^2} \right)
\]

\[ E_{\text{cell}} = 1.56 \text{ V} - 0.024 \text{ V} = 1.54 \text{ V} \]

20.98 The concentration of Br\(^{-}\) in solution will be 0.10 M, since the \( K_{sp} \) of AgBr is so small, the amount of dissociation of AgBr from the electrode will be negligible.

The reduction reaction will be

\[ \text{AgBr} + e^- \rightarrow \text{Ag} + \text{Br}^- \quad E^0 = 0.070 \text{ V} \]

The oxidation reaction will occur at the standard hydrogen electrode.

The net cell reaction is:

\[ 2\text{AgBr} + \text{H}_2 \rightarrow 2\text{Ag} + 2\text{Br}^- + 2\text{H}^+ \]

\[ E_{\text{cell}} = 0.070 \text{ V} - 0.000 \text{ V} = 0.070 \text{ V} \]

The potential for the constructed cell is calculated using the Nernst equation:

\[
E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0592 \text{ V}}{2} \log \left( \frac{[\text{Br}^-]^2[\text{H}^+]}{[\text{I}^-]^2} \right)
\]

\[ E_{\text{cell}} = 0.070 \text{ V} - (-0.0592) 
E_{\text{cell}} = 0.129 \text{ V} \]

20.99 Our strategy will be thus:

**Step A:**
Pressure H\(_2\) (wet) \rightarrow partial pressure H\(_2\) \rightarrow mol H\(_2\) \rightarrow \# e\(^-\) used

**Step B:**
Find total charge used = (current)(time)

**Step C:**
The charge per electron can be arrived at by:

\[ \text{Charge per } e^- = \text{total charge/total } \# e^- \text{ used} = \text{Step A/Step B} \]

**Step A:**
Pressure H\(_2\) (wet) \rightarrow partial pressure H\(_2\) \rightarrow mol H\(_2\) \rightarrow \# e^- used

The total pressure of wet hydrogen is 767 torr, but some of this is provided by water vapor. Consulting the water vapor pressure table in the appendices, we find that at 27 °C, the vapor pressure of water is 26.7 torr. Therefore pressure solely due to hydrogen gas (the partial pressure of hydrogen gas) is:

\[ P_{\text{H}_2} = 767 - 26.7 = 740 \text{ torr} \]

740 torr(1 atm/760 torr) = 0.974 atm

Using the ideal gas law,
PV = nRT
(0.974 atm)(0.288 L) = n(0.0821 L·atm mol\(^{-1}\)·K\(^{-1}\))(27 + 273K)
n = 0.0114 mol H\(_2\)

According to the electrolysis equation \(2\text{H}^+ + 2e^- \rightarrow \text{H}_2(g)\), 2 moles of electrons are required per mol of H\(_2\) gas formed. Therefore,
electrons = 0.0114 mol H\(_2\)(2 mol e\(^-\)/1 mol H\(_2\))(6.022 \times 10^{23} \text{ electrons/mol}) = 1.37 \times 10^{22} \text{ electrons}

**Step B:**
Total charge used = (1.22 A)(1800 s) = 2200 C

**Step C:**
Charge per e\(^-\) = total charge/total # e\(^-\) used = 2200 C/1.37 \times 10^{22} \text{ electrons} = 1.61 \times 10^{-19} \text{ C per electron}

(This is a very good estimate; the accepted value is 1.60 \times 10^{-19} \text{ C}.)

20.100 The oxidation reaction is:
\[
\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe} \quad E^o = -0.44 \text{ V}
\]
The reduction reaction is:
\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad E^o = 0.00 \text{ V}
\]
The overall cell reaction is
\[
2\text{H}^+ + \text{Fe} \rightarrow \text{H}_2 + \text{Fe}^{2+} \quad E_{cell}^o = 0.44 \text{ V}
\]
\[
E_{cell} = E_{cell}^o - \frac{0.0592 \text{ V}}{n} \log \left( \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^2} \right)
\]
\[
[\text{Fe}^{2+}] = 0.10 \text{ M}
\]
[H\(^+\)] is from the ionization of acetic acid
\[
K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.8 \times 10^{-5}
\]
\[
[H^+] = x \quad [\text{C}_2\text{H}_3\text{O}_2^-] = x \quad [\text{HC}_2\text{H}_3\text{O}_2] = 0.10 - x
\]
\[
1.8 \times 10^{-5} = \frac{x^2}{0.10 - x}
\]
Assume x is small compared to the concentration of HC\(_2\)H\(_3\)O\(_2\)
\[
x = 1.34 \times 10^{-3} \text{ M} = [\text{H}^+] = [\text{C}_2\text{H}_3\text{O}_2^-]
\]
\[
[\text{HC}_2\text{H}_3\text{O}_2] = 0.10 \text{ M}
\]
n = 2
\[
E_{cell} = 0.44 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \left( \frac{0.10}{1.34 \times 10^{-3}} \right)
\]
\[
E_{cell} = 0.44 \text{ V} - 0.14 \text{ V} = 0.30 \text{ V}
\]

