CHAPTER SEVENTEEN

ELECTROCHEMISTRY

Review of Oxidation - Reduction Reactions

13. Oxidation: increase in oxidation number; loss of electrons
   Reduction: decrease in oxidation number; gain of electrons

14. See Table 4.2 in Chapter 4 of the text for rules for assigning oxidation numbers.
   a. H (+1), O (-2), N (+5)
   b. Cl (-1), Cu (+2)
   c. O (0)
   d. H (+1), O (-1)
   e. Mg (+2), O (-2), S (+6)
   f. Ag (0)
   g. Pb (+2), O (-2), S (+6)
   h. O (-2), Pb (+4)
   i. Na (+1), O (-2), C (+3)
   j. O (-2), C (+4)
   k. (NH₄)₂Ce(SO₄)₄ contains NH₄⁺ ions and SO₄²⁻ ions. Thus, cerium exists as the Ce⁴⁺ ion.
      H (+1), N (-3), Ce (+4), S (+6), O (-2)
   l. O (-2), Cr (+3)

15. The species oxidized shows an increase in oxidation numbers and is called the reducing agent. The species reduced shows a decrease in oxidation numbers and is called the oxidizing agent. The pertinent oxidation numbers are listed by the substance oxidized and the substance reduced.

<table>
<thead>
<tr>
<th>Redox?</th>
<th>Ox. Agent</th>
<th>Red. Agent</th>
<th>Substance Oxidized</th>
<th>Substance Reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. Yes</td>
<td>H₂O</td>
<td>CH₄</td>
<td>CH₄ (C, -4 → +2)</td>
<td>H₂O (H, +1 → 0)</td>
</tr>
<tr>
<td>b. Yes</td>
<td>AgNO₃</td>
<td>Cu</td>
<td>Cu (0 → +2)</td>
<td>AgNO₃ (Ag, +1 → 0)</td>
</tr>
<tr>
<td>c. Yes</td>
<td>HCl</td>
<td>Zn</td>
<td>Zn (0 → +2)</td>
<td>HCl (H, +1 → 0)</td>
</tr>
<tr>
<td>d. No; There is no change in any of the oxidation numbers.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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16. See Chapter 4.10 of the text for rules on balancing oxidation-reduction reactions.

a. \( \text{Cr} \rightarrow \text{Cr}^{3+} + 3 \text{e}^- \)  \( \text{NO}_3^- \rightarrow \text{NO} \)
\[
4 \text{H}^+ + \text{NO}_3^- \rightarrow \text{NO} + 2 \text{H}_2\text{O}
\]
\[
3 \text{e}^- + 4 \text{H}^+ + \text{NO}_3^- \rightarrow \text{NO} + 2 \text{H}_2\text{O}
\]
\[
\text{Cr} \rightarrow \text{Cr}^{3+} + 3 \text{e}^-
\]
\[
3 \text{e}^- + 4 \text{H}^+ + \text{NO}_3^- \rightarrow \text{NO} + 2 \text{H}_2\text{O}
\]

\[
4 \text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) + \text{Cr}(s) \rightarrow \text{Cr}^{3+}(\text{aq}) + \text{NO(g)} + 2 \text{H}_2\text{O(l)}
\]

b. \( \text{Al} \rightarrow \text{Al}^{3+} + 3 \text{e}^- \) \( \times 5 \)
\[
\text{MnO}_4^- \rightarrow \text{Mn}^{2+}
\]
\[
8 \text{H}^+ + \text{MnO}_4^- \rightarrow \text{Mn}^{2+} + 4 \text{H}_2\text{O}
\]
\[
(5 \text{e}^- + 8 \text{H}^+ + \text{MnO}_4^- \rightarrow \text{Mn}^{2+} + 4 \text{H}_2\text{O}) \times 3
\]
\[
5 \text{Al} \rightarrow 5 \text{Al}^{3+} + 15 \text{e}^-
\]
\[
15 \text{e}^- + 24 \text{H}^+ + 3 \text{MnO}_4^- \rightarrow 3 \text{Mn}^{2+} + 12 \text{H}_2\text{O}
\]

\[
24 \text{H}^+(\text{aq}) + 3 \text{MnO}_4^-(\text{aq}) + 5 \text{Al(s)} \rightarrow 5 \text{Al}^{3+}(\text{aq}) + 3 \text{Mn}^{2+}(\text{aq}) + 12 \text{H}_2\text{O(l)}
\]

c. \( \text{Ce}^{4+} + \text{e}^- \rightarrow \text{Ce}^{3+} \) \( \times 6 \)
\[
\text{CH}_3\text{OH} \rightarrow \text{CO}_2
\]
\[
\text{H}_2\text{O} + \text{CH}_3\text{OH} \rightarrow \text{CO}_2 + 6 \text{H}^+
\]
\[
\text{H}_2\text{O} + \text{CH}_3\text{OH} \rightarrow \text{CO}_2 + 6 \text{H}^+ + 6 \text{e}^-
\]
\[
6 \text{Ce}^{4+} + 6 \text{e}^- \rightarrow 6 \text{Ce}^{3+}
\]
\[
\text{H}_2\text{O} + \text{CH}_3\text{OH} \rightarrow \text{CO}_2 + 6 \text{H}^+ + 6 \text{e}^-
\]
\[
\text{H}_2\text{O(l)} + \text{CH}_3\text{OH(aq)} + 6 \text{Ce}^{4+}(\text{aq}) \rightarrow 6 \text{Ce}^{3+}(\text{aq}) + \text{CO}_2(\text{g}) + 6 \text{H}^+(\text{aq})
\]

d. \( \text{PO}_3^{3-} \rightarrow \text{PO}_4^{3-} \)
\[
(\text{H}_2\text{O} + \text{PO}_3^{3-} \rightarrow \text{PO}_4^{3-} + 2 \text{H}^+ + 2 \text{e}^-) \times 3
\]
\[
\text{MnO}_4^- \rightarrow \text{MnO}_2
\]
\[
(3 \text{e}^- + 4 \text{H}^+ + \text{MnO}_4^- \rightarrow \text{MnO}_2 + 2 \text{H}_2\text{O}) \times 2
\]
\[
3 \text{H}_2\text{O} + 3 \text{PO}_3^{3-} \rightarrow 3 \text{PO}_4^{3-} + 6 \text{H}^+ + 6 \text{e}^-
\]
\[
6 \text{e}^- + 8 \text{H}^+ + 2 \text{MnO}_4^- \rightarrow 2 \text{MnO}_2 + 4 \text{H}_2\text{O}
\]
\[
2 \text{H}^+ + 2 \text{MnO}_4^- + 3 \text{PO}_3^{3-} \rightarrow 3 \text{PO}_4^{3-} + 2 \text{MnO}_2 + \text{H}_2\text{O}
\]

Now convert to a basic solution by adding 2 OH\(^-\) to both sides. \( 2 \text{H}^+ + 2 \text{OH}^- \rightarrow 2 \text{H}_2\text{O} \) on the reactant side. After converting H\(^+\) to OH\(^-\), simplify the overall equation by crossing off 1 H\(_2\)O on each side of the reaction. The overall balanced equation is:

\[
\text{H}_2\text{O(l)} + 2 \text{MnO}_4^-(\text{aq}) + 3 \text{PO}_3^{3-}(\text{aq}) \rightarrow 3 \text{PO}_4^{3-}(\text{aq}) + 2 \text{MnO}_2(\text{s}) + 2 \text{OH}^-(\text{aq})
\]

e. \( \text{Mg} \rightarrow \text{Mg(OH)}_2 \)
\[
\text{OC}^- \rightarrow \text{Cl}^-
\]
\[ 2 \text{H}_2\text{O} + \text{Mg} \rightarrow \text{Mg(OH)}_2 + 2 \text{H}^+ + 2 e^- \quad \quad 2 e^- + 2 \text{H}^+ + \text{OCl}^- \rightarrow \text{Cl}^- + \text{H}_2\text{O} \]

\[ 2 \text{H}_2\text{O} + \text{Mg} \rightarrow \text{Mg(OH)}_2 + 2 \text{H}^+ + 2 e^- \quad \quad 2 e^- + 2 \text{H}^+ + \text{OCl}^- \rightarrow \text{Cl}^- + \text{H}_2\text{O} \]

\[
\text{OCl}^-(aq) + \text{H}_2\text{O}(l) + \text{Mg}(s) \rightarrow \text{Mg(OH)}_2(s) + \text{Cl}^-(aq)
\]

The final overall reaction does not contain \( \text{H}^+ \), so we are done.

f. \( \text{H}_2\text{CO} \rightarrow \text{HCO}_3^- \)

\[
2 \text{H}_2\text{O} + \text{H}_2\text{CO} \rightarrow \text{HCO}_3^- + 5 \text{H}^+ + 4 e^- \quad (e^- + \text{Ag(NH}_3)_2^+ \rightarrow \text{Ag} + 2 \text{NH}_3) \times 4
\]

\[
2 \text{H}_2\text{O} + \text{H}_2\text{CO} \rightarrow \text{HCO}_3^- + 5 \text{H}^+ + 4 e^- \\
4 e^- + 4 \text{Ag(NH}_3)_2^- \rightarrow 4 \text{Ag} + 8 \text{NH}_3
\]

4 \( \text{Ag(NH}_3)_2^+ + 2 \text{H}_2\text{O} + \text{H}_2\text{CO} \rightarrow \text{HCO}_3^- + 5 \text{H}^+ + 4 \text{Ag} + 8 \text{NH}_3 \)

Convert to a basic solution by adding 5 \( \text{OH}^- \) to both sides (5 \( \text{H}^+ + 5 \text{OH}^- \rightarrow 5 \text{H}_2\text{O} \)). Then, cross off 2 \( \text{H}_2\text{O} \) on both sides, which gives the overall balanced equation:

\[
5 \text{OH}^-(aq) + 4 \text{Ag(NH}_3)_2^-(aq) + \text{H}_2\text{CO}(aq) \rightarrow \text{HCO}_3^-(aq) + 3 \text{H}_2\text{O}(l) + 4 \text{Ag}(s) + 8 \text{NH}_3(aq)
\]

**Questions**

17. In a galvanic cell, a spontaneous redox reaction occurs which produces an electric current. In an electrolytic cell, electricity is used to force a redox reaction that is not spontaneous to occur.

18. The salt bridge allows counter ions to flow into the two cell compartments to maintain electrical neutrality. Without a salt bridge, no sustained electron flow can occur.

19. a. Cathode: The electrode at which reduction occurs.

b. Anode: The electrode at which oxidation occurs.

c. Oxidation half-reaction: The half-reaction in which electrons are products. In a galvanic cell, the oxidation half-reaction always occurs at the anode.

d. Reduction half-reaction: The half-reaction in which electrons are reactants. In a galvanic cell, the reduction half-reaction always occurs at the cathode.

20. a. Purification by electrolysis is called electrefining. See the text for a discussion of the electrefining of copper. Electrefining is possible because of the selectivity of electrode reactions. The anode is made up of the impure metal. A potential is applied so just the metal of interest and all more easily oxidized metals are oxidized at the anode. The metal of interest is the only metal plated at the cathode due to the careful control of the potential applied. The metal ions that could plate out at the cathode in preference to the metal we are purifying will not be in solution, because these metals were not oxidized at the anode.

b. A more easily oxidized metal is placed in electrical contact with the metal we are trying to protect. It is oxidized in preference to the protected metal. The protected metal becomes the cathode.
21. As a battery discharges, $E_{\text{cell}}$ decreases, eventually reaching zero. A charged battery is not at equilibrium. At equilibrium, $E_{\text{cell}} = 0$ and $\Delta G = 0$. We get no work out of an equilibrium system. A battery is useful to us because it can do work as it approaches equilibrium.

22. Standard reduction potentials are an intensive property, i.e., they do not depend on how many times the reaction occurs. As long as the concentrations of ions and gases are $1 \ M$ or $1 \ \text{atm}$, standard reduction potentials and standard oxidation potentials are a constant and not dependent on the coefficients in the balanced equation.

23. Both fuel cells and batteries are galvanic cells. However, fuel cells, unlike batteries, have the reactants continuously supplied and can produce a current indefinitely.

24. Moisture must be present to act as a medium for ion flow between the anodic and cathodic regions. Salt provides ions necessary to complete the electrical circuit in the corrosion process. Together, salt and water make up the salt bridge in this spontaneous electrochemical process.

Three methods discussed in the text to prevent corrosion are galvanizing, alloying and cathodic protection. Galvanizing coats the metal of interest (usually iron) with zinc, which is an easily oxidized metal. Alloying mixes in metals that form durable, effective oxide coatings over the metal of interest. Cathodic protection connects, via a wire, a more easily oxidized metal to the metal we are trying to protect. The more active metal is preferentially oxidized, thus protecting our metal object from corrosion.

**Exercises**

**Galvanic Cells, Cell Potentials, Standard Reduction Potentials, and Free Energy**

25. A typical galvanic cell diagram is:

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\[ \text{Anode (oxidation)} \quad \text{Salt Bridge} \quad \text{Cathode (reduction)} \]
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The diagram for all cells will look like this. The contents of each half-cell compartment will be identified for each reaction, with all solute concentrations at $1.0 \ M$ and all gases at $1.0 \ \text{atm}$. For Exercises 17.25 and 17.26, the flow of ions through the salt bridge was not asked for in the questions. If asked, however, cations always flow into the cathode compartment, and anions always flow into the anode compartment. This is required to keep each compartment electrically neutral.
a. Table 17.1 of the text lists balanced reduction half-reactions for many substances. For this overall reaction, we need the Cl\textsubscript{2} to Cl\textsuperscript{-} reduction half-reaction and the Cr\textsuperscript{3+} to Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{2-} oxidation half-reaction. Manipulating these two half-reactions gives the overall balanced equation.

\[
\begin{align*}
(\text{Cl}_2 + 2e^- & \rightarrow 2\text{Cl}^-) \times 3 \\
7\text{H}_2\text{O} + 2\text{Cr}^{3+} & \rightarrow \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^-
\end{align*}
\]

\[
7\text{H}_2\text{O(l)} + 2\text{Cr}^{3+}(\text{aq}) + 3\text{Cl}_2(\text{g}) \rightarrow \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 6\text{Cl}^- (\text{aq}) + 14\text{H}^+(\text{aq})
\]

The contents of each compartment are:

Cathode: Pt electrode; Cl\textsubscript{2} bubbled into solution, Cl\textsuperscript{-} in solution

Anode: Pt electrode; Cr\textsuperscript{3+}, H\textsuperscript{+}, and Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{2-} in solution

We need a nonreactive metal to use as the electrode in each case, since all the reactants and products are in solution. Pt is a common choice. Another possibility is graphite.

b. \[
\begin{align*}
\text{Cu}^{2+} + 2e^- & \rightarrow \text{Cu} \\
\text{Mg} & \rightarrow \text{Mg}^{2+} + 2e^-
\end{align*}
\]

\[
\text{Cu}^{2+}(\text{aq}) + \text{Mg(s)} \rightarrow \text{Cu(s)} + \text{Mg}^{2+}(\text{aq})
\]

Cathode: Cu electrode; Cu\textsuperscript{2+} in solution; Anode: Mg electrode; Mg\textsuperscript{2+} in solution

26. Reference Exercise 17.25 for a typical galvanic cell diagram. The contents of each half-cell compartment are identified below with all solute concentrations at 1.0 M and all gases at 1.0 atm.

a. Reference Table 17.1 for the balanced half-reactions.

\[
\begin{align*}
5e^- + 6\text{H}^+ + \text{IO}_3^- & \rightarrow 1/2\text{I}_2 + 3\text{H}_2\text{O} \\
(\text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + e^-) \times 5
\end{align*}
\]

\[
6\text{H}^+ + \text{IO}_3^- + 5\text{Fe}^{2+} \rightarrow 5\text{Fe}^{3+} + 1/2\text{I}_2 + 3\text{H}_2\text{O}
\]

or $12\text{H}^+(\text{aq}) + 2\text{IO}_3^-(\text{aq}) + 10\text{Fe}^{2+}(\text{aq}) \rightarrow 10\text{Fe}^{3+}(\text{aq}) + \text{I}_2(\text{aq}) + 6\text{H}_2\text{O(l)}$

Cathode: Pt electrode; IO\textsuperscript{-}, I\textsubscript{2} and H\textsubscript{2}SO\textsubscript{4} (H\textsuperscript{+} source) in solution.

Note: I\textsubscript{2}(s) would make a poor electrode since it sublimes.

Anode: Pt electrode; Fe\textsuperscript{2+} and Fe\textsuperscript{3+} in solution

b. \[
\begin{align*}
(\text{Ag}^+ + e^- & \rightarrow \text{Ag}) \times 2 \\
\text{Zn} & \rightarrow \text{Zn}^{2+} + 2e^-
\end{align*}
\]

\[
\text{Zn(s)} + 2\text{Ag}^+(\text{aq}) \rightarrow 2\text{Ag(s)} + \text{Zn}^{2+}(\text{aq})
\]
Cathode: Ag electrode; Ag⁺ in solution; Anode: Zn electrode; Zn²⁺ in solution

27. To determine E° for the overall cell reaction, we must add the standard reduction potential to the standard oxidation potential (E°_{cell} = E°_{red} + E°_{ox}). Reference Table 17.1 for values of standard reduction potentials. Remember that E°_{red} = -E°_{ox} and that standard potentials are not multiplied by the integer used to obtain the overall balanced equation.

