Visualizing Concepts

20.1 In a Brensted-Lowry acid-base reaction, \( \text{H}^+ \) is transferred from the acid to the base. In a redox reaction, the substance being oxidized (the reductant) loses electrons and the substance being reduced (the oxidant) gains electrons. Furthermore, the number of electrons gained and lost must be equal. The concept of electron transfer from reductant to oxidant is clearly applicable to redox reactions. (The path of the transfer may or may not be direct, but ultimately electrons are transferred during redox reactions.)

20.2 (a) If a \( \text{Zn(s)} \) strip was placed in a \( \text{CdSO}_4(\text{aq}) \) solution, \( \text{Cd(s)} \) would form on the strip. Although \( E_{\text{red}}^\text{Zn} \) for \( \text{Zn}^{2+}(\text{aq}) \), -0.763 V, and \( \text{Cd}^{2+}(\text{aq}) \), -0.403 V, are both negative, the value for \( \text{Cd}^{2+} \) is larger (less negative), so it will be the reduced species in the redox reaction.

(b) If a \( \text{Cu(s)} \) strip was placed in a \( \text{AgNO}_3(\text{aq}) \) solution, \( \text{Ag(s)} \) would form on the strip. Although \( E_{\text{red}}^\text{Cu} \) for \( \text{Cu}^{2+}(\text{aq}) \), 0.337 V, and \( \text{Ag}^{+}(\text{aq}) \), 0.799 V, are both positive, the species with the larger \( E_{\text{red}}^\text{Cu} \) value, \( \text{Ag}^+ \), will be reduced in the reaction.

20.3 \( \text{Ni}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Ni(s)}, \quad E_{\text{red}}^\text{Ni} = -0.28 \text{ V}, \quad \text{cathode} \)

\( \text{Fe}^{3+}(\text{aq}) + 2e^- \rightarrow \text{Fe(s)}, \quad E_{\text{red}}^\text{Fe} = -0.44 \text{ V}, \quad \text{anode} \)

\( \text{Ni}^{2+}(\text{aq}) \) has the larger \( E_{\text{red}}^\text{Ni} \), so it will be reduced in the redox reaction. Reduction occurs at the cathode, so \( \text{Ni}^{2+}(\text{aq}) \) and \( \text{Ni(s)} \) will be in the cathode compartment and \( \text{Fe}^{3+}(\text{aq}) \) and \( \text{Fe(s)} \) will be in the anode compartment. The voltmeter will read:

\[
E_{\text{cell}} = E_{\text{red}}^\text{cathode} - E_{\text{red}}^\text{anode} = -0.28 \text{ V} - (-0.44 \text{ V}) = 0.16 \text{ V}
\]
20.4 The species with the largest $E^\circ$ is easiest to reduce, while the species with the smallest, most negative $E^\circ$ is easiest to oxidize.

(a) The species easiest to oxidize is at the bottom of Figure 20.14.

(b) The species easiest to reduce is at the top of Figure 20.14.

20.5 $A(aq) + B(aq) \rightarrow A^- (aq) + B^+ (aq)$

(a) A gains electrons; it is being reduced. B loses electrons; it is being oxidized.

(b) Reduction occurs at the cathode; oxidation occurs at the anode.

$A(aq) + 1e^- \rightarrow A^- (aq)$ occurs at the cathode.

$B(aq) \rightarrow B^+ (aq) + 1e^-$ occurs at the anode.

(c) In a voltaic cell, the anode is at higher potential energy than the cathode. The anode reaction, $B(aq) \rightarrow B^+ (aq) + 1e^-$, is higher in potential energy.

20.6

The main difference between a fuel cell and a battery is that a fuel cell is not self-contained. That is, there is a continuous supply of fuel (reductant) and oxidant to the cell, and continuous exhaust of products. The fuel cell produces electrical current as long as reactants are supplied. It never goes "dead."

20.7 Zinc, $E^\circ_{\text{Zn}} = -0.763 \text{ V}$, is more easily oxidized than iron, $E^\circ_{\text{Fe}} = -0.440 \text{ V}$. If conditions are favorable for oxidation, zinc will be preferentially oxidized, preventing iron from corroding. The protection lasts until all the Zn coating has reacted.