20.101 The approach is as follows:
Area x thickness Cr \rightarrow volume Cr \rightarrow mass Cr \rightarrow moles Cr \rightarrow # e^- needed \rightarrow current

\[
V_{Cr} = (\text{area})(\text{thickness}) = (1.00 \text{ m}^2)(5.0 \times 10^{-5} \text{ m}) = 5.0 \times 10^{-5} \text{ m}^3
\]
\[
e^- = \left(5.0 \times 10^{-5} \text{ m}^3\right) \left(\frac{100 \text{ cm}}{1 \text{ m}}\right)^3 \left(\frac{7.19 \text{ g Cr}}{1 \text{ cm}^3}\right) \frac{1 \text{ mol Cr}}{52.0 \text{ g Cr}} \left(\frac{6 \text{ F}}{1 \text{ mol Cr}}\right) \left(\frac{96,500 \text{ C}}{1 \text{ F}}\right)
\]
This is done in 4.50 hr (16,200 s). So the current must be:
Current = charge/time = \( \frac{4.00 \times 10^6 \text{ C}}{16,200 \text{ s}} = 247 \text{ A} \)

20.102 (a) First, we calculate the number of Coulombs:
1.50 A \times 30.0 \text{ min} \times 60 \text{ s/min} = 2.70 \times 10^3 \text{ A} \cdot \text{s} = 2.70 \times 10^3 \text{ C}

Then we determine the number of moles of electrons:
\[
\text{mole } e^- = \frac{2.70 \times 10^3 \text{ C}}{96,500 \text{ C/mol e}^-} = 0.0280 \text{ mol } e^-
\]

(b) \( 0.475 \text{ g} \div 50.9 \text{ g/mol} = 9.33 \times 10^{-3} \text{ mol V} \)

(c) \( (2.80 \times 10^{-2} \text{ mol } e^-)/(9.33 \times 10^{-3} \text{ mol V}) = 3.00 \text{ mol } e^-/\text{mol V} \)
The original oxidation state was V\(^{3+}\).

20.103

<table>
<thead>
<tr>
<th></th>
<th>( E^o ) (V)</th>
<th>Electron Affinity (kJ/mol)</th>
<th>Ionization Energy(^1) (kJ/mol)</th>
<th>Electronegativity</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(_2)</td>
<td>+2.87</td>
<td>-328</td>
<td>1682</td>
<td>4.1</td>
</tr>
<tr>
<td>Cl(_2)</td>
<td>+1.36</td>
<td>-348</td>
<td>1251</td>
<td>2.9</td>
</tr>
<tr>
<td>Br(_2)</td>
<td>+1.07</td>
<td>-325</td>
<td>1140</td>
<td>2.8</td>
</tr>
<tr>
<td>I(_2)</td>
<td>+0.54</td>
<td>-295</td>
<td>1008</td>
<td>2.2</td>
</tr>
<tr>
<td>Li(^+)</td>
<td>-3.05</td>
<td>-60</td>
<td>520</td>
<td>1.0</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>-2.71</td>
<td>-53</td>
<td>496</td>
<td>1.0</td>
</tr>
<tr>
<td>K(^+)</td>
<td>-2.92</td>
<td>-48</td>
<td>419</td>
<td>0.9</td>
</tr>
<tr>
<td>Rb(^+)</td>
<td>-2.93</td>
<td>-47</td>
<td>403</td>
<td>0.9</td>
</tr>
<tr>
<td>Cs(^+)</td>
<td>-2.92</td>
<td>-45</td>
<td>376</td>
<td>0.9</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>-2.32</td>
<td>+230</td>
<td>738</td>
<td>1.3</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>-2.76</td>
<td>+155</td>
<td>590</td>
<td>1.1</td>
</tr>
<tr>
<td>Sr(^{2+})</td>
<td>-2.89</td>
<td>+176</td>
<td>549</td>
<td>1.0</td>
</tr>
<tr>
<td>Ba(^{2+})</td>
<td>-2.90</td>
<td>+50</td>
<td>503</td>
<td>0.9</td>
</tr>
</tbody>
</table>