25a. \[ \text{E}_{\text{cell}}^0 = E_{\text{Cl}_2\rightarrow \text{Cl}^+}^0 + E_{\text{Zn}^{2+} \rightarrow \text{Zn}}^0 = 1.36 \text{ V} + (-1.33 \text{ V}) = 0.03 \text{ V} \]

25b. \[ \text{E}_{\text{cell}}^0 = E_{\text{Ca}^{2+} \rightarrow \text{Ca}}^0 + E_{\text{Mg}^{2+} \rightarrow \text{Mg}^{2+}}^0 = 0.34 \text{ V} + 2.37 \text{ V} = 2.71 \text{ V} \]

28.

26a. \[ \text{E}_{\text{cell}}^0 = E_{\text{Zn}^{2+} \rightarrow \text{Zn}}^0 + E_{\text{Fe}^{2+} \rightarrow \text{Fe}}^0 = 1.20 \text{ V} + (-0.77 \text{ V}) = 0.43 \text{ V} \]

26b. \[ \text{E}_{\text{cell}}^0 = E_{\text{Ag}^{+} \rightarrow \text{Ag}}^0 + E_{\text{Zn}^{2+} \rightarrow \text{Zn}^{2+}}^0 = 0.80 \text{ V} + 0.76 \text{ V} = 1.56 \text{ V} \]

29. Reference Exercise 17.25 for a typical galvanic cell design. The contents of each half-cell compartment are identified below with all solute concentrations at 1.0 M and all gases at 1.0 atm. For each pair of half-reactions, the half-reaction with the largest standard reduction potential will be the cathode reaction, and the half-reaction with the smallest reduction potential will be reversed to become the anode reaction. Only this combination gives a spontaneous overall reaction, i.e., a reaction with a positive overall standard cell potential. Note that in a galvanic cell as illustrated in Exercise 17.25, the cations in the salt bridge migrate to the cathode, and the anions migrate to the anode.

a. \[ \begin{align*}
\text{Cl}_2 + 2 \text{e}^- & \rightarrow 2 \text{Cl}^- \\
2 \text{Br}^- & \rightarrow \text{Br}_2 + 2 \text{e}^- 
\end{align*} \]

\[ \text{Cl}_2(g) + 2 \text{Br}^-(aq) \rightarrow \text{Br}_2(aq) + 2 \text{Cl}^-(aq) \quad \text{\textit{E}}_{\text{cell}}^0 = 0.27 \text{ V} \]

The contents of each compartment are:

Cathode: Pt electrode; Cl₂(g) bubbled in, Cl⁻ in solution

Anode: Pt electrode; Br₂ and Br⁻ in solution

b. \[ \begin{align*}
(2 \text{e}^- + 2 \text{H}^+ + \text{IO}_3^- & \rightarrow \text{IO}_4^- + \text{H}_2\text{O}) \times 5 \\
(4 \text{H}_2\text{O} + \text{Mn}^{2+} & \rightarrow \text{MnO}_4^- + 8 \text{H}^+ + 5 \text{e}^-) \times 2
\end{align*} \]

\[ 10 \text{H}^+ + 5 \text{IO}_3^- + 8 \text{H}_2\text{O} + 2 \text{Mn}^{2+} \rightarrow 5 \text{IO}_4^- + 5 \text{H}_2\text{O} + 2 \text{MnO}_4^- + 16 \text{H}^+ \quad \text{\textit{E}}_{\text{cell}}^0 = 0.09 \text{ V} \]

This simplifies to:

\[ 3 \text{H}_2\text{O(l)} + 5 \text{IO}_3^-(aq) + 2 \text{Mn}^{2+}(aq) \rightarrow 5 \text{IO}_4^-(aq) + 2 \text{MnO}_4^-(aq) + 6 \text{H}^+(aq) \quad \text{\textit{E}}_{\text{cell}}^0 = 0.09 \text{ V} \]

Cathode: Pt electrode; IO₃⁻, IO₄⁻, and H₂SO₄ (as a source of H⁺) in solution

Anode: Pt electrode; Mn²⁺, MnO₄⁻ and H₂SO₄ in solution
30. Reference Exercise 17.25 for a typical galvanic cell design. The contents of each half-cell compartment are identified below, with all solute concentrations at 1.0 \( M \) and all gases at 1.0 atm.

a. \[ \begin{align*}
H_2O_2 + 2 H^+ + 2 e^- & \rightarrow 2 H_2O \\
H_2O_2 & \rightarrow O_2 + 2 H^+ + 2 e^- 
\end{align*} \]

\( E^\circ = 1.78 \text{ V} \)

\( -E^\circ = -0.68 \text{ V} \)

\[ 2 H_2O_2(aq) \rightarrow 2 H_2O(l) + O_2(g) \] \( \Delta E^\circ_{\text{cell}} = 1.10 \text{ V} \)

Cathode: Pt electrode; \( H_2O_2 \) and \( H^+ \) in solution

Anode: Pt electrode; \( O_2(g) \) bubbled in, \( H_2O_2 \) and \( H^+ \) in solution

b. \[ \begin{align*}
(Fe^{3+} + 3 e^- \rightarrow Fe) \times 2 & \quad E^\circ = -0.036 \text{ V} \\
(Mn \rightarrow Mn^{2+} + 2 e^-) \times 3 & \quad -E^\circ = 1.18 \text{ V} 
\end{align*} \]

\[ 2 Fe^{3+}(aq) + 3 Mn(s) \rightarrow 2 Fe(s) + 3 Mn^{2+}(aq) \] \( \Delta E^\circ_{\text{cell}} = 1.14 \text{ V} \)

Cathode: Fe electrode; \( Fe^{3+} \) in solution; Anode: Mn electrode; \( Mn^{2+} \) in solution

31. In standard line notation, the anode is listed first and the cathode is listed last. A double line separates the two compartments. By convention, the electrodes are on the ends with all solutes and gases towards the middle. A single line is used to indicate a phase change. We also include all concentrations.

25a. Pt | \( Cr^{3+} (1.0 \text{ M}), Cr_2O_7^{2-} (1.0 \text{ M}), H^+ (1.0 \text{ M}) \) || \( Cl^- (1.0 \text{ atm}) | Cl^+ (1.0 \text{ M}) | Pt \)

25b. Mg | \( Mg^{2+} (1.0 \text{ M}) || Cu^{2+} (1.0 \text{ M}) | Cu \)

29a. Pt | \( Br^- (1.0 \text{ M}), Br_2 (1.0 \text{ M}) || Cl^- (1.0 \text{ atm}) | Cl^+ (1.0 \text{ M}) | Pt \)

29b. Pt | \( Mn^{3+} (1.0 \text{ M}), MnO_4^- (1.0 \text{ M}), H^+ (1.0 \text{ M}) || IO_3^- (1.0 \text{ M}), H^+ (1.0 \text{ M}), IO_5^- (1.0 \text{ M}) | Pt \)

32. 26a. Pt | \( Fe^{2+} (1.0 \text{ M}), Fe^{3+} (1.0 \text{ M}) || IO_3^- (1.0 \text{ M}), H^+ (1.0 \text{ M}), I_2 (1.0 \text{ M}) | Pt \)

32b. Zn | \( Zn^{2+} (1.0 \text{ M}) || Ag^+ (1.0 \text{ M}) | Ag \)

30a. Pt | \( H_2O_2 (1.0 \text{ M}), H^+ (1.0 \text{ M}) | O_2 (1.0 \text{ atm}) || H_2O_2 (1.0 \text{ M}), H^+ (1.0 \text{ M}) | Pt \)

30b. Mn | \( Mn^{2+} (1.0 \text{ M}) || Fe^{3+} (1.0 \text{ M}) | Fe \)

33. Locate the pertinent half-reactions in Table 17.1, and then figure which combination will give a positive standard cell potential. In all cases, the anode compartment contains the species with the smallest standard reduction potential. For part a, the copper compartment is the anode, and in part b, the cadmium compartment is the anode.
a. $\text{Au}^{3+} + 3 e^- \rightarrow \text{Au} \quad \text{E}^\circ = 1.50 \text{ V}$

$$\left(\text{Cu}^+ \rightarrow \text{Cu}^{2+} + e^-\right) \times 3$$

$$\text{Au}^{3+}(aq) + 3 \text{Cu}^+(aq) \rightarrow \text{Au(s)} + 3 \text{Cu}^{2+}(aq) \quad \text{E}^\circ_{\text{cell}} = 1.34 \text{ V}$$

b. $\left(\text{VO}_2^{+} + 2 \text{H}^+ + e^- \rightarrow \text{VO}^{2+} + \text{H}_2\text{O}\right) \times 2 \quad \text{E}^\circ = 1.00 \text{ V}$

$$\text{Cd} \rightarrow \text{Cd}^{2+} + 2e^- \quad \text{E}^\circ = 0.40 \text{ V}$$

$$2 \text{VO}_2^{+}(aq) + 4 \text{H}^+(aq) + \text{Cd(s)} \rightarrow 2 \text{VO}^{2+}(aq) + 2 \text{H}_2\text{O}(l) + \text{Cd}^{2+}(aq) \quad \text{E}^\circ_{\text{cell}} = 1.40 \text{ V}$$

34. a. $\left(\text{H}_2\text{O}_2 + 2 \text{H}^+ + 2 e^- \rightarrow 2 \text{H}_2\text{O}\right) \times 3 \quad \text{E}^\circ = 1.78 \text{ V}$

$$2 \text{Cr}^{3+} + 7 \text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6 e^- \quad \text{E}^\circ = -1.33 \text{ V}$$

$$3 \text{H}_2\text{O}_2(aq) + 2 \text{Cr}^{3+}(aq) + \text{H}_2\text{O}(l) \rightarrow \text{Cr}_2\text{O}_7^{2-}(aq) + 8 \text{H}^+(aq) \quad \text{E}^\circ_{\text{cell}} = 0.45 \text{ V}$$

b. $\left(2 \text{H}^+ + 2 e^- \rightarrow \text{H}_2\right) \times 3 \quad \text{E}^\circ = 0.00 \text{ V}$

$$\text{(Al} \rightarrow \text{Al}^{3+} + 3 e^-\times 2 \quad -\text{E}^\circ = 1.66 \text{ V}$$

$$6 \text{H}^+(aq) + 2 \text{Al}(s) \rightarrow 3 \text{H}_2(g) + 2 \text{Al}^{3+}(aq) \quad \text{E}^\circ_{\text{cell}} = 1.66 \text{ V}$$

35. a. $2 \text{Ag}^+ + 2 e^- \rightarrow 2 \text{Ag} \quad \text{E}^\circ = 0.80 \text{ V}$

$$\text{Cu} \rightarrow \text{Cu}^{2+} + 2 e^- \quad -\text{E}^\circ = -0.34 \text{ V}$$

$$2 \text{Ag}^+ + \text{Cu} \rightarrow \text{Cu}^{2+} + 2 \text{Ag} \quad \text{E}^\circ_{\text{cell}} = 0.46 \text{ V}$$

Spontaneous at standard conditions ($\text{E}^\circ_{\text{cell}} > 0$).

b. $\text{Zn}^{2+} + 2 e^- \rightarrow \text{Zn} \quad \text{E}^\circ = -0.76 \text{ V}$

$$\text{Ni} \rightarrow \text{Ni}^{2+} + 2 e^- \quad -\text{E}^\circ = 0.23 \text{ V}$$

$$\text{Zn}^{2+} + \text{Ni} \rightarrow \text{Zn} + \text{Ni}^{2+} \quad \text{E}^\circ_{\text{cell}} = -0.53 \text{ V}$$

Not spontaneous at standard conditions ($\text{E}^\circ_{\text{cell}} < 0$).

36. a. $\left(5 e^- + 8 \text{H}^+ + \text{MnO}_4^- \rightarrow \text{Mn}^{2+} + 4 \text{H}_2\text{O}\right) \times 2 \quad \text{E}^\circ = 1.51 \text{ V}$

$$\left(2 \text{I}^- \rightarrow \text{I}_2 + 2 e^-\right) \times 5 \quad -\text{E}^\circ = -0.54 \text{ V}$$

$$16 \text{H}^+ + 2 \text{MnO}_4^- + 10 \text{I}^- \rightarrow 5 \text{I}_2 + 2 \text{Mn}^{2+} + 8 \text{H}_2\text{O} \quad \text{E}^\circ_{\text{cell}} = 0.97 \text{ V}$$

Spontaneous

b. $\left(5 e^- + 8 \text{H}^+ + \text{MnO}_4^- \rightarrow \text{Mn}^{2+} + 4 \text{H}_2\text{O}\right) \times 2 \quad \text{E}^\circ = 1.51 \text{ V}$

$$\left(2 \text{F}^- \rightarrow \text{F}_2 + 2 e^-\right) \times 5 \quad -\text{E}^\circ = -2.87 \text{ V}$$

$$16 \text{H}^+ + 2 \text{MnO}_4^- + 10 \text{F}^- \rightarrow 5 \text{F}_2 + 2 \text{Mn}^{2+} + 8 \text{H}_2\text{O} \quad \text{E}^\circ_{\text{cell}} = -1.36 \text{ V}$$

Not spontaneous

37. $\text{Cl}_2 + 2 e^- \rightarrow 2 \text{Cl}^- \quad \text{E}^\circ = 1.36 \text{ V}$

$$\left(\text{ClO}_2^- \rightarrow \text{ClO}_2 + e^-\right) \times 2 \quad -\text{E}^\circ = -0.954 \text{ V}$$

$$2 \text{ClO}_2(aq) + \text{Cl}_2(g) \rightarrow 2 \text{ClO}_2(aq) + 2 \text{Cl}^-(aq) \quad \text{E}^\circ_{\text{cell}} = 0.41 \text{ V} = 0.41 \text{ J/C}$$

$$\Delta G^\circ = -nF\text{E}^\circ_{\text{cell}} = -(2 \text{ mol e}^\circ)(96,485 \text{ C/mol e}^\circ)(0.41 \text{ J/C}) = -7.9 \times 10^4 \text{ J} = -79 \text{ kJ}$$
38. a. 

\[
\begin{align*}
(4 \text{H}^+ + \text{NO}_3^- + 3 \text{e}^- & \rightarrow \text{NO} + 2 \text{H}_2\text{O}) \times 2 \\
(\text{Mn} & \rightarrow \text{Mn}^{2+} + 2 \text{e}^-) \times 3
\end{align*}
\]

\[E^\circ = 0.96 \text{ V}\]

\[-E^\circ = 1.18 \text{ V}\]

\[
3 \text{Mn(s)} + 8 \text{H}^+(\text{aq}) + 2 \text{NO}_3^-(\text{aq}) \rightarrow 2 \text{NO(g)} + 4 \text{H}_2\text{O(l)} + 3 \text{Mn}^{2+}(\text{aq}) \quad E^\circ_{\text{cell}} = 2.14 \text{ V}
\]

\[
(2 \text{e}^- + 2 \text{H}^+ + \text{IO}_4^- \rightarrow \text{IO}_3^- + \text{H}_2\text{O}) \times 5
\]

\[E^\circ = 1.60 \text{ V}\]

\[-E^\circ = -1.51 \text{ V}\]

\[
5 \text{IO}_4^-(\text{aq}) + 2 \text{Mn}^{2+}(\text{aq}) + 3 \text{H}_2\text{O(l)} \rightarrow 5 \text{IO}_3^-(\text{aq}) + 2 \text{MnO}_4^-(\text{aq}) + 6 \text{H}^+(\text{aq}) \quad E^\circ_{\text{cell}} = 0.09 \text{ V}
\]

b. Nitric acid oxidation (see above for \(E^\circ_{\text{cell}}\)): 

\[
\Delta G^\circ = -nFE^\circ_{\text{cell}} = -(6 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)(2.14 \text{ J/C}) = -1.24 \times 10^6 \text{ J} = -1240 \text{ kJ}
\]

Periodate oxidation (see above for \(E^\circ_{\text{cell}}\)): 

\[
\Delta G^\circ = -(10 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)(0.09 \text{ J/C})(1 \text{ kJ/1000 J}) = -90 \text{ kJ}
\]

39. Since the cells are at standard conditions, \(w_{\text{max}} = \Delta G = \Delta G^\circ = -nFE^\circ_{\text{cell}}\). See Exercise 17.33 for the balanced overall equations and for \(E^\circ_{\text{cell}}\).