20.8 Unintended oxidation reactions in the body lead to unwanted health effects, just as unwanted oxidation of metals leads to corrosion. Antioxidants probably have modes of action similar to anti-corrosion agents. They can preferentially react with oxidizing agents (cathodic protection), create conditions that are unfavorable to the oxidation-reduction reaction, or physically coat or surround the molecule being oxidized to prevent the oxidant from attacking it. The first of these modes of action is likely to be safest in biological systems. Adjusting reaction conditions in our body can be dangerous, and physical protection is unlikely to provide lasting protection against oxidation. Anti-oxidants are likely to be reductants that preferentially react with oxidizing agents.

Oxidation States

20.9 (a) Oxidation is the loss of electrons.
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(b) The electrons appear on the products side (right side) of an oxidation half-reaction.

(c) The oxidant is the reactant that is reduced; it gains the electrons that are lost by the substance being oxidized.

(d) An oxidizing agent is the substance that promotes oxidation. That is, it gains electrons that are lost by the substance being oxidized. It is the same as the oxidant.

20.10 (a) Reduction is the gain of electrons.

(b) The electrons appear on the reactants side (left side) of a reduction half-reaction.

(c) The reductant is the reactant that is oxidized; it provides the electrons that are gained by the substance being reduced.

(d) A reducing agent is the substance that promotes reduction. It donates the electrons gained by the substance that is reduced. It is the same as the reductant.

20.11 (a) True.

(b) False. Fe$^{3+}$ is reduced to Fe$^{2+}$, so it is the oxidizing agent, and Co$^{2+}$ is the reducing agent.

(c) True.

20.12 (a) False. If something is reduced, it gains electrons.

(b) True.

(c) True. Oxidation can be thought of as a gain of oxygen atoms. Looking forward, this view will be useful for organic reactions, Chapter 25.

20.13 Analyze/Plan. Given a chemical equation, we are asked to indicate which elements undergo a change in oxidation number and the magnitude of the change. Assign oxidation numbers according to the rules given in Section 4.4. Note the changes and report the magnitudes. Solve.

(a) I is reduced from +5 to 0; C is oxidized from +2 to +4.

(b) Hg is reduced from +2 to 0; N is oxidized from -2 to 0.

(c) N is reduced from +5 to +2; S is oxidized from -2 to 0.

(d) Cl is reduced from +4 to +3; O is oxidized from -1 to 0.

20.14 (a) No oxidation-reduction

(b) I is oxidized from -1 to +5; Cl is reduced from +1 to -1.

(c) S is oxidized from +4 to +6; N is reduced from +5 to +2.

(d) S is reduced from +6 to +4; Br is oxidized from -1 to 0.

Balancing Oxidation-Reduction Reactions

20.15 Analyze/Plan. Write the balanced chemical equation and assign oxidation numbers. The substance oxidized is the reductant and the substance reduced is the oxidant. Solve.
20

Solutions to Exercises

(a) $\text{TiCl}_4(\text{g}) + 2\text{Mg}(\text{l}) \rightarrow \text{Ti}(\text{s}) + 2\text{MgCl}_2(\text{l})$
(b) $\text{Mg}(\text{l})$ is oxidized; $\text{TiCl}_4(\text{g})$ is reduced.
(c) $\text{Mg}(\text{l})$ is the reductant; $\text{TiCl}_4(\text{g})$ is the oxidant.

20.16

(a) $2\text{N}_2\text{H}_4(\text{g}) + \text{N}_2\text{O}_4(\text{g}) \rightarrow 3\text{N}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$
(b) $\text{N}_2\text{H}_4(\text{g})$ is oxidized; $\text{N}_2\text{O}_4(\text{g})$ is reduced.
(c) $\text{N}_2\text{O}_4(\text{g})$ serves as the oxidizing agent; it is itself reduced. $\text{N}_2\text{H}_4(\text{g})$ serves as the reducing agent; it is itself oxidized.