(1) [wiki.chemeddl.org](http://wiki.chemeddl.org)

(a) Reduction potentials decrease in the same order as electronegativity and ionization energy. Electron affinity follows no pattern.

(b) Reduction potentials and the properties decrease going down the family, though Li is out of order due to its small size and larger effective nuclear charge compared to the other members of the family.

(c) Reduction potentials and the properties decrease going down the family though the electron affinity value for Sr\(^{2+}\) is out of order.
Chapter 20

\[ E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{RT}{nF} \ln \left[ \text{Cl}^- \right] \]

\[ 0.0478 \text{ V} = 0.2223 \text{ V} - \frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{1(96,500 \text{ C mol}^{-1})} \ln \left[ \text{Cl}^- \right] \]

\[ -0.1745 \text{ V} = \frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{1(96,500 \text{ C mol}^{-1})} \ln \left[ \text{Cl}^- \right] \]

\[ -6.797 \text{ V} = \ln \left[ \text{Cl}^- \right] \]

\[ 1.117 \times 10^{-3} = \left[ \text{Cl}^- \right] \]

20.105 The half–reactions diagrammed in this problem are:

- \( \text{Ag(s)} \rightarrow \text{Ag}^+(aq) + e^- \) anode \( E^\circ = -0.80 \text{ V} \)
- \( \text{Fe}^{3+}(aq) + e^- \rightarrow \text{Fe}^{2+}(aq) \) cathode \( E^\circ = 0.77 \text{ V} \)

\[ E_{\text{cell}}^{\ominus} = E_{\text{reduction}}^{\ominus} - E_{\text{oxidation}}^{\ominus} = 0.77 \text{ V} - 0.80 \text{ V} = -0.03 \text{ V} \]

\[ E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{0.0592 \text{ V}}{1} \log \left[ \frac{\text{Fe}^{2+}}{\text{Fe}^{3+}} \right] \]

\[ = -0.03 \text{ V} - \frac{0.0592 \text{ V}}{1} \log \left[ \frac{3.0 \times 10^{-4}}{1.1 \times 10^{-3}} \right] = +0.09 \text{ V} \]

As stated, being a galvanic cell, and using conventions in cell notation, the left-side half–cell is the anode and negatively charged, and the right–side half–cell is the cathode and positively charged. The equation for the spontaneous cell reaction is \( \text{Fe}^{3+}(1.1 \times 10^{-3} \text{ M}) + \text{Ag(s)} \rightarrow \text{Ag}^+(3.0 \times 10^{-4} \text{ M}) + \text{Fe}^{2+}(0.040 \text{ M}) \). This is an example of a concentration cell.

**Multi-Concept Problems**

20.106 The electrolysis of NaCl solution results in the reduction of water, together with the formation of hydroxide ion: \( 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^- (aq) \). The number of Coulombs is: \( 2.00 \text{ A} \times 20.0 \text{ min} \times 60 \text{ s/min} = 2.40 \times 10^3 \text{ C} \). The number of moles of \( \text{OH}^- \) is:

\[ \text{mol OH}^- = \left(2.40 \times 10^3 \text{ C}\right) \left(\frac{1 \text{ mol e}^-}{96,500 \text{ C}}\right) \left(\frac{2 \text{ mol OH}^-}{2 \text{ mol e}^-}\right) = 0.0249 \text{ mol OH}^- \]

The volume of acid solution that will neutralize this much \( \text{OH}^- \) is:

\[ \text{mL HCl} = \left(0.0249 \text{ mol OH}^-\right) \left(\frac{1 \text{ mol HCl}}{1 \text{ mol OH}^-}\right) \left(\frac{1000 \text{ mL HCl}}{0.620 \text{ mol HCl}}\right) = 40.1 \text{ mL HCl} \]