33a. \(w_{\text{max}} = -(3 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)(1.34 \text{ J/C}) = -3.88 \times 10^5 \text{ J} = -388 \text{ kJ}\)

33b. \(w_{\text{max}} = -(2 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)(1.40 \text{ J/C}) = -2.70 \times 10^5 \text{ J} = -270 \text{ kJ}\)

40. Since the cells are at standard conditions, \(w_{\text{max}} = \Delta G = \Delta G^\circ = -nFE^\circ_{\text{cell}}\). See Exercise 17.34 for the balanced overall equations and for \(E^\circ_{\text{cell}}\).

34a. \(w_{\text{max}} = -(6 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)(0.45 \text{ J/C}) = -2.6 \times 10^5 \text{ J} = -260 \text{ kJ}\)

34b. \(w_{\text{max}} = -(6 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)(1.66 \text{ J/C}) = -9.61 \times 10^5 \text{ J} = -961 \text{ kJ}\)

41. \(\text{CH}_3\text{OH(l)} + 3/2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O(l)} \quad \Delta G^\circ = 2(-237) + (-394) - [-166] = -702 \text{ kJ}\)

The balanced half-reactions are:

\[
\begin{align*}
\text{H}_2\text{O} + \text{CH}_3\text{OH} & \rightarrow \text{CO}_2 + 6 \text{H}^+ + 6 \text{e}^- \\
\text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- & \rightarrow 2 \text{H}_2\text{O}
\end{align*}
\]

For 3/2 mol \(\text{O}_2\), 6 moles of electrons will be transferred (\(n = 6\)).

\[
\Delta G^\circ = -nFE^\circ, \quad E^\circ = \frac{-\Delta G^\circ}{nF} = \frac{-(-702,000 \text{ J})}{(6 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)} = 1.21 \text{ J/C} = 1.21 \text{ V}
\]

42. \(\text{Fe}^{2+} + 2 \text{e}^- \rightarrow \text{Fe} \quad E^\circ = -0.44 \text{ V} = -0.44 \text{ J/C}\)

\[
\Delta G^\circ = -nFE^\circ = -(2 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)(-0.44 \text{ J/C})(1 \text{ kJ/1000 J}) = 85 \text{ kJ}
\]

85 kJ = 0 - \(\Delta G^\circ_{\text{Fe}^{2+} + \text{e}^-}\), \(\Delta G^\circ_{\text{Fe}^{2+}} = -85 \text{ kJ}\)
We can get $\Delta G_{\text{Fe}^{2+}\text{Fe}^{3+}}^o$ two ways. Consider: $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$ $E^o = 0.77 \text{ V}$

$\Delta G^o = -(1 \text{ mol e})(96,485 \text{ C/mol e})(0.77 \text{ J/C}) = -74,300 \text{ J} = -74 \text{ kJ}$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G^o$</th>
<th>$\Delta G_{\text{Fe}^{2+}\text{Fe}^{3+}}^o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + e^-$</td>
<td>$74 \text{ kJ}$</td>
<td>$-74 \text{ kJ/mol}$</td>
</tr>
<tr>
<td>$\text{Fe} \rightarrow \text{Fe}^{2+} + 2 e^-$</td>
<td>$-85 \text{ kJ}$</td>
<td></td>
</tr>
</tbody>
</table>

or consider: $\text{Fe}^{3+} + 3 e^- \rightarrow \text{Fe}$ $E^o = -0.036 \text{ V}$

$\Delta G^o = -(3 \text{ mol e})(96,485 \text{ C/mol e})(-0.036 \text{ J/C}) = 10,400 \text{ J} = 10 \text{ kJ}$

$10 \text{. kJ} = 0 - [\Delta G_{\text{Fe}^{2+}\text{Fe}^{3+}}^o + 0], \quad \Delta G_{\text{Fe}^{2+}\text{Fe}^{3+}}^o = -10 \text{. kJ/mol}; \text{ Round-off error explains the 1 kJ discrepancy.}$

43. Good oxidizing agents are easily reduced. Oxidizing agents are on the left side of the reduction half-reactions listed in Table 17.1. We look for the largest, most positive standard reduction potentials to correspond to the best oxidizing agents. The ordering from worst to best oxidizing agents is:

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E^o(\text{V})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$^+$</td>
<td>-2.92</td>
</tr>
<tr>
<td>H$^+$</td>
<td>-0.83</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>-0.40</td>
</tr>
<tr>
<td>I$_2$</td>
<td>0.54</td>
</tr>
<tr>
<td>AuCl$_3$</td>
<td>0.99</td>
</tr>
<tr>
<td>IO$_4$</td>
<td>1.20</td>
</tr>
</tbody>
</table>

44. Good reducing agents are easily oxidized. The reducing agents are on the right side of the reduction half-reactions listed in Table 17.1. The best reducing agents have the most negative standard reduction potentials ($E^o$) or the most positive standard oxidation potentials, $E^o_{\text{red}}$ ($= -E^o$).

- $E^- < \text{Cr}^{3+} < \text{Fe}^{2+} < \text{H}_2 < \text{Zn} < \text{Li}$
- $E^o(\text{V})$: -2.87, -1.33, -0.77, 0.00, 0.76, 3.05

45. a. $2 \text{H}^+ + 2 e^- \rightarrow \text{H}_2$ $E^o = 0.00 \text{ V}; \quad \text{Cu} \rightarrow \text{Cu}^{2+} + 2 e^- \quad E^o = -0.34 \text{ V}$

$E^o_{\text{cell}} = -0.34 \text{ V}; \text{ No, H}^+ \text{ cannot oxidize Cu to Cu}^{2+} \text{ at standard conditions (}E^o_{\text{cell}} < 0).$  

b. $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$ $E^o = 0.77 \text{ V}; \quad 2 \text{I}^- \rightarrow \text{I}_2 + 2 e^- \quad -E^o = -0.54 \text{ V}$

$E^o_{\text{cell}} = 0.77 - 0.54 = 0.23 \text{ V}; \text{ Yes, Fe}^{3+} \text{ can oxidize I}^- \text{ to I}_2.$

c. $\text{H}_2 \rightarrow 2 \text{H}^+ + 2 e^-$ $E^o = 0.00 \text{ V}; \quad \text{Ag}^+ + e^- \rightarrow \text{Ag} \quad E^o = 0.80 \text{ V}$

$E^o_{\text{cell}} = 0.80 \text{ V}; \text{ Yes, H}_2 \text{ can reduce Ag}^+ \text{ to Ag at standard conditions (}E^o_{\text{cell}} > 0).$  

d. $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-$ $-E^o = -0.77 \text{ V}; \quad \text{Cr}^{3+} + e^- \rightarrow \text{Cr}^{2+} \quad E^o = -0.50 \text{ V}$

$E^o_{\text{cell}} = -0.50 - 0.77 = -1.27 \text{ V}; \text{ No, Fe}^{2+} \text{ cannot reduce Cr}^{3+} \text{ to Cr}^{2+} \text{ at standard conditions.}$

46. $\text{Cl}_2 + 2 e^- \rightarrow 2 \text{Cl}^-$ $E^o = 1.36 \text{ V}$  

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

$\text{Pb}^{2+} + 2 e^- \rightarrow \text{Pb} \quad E^o = -0.13 \text{ V}$  

$\text{Zn}^{2+} + 2 e^- \rightarrow \text{Zn} \quad E^o = -0.76 \text{ V}$
### CHAPTER 17  ELECTROCHEMISTRY

\[ \text{Na}^+ + e^- \rightarrow \text{Na} \quad E^\circ = -2.71 \text{ V} \]

a. Oxidizing agents (species reduced) are on the left side of the above reduction half-reactions. Of the species available, Ag would be the best oxidizing agent since it has the largest \( E^\circ \) value. Note that Cl\(^-\) is a better oxidizing agent than Ag\(^+\), but it is not one of the choices listed.

b. Reducing agents (species oxidized) are on the right side of the reduction half-reactions. Of the species available, Zn would be the best reducing agent since it has the largest \(-E^\circ\) value.

c. \( \text{SO}_4^{2-} + 4 \text{H}^+ + 2 e^- \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{O} \quad E^\circ = 0.20 \text{ V} \); \( \text{SO}_4^{2-} \) can oxidize Pb and Zn at standard conditions. When \( \text{SO}_4^{2-} \) is coupled with these reagents, \( E^\circ_{\text{cell}} \) is positive.

d. \( \text{Al} \rightarrow \text{Al}^{3+} + 3 e^- \quad -E^\circ = 1.66 \text{ V} \); Al can oxidize Ag\(^+\) and Zn\(^{2+}\) at standard conditions since \( E^\circ_{\text{cell}} > 0 \).

47. a. \( 2 \text{Br}^- \rightarrow \text{Br}_2 + 2 e^- \quad -E^\circ = -1.09 \text{ V} \); \( 2 \text{Cl}^- \rightarrow \text{Cl}_2 + 2 e^- \quad -E^\circ = -1.36 \text{ V} \); \( E^\circ > 1.09 \text{ V} \) to oxidize \( \text{Br}^-\); \( E^\circ < 1.36 \text{ V} \) to not oxidize \( \text{Cl}^-\). Cr\(_{2+}\), \( \text{O}_2\), MnO\(_2\), and IO\(_3^-\) are all possible since when all of these oxidizing agents are coupled with \( \text{Br}^-\), \( E^\circ_{\text{cell}} > 0 \), and when coupled with \( \text{Cl}^-\), \( E^\circ_{\text{cell}} < 0 \) (assuming standard conditions).

b. \( \text{Mn} \rightarrow \text{Mn}^{2+} + 2 e^- \quad -E^\circ = 1.18; \quad \text{Ni} \rightarrow \text{Ni}^{2+} + 2 e^- \quad -E^\circ = 0.23 \text{ V} \); Any oxidizing agent with \(-0.23 \text{ V} > E^\circ > -1.18 \text{ V} \) will work. PbSO\(_4\), Cd\(^{2+}\), Fe\(^{3+}\), Cr\(^{3+}\), Zn\(^{2+}\), and H\(_2\)O will be able to oxidize Mn but not Ni (assuming standard conditions).

48. a. \( \text{Cu}^{2+} + 2 e^- \rightarrow \text{Cu} \quad E^\circ = 0.34 \text{ V} \); \( \text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+ \quad E^\circ = 0.16 \text{ V} \); To reduce \( \text{Cu}^{2+} \) to Cu but not reduce \( \text{Cu}^+ \) to Cu\(^+\), the reducing agent must have a standard oxidation potential \( (E^\circ = -E^\circ) \) between \(-0.34 \text{ V} \) and \(-0.16 \text{ V} \) (so \( E^\circ_{\text{cell}} \) is positive only for the \( \text{Cu}^{2+} \) to Cu reduction). The reducing agents (species oxidized) are on the right side of the half-reactions in Table 17.1. The reagents at standard conditions which have \( E^\circ_{\text{cell}} \) (\( = -E^\circ \)) between \(-0.34 \text{ V} \) and \(-0.16 \text{ V} \) are Ag (in 1.0 M Cl\(^-\)) and H\(_2\)SO\(_4\).

b. \( \text{Br}_2 + 2 e^- \rightarrow 2 \text{Br}^- \quad E^\circ = 1.09 \text{ V} \); \( \text{I}_2 + 2 e^- \rightarrow 2 \text{I}^- \quad E^\circ = 0.54 \text{ V} \); From Table 17.1, VO\(^2+\), Au (in 1.0 M Cl\(^-\)), NO, ClO\(_3^-\), Hg\(_{2+}\), Ag, Hg\(_{2+}\), Fe\(_{3+}\), H\(_2\)O\(_2\), and MnO\(_4^-\) are all capable at standard conditions of reducing \( \text{Br}_2 \) to \( \text{Br}^- \) but not reducing \( \text{I}_2 \) to \( \text{I}^- \). When these reagents are coupled with \( \text{Br}_2\), \( E^\circ_{\text{cell}} > 0 \), and when coupled with \( \text{I}_2\), \( E^\circ_{\text{cell}} < 0 \).

49. \[
\begin{align*}
\text{ClO}^- + \text{H}_2\text{O} + 2 e^- & \rightarrow 2 \text{OH}^- + \text{Cl}^- & E^\circ = 0.90 \text{ V} \\
2 \text{NH}_3 + 2 \text{OH}^- & \rightarrow \text{N}_2\text{H}_4 + 2 \text{H}_2\text{O} + 2 e^- & -E^\circ = 0.10 \text{ V}
\end{align*}
\]

Since \( E^\circ_{\text{cell}} \) is positive for this reaction, then at standard conditions ClO\(^-\) can spontaneously oxidize NH\(_3\) to the somewhat toxic N\(_2\)H\(_4\).

50. \[
\begin{align*}
\text{Tl}^{3+} + 2 e^- & \rightarrow \text{Tl}^+ & E^\circ = 1.25 \text{ V} \\
3 \text{I}^- & \rightarrow \text{I}_3^- + 2 e^- & -E^\circ = -0.55 \text{ V}
\end{align*}
\]

Since \( E^\circ_{\text{cell}} \) is positive for this reaction, then at standard conditions Tl\(^3+\) can spontaneously oxidize I\(_3^-\) to the somewhat toxic Tl\(^+\).
In solution, $\text{Tl}^+$ can oxidize $\text{I}^-$ to $\text{I}_3^-$. Thus, we expect $\text{TlI}_3$ to be thallium(I) triiodide.

**The Nernst Equation**

51. \[
\begin{align*}
\text{H}_2\text{O}_2 + 2 \text{H}^+ + 2 e^- & \rightarrow 2 \text{H}_2\text{O} \\
\text{(Ag} \rightarrow \text{Ag}^+ + e^-) \times 2
\end{align*}
\]

\[E^\circ = 1.78 \text{ V}\]

\[E^\circ = -0.80 \text{ V}\]

\[
\text{H}_2\text{O}_2(\text{aq}) + 2 \text{H}^+(\text{aq}) + 2 \text{Ag(s)} \rightarrow 2 \text{H}_2\text{O(l)} + 2 \text{Ag}^-(\text{aq})
\]

\[E^\circ_{\text{cell}} = 0.98 \text{ V}\]

a. A galvanic cell is based on spontaneous chemical reactions. At standard conditions, this reaction produces a voltage of 0.98 V. Any change in concentration that increases the tendency of the forward reaction to occur will increase the cell potential. Conversely, any change in concentration that decreases the tendency of the forward reaction to occur (increases the tendency of the reverse reaction to occur) will decrease the cell potential. Using Le Chatelier’s principle, increasing the reactant concentrations of $\text{H}_2\text{O}_2$ and $\text{H}^+$ at 1.0 $M$ to 2.0 $M$ will drive the forward reaction further to right (will further increase the tendency of the forward reaction to occur). Therefore, $E_{\text{cell}}$ will be greater than $E^\circ_{\text{cell}}$.

b. Here, we decreased the reactant concentration of $\text{H}^+$ and increased the product concentration of $\text{Ag}^-$ from the standard conditions. This decreases the tendency of the forward reaction to occur which will decrease $E_{\text{cell}}$ as compared to $E^\circ_{\text{cell}}$ ($E_{\text{cell}} < E^\circ_{\text{cell}}$).

52. The concentrations of $\text{Fe}^{2+}$ in the two compartments are now 0.01 $M$ and $1 \times 10^{-7}$ $M$. The driving force for this reaction is to equalize the $\text{Fe}^{2+}$ concentrations in the two compartments. This occurs if the compartment with $1 \times 10^{-7}$ $M$ $\text{Fe}^{2+}$ becomes the anode ($\text{Fe}$ will be oxidized to $\text{Fe}^{3+}$) and the compartment with the 0.01 $M$ $\text{Fe}^{2+}$ becomes the cathode ($\text{Fe}^{2+}$ will be reduced to Fe). Electron flow, as always for galvanic cells, goes from the anode to the cathode, so electron flow will go from the right compartment ($[\text{Fe}^{2+}] = 1 \times 10^{-7}$ $M$) to the left compartment ($[\text{Fe}^{2+}] = 0.01$ $M$).