20.17

*Analyze/Plan.* Follow the logic in Sample Exercises 20.2 and 20.3. If the half-reaction occurs in basic solution, balance as in acid, then add $\text{OH}^-$ to each side. *Solve.*

(a) $\text{Sn}^{2+}(\text{aq}) \rightarrow \text{Sn}^{4+}(\text{aq}) + 2\text{e}^-$, oxidation
(b) $\text{TiO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{Ti}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$, reduction
(c) $\text{ClO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow \text{Cl}^-(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$, reduction
(d) $4\text{OH}^-\text{(aq)} \rightarrow \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^-$, oxidation
(e) $\text{SO}_4^{2-}(\text{aq}) + 2\text{OH}^-\text{(aq)} \rightarrow \text{SO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^-$, oxidation
(f) $\text{N}_2(\text{g}) + 8\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{NH}_3(\text{aq})$, reduction
(g) $\text{N}_2(\text{g}) + 6\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{NH}_3(\text{g}) + \text{OH}^-\text{(aq)}$, reduction

20.18

(a) $\text{Mo}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Mo}(\text{s})$, reduction
(b) $\text{H}_2\text{SO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^-$, oxidation
(c) $\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \rightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$, reduction
(d) $\text{Mn}^{2+}(\text{aq}) + 4\text{OH}^-(\text{aq}) \rightarrow \text{MnO}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^-$, oxidation
(e) $\text{Cr(OH)}_2(\text{s}) + 5\text{OH}^-(\text{aq}) \rightarrow \text{CrO}_4^{2-}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) + 3\text{e}^-$, oxidation
(f) $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$, reduction
(g) $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$, reduction

20.19

*Analyze/Plan.* Follow the logic in Sample Exercises 20.2 and 20.3 to balance the given equations. Use the method in Sample Exercise 20.1 to identify oxidizing and reducing agents. *Solve.*

(a) $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + \text{I}^-\text{(aq)} + 8\text{H}^+(\text{aq}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + \text{IO}_3^-(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$
   oxidizing agent, $\text{Cr}_2\text{O}_7^{2-}$; reducing agent, $\text{I}^-$
(b) The half-reactions are:
   4[$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$]
   5[$\text{CH}_3\text{OH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HCO}_2\text{H}(\text{aq}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$]
   $4\text{MnO}_4^-(\text{aq}) + 5\text{CH}_3\text{OH}(\text{aq}) + 12\text{H}^+(\text{aq}) \rightarrow 4\text{Mn}^{2+}(\text{aq}) + 5\text{HCO}_2\text{H}(\text{aq}) + 11\text{H}_2\text{O}(\text{l})$
   oxidizing agent, $\text{MnO}_4^-$; reducing agent, $\text{CH}_3\text{OH}$
Solutions to Exercises

(c) \( \ce{I_2(s) + 6H_2O(l) \rightarrow 2IO_3^-(aq) + 12H^+(aq) + 10e^-} \)

\( 5\ce{OCl^- (aq) + 2H^+ (aq) + 2e^- \rightarrow Cl^- (aq) + H_2O(l)} \)

\( \ce{I_2(s) + 5OCl^- (aq) + H_2O(l) \rightarrow 2IO_3^-(aq) + 5Cl^- (aq) + 2H^+ (aq)} \)

oxidizing agent, \( \ce{OCl^-} \); reducing agent, \( \ce{I_2} \)

(d) \( \ce{As_2O_3(s) + 5H_2O(l) \rightarrow 2H_3AsO_4(aq) + 4H^+(aq) + 4e^-} \)

\( 2\ce{NO_3^- (aq) + 6H^+(aq) + 4e^- \rightarrow N_2O_3(aq) + 3H_2O(l)} \)

\( \ce{As_2O_3(s) + 2NO_3^-(aq) + 2H_2O(l) + 2H^+(aq) \rightarrow 2H_3AsO_4(aq) + N_2O_3(aq)} \)

oxidizing agent, \( \ce{NO_3^-} \); reducing agent, \( \ce{As_2O_3} \)

(e) \( \ce{2[MnO_4^- (aq) + 2H_2O(l) + 3e^- \rightarrow MnO_2(s) + 4OH^-]} \)