20.107 The electrolysis of NaCl solution results in the reduction of water, together with the formation of chlorine gas and hydroxide ion: \( 2\text{Cl}^- (aq) \rightarrow \text{Cl}_2(g) + 2e^- \). The number of Coulombs is: \( 2.50 \text{ A} \times 15.0 \text{ min} \times 60 \text{ s/min} = 2.25 \times 10^3 \text{ C} \). The number of moles of \( \text{Cl}_2 \) gas collected is:

\[ \text{mol Cl}_2 = \left(2.25 \times 10^3 \text{ C}\right) \left(\frac{1 \text{ mol e}^-}{96,500 \text{ C}}\right) \left(\frac{1 \text{ mol Cl}_2}{2 \text{ mol e}^-}\right) = 0.0117 \text{ mol Cl}_2 \]

The volume of \( \text{Cl}_2 \) gas that is collected is:
\[ V = \frac{nRT}{P} = \frac{(0.0117 \text{ mol})(0.0821 \frac{\text{L atm}}{\text{mol K}})(298 \text{ K})}{(750 \text{ torr} - 23.76 \text{ torr})
\left( \frac{1 \text{ atm}}{760 \text{ torr}} \right) = 0.299 \text{ L} = 299 \text{ mL} \]

20.108 \( 2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g) \)

The number of Coulombs is: \( 15.00 \text{ min} \times 60 \text{ s/min} \times 0.750 \text{ C/s} = 675 \text{ C} \).

The number of moles of \( \text{H}_2 \) is:

\[ \text{mol H}_2 = \left( 675 \text{ C} \right) \left( \frac{1 \text{ mol e}^-}{96,500 \text{ C}} \right) \left( \frac{1 \text{ mol H}_2}{2 \text{ mol e}^-} \right) = 3.50 \times 10^{-3} \text{ mol H}_2 \]

Finally, we calculate the volume of \( \text{H}_2 \) gas:

\[ V = \frac{nRT}{P} = \frac{(0.00350 \text{ mol})(0.0821 \frac{\text{L atm}}{\text{mol K}})(293 \text{ K})}{(735 \text{ torr})
\left( \frac{1 \text{ atm}}{760 \text{ torr}} \right) = 0.0870 \text{ L} = 87.0 \text{ mL} \]

20.109 In the iron half–cell, we are initially given:

\( 0.0500 \text{ L} \times 0.100 \text{ mol/L} = 5.00 \times 10^{-3} \text{ mol Fe}^{2+}(aq) \)

The precipitation of \( \text{Fe(OH)}_2(s) \) consumes some of the added hydroxide ion, as well as some of the iron ion: \( \text{Fe}^{2+}(aq) + 2\text{OH}^- (aq) \rightarrow \text{Fe(OH)}_2(s) \). The number of moles of \( \text{OH}^- \) that have been added to the iron half–cell is:

\[ 0.500 \text{ mol/L} \times 0.0500 \text{ L} = 2.50 \times 10^{-2} \text{ mol OH}^- \]

The stoichiometry of the precipitation reaction requires that the following number of moles of \( \text{OH}^- \) be consumed on precipitation of \( 5.00 \times 10^{-3} \text{ mol of Fe(OH)}_2(s) \):

\[ 5.00 \times 10^{-3} \text{ mol Fe(OH)}_2 \times (2 \text{ mol OH}^-/\text{mol Fe(OH)}_2) = 1.00 \times 10^{-2} \text{ mol OH}^- \]

The number of moles of \( \text{OH}^- \) that are unprecipitated in the iron half–cell is:

\[ 2.50 \times 10^{-2} \text{ mol} - 1.00 \times 10^{-2} \text{ mol} = 1.50 \times 10^{-2} \text{ mol OH}^- \]

Since the resulting volume is \( 50.0 \text{ mL} + 50.0 \text{ mL} \), the concentration of hydroxide ion in the iron half–cell becomes, upon precipitation of the \( \text{Fe(OH)}_2 \):

\[ [\text{OH}^-] = 1.50 \times 10^{-2} \text{ mol/0.100 L} = 0.150 \text{ M OH}^- \]