53. For concentration cells, the driving force for the reaction is the difference in ion concentrations between the anode and cathode. In order to equalize the ion concentrations, the anode always has the smaller ion concentration. The general setup for this concentration cell is:

\[
\begin{align*}
\text{Cathode:} & \quad \text{Ag}^+(x \ M) + e^- \rightarrow \text{Ag} \quad E^\circ = 0.80 \text{ V} \\
\text{Anode:} & \quad \text{Ag} \rightarrow \text{Ag}^+(y \ M) + e^- \quad -E^\circ = -0.80 \text{ V}
\end{align*}
\]

\[
\text{Ag}^+(\text{cathode, } x \ M) \rightarrow \text{Ag}^+ (\text{anode, } y \ M) 
\]

\[E^\circ_{\text{cell}} = 0.00 \text{ V}\]

\[
E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log Q = -\frac{0.0591}{1} \log \frac{[\text{Ag}^+]_{\text{anode}}}{[\text{Ag}^+]_{\text{cathode}}}
\]

For each concentration cell, we will calculate the cell potential using the above equation. Remember that the anode always has the smaller ion concentration.

a. Since both compartments are at standard conditions ($[\text{Ag}^+] = 1.0 \ M$) then $E_{\text{cell}} = E^\circ_{\text{cell}} = 0 \text{ V}$. No voltage is produced since no reaction occurs. Concentration cells only produce a voltage when the ion concentrations are not equal.

b. Cathode = 2.0 $M$ $\text{Ag}^+$; Anode = 1.0 $M$ $\text{Ag}^+$; Electron flow is always from the anode to the
cathode, so electrons flow to the right in the diagram.

\[
E_{\text{cell}} = \frac{-0.0591}{n} \log \frac{[\text{Ag}^+]_{\text{anode}}}{[\text{Ag}^+]_{\text{cathode}}} = \frac{-0.0591}{1} \log \frac{1.0}{2.0} = 0.018 \text{ V}
\]

c. Cathode = 1.0 \text{ M } \text{Ag}^+; \text{ Anode} = 0.10 \text{ M } \text{Ag}^+; \text{ Electrons flow to the left in the diagram.}

\[
E_{\text{cell}} = \frac{-0.0591}{n} \log \frac{[\text{Ag}^+]_{\text{anode}}}{[\text{Ag}^+]_{\text{cathode}}} = \frac{-0.0591}{1} \log \frac{0.10}{1.0} = 0.059 \text{ V}
\]

d. Cathode = 1.0 \text{ M } \text{Ag}^+; \text{ Anode} = 4.0 \times 10^{-5} \text{ M } \text{Ag}^+; \text{ Electrons flow to the left in the diagram.}

\[
E_{\text{cell}} = \frac{-0.0591}{1} \log \frac{4.0 \times 10^{-5}}{1.0} = 0.26 \text{ V}
\]

e. Since the ion concentrations are the same, then \( \log ([\text{Ag}^+]_{\text{anode}}/[\text{Ag}^+]_{\text{cathode}}) = \log (1.0) = 0 \) and \( E_{\text{cell}} = 0 \). No electron flow occurs.

54. As is the case for all concentration cells, \( E^\circ_{\text{cell}} = 0 \), and the smaller ion concentration is always in the anode compartment. The general Nernst equation for the \text{Ni} | \text{Ni}^{2+} (x \text{ M}) || \text{Ni}^{2+} (y \text{ M}) | \text{Ni} concentration cell is:

\[
E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log Q = \frac{-0.0591}{2} \log \frac{[\text{Ni}^{2+}]_{\text{anode}}}{[\text{Ni}^{2+}]_{\text{cathode}}}
\]

a. Since both compartments are at standard conditions ([\text{Ni}^{2+}] = 1.0 \text{ M}), then \( E_{\text{cell}} = E^\circ_{\text{cell}} = 0 \text{ V} \). No electron flow occurs.

b. Cathode = 2.0 \text{ M } \text{Ni}^{2+}; \text{ Anode} = 1.0 \text{ M } \text{Ni}^{2+}; \text{ Electron flow is always from the anode to the cathode, so electrons flow to the right in the diagram.}

\[
E_{\text{cell}} = \frac{-0.0591}{2} \log \frac{1.0}{2.0} = 8.9 \times 10^{-3} \text{ V}
\]

c. Cathode = 1.0 \text{ M } \text{Ni}^{2+}; \text{ Anode} = 0.10 \text{ M } \text{Ni}^{2+}; \text{ Electrons flow to the left in the diagram.}

\[
E_{\text{cell}} = \frac{-0.0591}{2} \log \frac{0.10}{1.0} = 0.030 \text{ V}
\]

d. Cathode = 1.0 \text{ M } \text{Ni}^{2+}; \text{ Anode} = 4.0 \times 10^{-3} \text{ M } \text{Ni}^{2+}; \text{ Electrons flow to the left in the diagram.}

\[
E_{\text{cell}} = \frac{-0.0591}{2} \log \frac{4.0 \times 10^{-3}}{1.0} = 0.13 \text{ V}
\]

e. Since both concentrations are equal, \( \log (2.5/2.5) = \log 1.0 = 0 \) and \( E_{\text{cell}} = 0 \). No electron flow occurs.

55. \[
5 \text{ e}^- + 8 \text{ H}^+ + \text{MnO}_4^- \rightarrow \text{Mn}^{2+} + 4 \text{ H}_2\text{O} \]

\[
(\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-) \times 5
\]

\[
E^\circ = 1.51 \text{ V}
\]

\[
-E^\circ = -0.77 \text{ V}
\]

8 \text{ H}^+(aq) + \text{MnO}_4^-(aq) + 5 \text{ Fe}^{2+}(aq) \rightarrow 5 \text{ Fe}^{3+}(aq) + \text{Mn}^{2+}(aq) + 4 \text{ H}_2\text{O(l)} \]

\[
E^\circ_{\text{cell}} = 0.74 \text{ V}
\]
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\[ E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log Q = 0.74 \text{ V} - \frac{0.0591}{5} \log \frac{[\text{Fe}^{3+}]^5 [\text{Mn}^{2+}]}{[\text{Fe}^{2+}]^5 [\text{MnO}_4^-] [\text{H}^+]^6}; \text{ pH = 4.0 so } \text{H}^+ = 1 \times 10^{-4} \text{ M} \]

\[ E_{\text{cell}} = 0.74 - \frac{0.0591 \log (1 \times 10^{-9})^5 (1 \times 10^{-4})}{5} (1 \times 10^{-3}) (1 \times 10^{-2}) (1 \times 10^{-4})^6 \]

\[ E_{\text{cell}} = 0.74 - 0.0591 \log (1 \times 10^{13}) = 0.74 \text{ V} - 0.15 \text{ V} = 0.59 \text{ V} = 0.6 \text{ V} \text{ (1 sig. fig. due to concentrations)} \]

Yes, \( E_{\text{cell}} > 0 \) so the reaction will occur as written.

56. \( n = 2 \) for this reaction (lead goes from Pb → Pb\(^{2+}\) in PbSO\(_4\)).

\[ E = E^\circ - \frac{0.0591}{2} \log \frac{1}{[\text{H}^+]^2 [\text{HSO}_4^-]^2} = 2.04 \text{ V} - \frac{0.0591}{2} \log \frac{1}{(4.5)^2 (4.5)^2} \]

\[ E = 2.04 \text{ V} + 0.077 \text{ V} = 2.12 \text{ V} \]

57. \( \text{Cu}^{2+} + 2 e^- \rightarrow \text{Cu} \)

\( \text{Zn} \rightarrow \text{Zn}^{2+} + 2 e^- \)

\( \text{Cu}^{2+} (\text{aq}) + \text{Zn}(s) \rightarrow \text{Zn}^{2+} (\text{aq}) + \text{Cu}(s) \quad E^\circ_{\text{cell}} = 1.10 \text{ V} \)

Since \( \text{Zn}^{2+} \) is a product in the reaction, the \( \text{Zn}^{2+} \) concentration increases from 1.00 \( M \) to 1.20 \( M \). This means that the reactant concentration of \( \text{Cu}^{2+} \) must decrease from 1.00 \( M \) to 0.80 \( M \) (from the 1:1 mol ratio in the balanced reaction).

\[ E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log Q = 1.10 \text{ V} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \]

\[ E_{\text{cell}} = 1.10 \text{ V} - \frac{0.0591}{2} \log \frac{1.20}{0.80} = 1.10 \text{ V} - 0.0052 \text{ V} = 1.09 \text{ V} \]

58. \( (\text{Pb}^{2+} + 2 e^- \rightarrow \text{Pb}) \times 3 \)

\( (\text{Al} \rightarrow \text{Al}^{3+} + 3 e^-) \times 2 \)

\( E^\circ = -0.13 \text{ V} \quad -E^\circ = 1.66 \text{ V} \)

\[ 3 \text{ Pb}^{2+}(\text{aq}) + 2 \text{ Al}(s) \rightarrow 3 \text{ Pb}(s) + 2 \text{ Al}^{3+}(\text{aq}) \quad E^\circ_{\text{cell}} = 1.53 \text{ V} \]

From the balanced reaction, when the \( \text{Al}^{3+} \) has increased by 0.60 mol/L (\( \text{Al}^{3+} \) is a product in the spontaneous reaction), then the \( \text{Pb}^{2+} \) concentration has decreased by \( 3/2 \) (0.60 mol/L) = 0.90 \( M \).

\[ E_{\text{cell}} = 1.53 \text{ V} - \frac{0.0591}{6} \log \frac{[\text{Al}^{3+}]^2}{[\text{Pb}^{2+}]^3} = 1.53 - \frac{0.0591}{6} \log \frac{(1.60)^2}{(0.10)^3} \]

\[ E_{\text{cell}} = 1.53 \text{ V} - 0.034 \text{ V} = 1.50 \text{ V} \]

59. \( \text{Cu}^{2+}(\text{aq}) + \text{H}_2(g) \rightarrow 2 \text{ H}^+(\text{aq}) + \text{Cu(s)} \quad E^\circ_{\text{cell}} = 0.34 \text{ V} - 0.00 \text{ V} = 0.34 \text{ V} \); \( n = 2 \) mol electrons

Since \( P_{\text{H}_2} = 1.0 \text{ atm and } [\text{H}^+] = 1.0 \text{ M} \):

\[ E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2} \log \frac{1}{[\text{Cu}^{2+}]} \]
a.  \( E_{\text{cell}} = 0.34 \text{ V} - \frac{0.0591}{2} \log \frac{1}{2.5 \times 10^{-4}} = 0.34 \text{ V} - 0.11 \text{ V} = 0.23 \text{ V} \)

b. \( 0.195 \text{ V} = 0.34 \text{ V} - \frac{0.0591}{2} \log \frac{1}{[\text{Cu}^{2+}]} \), \( \log \frac{1}{[\text{Cu}^{2+}]} = 4.91 \), \([\text{Cu}^{2+}] = 10^{-4.91} = 1.2 \times 10^{-4} \text{ M} \)

Note: When determining exponents, we will carry extra significant figures.

60. \( 3 \text{ Ni}^{2+}(\text{aq}) + 2 \text{ Al}(s) \rightarrow 2 \text{ Al}^{3+}(\text{aq}) + 3 \text{ Ni}(s) \)  \( E_{\text{cell}} = -0.23 + 1.66 = 1.43 \text{ V} \); \( n = 6 \text{ mol electrons} \)

a. \( E_{\text{cell}} = 1.43 \text{ V} - \frac{0.0591}{6} \log \frac{[\text{Al}^{3+}]^2}{[\text{Ni}^{2+}]^3} = 1.43 - \frac{0.0591}{6} \log \frac{(7.2 \times 10^{-3})^2}{(1.0)^3} \)

\( E_{\text{cell}} = 1.43 \text{ V} - (-0.042 \text{ V}) = 1.47 \text{ V} \)

b. \( 1.62 \text{ V} = 1.43 \text{ V} - \frac{0.0591}{6} \log \frac{[\text{Al}^{3+}]^2}{(1.0)^3} \), \( \log [\text{Al}^{3+}]^2 = -19.29 \)

\([\text{Al}^{3+}]^2 = 10^{-19.29} \), \([\text{Al}^{3+}] = 2.3 \times 10^{-10} \text{ M} \)

61. \( \text{Cu}^{2+}(\text{aq}) + \text{H}_2(\text{g}) \rightarrow 2 \text{ H}^+(\text{aq}) + \text{Cu}(s) \)  \( E_{\text{cell}} = 0.34 \text{ V} - 0.00 \text{ V} = 0.34 \text{ V} \); \( n = 2 \)

Since \( P_{\text{H}_2} = 1.0 \text{ atm} \) and \([\text{H}^+] = 1.0 \text{ M} \): \( E_{\text{cell}} = E_{\text{cell}}^o - \frac{0.0591}{2} \log \frac{1}{[\text{Cu}^{2+}]} \)

Use the \( K_p \) expression to calculate the \( \text{Cu}^{2+} \) concentration in the cell.

\( \text{Cu}_2(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2 \text{ OH}^-(\text{aq}) \)  \( K_p = 1.6 \times 10^{-19} = [\text{Cu}^{2+}][\text{OH}^-]^2 \)

From problem, \([\text{OH}^-] = 0.10 \text{ M} \), so: \([\text{Cu}^{2+}] = \frac{1.6 \times 10^{-19}}{(0.10)^2} = 1.6 \times 10^{-17} \text{ M} \)

\( E_{\text{cell}} = E_{\text{cell}}^o - \frac{0.0591}{2} \log \frac{1}{[\text{Cu}^{2+}]} = 0.34 \text{ V} - \frac{0.0591}{2} \log \frac{1}{1.6 \times 10^{-17}} = 0.34 - 0.50 = -0.16 \text{ V} \)

Since \( E_{\text{cell}} < 0 \), the forward reaction is not spontaneous, but the reverse reaction is spontaneous. The Cu electrode becomes the anode and \( E_{\text{cell}} = 0.16 \text{ V} \) for the reverse reaction. The cell reaction is: \( 2 \text{ H}^+(\text{aq}) + \text{Cu}(s) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{H}_2(\text{g}). \)

62. \( 3 \text{ Ni}^{2+}(\text{aq}) + 2 \text{ Al}(s) \rightarrow 2 \text{ Al}^{3+}(\text{aq}) + 3 \text{ Ni}(s) \)  \( E_{\text{cell}} = -0.23 + 1.66 = 1.43 \text{ V} \); \( n = 6 \)

\( E_{\text{cell}} = E_{\text{cell}}^o - \frac{0.0591}{n} \log \frac{[\text{Al}^{3+}]^2}{[\text{Ni}^{2+}]^3}, 1.82 \text{ V} = 1.43 \text{ V} - \frac{0.0591}{6} \log \frac{[\text{Al}^{3+}]^2}{(1.0)^3} \)

\( \log [\text{Al}^{3+}]^2 = -39.59 \), \([\text{Al}^{3+}]^2 = 10^{-39.59} \), \([\text{Al}^{3+}] = 1.6 \times 10^{-20} \text{ M} \)

\( \text{Al}_2(\text{aq}) \leftrightarrow \text{Al}^{3+}(\text{aq}) + 3 \text{ OH}^-(\text{aq}) \)  \( K_p = [\text{Al}^{3+}][\text{OH}^-]^3 \); From the problem, \([\text{OH}^-] = 1.0 \times 10^{-4} \text{ M} \).
\[ K_{sp} = (1.6 \times 10^{-20}) (1.0 \times 10^{-4})^3 = 1.6 \times 10^{-32} \]

63. See Exercises 17.25, 17.27 and 17.29 for balanced reactions and standard cell potentials. Balanced reactions are necessary to determine \( n \), the moles of electrons transferred.

25a. \( 7 \text{ H}_2\text{O} + 2 \text{ Cr}^{3+} + 3 \text{ Cl}_2 \rightarrow \text{ Cr}_2\text{O}_7^{2-} + 6 \text{ Cl}^- + 14 \text{ H}^+ \quad E^\circ_{\text{cell}} = 0.03 \text{ V} = 0.03 \text{ J/C} \)

\[ \Delta G^\circ = -nFE^\circ_{\text{cell}} = -(6 \text{ mol e}^\circ)(96,485 \text{ C/mol e}^\circ)(0.03 \text{ J/C}) = -1.7 \times 10^4 \text{ J} = -20 \text{ kJ} \]

\[ E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log Q: \text{ At equilibrium, } E_{\text{cell}} = 0 \text{ and } Q = K, \text{ so } E^\circ_{\text{cell}} = \frac{0.0591}{n} \log K \]

\[ \log K = \frac{nE^\circ}{0.0591} = 6(0.03) = 0.35, \quad K = 10^{0.5} = 1 \times 10^1 \]

Note: When determining exponents, we will round off to the correct number of significant figures after the calculation is complete in order to help eliminate excessive round-off error.