\( \ce{Br^-(aq) + 6OH^- (aq) \rightarrow BrO_3^-(aq) + 3H_2O(l) + 6e^-} \)

\( \ce{2[MnO_4^- (aq) + Br^- (aq) + H_2O(l) \rightarrow 2MnO_2(s) + BrO_3^- (aq) + 2OH^- (aq)} \)

oxidizing agent, \( \ce{MnO_4^-} \); reducing agent, \( \ce{Br^-} \)

(f) \( \ce{Pb(OH)_2(s) + ClO^- (aq) \rightarrow PbO_2(s) + Cl^- (aq) + 2OH^- (aq) + H_2O(l)} \)

oxidizing agent, \( \ce{ClO^-} \); reducing agent, \( \ce{Pb(OH)_2} \)

20.20

(a) \( \ce{3[NO_2^- (aq) + H_2O(l) \rightarrow NO_3^- (aq) + 2H^+(aq) + 2e^-]} \)

\( \ce{Cr_2O_7^{2-} (aq) + 14H^+ (aq) + 6e^- \rightarrow 2Cr^{3+} (aq) + 7H_2O(l)} \)

Net: \( \ce{3NO_2^- (aq) + Cr_2O_7^{2-} (aq) + 8H^+ (aq) \rightarrow 3NO_3^- (aq) + 2Cr^{3+} (aq) + 4H_2O(l)} \)

oxidizing agent, \( \ce{Cr_2O_7^{2-}} \); reducing agent, \( \ce{NO_2^-} \)

(b) \( \ce{4[As(s) + 3H_2O(l) \rightarrow H_3AsO_3(aq) + 3H^+(aq) + 3e^-]} \)

\( \ce{3[ClO_3^- (aq) + 5H^+(aq) + 4e^- \rightarrow HClO(aq) + 2H_2O(l)]} \)

Net: \( \ce{4As(s) + 3ClO_3^- (aq) + 6H_2O(l) + 3H^+(aq) \rightarrow 4H_3AsO_3(aq) + 3HClO(aq)} \)

oxidizing agent, \( \ce{ClO_3^-} \); reducing agent, \( \ce{As} \)

(c) \( \ce{2[Cr_2O_7^{2-} (aq) + 14H^+ (aq) + 6e^- \rightarrow 2Cr^{3+} (aq) + 7H_2O(l)]} \)

\( \ce{3(CH_3OH)(aq) + H_2O(l) \rightarrow HCO_2H(aq) + 4H^+(aq) + 4e^-} \)

Net: \( \ce{2Cr_2O_7^{2-} (aq) + 3CH_3OH(aq) + 16H^+ (aq) \rightarrow 4Cr^{3+} (aq) + 3HCO_2H(aq) + 11H_2O(l)} \)

oxidizing agent, \( \ce{Cr_2O_7^{2-}} \); reducing agent, \( \ce{CH_3OH} \)

(d) \( \ce{2[MnO_4^- (aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+} (aq) + 4H_2O(l)]} \)

\( \ce{5[2Cl^- (aq) \rightarrow Cl_2(aq) + 2e^-]} \)

Net: \( \ce{2MnO_4^- (aq) + 10Cl^- (aq) + 16H^+ (aq) \rightarrow 2Mn^{2+} (aq) + 5Cl_2(g) + 8H_2O(l)} \)

oxidizing agent, \( \ce{MnO_4^-} \); reducing agent, \( \ce{Cl^-} \)

(e) \( \ce{H_2O_2(aq) + 2e^- \rightarrow O_2(g) + 2H^+(aq)} \)

Since the reaction is in base, the \( \ce{H^+} \) can be "neutralized" by adding 2\( \ce{OH^-} \) to each side of the equation to give \( \ce{H_2O_2(aq) + 2OH^- (aq) \rightarrow O_2(g) + 2H_2O(l) + 2e^-} \). The other half reaction is \( 2[\ce{ClO_2(aq) + e^- \rightarrow ClO_2^-(aq)}] \).
20.21 (a) The reaction $\text{Cu}^{2+}(aq) + \text{Zn}(s) \rightarrow \text{Cu}(s) + \text{Zn}^{2+}(aq)$ is occurring in both figures. In Figure 20.3, the reactants are in contact, and the concentrations of the ions in solution aren’t specified. In Figure 20.4 the oxidation half-reaction and reduction half-reaction are occurring in separate compartments, joined by a porous connector. The concentrations of the two solutions are initially 1.0 M. In Figure 20.4, electrical current is isolated and flows through the voltmeter. In Figure 20.3, the flow of electrons cannot be isolated or utilized.