We have assumed that the iron hydroxide that forms in the above precipitation reaction is completely insoluble. This is not accurate, though, because some small amount does dissolve in water according to the following equilibrium:

\[ \text{Fe(OH)}_2(s) \sqsubset \text{Fe}^{2+}(aq) + 2\text{OH}^- (aq) \]

This means that the true \([\text{OH}^-]\) is slightly higher than \( 0.150 \text{ M} \) as calculated above. Thus we must set up the usual equilibrium table, in order to analyze the extent to which \( \text{Fe(OH)}_2(s) \) dissolves in \( 0.150 \text{ M OH}^- \) solution:

<table>
<thead>
<tr>
<th></th>
<th>([\text{Fe}^{2+}])</th>
<th>([\text{OH}^-])</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>–</td>
<td>0.150</td>
</tr>
<tr>
<td>C</td>
<td>+x</td>
<td>+2x</td>
</tr>
<tr>
<td>E</td>
<td>+x</td>
<td>0.150+2x</td>
</tr>
</tbody>
</table>

The quantity \( x \) in the above table is the molar solubility of \( \text{Fe(OH)}_2 \) in the solution that is formed in the iron half–cell.
$K_{sp} = [\text{Fe}^{2+}][\text{OH}^-]^2 = (x)(0.150 + 2x)^2$

The standard cell potential is:

$$E^\circ_{\text{cell}} = E^\circ_{\text{reduction}} - E^\circ_{\text{oxidation}} = 0.3419 \text{ V} - (-0.447 \text{ V}) = 0.7889 \text{ V}$$

The Nernst equation is:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln \frac{[\text{Fe}^{2+}]}{[\text{Cu}^{2+}]}$$

$$1.175 = 0.7889 - \frac{(8.314 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})}{2(96,500 \text{ C mol}^{-1})} \ln \frac{[\text{Fe}^{2+}]}{[1.00]}$$

$$1.175 = 0.7889 - 0.01284 \ln [\text{Fe}^{2+}]$$

$$\ln [\text{Fe}^{2+}] = -30.07$$

$$[\text{Fe}^{2+}] = 8.72 \times 10^{-14} \text{ M}$$

This is the concentration of Fe$^{2+}$ in the saturated solution, and it is the value to be used for $x$ in the above expression for $K_{sp}$.

$$K_{sp} = (x)(0.150 + 2x)^2 = (8.72 \times 10^{-14})(0.150 + (2)(8.72 \times 10^{-14}))^2$$

$$K_{sp} = 1.96 \times 10^{-15}$$

20.110 The desired reaction is:

$$\text{AgBr(s)} \rightleftharpoons \text{Ag}^+(aq) + \text{Br}^-(aq)$$

While this does not look like an oxidation-reduction reaction, we can use Hess’s law and the half-reaction provided in the problem to construct the desired reaction. Reverse the direction of the first reaction and keep the second reaction in the given direction. Be sure to change the sign of the cell potential when the reaction direction is changed.

$$\text{Ag} \rightarrow \text{Ag}^+ + e^- \quad E^\circ = -0.80 \text{ V}$$

$$\text{AgBr} \rightarrow \text{Ag} + \text{Br}^- + e^- \quad E^\circ = +0.07 \text{ V}$$

Sum the two reactions and their cell potentials:

$$\text{AgBr} \rightarrow \text{Ag}^+ + \text{Br}^- \quad E^\circ_{\text{cell}} = -0.73 \text{ V}$$

Now use the Nernst equation to determine the equilibrium constant for the reaction.

At equilibrium, $E_{\text{cell}} = 0$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592 \text{ V}}{I} \log \left[ \frac{[\text{Ag}^+]}{[\text{Br}^-]} \right]$$

$$\log \left[ \frac{[\text{Ag}^+]}{[\text{Br}^-]} \right] = \log K_{sp} (\text{AgBr}) = \frac{-0.73 \text{ V}}{0.0592 \text{ V}} = -12.3$$

$$K_{sp} = 4.7 \times 10^{-13}$$

20.111 The range of moles of Cl$^-$ is:
Chapter 20

0.096 M x 3.00 mL = 0.288 mmol Cl\(^-\)
0.106 M x 3.00 mL = 0.318 mmol Cl\(^-\)

\[
\text{Coulombs} = 0.288 \text{ mmol} \times \left( \frac{1 \text{ mol}}{1000 \text{ mmol}} \right) \left( \frac{1 \text{ mol e}^-}{1 \text{ mol Cl}^-} \right) \left( \frac{96,500 \text{ C}}{1 \text{ mol e}^-} \right) = 27.8 \text{ C}
\]