25b. \( \Delta G^\circ = -(2 \text{ mol e}^\circ)(96,485 \text{ C/mol e}^\circ)(2.71 \text{ J/C}) = -5.23 \times 10^4 \text{ J} = -523 \text{ kJ} \)

\[ \log K = \frac{2(2.71)}{0.0591} = 91.709, \quad K = 5.12 \times 10^{91} \]

29a. \( \Delta G^\circ = -(2 \text{ mol e}^\circ)(96,485 \text{ C/mol e}^\circ)(0.27 \text{ J/C}) = -5.21 \times 10^4 \text{ J} = -52 \text{ kJ} \)

\[ \log K = \frac{2(0.27)}{0.0591} = 9.14, \quad K = 1.4 \times 10^9 \]

29b. \( \Delta G^\circ = -(10 \text{ mol e}^\circ)(96,485 \text{ C/mol e}^\circ)(0.09 \text{ J/C}) = -8.7 \times 10^4 \text{ J} = -90 \text{ kJ} \)

\[ \log K = \frac{10(0.09)}{0.0591} = 15.23, \quad K = 2 \times 10^{15} \]

64. \( \Delta G^\circ = -nFE^\circ_{\text{cell}}; \quad E^\circ_{\text{cell}} = \frac{0.0591}{n} \log K, \quad \log K = \frac{nE^\circ}{0.0591} \)

26a. \( \Delta G^\circ = -(10 \text{ mol e}^\circ)(96,485 \text{ C/mol e}^\circ)(0.43 \text{ J/C}) = -4.1 \times 10^5 \text{ J} = -410 \text{ kJ} \)

\[ \log K = \frac{10(0.43)}{0.0591} = 72.76, \quad K = 10^{72.76} = 5.8 \times 10^{72} \]

26b. \( \Delta G^\circ = -(2 \text{ mol e}^\circ)(96,485 \text{ C/mol e}^\circ)(1.56 \text{ J/C}) = -3.01 \times 10^5 \text{ J} = -301 \text{ kJ} \)

\[ \log K = \frac{2(1.56)}{0.0591} = 52.792, \quad K = 6.19 \times 10^{52} \]

30a. \( \Delta G^\circ = -(2 \text{ mol e}^\circ)(96,485 \text{ C/mol e}^\circ)(1.10 \text{ J/C}) = -2.12 \times 10^5 \text{ J} = -212 \text{ kJ} \)

\[ \log K = \frac{2(1.10)}{0.0591} = 37.225, \quad K = 1.68 \times 10^{37} \]

30b. \( \Delta G^\circ = -(6 \text{ mol e}^\circ)(96,485 \text{ C/mol e}^\circ)(1.14 \text{ J/C}) = -6.60 \times 10^5 \text{ J} = -660 \text{ kJ} \)

\[ \log K = \frac{6(1.14)}{0.0591} = 115.736, \quad K = 5.45 \times 10^{115} \]
65.  a. Possible reaction: \( \text{I}_2(s) + 2 \text{Cl}^-(aq) \to 2 \text{I}^-(aq) + \text{Cl}_2(g) \) \( \Delta E_{\text{cell}} = 0.54 \text{ V} - 1.36 \text{ V} = -0.82 \text{ V} \)
This reaction is not spontaneous at standard conditions since \( \Delta E_{\text{cell}} < 0 \). No reaction occurs.

b. Possible reaction: \( \text{Cl}_2(g) + 2 \text{I}^-(aq) \to \text{I}_2(s) + 2 \text{Cl}^-(aq) \) \( \Delta E_{\text{cell}} = 0.82 \text{ V} \); This reaction is spontaneous at standard conditions since \( \Delta E_{\text{cell}} > 0 \). The reaction will occur.

\[ \Delta G^0 = -nFE_{\text{cell}} = -(2 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)(0.82 \text{ J/C}) = -1.6 \times 10^7 \text{ J} = -160 \text{ kJ} \]

\[ E^0 = \frac{0.0591}{n} \log K, \log K = \frac{nE^0}{0.0591} = \frac{2(0.82)}{0.0591} = 27.75, \ K = 10^{27.75} = 5.6 \times 10^{27} \]

c. Possible reaction: \( 2 \text{Ag}(s) + \text{Cu}^{2+}(aq) \to \text{Cu}(s) + 2 \text{Ag}^+(aq) \) \( \Delta E_{\text{cell}} = -0.46 \text{ V} \); No reaction occurs.

d. Fe\(^{3+}\) can be oxidized or reduced. The other species present are H\(^+\), SO\(_4^{2-}\), H\(_2\)O, and O\(_2\) from air. Only O\(_2\) in the presence of H\(^+\) has a large enough standard reduction potential to oxidize Fe\(^{3+}\) to Fe\(^{2+}\) (resulting in \( \Delta E_{\text{cell}} > 0 \)). All other combinations, including the possible reduction of Fe\(^{2+}\), give negative cell potentials. The spontaneous reaction is:

\[ 4 \text{Fe}^{2+}(aq) + 4 \text{H}^+(aq) + \text{O}_2(g) \to 4 \text{Fe}^{3+}(aq) + 2 \text{H}_2\text{O}(l) \] \( \Delta E_{\text{cell}} = 1.23 - 0.77 = 0.46 \text{ V} \)

\[ \Delta G^0 = -nFE_{\text{cell}} = -(4 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)(0.46 \text{ J/C})(1 \text{ kJ/1000 J}) = -180 \text{ kJ} \]

\[ \log K = \frac{4(0.46)}{0.0591} = 31.13, \ K = 1.3 \times 10^{27} \]

66.  a. Cu\(^+\) + e\(^-\) \to Cu \( E^0 = 0.52 \text{ V} \)
Cu\(^+\) \to Cu\(^{2+}\) + e\(^-\) \( -E^0 = -0.16 \text{ V} \)

\[ 2 \text{Cu}^+(aq) \to \text{Cu}^{2+}(aq) + \text{Cu}(s) \] \( \Delta E_{\text{cell}} = 0.36 \text{ V}; \text{ Spontaneous} \)

\[ \Delta G^0 = -nFE_{\text{cell}} = -(1 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)(0.36 \text{ J/C})(1 \text{ kJ/1000 J}) = -34,700 \text{ J} = -35 \text{ kJ} \]

\[ E_{\text{cell}} = \frac{0.0591}{n} \log K, \log K = \frac{nE^0}{0.0591} = \frac{1(0.36)}{0.0591} = 6.09, \ K = 10^{26.99} = 1.2 \times 10^6 \]

b. Fe\(^{3+}\) + 2 e\(^-\) \to Fe \( E^0 = -0.44 \text{ V} \)
(Fe\(^{3+}\) \to Fe\(^{2+}\) + e\(^-\)) \times 2 \( -E^0 = -0.77 \text{ V} \)

\[ 3 \text{Fe}^{2+}(aq) \to 2 \text{Fe}^{3+}(aq) + \text{Fe}(s) \] \( \Delta E_{\text{cell}} = -1.21 \text{ V}; \text{ Not spontaneous} \)

c. HClO\(_2\) + 2 H\(^+\) + 2 e\(^-\) \to HClO + H\(_2\)O \( E^0 = 1.65 \text{ V} \)
HClO\(_2\) + H\(_2\)O \to ClO\(^3-\) + 3 H\(^+\) + 2 e\(^-\) \( -E^0 = -1.21 \text{ V} \)

\[ 2 \text{HClO}_2(aq) \to \text{ClO}_3^-(aq) + \text{H}^+(aq) + \text{HClO}(aq) \] \( \Delta E_{\text{cell}} = 0.44 \text{ V}; \text{ Spontaneous} \)
\[
\Delta G^0 = -nF \frac{E^0}{cell} = -(2 \text{ mol e}^\cdot)(96,485 \text{ C/mol e}^\cdot)(0.44 \text{ J/C}) = -84,900 \text{ J} = -85 \text{ kJ}
\]

\[
\log K = \frac{nE^0}{0.0591} = \frac{2(0.44)}{0.0591} = 14.89, \ K = 7.8 \times 10^{14}
\]

67. a. \( Au^{3+} + 3 e^- \rightarrow Au \quad E^0 = 1.50 \text{ V} \)

\[
\text{Au}^{3+} (\text{aq}) + 3 \text{ Tl}(s) \rightarrow \text{Au}(s) + 3 \text{Tl}^+(aq) \quad E^0_{\text{cell}} = 1.84 \text{ V}
\]

b. \( \Delta G^0 = -nF \frac{E^0}{cell} = -(3 \text{ mol e}^\cdot)(96,485 \text{ C/mol e}^\cdot)(1.84 \text{ J/C}) = -5.33 \times 10^4 \text{ J} = -533 \text{ kJ} \)

\[
\log K = \frac{nE^0}{0.0591} = \frac{3(1.84)}{0.0591} = 93.401, \ K = 10^{93.401} = 2.52 \times 10^{93}
\]

c. \( E_{\text{cell}} = 1.84 \text{ V} - \frac{0.0591}{3} \log \left[ \frac{\text{Tl}^+}{\text{Au}^{3+}} \right] = 1.84 - \frac{0.0591}{3} \log \left( 1.0 \times 10^{-6} \right) = 2.04 \text{ V}
\)

68. \( (\text{Cr}^{2+} \rightarrow \text{Cr}^{3+} + e^-) \times 2 \)

\[
\text{Co}^{2+} + 2 e^- \rightarrow \text{Co} \quad 2 \text{ Cr}^{2+} + \text{Co}^{2+} \rightarrow 2 \text{ Cr}^{3+} + \text{Co}
\]

\[
E^o_{\text{cell}} = \frac{0.0591}{n} \log K = \frac{0.0591}{2} \log (2.79 \times 10^7) = 0.220 \text{ V}
\]

\[
E = E^0 - \frac{0.0591}{n} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Cr}^{2+}]^2[\text{Co}^{2+}]} = 0.220 \text{ V} - \frac{0.0591}{2} \log \frac{(2.0)^2}{(0.30)^2(0.20)} = 0.151 \text{ V}
\]

\( \Delta G = -nF E = -(2 \text{ mol e}^\cdot)(96,485 \text{ C/mol e}^\cdot)(0.151 \text{ J/C}) = -2.91 \times 10^4 \text{ J} = -29.1 \text{ kJ} \)

69. \( \text{CdS} + 2 e^- \rightarrow \text{Cd} + S^2^- \quad E^0 = -1.21 \text{ V} \)

\[
\text{Cd} \rightarrow \text{Cd}^{2+} + 2 e^- \quad -E^0 = 0.402 \text{ V}
\]

\[
\text{CdS(s)} \rightarrow \text{Cd}^{2+}(aq) + S^2-(aq) \quad E^0_{\text{cell}} = -0.81 \text{ V} \quad K_{sp} = ?
\]

\[
\log K_{sp} = \frac{nF E^0}{0.0591} = \frac{2(-0.81)}{0.0591} = -27.41, \quad K_{sp} = 10^{-27.41} = 3.9 \times 10^{-28}
\]

70. \( \text{Al}^{3+} + 3 e^- \rightarrow \text{Al} \quad E^0 = -1.66 \text{ V} \)

\[
\text{Al} + 6 F^- \rightarrow \text{AlF}_3^- + 3 e^- \quad -E^0 = 2.07 \text{ V}
\]
### Electrochemistry

\[
\text{Al}^{3+} (aq) + 6 \text{F}^-(aq) \rightarrow \text{AlF}_3^{4-} (aq) \quad E_{\text{cell}}^o = 0.41 \text{ V} \quad K = ?
\]

\[
\log K = \frac{nE^o}{0.0591} = \frac{3(0.41)}{0.0591} = 20.81, \quad K = 10^{20.81} = 6.5 \times 10^{20}
\]

71. \[
\begin{align*}
\text{Ag}^+ + e^- & \rightarrow \text{Ag}^0 
E^o = 0.80 \text{ V} \\
\text{Ag} + 2 \text{S}_2\text{O}_3^{2-} & \rightarrow \text{Ag(S}_2\text{O}_3)_2^{2-} + e^- 
-E^o = -0.017 \text{ V}
\end{align*}
\]

\[
\text{Ag}^+(aq) + 2 \text{S}_2\text{O}_3^{2-}(aq) \rightarrow \text{Ag(S}_2\text{O}_3)_2^{2-}(aq) 
E_{\text{cell}}^o = 0.78 \text{ V} \quad K = ?
\]

For this overall reaction, \( E_{\text{cell}}^o = \frac{0.0591}{n} \log K \)

\[
\log K = \frac{nE^o}{0.0591} = \frac{(1)(0.78)}{0.0591} = 13.20, \quad K = 10^{13.20} = 1.6 \times 10^{13}
\]

72. \[
\begin{align*}
\text{CuI} + e^- & \rightarrow \text{Cu}^+ + \text{I}^- 
E_{\text{cell}}^o = ? \\
\text{Cu}^+ & \rightarrow \text{Cu}^+ + e^- 
-E^o = -0.52 \text{ V}
\end{align*}
\]

\[
\text{CuI(s)} \rightarrow \text{Cu}^+(aq) + \text{I}^-(aq) 
E_{\text{cell}}^o = E_{\text{cell}}^o - 0.52 \text{ V}
\]

For this overall reaction, \( K = K_{sp} = 1.1 \times 10^{-12} \):

\[
E_{\text{cell}}^o = \frac{0.0591}{n} \log K_{sp} = \frac{0.0591}{1} \log (1.1 \times 10^{-12}) = -0.71 \text{ V}
\]

\[
E_{\text{cell}}^o = -0.71 \text{ V} = E_{\text{cell}}^o - 0.52, \quad E_{\text{cell}}^o = -0.19 \text{ V}
\]

### Electrolysis

73. a. \( \text{Al}^{3+} + 3 e^- \rightarrow \text{Al}; \) 3 mol e\(^-\) are needed to produce 1 mol Al from Al\(^{3+}\).

\[
1.0 \times 10^3 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \times \frac{3 \text{ mol e}^-}{1 \text{ mol Al}} \times \frac{96,485 \text{ C}}{1 \text{ mol e}^-} \times \frac{1 \text{ s}}{100.0 \text{ C}} = 1.07 \times 10^4 \text{ s} = 30 \text{ hours}
\]

b. \( 1.0 \text{ g Ni} \times \frac{1 \text{ mol Ni}}{58.69 \text{ g Ni}} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Ni}} \times \frac{96,485 \text{ C}}{1 \text{ mol e}^-} \times \frac{1 \text{ g}}{100.0 \text{ C}} = 33 \text{ s} \)

c. \( 5.0 \text{ mol Ag} \times \frac{1 \text{ mol e}^-}{1 \text{ mol Ag}} \times \frac{96,485 \text{ C}}{1 \text{ mol e}^-} \times \frac{1 \text{ s}}{100.0 \text{ C}} = 4.8 \times 10^3 \text{ s} = 1.3 \text{ hours} \)

74. The oxidation state of bismuth in BiO\(^+\) is +3 because oxygen has a -2 oxidation state in this ion. Therefore, 3 moles of electrons are required to reduce the bismuth in BiO\(^+\) to Bi(s).

\[
10.0 \text{ g Bi} \times \frac{1 \text{ mol Bi}}{209.0 \text{ g Bi}} \times \frac{3 \text{ mol e}^-}{1 \text{ mol Bi}} \times \frac{96,485 \text{ C}}{1 \text{ mol e}^-} \times \frac{1 \text{ s}}{25.0 \text{ C}} = 554 \text{ s} = 9.23 \text{ min}
\]

75. \[
15 \text{ A} = \frac{15 \text{ C}}{60 \text{ g}} \times \frac{60 \text{ min}}{1 \text{ h}} = 5.4 \times 10^4 \text{ C of charge passed in 1 hour}
\]
a. \[ 5.4 \times 10^4 \ \text{C} \times \frac{1 \ \text{mol} \ \text{e}^-}{96,485 \ \text{C}} \times \frac{1 \ \text{mol} \ \text{Co}^4}{2 \ \text{mol} \ \text{e}^-} \times \frac{58.93 \ \text{g} \ \text{Co}}{1 \ \text{mol} \ \text{Co}} = 16 \ \text{g} \ \text{Co} \]

b. \[ 5.4 \times 10^4 \ \text{C} \times \frac{1 \ \text{mol} \ \text{e}^-}{96,485 \ \text{C}} \times \frac{1 \ \text{mol} \ \text{Hf}^{4+}}{4 \ \text{mol} \ \text{e}^-} \times \frac{178.5 \ \text{g} \ \text{Hf}}{1 \ \text{mol} \ \text{Hf}} = 25 \ \text{g} \ \text{Hf} \]

c. \[ 2 \ \text{I} \rightarrow \text{I}_2 + 2 \ \text{e}^-; \ 5.4 \times 10^4 \ \text{C} \times \frac{1 \ \text{mol} \ \text{I}^-}{96,485 \ \text{C}} \times \frac{1 \ \text{mol} \ \text{I}_2}{2 \ \text{mol} \ \text{e}^-} \times \frac{253.8 \ \text{g} \ \text{I}_2}{1 \ \text{mol} \ \text{I}_2} = 71 \ \text{g} \ \text{I}_2 \]

d. \[ \text{CrO}_3(l) \rightarrow \text{Cr}^{6+} + 3 \ \text{O}^2-; \ 6 \ \text{mol} \ \text{e}^- \text{ are needed to produce } 1 \ \text{mol} \ \text{Cr} \text{ from molten } \text{CrO}_3. \]
\[ 5.4 \times 10^4 \ \text{C} \times \frac{1 \ \text{mol} \ \text{e}^-}{96,485 \ \text{C}} \times \frac{1 \ \text{mol} \ \text{Cr}^{6+}}{6 \ \text{mol} \ \text{e}^-} \times \frac{52.00 \ \text{g} \ \text{Cr}^{6+}}{1 \ \text{mol} \ \text{Cr}^{6+}} = 4.9 \ \text{g} \ \text{Cr} \]