(b) In the cathode compartment of the voltaic cell in Figure 20.5, Cu$^{2+}$ cations are reduced to Cu atoms, decreasing the number of positively charged particles in the compartment. Na$^+$ cations are drawn into the compartment to maintain charge balance as Cu$^{2+}$ ions are removed.

20.22 (a) The porous glass dish in Figure 20.4 provides a mechanism by which ions not directly involved in the redox reaction can migrate into the anode and cathode compartments to maintain charge neutrality of the solutions. Ionic conduction within the cell, through the glass disk, completes the cell circuit.

(b) In the anode compartment of Figure 20.5, Zn atoms are oxidized to Zn$^{2+}$ cations, increasing the number of positively charged particles in the compartment. NO$_3^-$ anions migrate into the compartment to maintain charge balance as Zn$^{2+}$ ions are produced.

20.23 Analyze/Plan. Follow the logic in Sample Exercise 20.4. Solve.

(a) Fe(s) is oxidized, Ag$^+$ (aq) is reduced.

(b) Ag$^+$ (aq) + e$^-$ → Ag(s); Fe(s) → Fe$^{2+}$(aq) + 2e$^-$

(c) Fe(s) is the anode, Ag(s) is the cathode.

(d) Fe(s) is negative; Ag(s) is positive.

(e) Electrons flow from the Fe(-) electrode toward the Ag(+) electrode.

(f) Cations migrate toward the Ag(s) cathode; anions migrate toward the Fe(s) anode.

20.24 (a) Al(s) is oxidized, Ni$^{2+}$(aq) is reduced.

(b) Al(s) → Al$^{3+}$(aq) + 3e$^-”; Ni$^{2+}$(aq) + 2e$^-” → Ni(s)

(c) Al(s) is the anode; Ni(s) is the cathode.
(d) Al(s) is negative (-); Ni(s) is positive (+).
(e) Electrons flow from the Al(-) electrode toward the Ni(+) electrode.
(e) Cations migrate toward the Ni(s) cathode; anions migrate toward the Al(s) anode.

Cell EMF under Standard Conditions

20.25  
(a) \textit{Electromotive force}, \textit{emf}, is the driving force that causes electrons to flow through the external circuit of a voltaic cell. It is the potential energy difference between an electron at the anode and an electron at the cathode.
(b) One \textit{volt} is the potential energy difference required to impart 1 J of energy to a charge of 1 coulomb. 1 V = 1 J/C.
(c) \textit{Cell potential}, \text{E}_{\text{cell}} is the emf of an electrochemical cell.

20.26  
(a) In a voltaic cell, the anode has the higher potential energy for electrons. To achieve a lower potential energy, electrons flow from the anode to the cathode.
(b) The units of electrical potential are volts. A potential of one volt imparts one joule of energy to one coulomb of charge.
(c) A \textit{standard} cell potential describes the potential of an electrochemical cell where all components are present at standard conditions: elements in their standard states, gases at 1 atm pressure and 1 M aqueous solutions.

20.27  
(a) \(2\text{H}^+ \text{(aq)} + 2e^- \rightarrow \text{H}_2\text{(g)}\)
(b) A \textit{standard} hydrogen electrode is a hydrogen electrode where the components are at standard conditions, 1 M \text{H}^+ \text{(aq)} and \text{H}_2\text{(g)} at 1 atm.
(c) The platinum foil in an SHE serves as an inert electron carrier and a solid reaction surface.

20.28  
(a) \(\text{H}_2\text{(g)} \rightarrow 2\text{H}^+ \text{(aq)} + 2e^-\)
(b) The platinum electrode serves as a reaction surface; the greater the surface area, the more \text{H}_2 or \text{H}^+ that can be adsorbed onto the surface to facilitate the flow of electrons.