The time that will be required is:
\[
\text{seconds} = \left( \frac{27.8 \text{ C}}{0.500 \text{ C}} \right) = 55.6 \text{ s}
\]

\[
\text{Coulombs} = 0.318 \text{ mmol} \times \left( \frac{1 \text{ mol}}{1000 \text{ mmol}} \right) \left( \frac{1 \text{ mol e}^-}{1 \text{ mol Cl}^-} \right) \left( \frac{96,500 \text{ C}}{1 \text{ mol e}^-} \right) = 30.7 \text{ C}
\]

\[
\text{seconds} = \left( \frac{30.7 \text{ C}}{0.500 \text{ C}} \right) = 61.4 \text{ s}
\]

The range of time is thus, 55.6 to 61.4 seconds to precipitate the chloride ions as AgCl.

The electrolysis of NaCl solution results in the reduction of water, together with the formation of hydroxide ion: \(2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2(g) + 2\text{OH}^- (aq)\). The number of seconds is: \(25.0 \text{ min} \times 60 \text{ s/min} = 1.50 \times 10^3 \text{ s}\).

The number of moles of OH\(^-\) is:
\[
\text{mol OH}^- = (15.5 \text{ mL H}^+) \left( \frac{0.250 \text{ mol H}^+}{1000 \text{ mL H}^+} \right) \left( \frac{1 \text{ mol OH}^-}{1 \text{ mol H}^+} \right) = 3.87 \times 10^{-3} \text{ mol OH}^-
\]

The number of Coulombs that will form this much OH\(^-\) is:
\[
\text{Coulombs} = \left( 3.87 \times 10^{-3} \text{ mol OH}^- \right) \left( \frac{2 \text{ mol e}^-}{2 \text{ mol OH}^-} \right) \left( \frac{96,500 \text{ C}}{1 \text{ mol e}^-} \right) = 3.74 \times 10^2 \text{ C}
\]

The average current in amperes is:
\[
\text{Current} = \frac{3.74 \times 10^2 \text{ C}}{1.50 \times 10^3 \text{ s}} = 0.250 \text{ A}
\]

\[
\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(g)
\]

\[
\Delta G^\circ_T = \Delta H^\circ_{298} - T\Delta S^\circ_{298}
\]

\[
= (1 \text{ mol H}_2\text{O})(-241.8 \text{ kJ mol}^{-1}) \left( \frac{1000 \text{ J}}{1 \text{ kJ}} \right) - 383 \text{ K}[(1 \text{ mol H}_2\text{O})(188.7 \text{ J mol}^{-1} \text{ K}^{-1})]
\]

\[
- [(1 \text{ mol H}_2)(130.6 \text{ J mol}^{-1} \text{ K}^{-1}) + (\frac{1}{2} \text{ mol O}_2)(205.0 \text{ J mol}^{-1} \text{ K}^{-1})]
\]

\[
= -2.248 \times 10^5 \text{ J or 224.8 kJ}
\]

The is the maximum amount of work obtained by the reaction of one mole of hydrogen gas.
\[
\left(2.248 \times 10^5 \text{ J} \right) \left(\frac{1 \text{ watt}}{1 \text{ J/s}}\right) = 2.248 \times 10^5 \text{ watt s}
\]

Therefore, one mole of hydrogen gas will produce 224.8 kW s. We want enough hydrogen gas to produce 1 kW s.

The mass of H\(_2\), at 100\% efficiency would be:

\[
(1 \text{ kW s}) \left(\frac{1 \text{ mol H}_2}{224.8 \text{ kW s}}\right) \left(\frac{2.02 \text{ g}}{\text{ mol H}_2}\right) = 8.98 \times 10^{-3} \text{ g H}_2
\]

Since the efficiency is only 70\% we will need:

\[
\frac{8.98 \times 10^{-3} \text{ g}}{0.70} = 1.28 \times 10^{-2} \text{ g H}_2
\]