76. \[ \text{Al} \text{ is in the } +3 \text{ oxidation in } \text{Al}_2\text{O}_3, \text{ so } 3 \ \text{mol} \ \text{e}^- \text{ are needed to convert } \text{Al}^{3+} \text{ into } \text{Al(s)}. \]
\[ 2.00 \ \text{h} \times \frac{60 \ \text{min}}{1 \ \text{h}} \times \frac{60 \ \text{s}}{1 \ \text{min}} \times \frac{1.00 \times 10^6 \ \text{C}}{1 \ \text{mol} \ \text{e}^-} \times \frac{1 \ \text{mol} \ \text{e}^-}{96,485 \ \text{C}} \times \frac{1 \ \text{mol} \ \text{Al}}{3 \ \text{mol} \ \text{e}^-} \times \frac{26.98 \ \text{g} \ \text{Al}}{1 \ \text{mol} \ \text{Al}} = 6.71 \times 10^5 \ \text{g} \]

77. \[ 1397 \ \text{s} \times \frac{6.50 \ \text{C}}{\text{g}} \times \frac{1 \ \text{mol} \ \text{e}^-}{96,485 \ \text{C}} \times \frac{1 \ \text{mol} \ \text{M}}{3 \ \text{mol} \ \text{e}^-} = 3.14 \times 10^{-2} \ \text{mol} \ \text{M} \ \text{where M} = \text{unknown metal} \]
\[ \text{Molar mass} = \frac{1.41 \ \text{g} \ \text{M}}{3.14 \times 10^{-2} \ \text{mol} \ \text{M}} = 44.9 \ \text{g/mol}; \ \text{The element is scandium. Sc forms } 3+ \text{ ions.} \]

78. \[ \text{Alkaline earth metals form } +2 \text{ ions, so } 2 \ \text{mol of } \text{e}^- \text{ are transferred to form the metal, M.} \]
\[ \text{mol} \ \text{M} = 748 \ \text{s} \times \frac{5.00 \ \text{C}}{\text{g}} \times \frac{1 \ \text{mol} \ \text{e}^-}{96,485 \ \text{C}} \times \frac{1 \ \text{mol} \ \text{M}}{2 \ \text{mol} \ \text{e}^-} = 1.94 \times 10^{-2} \ \text{mol} \ \text{M} \]
\[ \text{molar mass of } \text{M} = \frac{0.471 \ \text{g} \ \text{M}}{1.94 \times 10^{-2} \ \text{mol} \ \text{M}} = 24.3 \ \text{g/mol}; \ \text{MgCl}_2 \text{ was electrolyzed.} \]

79. \[ \text{F}_2 \text{ is produced at the anode: } 2 \ \text{F}^- \rightarrow \text{F}_2 + 2 \ \text{e}^- \]
\[ 2.00 \ \text{h} \times \frac{60 \ \text{min}}{1 \ \text{h}} \times \frac{60 \ \text{s}}{1 \ \text{min}} \times \frac{10.0 \ \text{C}}{1 \ \text{mol} \ \text{e}^-} \times \frac{1 \ \text{mol} \ \text{F}_2}{96,485 \ \text{C}} = 0.746 \ \text{mol} \ \text{e}^- \]
\[ 0.746 \ \text{mol} \ \text{e}^- \times \frac{1 \ \text{mol} \ \text{F}_2}{2 \ \text{mol} \ \text{e}^-} = 0.373 \ \text{mol} \ \text{F}_2; \ \text{PV} = \text{nRT}, \ \frac{\text{V}}{\text{P}} = \frac{\text{nRT}}{\text{P}} \]
\[ \frac{\text{V}}{\text{P}} = \frac{(0.373 \ \text{mol}) (0.08206 \ \text{L} \cdot \text{atm/K/mol}) (298 \ \text{K})}{1.00 \ \text{atm}} = 9.12 \ \text{L} \ \text{F}_2 \]

\[ \text{K is produced at the cathode: } \text{K}^+ + \text{e}^- \rightarrow \text{K} \]
0.746 mol e⁻ × \( \frac{1 \text{ mol K}}{\text{mol e}^-} \) × \( \frac{39.10 \text{ g K}}{\text{mol K}} \) = 29.2 g K

### 80.

The half-reactions for the electrolysis of water are:

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

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

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

Note: \( 4 \text{H}^+ + 4 \text{OH}^- \rightarrow 4 \text{H}_2\text{O} \) and \( n = 4 \) for this reaction as it is written.

\[
15.0 \text{ min} \times \frac{60 \text{ g}}{\text{min}} \times \frac{2.50 \text{ C}}{96,485 \text{ C}} \times \frac{2 \text{ mol H}_2}{1 \text{ mol e}^-} = 1.17 \times 10^{-2} \text{ mol H}_2
\]

At STP, 1 mole of an ideal gas occupies a volume of 22.42 L (see Chapter 5 of the text).

\[
1.17 \times 10^{-2} \text{ mol H}_2 \times \frac{22.42 \text{ L}}{1 \text{ mol H}_2} = 0.262 \text{ L} = 262 \text{ mL} \text{ H}_2
\]

\[
1.17 \times 10^{-2} \text{ mol H}_2 \times \frac{1 \text{ mol O}_2}{2 \text{ mol H}_2} \times \frac{22.42 \text{ L}}{1 \text{ mol O}_2} = 0.131 \text{ L} = 131 \text{ mL} \text{ O}_2
\]

### 81.

\[
\frac{150. \times 10^5 \text{ g C}_6\text{H}_5\text{N}_2}{\text{h}} \times \frac{1 \text{ h}}{60 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} \times \frac{1 \text{ mol C}_6\text{H}_5\text{N}_2}{90.12 \text{ g C}_6\text{H}_5\text{N}_2} \times \frac{2 \text{ mol e}^-}{1 \text{ mol C}_6\text{H}_5\text{N}_2} \times \frac{96,485 \text{ C}}{1 \text{ mol e}^-} = 7.44 \times 10^4 \text{ C/s or a current of } 7.44 \times 10^4 \text{ A}
\]

### 82.

\[
\text{Al}^{3+} + 3 \text{ e}^- \rightarrow \text{Al}; \ 3 \text{ mol e}^- \text{ are needed to produce Al from } \text{Al}^{3+}
\]

\[
2000 \text{ lb Al} \times \frac{453.6 \text{ g}}{1 \text{ lb}} \times \frac{1 \text{ mol Al}}{26.98 \text{ g}} \times \frac{3 \text{ mol e}^-}{1 \text{ mol Al}} \times \frac{96,485 \text{ C}}{1 \text{ mol e}^-} = 1 \times 10^{10} \text{ C of electricity needed}
\]

\[
\frac{1 \times 10^{10} \text{ C}}{24 \text{ h}} \times \frac{1 \text{ h}}{60 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} = 1 \times 10^5 \text{ C/s} = 1 \times 10^5 \text{ A}
\]

### 83.

\[
2.30 \text{ min} \times \frac{60 \text{ s}}{\text{min}} = 138 \text{ s}; \ 138 \text{ s} \times \frac{2.00 \text{ C}}{\text{g}} \times \frac{1 \text{ mol e}^-}{96,485 \text{ C}} \times \frac{1 \text{ mol Ag}}{1 \text{ mol e}^-} = 2.86 \times 10^{-3} \text{ mol Ag}
\]

\[
[\text{Ag}^-] = 2.86 \times 10^{-3} \text{ mol Ag}^-/0.250 \text{ L} = 1.14 \times 10^{-2} \text{ M}
\]

### 84.

\[
0.50 \text{ L} \times 0.010 \text{ mol Pt}^+/\text{L} = 5.0 \times 10^{-3} \text{ mol Pt}^+
\]

To plate out 99% of the Pt\(^{3+}\), we will produce \(0.99 \times 5.0 \times 10^{-3} \text{ mol Pt} \).

\[
0.99 \times 5.0 \times 10^{-3} \text{ mol Pt} \times \frac{4 \text{ mol e}^-}{\text{mol Pt}} \times \frac{96,485 \text{ C}}{1 \text{ mol e}^-} \times \frac{1 \text{ s}}{4.00 \text{ C}} = 480 \text{ s}
\]
85. \( \text{Au}^{3+} + 3 \text{e}^- \rightarrow \text{Au} \quad \text{E}^\circ = 1.50 \text{ V} \)
\( \text{Ni}^{2+} + 2 \text{e}^- \rightarrow \text{Ni} \quad \text{E}^\circ = -0.23 \text{ V} \)
\( \text{Ag}^+ + \text{e}^- \rightarrow \text{Ag} \quad \text{E}^\circ = 0.80 \text{ V} \)
\( \text{Cd}^{2+} + 2 \text{e}^- \rightarrow \text{Cd} \quad \text{E}^\circ = -0.40 \text{ V} \)
\( 2 \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^- \quad \text{E}^\circ = -0.83 \text{ V} \)

\( \text{Au(s)} \) will plate out first since it has the most positive reduction potential, followed by \( \text{Ag(s)} \), which is followed by \( \text{Ni(s)} \), and finally \( \text{Cd(s)} \) will plate out last since it has the most negative reduction potential of the metals listed.

86. Species present: \( \text{Fe}^{2+}, \text{SO}_4^{2-}, \text{H}^+ \) and \( \text{H}_2\text{O} \). The possible cathode reactions are:

\[
\begin{align*}
\text{SO}_4^{2-} + 4 \text{H}^+ + 2 \text{e}^- & \rightarrow \text{H}_2\text{SO}_3 + \text{H}_2\text{O} \quad \text{E}^\circ = 0.20 \text{ V} \\
2 \text{H}^+ + 2 \text{e}^- & \rightarrow \text{H}_2 \quad \text{E}^\circ = 0.00 \text{ V} \\
\text{Fe}^{2+} + 2 \text{e}^- & \rightarrow \text{Fe} \quad \text{E}^\circ = -0.44 \text{ V} \\
2 \text{H}_2\text{O} + 2 \text{e}^- & \rightarrow \text{H}_2 + 2 \text{OH}^- \quad \text{E}^\circ = -0.83 \text{ V}
\end{align*}
\]

Reduction of \( \text{SO}_4^{2-} \) will occur at the cathode since \( \text{SO}_4^{2-} \) is most positive. The possible anode reactions are:

\[
\begin{align*}
\text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + \text{e}^- \quad -\text{E}^\circ = -0.77 \text{ V} \\
2 \text{H}_2\text{O} & \rightarrow \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \quad -\text{E}^\circ = -1.23 \text{ V}
\end{align*}
\]

Oxidation of \( \text{Fe}^{2+} \) will occur at the anode since \( \text{Fe}^{2+} \) is most positive.

87. Reduction occurs at the cathode, and oxidation occurs at the anode. First, determine all the species present, then look up pertinent reduction and/or oxidation potentials in Table 17.1 for all these species. The cathode reaction will be the reaction with the most positive reduction potential, and the anode reaction will be the reaction with the most positive oxidation potential.

a. Species present: \( \text{Ni}^{2+} \) and \( \text{Br}^- \); \( \text{Ni}^{2+} \) can be reduced to \( \text{Ni} \), and \( \text{Br}^- \) can be oxidized to \( \text{Br}_2 \) (from Table 17.1). The reactions are:

\[
\begin{align*}
\text{Cathode: } \text{Ni}^{2+} + 2\text{e}^- & \rightarrow \text{Ni} \quad \text{E}^\circ = -0.23 \text{ V} \\
\text{Anode: } 2 \text{Br}^- & \rightarrow \text{Br}_2 + 2 \text{e}^- \quad -\text{E}^\circ = -1.09 \text{ V}
\end{align*}
\]

b. Species present: \( \text{Al}^{3+} \) and \( \text{F}^- \); \( \text{Al}^{3+} \) can be reduced, and \( \text{F}^- \) can be oxidized. The reactions are:

\[
\begin{align*}
\text{Cathode: } \text{Al}^{3+} + 3 \text{e}^- & \rightarrow \text{Al} \quad \text{E}^\circ = -1.66 \text{ V} \\
\text{Anode: } 2 \text{F}^- & \rightarrow \text{F}_2 + 2 \text{e}^- \quad -\text{E}^\circ = -2.87 \text{ V}
\end{align*}
\]

c. Species present: \( \text{Mn}^{2+} \) and \( \text{I}^- \); \( \text{Mn}^{2+} \) can be reduced, and \( \text{I}^- \) can be oxidized. The reactions are:

\[
\begin{align*}
\text{Cathode: } \text{Mn}^{2+} + 2 \text{e}^- & \rightarrow \text{Mn} \quad \text{E}^\circ = -1.18 \text{ V} \\
\text{Anode: } 2 \text{I}^- & \rightarrow \text{I}_2 + 2 \text{e}^- \quad -\text{E}^\circ = -0.54 \text{ V}
\end{align*}
\]

88. These are all in aqueous solutions, so we must also consider the reduction and oxidation of \( \text{H}_2\text{O} \) in addition to the potential redox reactions of the ions present. For the cathode reaction, the species with
the most positive reduction potential will be reduced, and for the anode reaction, the species with the most positive oxidation potential will be oxidized.

a. Species present: \( \text{Ni}^{2+}, \text{Br}^- \) and \( \text{H}_2\text{O} \). Possible cathode reactions are:

\[
\begin{align*}
\text{Ni}^{2+} + 2e^- & \rightarrow \text{Ni} & E^\circ = -0.23 \text{ V} \\
2 \text{H}_2\text{O} + 2e^- & \rightarrow \text{H}_2 + 2 \text{OH}^- & E^\circ = -0.83 \text{ V}
\end{align*}
\]

Since it is easier to reduce \( \text{Ni}^{2+} \) than \( \text{H}_2\text{O} \) (assuming standard conditions), \( \text{Ni}^{2+} \) will be reduced by the above cathode reaction.

Possible anode reactions are:

\[
\begin{align*}
2 \text{Br}^- & \rightarrow \text{Br}_2 + 2e^- & E^\circ = -1.09 \text{ V} \\
2 \text{H}_2\text{O} & \rightarrow \text{O}_2 + 4 \text{H}^+ + 4e^- & E^\circ = -1.23 \text{ V}
\end{align*}
\]

Since \( \text{Br}^- \) is easier to oxidize than \( \text{H}_2\text{O} \) (assuming standard conditions), then \( \text{Br}^- \) will be oxidized by the above anode reaction.

b. Species present: \( \text{Al}^{3+}, \text{F}^- \) and \( \text{H}_2\text{O} \); \( \text{Al}^{3+} \) and \( \text{H}_2\text{O} \) can be reduced. The reduction potentials are \( E^\circ = -1.66 \text{ V} \) for \( \text{Al}^{3+} \) and \( E^\circ = -0.83 \text{ V} \) for \( \text{H}_2\text{O} \) (assuming standard conditions). \( \text{H}_2\text{O} \) will be reduced at the cathode (\( 2 \text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2 \text{OH}^- \)).

\( \text{F}^- \) and \( \text{H}_2\text{O} \) can be oxidized. The oxidation potentials are \(-E^\circ = -2.87 \text{ V} \) for \( \text{F}^- \) and \(-E^\circ = -1.23 \text{ V} \) for \( \text{H}_2\text{O} \) (assuming standard conditions). From the potentials, we would predict \( \text{H}_2\text{O} \) to be oxidized at the anode (\( 2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{H}^+ + 4e^- \)).

c. Species present: \( \text{Mn}^{2+}, \text{I}^- \) and \( \text{H}_2\text{O} \); \( \text{Mn}^{2+} \) and \( \text{H}_2\text{O} \) can be reduced. The possible cathode reactions are:

\[
\begin{align*}
\text{Mn}^{2+} + 2e^- & \rightarrow \text{Mn} & E^\circ = -1.18 \text{ V} \\
2 \text{H}_2\text{O} + 2e^- & \rightarrow \text{H}_2 + 2 \text{OH}^- & E^\circ = -0.83 \text{ V}
\end{align*}
\]

Reduction of \( \text{H}_2\text{O} \) will occur at the cathode since \( E^\circ_{\text{Mn}} \) is most positive.

\( \text{I}^- \) and \( \text{H}_2\text{O} \) can be oxidized. The possible anode reactions are:

\[
\begin{align*}
2 \text{I}^- & \rightarrow \text{I}_2 + 2e^- & E^\circ = -0.54 \text{ V} \\
2 \text{H}_2\text{O} & \rightarrow \text{O}_2 + 4 \text{H}^+ + 4e^- & E^\circ = -1.23 \text{ V}
\end{align*}
\]

Oxidation of \( \text{I}^- \) will occur at the anode since \( -E^\circ_{\text{I}} \) is most positive.

**Additional Exercises**

89. The half-reaction for the SCE is:

\[
\text{Hg}_2\text{Cl}_2 + 2e^- \rightarrow 2 \text{Hg} + 2 \text{Cl}^- \quad E^\circ_{\text{SCE}} = 0.242 \text{ V}
\]
For a spontaneous reaction to occur, $E_{\text{cell}}$ must be positive. Using the standard reduction potentials in Table 17.1 and the given SCE potential, deduce which combination will produce a positive overall cell potential.

a. $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ \hspace{1cm} $E^0 = 0.34 \text{ V}$

$$E_{\text{cell}} = 0.34 - 0.242 = 0.10 \text{ V}; \text{ SCE is the anode.}$$

b. $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$ \hspace{1cm} $E^0 = 0.77 \text{ V}$

$$E_{\text{cell}} = 0.77 - 0.242 = 0.53 \text{ V}; \text{ SCE is the anode.}$$

c. $\text{AgCl} + e^- \rightarrow \text{Ag} + \text{Cl}^-$ \hspace{1cm} $E^0 = 0.22 \text{ V}$

$$E_{\text{cell}} = 0.242 - 0.22 = 0.02 \text{ V}; \text{ SCE is the cathode.}$$

d. $\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$ \hspace{1cm} $E^0 = -1.66 \text{ V}$

$$E_{\text{cell}} = 0.242 + 1.66 = 1.90 \text{ V}; \text{ SCE is the cathode.}$$

e. $\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$ \hspace{1cm} $E^0 = -0.23 \text{ V}$

$$E_{\text{cell}} = 0.242 + 0.23 = 0.47 \text{ V}; \text{ SCE is the cathode.}$$

90. The potential oxidizing agents are $\text{NO}_3^-$ and $\text{H}^+$. Hydrogen ion cannot oxidize Pt under either condition. Nitrate cannot oxidize Pt unless there is $\text{Cl}^-$ in the solution. Aqua regia has both $\text{Cl}^-$ and $\text{NO}_3^-$. The overall reaction is:

$$\text{(NO}_3^- + 4 \text{H}^+ + 3e^- \rightarrow \text{NO} + 2 \text{H}_2\text{O}) \times 2 \quad E^0 = 0.96 \text{ V}$$
$$\text{(4 Cl}^- + \text{Pt} \rightarrow \text{PtCl}^{2+} + 2e^-) \times 3 \quad -E^0 = -0.755 \text{ V}$$
$$\frac{12 \text{Cl}(aq) + 3 \text{Pt}(s) + 2 \text{NO}_3^-(aq) + 8 \text{H}^+(aq) \rightarrow 3 \text{PtCl}_2^{2+}(aq) + 2 \text{NO}(g) + 4 \text{H}_2\text{O}(l)}{E_{\text{cell}}^0 = 0.21 \text{ V}}$$

91. $2 \text{Ag}^+(aq) + \text{Cu}(s) \rightarrow \text{Cu}^{2+}(aq) + 2 \text{Ag}(s)$ \hspace{1cm} $E_{\text{cell}}^0 = 0.80 - 0.34 \text{ V} = 0.46 \text{ V}$; A galvanic cell produces a voltage as the forward reaction occurs. Any stress that increases the tendency of the forward reaction to occur will increase the cell potential, while a stress that decreases the tendency of the forward reaction to occur will decrease the cell potential.

a. Added $\text{Cu}^{2+}$ (a product ion) will decrease the tendency of the forward reaction to occur, which will decrease the cell potential.

b. Added $\text{NH}_3$ removes $\text{Cu}^{2+}$ in the form of $\text{Cu(NH}_3)_2^{2+}$. Removal of a product ion will increase the tendency of the forward reaction to occur, which will increase the cell potential.

c. Added $\text{Cl}^-$ removes $\text{Ag}^+$ in the form of $\text{AgCl}(s)$. Removal of a reactant ion will decrease the tendency of the forward reaction to occur, which will decrease the cell potential.
d. \( Q_i = \frac{[\text{Cu}^{2+}]_o}{[\text{Ag}^{+}]_o^2} \); As the volume of solution is doubled, each concentration is halved.

\[
Q_2 = \frac{1/2 [\text{Cu}^{2+}]_o}{(1/2 [\text{Ag}^{+}]_o)^2} = \frac{2[\text{Cu}^{2+}]_o}{[\text{Ag}^{+}]_o^2} = 2 \ Q_i
\]

The reaction quotient is doubled as the concentrations are halved. Since reactions are spontaneous when \( Q < K \) and since \( Q \) increases when the solution volume doubles, the reaction is closer to equilibrium, which will decrease the cell potential.

e. Since \( \text{Ag(s)} \) is not a reactant in this spontaneous reaction, and since solids do not appear in the reaction quotient expressions, replacing the silver electrode with a platinum electrode will have no effect on the cell potential.

92. \( \text{(Al}^3+ + 3 \text{e}^- \rightarrow \text{Al}) \times 2 \) \( \text{E}^\circ = -1.66 \text{ V} \)

\( \text{(M} \rightarrow \text{M}^{2+} + 2 \text{e}^- \) \( \times 3 \)

\( \text{E}^\circ = ? \)

\( 3 \text{M(s)} + 2 \text{Al}^{3+}(\text{aq}) \rightarrow 2 \text{Al(s)} + 3 \text{M}^{2+}(\text{aq}) \)

\( \text{E}^\circ_{\text{cell}} = -\text{E}^\circ - 1.66 \text{ V} \)

\( \Delta G^\circ = -nF \text{E}^\circ_{\text{cell}} = -411 \times 10^3 \text{ J} = -(6 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)(\text{E}^\circ_{\text{cell}}) \)

\( \text{E}^\circ_{\text{cell}} = 0.71 \text{ V} \)

\( \text{E}^\circ_{\text{cell}} = -\text{E}^\circ - 1.66 \text{ V} = 0.71 \text{ V}, \ -\text{E}^\circ = 2.37 \) or \( \text{E}^\circ = -2.37 \)

From table 17.1, the reduction potential for \( \text{Mg}^{2+} + 2 \text{e}^- \rightarrow \text{Mg} \) is \(-2.37 \text{ V}, \) which fits the data. Hence, the metal is magnesium.

93. a. \( \Delta G^\circ = \sum n_y \Delta G^\circ_{\text{products}} - \sum n_x \Delta G^\circ_{\text{reactants}} = 2(-480.) + 3(86) - 3(-40.) = -582 \text{ kJ} \)

From oxidation numbers, \( n = 6. \) \( \Delta G^\circ = -nFE^\circ, \ \text{E}^\circ = \frac{-\Delta G^\circ}{nF} = \frac{-(-582,000 \text{ J})}{6(96,485 \text{ C})} = 1.01 \text{ V} \)

\( \log K = \frac{-\text{E}^\circ}{0.0591} = \frac{6(1.01)}{0.0591} = 102.538, \ K = 10^{102.538} = 3.45 \times 10^{102} \)

b. \( 2 \text{e}^- + \text{Ag}_2 \text{S} \rightarrow 2 \text{Ag} + \text{S}^2- \) \( \times 3 \)

\( \text{(Al} \rightarrow \text{Al}^{3+} + 3 \text{e}^- \) \( \times 2 \)

\( \text{E}^\circ_{\text{al}_{\text{2S}}} = ? \)

\( 3 \text{Ag}_2 \text{S(s)} + 2 \text{Al(s)} \rightarrow 6 \text{Ag(s)} + 3 \text{S}^2-(\text{aq}) + 2 \text{Al}^{3+}(\text{aq}) \)

\( \text{E}^\circ_{\text{cell}} = 1.01 \text{ V} = \text{E}^\circ_{\text{Ag}_{2S}} + 1.66 \text{V} \)

\( \text{E}^\circ_{\text{al}_{\text{2S}}} = 1.01 \text{ V} - 1.66 \text{ V} = -0.65 \text{ V} \)

94. \( \text{Zn} \rightarrow \text{Zn}^{2+} + 2 \text{e}^- \ -\text{E}^\circ = 0.76 \text{ V}; \ \text{Fe} \rightarrow \text{Fe}^{2+} + 2 \text{e}^- \ -\text{E}^\circ = 0.44 \text{ V} \)

It is easier to oxidize Zn than Fe, so the Zn would be oxidized, protecting the iron of the Monitor’s hull.

95. From Exercise 17.27a: \( 3 \text{Cl}_2(\text{g}) + 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O(l)} \rightarrow 14 \text{H}^+(\text{aq}) + \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 6 \text{Cl}^-\text{(aq)} \)

\( \text{E}^\circ_{\text{cell}} = 0.03 \text{ V} \)
CHAPTER 17  ELECTROCHEMISTRY

When $K \cdot Cr_2O_7^2-$ and $Cl^-$ are added to concentrated $H_2SO_4$, $Q$ becomes a large number due to $H^+\text{]}^{14}$ term. The log of a large number is positive. $E_{cell}$ becomes negative, which means the reverse reaction becomes spontaneous. The pungent fumes were $Cl_2(g)$.

96. Aluminum has the ability to form a durable oxide coating over its surface. Once the $HCl$ dissolves this oxide coating, $Al$ is exposed to $H^+$ and is easily oxidized to $Al^{3+}$, i.e., the $Al$ foil disappears after the oxide coating is dissolved.

97. Consider the strongest oxidizing agent combined with the strongest reducing agent from Table 17.1:

$$F_2 + 2 e^- \rightarrow 2 F^- \quad E^\circ = 2.87 \text{ V}$$

$$\text{(Li} \rightarrow \text{Li}^+ + e^-) \times 2 \quad -E^\circ = 3.05 \text{ V}$$

$$F_2(g) + 2 \text{Li(s)} \rightarrow 2 \text{Li}^+(aq) + 2 F^- (aq) \quad E^\circ_{cell} = 5.92 \text{ V}$$

The claim is impossible. The strongest oxidizing agent and reducing agent when combined only give an $E^\circ_{cell}$ value of about 6 V.

98. $2 H_2(g) + O_2(g) \rightarrow 2 H_2O(l)$; Oxygen goes from the zero oxidation state to the -2 oxidation state in $H_2O$. Since two mol $O$ appear in the balanced reaction, then $n = 4$ mol electrons transferred.

a. $E^\circ_{cell} = \frac{0.0591}{n} \log K = \frac{0.0591}{4} \log (1.28 \times 10^{15})$, $E^\circ_{cell} = 1.23 \text{ V}$

$$\Delta G^\circ = -nF E^\circ_{cell} = -(4 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)(1.23 \text{ J/C}) = -4.75 \times 10^4 \text{ J} = -475 \text{ kJ}$$

b. Since mol of gas decrease as reactants are converted into products, then $\Delta S^\circ$ will be negative (unfavorable). Since the value of $\Delta G^\circ$ is negative, then $\Delta H^\circ$ must be negative ($\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$).

c. $\Delta G = w_{max} = \Delta H - T\Delta S$. Since $\Delta S$ is negative, then as $T$ increases, $\Delta G$ becomes more positive (closer to zero). Therefore, $w_{max}$ will decrease as $T$ increases.

99. a. $O_2 + 2 H_2O + 4 e^- \rightarrow 4 OH^- \quad E^\circ = 0.40 \text{ V}$

$$\text{(H}_2 + 2 \text{OH}^- \rightarrow 2 \text{H}_2O + 2 e^-) \times 2 \quad -E^\circ = 0.83 \text{ V}$$

$$2 \text{H}_2(g) + O_2(g) \rightarrow 2 \text{H}_2O(l) \quad E^\circ_{cell} = 1.23 \text{ V} = 1.23 \text{ J/C}$$

Since standard conditions are assumed, then $w_{max} = \Delta G^\circ$ for 2 mol $H_2O$ produced.

$$\Delta G^\circ = -nF E^\circ_{cell} = -(4 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)(1.23 \text{ J/C}) = -475,000 \text{ J} = -475 \text{ kJ}$$

For $1.00 \times 10^3$ g $H_2O$ produced, $w_{max}$ is:

$$1.00 \times 10^3 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} \times \frac{-475 \text{ kJ}}{2 \text{ mol } H_2O} = -13,200 \text{ kJ} = w_{max}$$
The work done can be no larger than the free energy change. The best that could happen is that all of the free energy released would go into doing work, but this does not occur in any real process since there is always waste energy in a real process. Fuel cells are more efficient in converting chemical energy into electrical energy; they are also less massive. The major disadvantage is that they are expensive. In addition, H₂(g) and O₂(g) are an explosive mixture if ignited; much more so than fossil fuels.

100. Cadmium goes from the zero oxidation state to the +2 oxidation state in Cd(OH)₂. Since one mol of Cd appears in the balanced reaction, then n = 2 mol electrons transferred. At standard conditions:

\[ w_{\text{max}} = \Delta G^\circ = -nF \Delta E^\circ, \quad w = -(2 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)(1.10 \text{ J/C}) = -2.12 \times 10^5 \text{ J} = -212 \text{ kJ} \]

101. \((CO + O_2^- \rightarrow CO_2^- + 2 e^-)\times 2\)

\[ \text{O}_2 + 4 e^- \rightarrow 2 O_2^- \]

\[ 2 \text{ CO} + \text{O}_2 \rightarrow 2 \text{ CO}_2 \]

\[ \Delta G = -nFE, \quad E = \frac{-\Delta G}{nF} = \frac{-(380 \times 10^3 \text{ J})}{(4 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)} = 0.98 \text{ V} \]

102. In the electrolysis of aqueous sodium chloride, H₂O is reduced in preference to Na⁺, and Cl⁻ is oxidized in preference to H₂O. The anode reaction is \(2 \text{Cl}^- \rightarrow \text{Cl}_2 + 2 e^-\), and the cathode reaction is \(2 \text{H}_2\text{O} + 2 e^- \rightarrow \text{H}_2 + 2 \text{OH}^-\). The overall reaction is:

\[ 2 \text{H}_2\text{O}(l) + 2 \text{Cl}^- (\text{aq}) \rightarrow \text{Cl}_2(g) + \text{H}_2(g) + 2 \text{OH}^- (\text{aq}). \]

From the 1:1 mol ratio between Cl₂ and H₂ in the overall balanced reaction, if 257 L of Cl₂(g) are produced, then 257 L of H₂(g) will also be produced since moles and volume of gas are directly proportional at constant T and P (see Chapter 5 of text).

103. mol e⁻ = 50.0 min × \(\frac{60 \text{ g}}{\text{min}}\) × \(\frac{2.50 \text{ C}}{\text{g}}\) × \(\frac{1 \text{ mol e}^-}{96,485 \text{ C}}\) = 7.77 × 10⁻² mol e⁻

\[ \text{mol Ru} = 2.618 \text{ g Ru} \times \frac{\text{1 mol Ru}}{101.1 \text{ g Ru}} = 2.590 \times 10^-2 \text{ mol Ru} \]

\[ \frac{\text{mol e}^-}{\text{mol Ru}} = \frac{7.77 \times 10^-2 \text{ mol e}^-}{2.590 \times 10^-2 \text{ mol Ru}} = 3.00; \text{ The charge on the ruthenium ions is +3 (Ru}^{3+} + 3 \text{ e}^- \rightarrow \text{Ru}). \]

104. \(15 \text{ kWh} = \frac{15,000 \text{ J}}{\text{s}} \times \frac{60 \text{ g}}{\text{min}} \times \frac{60 \text{ min}}{\text{h}} = 5.4 \times 10^7 \text{ J or } 5.4 \times 10^4 \text{ kJ} \text{ (Hall process)} \)

To melt 1.0 kg Al requires: \(1.0 \times 10^3 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g}} \times \frac{10.7 \text{ kJ}}{\text{mol Al}} = 4.0 \times 10^2 \text{ kJ} \)

It is feasible to recycle Al by melting the metal because, in theory, it takes less than 1% of the energy required to produce the same amount of Al by the Hall process.
Challenge Problems

105. \( \Delta G^\circ = -nF \Delta E^\circ = \Delta H^\circ - T \Delta S^\circ \), \( \Delta E^\circ = \frac{T \Delta S^\circ - \Delta H^\circ}{nF} \).

If we graph \( \Delta E^\circ \) vs. \( T \) we should get a straight line \( y = mx + b \). The slope of the line is equal to \( \Delta S^\circ/nF \), and the y-intercept is equal to \( -\Delta H^\circ/nF \). From the equation above, \( \Delta E^\circ \) will have a small temperature dependence when \( \Delta S^\circ \) is close to zero.

106. a. We can calculate \( \Delta G^\circ \) from \( \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \) and then \( \Delta E^\circ \) from \( \Delta G^\circ = -nF \Delta E^\circ \); or we can use the equation derived in Exercise 17.105. For this reaction, \( n = 2 \) (from oxidation states).

\[
\Delta G^\circ = \frac{T \Delta S^\circ - \Delta H^\circ}{nF} = \frac{(253 K)(263.5 J/K) + 315.9 \times 10^3 J}{(2 \text{ mol } e^-)(96,485 C/mol e^-)} = 1.98 \text{ J/C} = 1.98 \text{ V}
\]

b. \( \Delta E^\circ = \frac{RT}{nF} \ln Q = 1.98 \text{ V} - \frac{RT}{nF} \ln \left( \frac{1}{[	ext{H}^+][\text{HSO}_4^-]^2} \right) \)

\[
E_{20} = 1.98 \text{ V} - \frac{(8.3145 \text{ J/K} \cdot \text{mol})(253 K)}{(2 \text{ mol } e^-)(96,485 \text{ C/mol e^-})} \ln \left( \frac{1}{(4.5)^2(4.5)^2} \right) = 1.98 \text{ V} + 0.066 \text{ V} = 2.05 \text{ V}
\]

c. From Exercise 17.56, \( E = 2.12 \text{ V} \) at 25°C. As the temperature decreases, the cell potential decreases. Also, oil becomes more viscous at lower temperatures, which adds to the difficulty of starting an engine on a cold day. The combination of these two factors results in batteries failing more often on cold days than on warm days.

107. \( (\text{Ag}^+ + e^- \rightarrow \text{Ag}) \times 2 \) \( \text{E}^\circ = 0.80 \text{ V} \)

\( \text{Pb} \rightarrow \text{Pb}^{2+} + 2 e^- \) \( \text{E}^\circ = (-0.13) \)

\[
2 \text{ Ag}^+ + \text{Pb} \rightarrow 2 \text{ Ag} + \text{Pb}^{2+} \quad \text{E}^\circ_{\text{cell}} = 0.93 \text{ V}
\]

\[
\text{E} = \text{E}^\circ - \frac{0.0591}{n} \log \left( \frac{[\text{Pb}^{2+}]}{[\text{Ag}^+]^2} \right) = 0.83 \text{ V} = 0.93 \text{ V} - \frac{0.0591}{2} \log \left( \frac{1.8}{[\text{Ag}^+]^2} \right)
\]

\[
\log \left( \frac{1.8}{[\text{Ag}^+]^2} \right) = \frac{0.10(2)}{0.0591} = 3.4, \quad \frac{(1.8)}{[\text{Ag}^+]^2} = 10^{3.4}, \quad [\text{Ag}^+] = 0.027 \text{ M}
\]

\[
\text{Ag}_2\text{SO}_4(s) \rightleftharpoons 2 \text{ Ag}^+(aq) + \text{SO}_4^{2-}(aq) \quad K_{sp} = [\text{Ag}^+]^2[\text{SO}_4^{2-}]
\]

Initial \( s = \text{solubility (mol/L)} \) \( 0 \) \( 0 \)

Equil. \( 2s \) \( s \)

From problem: \( 2s = 0.027 \text{ M} \), \( s = 0.027/2 \)

\[
K_{sp} = (2s)^2(s) = (0.027)^2(0.027/2) = 9.8 \times 10^{-6}
\]

108. a. \( \text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s) \) \( \text{E}^\circ_{\text{cell}} = 1.10 \text{ V} \), \( \text{E}^\circ_{\text{cell}} = 1.10 \text{ V} - \frac{0.0591}{2} \log \left( \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right) \)
cell $E_{\text{cell}} = 1.10 \text{ V} - \frac{0.0591}{2} \log \frac{0.10}{2.50} = 1.10 \text{ V} + 0.041 \text{ V} = 1.14 \text{ V}$

b. $10.0 \text{ h} \times \frac{60 \text{ min}}{\text{h}} \times \frac{60 \text{ g}}{\text{min}} \times \frac{10.0 \text{ C}}{\text{mol e}^-} \times \frac{1 \text{ mol Cu}}{96,485 \text{ C}} \times \frac{1 \text{ mol Cu}}{2 \text{ mol e}^-} = 1.87 \text{ mol Cu produced}$

The Cu$^{2+}$ concentration will decrease by $1.87 \text{ mol/L}$, and the Zn$^{2+}$ concentration will increase by $1.87 \text{ mol/L}$.

$$[\text{Cu}^{2+}] = 2.50 - 1.87 = 0.63 \text{ M}; \quad [\text{Zn}^{2+}] = 0.10 + 1.87 = 1.97 \text{ M}$$

$E_{\text{cell}} = 1.10 \text{ V} - \frac{0.0591}{2} \log \frac{1.97}{0.63} = 1.10 \text{ V} - 0.015 \text{ V} = 1.09 \text{ V}$

c. $1.87 \text{ mol Zn consumed} \times \frac{65.38 \text{ g Zn}}{\text{mol Zn}} = 122 \text{ g Zn}; \quad \text{Mass of electrode} = 200. - 122 = 78 \text{ g Zn}$

$1.87 \text{ mol Cu formed} \times \frac{63.55 \text{ g Cu}}{\text{mol Cu}} = 119 \text{ g Cu}; \quad \text{Mass of electrode} = 200. + 119 = 319 \text{ g Cu}$

d. Three things could possibly cause this battery to go dead:

1. All of the Zn is consumed.
2. All of the Cu$^{2+}$ is consumed.
3. Equilibrium is reached ($E_{\text{cell}} = 0$).

We began with $2.50 \text{ mol Cu}^{2+}$ and $200. \text{ g Zn} \times 1 \text{ mol Zn}/65.38 \text{ g Zn} = 3.06 \text{ mol Zn}$. Cu$^{2+}$ is the limiting reagent and will run out first. To react all the Cu$^{2+}$ requires:

$$2.50 \text{ mol Cu}^{2+} \times \frac{2 \text{ mol e}^-}{\text{mol Cu}^{2+}} \times \frac{96,485 \text{ C}}{\text{mol e}^-} \times \frac{1 \text{ g}}{10.0 \times 0.0591 \times \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \times \frac{1 \text{ h}}{2}} = 13.4 \text{ h}$$

For equilibrium to be reached:

$$E = E^\circ - \frac{0.0591}{2} \log \frac{\text{P}_{\text{H}_2}}{[\text{H}^+]} - E^\circ = -(-0.440 \text{ V})$$

$$[\text{Zn}^{2+}] = K = 10^{2(1.10)0.0591} = 1.68 \times 10^{37}$$

This is such a large equilibrium constant that virtually all of the Cu$^{2+}$ must react to reach equilibrium. So, the battery will go dead in 13.4 hours.

109. $2 \text{ H}^+ + 2 \text{ e}^- \rightarrow \text{H}_2 \quad E^\circ = 0.000 \text{ V}$

$\text{Fe} \rightarrow \text{Fe}^{2+} + 2 \text{ e}^- \quad -E^\circ = -(-0.440 \text{ V})$

$$\text{E}_{\text{cell}} = E^\circ - \frac{0.0591}{n} \log Q, \quad \text{where} \quad n = 2 \quad \text{and} \quad Q = \frac{\text{P}_{\text{H}_2} \times [\text{Fe}^{2+}]}{[\text{H}^+]^2}$$

To determine $K_a$ for the weak acid, first use the electrochemical data to determine the H$^+$ concentration in the half-cell containing the weak acid.

$$0.333 \text{ V} = 0.440 \text{ V} - \frac{0.0591}{2} \log \frac{1.00 \times 10^{-2}}{[\text{H}^+]^2}$$
Now we can solve for the $K_a$ value of the weak acid HA through the normal setup for a weak acid problem.

\[
\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}
\]

Initial: $1.00 \text{ M}$
Equil.: $1.00 - x \quad x \quad x$

\[
K_a = \frac{x^2}{1.00 - x}
\]

where $x = [\text{H}^+] = 4.89 \times 10^{-4} \text{ M}$, $K_a = \frac{(4.89 \times 10^{-4})^2}{1.00 - 4.89 \times 10^{-4}} = 2.39 \times 10^{-7}

110. a. Nonreactive anions are present in each half-cell to balance the cation charges.

b. $\text{Au}^{3+}(aq) + 3 \text{ Fe}^{2+}(aq) \rightarrow 3 \text{ Fe}^{3+}(aq) + \text{Au}(s) \quad E_{\text{cell}}^o = 1.50 - 0.77 = 0.73 \text{ V}$

\[
E_{\text{cell}} = E_{\text{cell}}^o - \frac{0.0591}{n} \log Q = 0.73 \text{ V} - \frac{0.0591}{3} \log \frac{\left[\text{Fe}^{2+}\right]^3}{\left[\text{Au}^{3+}\right] \left[\text{Fe}^{3+}\right]^3}
\]

Since $[\text{Fe}^{3+}] = [\text{Fe}^{2+}] = 1.0 \text{ M}$: $0.31 \text{ V} = 0.73 \text{ V} - \frac{0.0591}{3} \log \frac{1}{[\text{Au}^{3+}]}$

\[
3(-0.42) = -\log \frac{1}{[\text{Au}^{3+}]} \quad \log [\text{Au}^{3+}] = -21.32, \quad [\text{Au}^{3+}] = 10^{-21.32} = 4.8 \times 10^{-22} \text{ M}
\]

$\text{Au}^{3+} + 4 \text{ Cl}^- \rightarrow \text{AuCl}_4^-$; Since the equilibrium $\text{Au}^{3+}$ concentration is so small, assume $[\text{AuCl}_4^-] = [\text{Au}^{3+}] = 1.0 \text{ M}$, i.e., assume $K$ is large, so the reaction essentially goes to completion.

\[
K = \frac{[\text{AuCl}_4^-]}{[\text{Au}^{3+}] \left[\text{Cl}^-\right]^4} = \frac{1.0}{(4.8 \times 10^{-22})(0.10)^4} = 2.1 \times 10^{25}; \quad \text{Assumption good (K is large).}
\]
111. a. \[ E_{\text{cell}} = E_{\text{ref}} + 0.05916 \text{pH} \]
\[ 0.480 \text{ V} = 0.250 \text{ V} + 0.05916 \text{ pH} \]
\[ \text{pH} = \frac{0.480 - 0.250}{0.05916} = 3.888; \quad \text{Uncertainty} = \pm 1 \text{ mV} = \pm 0.001 \text{ V} \]

\[ \text{pH}_{\text{max}} = \frac{0.481 - 0.250}{0.05916} = 3.905; \quad \text{pH}_{\text{min}} = \frac{0.479 - 0.250}{0.05916} = 3.871 \]

So, if the uncertainty in potential is \( \pm 0.001 \text{ V} \), the uncertainty in pH is \( \pm 0.017 \) or about \( \pm 0.02 \) pH units. For this measurement, \( [H^+] = 10^{-3.888} = 1.29 \times 10^{-4} \text{ M} \). For an error of +1 mV, \( [H^+] = 10^{-3.905} = 1.24 \times 10^{-4} \text{ M} \). For an error of -1 mV, \( [H^+] = 10^{-3.871} = 1.35 \times 10^{-4} \text{ M} \). So, the uncertainty in \([H^+]\) is \( \pm 0.06 \times 10^{-4} \text{ M} = \pm 6 \times 10^{-6} \text{ M} \).

b. From part a, we will be within \( \pm 0.02 \) pH units if we measure the potential to the nearest \( \pm 0.001 \) V (1 mV).

112. a. From Table 17.1: \[ 2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^- \quad E^\circ = -0.83 \text{ V} \]

\[ E_{\text{cell}} = E_{\text{H}_2\text{O}} - E_{\text{Zr}} = -0.83 \text{ V} + 2.36 \text{ V} = 1.53 \text{ V} \]

Yes, the reduction of \( \text{H}_2\text{O} \) to \( \text{H}_2 \) by \( \text{Zr} \) is spontaneous at standard conditions since \( E_{\text{cell}}^\circ > 0 \).

b. \[
\begin{align*}
(2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^-) \times 2 \\
\text{Zr} + 4 \text{OH}^- \rightarrow \text{ZrO}_2\cdot\text{H}_2\text{O} + \text{H}_2\text{O} + 4 \text{e}^- \\
3 \text{H}_2\text{O}(l) + \text{Zr}(s) \rightarrow 2 \text{H}_2(g) + \text{ZrO}_2\cdot\text{H}_2\text{O}(s)
\end{align*}
\]

c. \[ \Delta G^\circ = -nFE^\circ = -(4 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)(1.53 \text{ J/C}) = -5.90 \times 10^4 \text{ J} = -590 \text{ kJ} \]

\[ E = E^\circ - \frac{0.0591}{n} \log Q; \quad \text{At equilibrium}, \ E = 0 \text{ and } Q = K. \]

\[ E^\circ = \frac{0.0591}{n} \log K, \quad \log K = \frac{4(1.53)}{0.0591} = 104, \quad K \approx 10^{104} \]

d. \[ 1.00 \times 10^7 \text{ kg Zr } \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{1 \text{ mol Zr}}{91.22 \text{ g Zr}} \times \frac{2 \text{ mol H}_2}{1 \text{ mol Zr}} = 2.19 \times 10^4 \text{ mol H}_2 \]

\[ 2.19 \times 10^4 \text{ mol H}_2 \times \frac{2.016 \text{ g H}_2}{\text{mol H}_2} = 4.42 \times 10^4 \text{ g H}_2 \]

\[ V = \frac{nRT}{P} = \frac{(2.19 \times 10^4 \text{ mol})(0.08206 \text{ L atm/mol K})(1273 \text{ K})}{1.0 \text{ atm}} = 2.3 \times 10^6 \text{ L H}_2 \]

e. Probably yes; Less radioactivity overall was released by venting the \( \text{H}_2 \) than what would have been released if the \( \text{H}_2 \) had exploded inside the reactor (as happened at Chernobyl). Neither
alternative is pleasant, but venting the radioactive hydrogen is the less unpleasant of the two alternatives.

113. a. \[
\begin{align*}
\text{(Ag}^+ + e^- \rightarrow \text{Ag}) \times 2 \\
\text{Cu} \rightarrow \text{Cu}^{2+} + 2 e^- 
\end{align*}
\]
E° = 0.80 V

\[
-\text{E}° = -0.34 \text{ V}
\]

\[
2 \text{Ag}^+(aq) + \text{Cu(s)} \rightarrow 2 \text{Ag(s)} + \text{Cu}^{2+}(aq)
\]
E°_{cell} = 0.46 V

\[
E_{\text{cell}} = E°_{\text{cell}} - \frac{0.0591}{n} \log Q
\]

where n = 2 and Q = \frac{[\text{Cu}^{2+}]}{([\text{Ag}^+]^2}

To calculate E_{cell}, we need to use the K_{sp} data to determine [Ag^+].

\[
\text{AgCl(s)} \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)
\]

\[K_{sp} = 1.6 \times 10^{-10} = [\text{Ag}^+] [\text{Cl}^-]
\]

Initial
\[
\begin{array}{c}
\text{Ag}^+ \text{ (aq)} \\
\text{Cl}^- \text{ (aq)} \\
0 \\
0
\end{array}
\]

Equil.
\[
\begin{array}{c}
\text{Ag}^+ \text{ (aq)} \\
\text{Cl}^- \text{ (aq)} \\
s \\
s
\end{array}
\]

K_{sp} = 1.6 \times 10^{-10} = s^2, \quad s = [\text{Ag}^+] = 1.3 \times 10^{-5} \text{ mol/L}

\[
E_{\text{cell}} = 0.46 \text{ V} - \frac{0.0591}{2} \log \frac{2.0}{(1.3 \times 10^{-5})^2} = 0.46 \text{ V} - 0.30 = 0.16 \text{ V}
\]

b. \[
\text{Cu}^{2+}(aq) + 4 \text{NH}_3(aq) \rightleftharpoons \text{Cu(NH}_3)_4^{2+}(aq)
\]
K = 1.0 \times 10^{13} = \frac{[\text{Cu(NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4}

Since K is very large for the formation of Cu(NH}_3)_4^{2+}, the forward reaction is dominant. At equilibrium, essentially all of the 2.0 M Cu^{2+} will react to form 2.0 M Cu(NH}_3)_4^{2+}. This reaction requires 8.0 M NH}_3 to react with all of the Cu^{2+} in the balanced equation. Therefore, the mol of NH}_3 added to 1.0 L solution will be larger than 8.0 mol since some NH}_3 must be present at equilibrium. In order to calculate how much NH}_3 is present at equilibrium, we need to use the electrochemical data to determine the Cu^{2+} concentration.

\[
E_{\text{cell}} = E°_{\text{cell}} - \frac{0.0591}{2} \log Q, \quad 0.52 \text{ V} = 0.46 \text{ V} - \frac{0.0591}{2} \log \frac{[\text{Cu}^{2+}]}{(1.3 \times 10^{-5})^2}
\]

\[
\log \frac{[\text{Cu}^{2+}]}{(1.3 \times 10^{-5})^2} = -0.06(2) = -2.03, \quad \frac{[\text{Cu}^{2+}]}{(1.3 \times 10^{-5})^2} = 10^{-2.03} = 9.3 \times 10^{-3}
\]

\[[\text{Cu}^{2+}] = 1.6 \times 10^{-12} = 2 \times 10^{-12} \text{ M} \quad \text{(We carried extra significant figures in the calculation.)}
\]

Note: Our assumption that the 2.0 M Cu^{2+} essentially reacts to completion is excellent as only 2 \times 10^{-12} M Cu^{2+} remains after this reaction. Now we can solve for the equilibrium [NH}_3].
K = 1.0 \times 10^{13} = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = \frac{(2.0)}{\left(2 \times 10^{-13}\right)[\text{NH}_3]^4}, \quad [\text{NH}_3] = 0.6 \, M

Since 1.0 \, L of solution is present, then 0.6 \, mol \, NH_3 remains at equilibrium. The total mol of NH_3 added is 0.6 \, mol plus the 8.0 \, mol NH_3 necessary to form 2.0 \, M \text{Cu}(\text{NH}_3)_2^{2+}. Therefore, 8.0 + 0.6 = 8.6 \, mol \, NH_3 were added.