(c) 

\[ H_2(g), 1 \text{ atm} \]

\[ \begin{array}{c}
\text{H}_2\text{(g)} \\
\text{H}^+(\text{aq}, 1 \text{ M})
\end{array} \]
A standard reduction potential is the relative potential of a reduction half-reaction measured at standard conditions, 1 M aqueous solution and 1 atm gas pressure.

(b) \( E^{\circ}_{\text{red}} = 0 \text{ V} \) for a standard hydrogen electrode.

(c) The reduction of Ag\(^+\) (aq) to Ag(s) is much more energetically favorable, because it has a substantially more positive \( E^{\circ}_{\text{red}} \) (0.799 V) than the reduction of Sn\(^2+\)(aq) to Sn(s) (-0.136 V).

It is not possible to measure the standard reduction potential of a single half-reaction because each voltaic cell consists of two half-reactions and only the potential of a complete cell can be measured.

(b) The standard reduction potential of a half-reaction is determined by combining it with a reference half-reaction of known potential and measuring the cell potential. Assuming the half-reaction of interest is the reduction half-reaction:

\[
E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red (cathode)}} - E^{\circ}_{\text{red (anode)}} = E^{\circ}_{\text{red (unknown)}} - E^{\circ}_{\text{red (reference)}};
\]

\[
E^{\circ}_{\text{red (unknown)}} = E^{\circ}_{\text{cell}} + E^{\circ}_{\text{red (reference)}}.
\]

(c) \( \text{Cd}^{2+}(aq) + 2e^- \rightarrow \text{Cd}(s) \ E^o = -0.403 \text{ V} \)

\( \text{Ca}^{2+}(aq) + 2e^- \rightarrow \text{Ca}(s) \ E^o = -2.87 \text{ V} \)

The reduction of \( \text{Ca}^{2+}(aq) \) to \( \text{Ca}(s) \) is the more energetically unfavorable reduction because it has a more negative \( E^o \) value.

20.31 **Analyze/Plan.** Follow the logic in Sample Exercise 20.5. **Solve.**

(a) The two half-reactions are:

\( \text{Ti}^{3+}(aq) + 2e^- \rightarrow \text{Ti}^{1+}(aq) \quad \text{cathode} \ E^{\circ}_{\text{red}} = ? \)

\( 2[\text{Cr}^{2+}(aq) \rightarrow \text{Cr}^{3+}(aq) + e^-] \quad \text{anode} \ E^{\circ}_{\text{red}} = -0.41 \text{ V} \)

(b) \( E_{\text{cell}} = E^{\circ}_{\text{red (cathode)}} - E^{\circ}_{\text{red (anode)}}, 1.19 \text{ V} = E^{\circ}_{\text{red}} - (-0.41 \text{ V}) ; \)

\( E^{\circ}_{\text{red}} = 1.19 \text{ V} - 0.41 \text{ V} = 0.78 \text{ V} \)

(c) Note that because \( \text{Cr}^{2+}(aq) \) is readily oxidized, it would be necessary to keep oxygen out of the left-hand cell compartment.
Solutions to Exercises

20.32
(a) \( \text{PdCl}_2\text{aq} + 2e^- \rightarrow \text{Pd(s)} + 4\text{Cl}^- \) cathode \( E_{\text{red}}^* = ? \)
\( \text{Cd(s)} \rightarrow \text{Cd}^{2+}\text{aq} + 2e^- \) anode \( E_{\text{red}}^* = -0.403 \text{ V} \)

(b) \( E_{\text{cell}}^* = E_{\text{red}}^* \) (cathode) - \( E_{\text{red}}^* \) (anode); 1.03 V = \( E_{\text{red}}^* \) (-0.403 V);
\( E_{\text{red}}^* = 1.03 \text{ V} - 0.403 = 0.63 \text{ V} \)

(c) 

\[
\begin{align*}
\text{Solution Contains} & \quad \text{Cd}^{2+}\text{aq} \\
\text{Solution Contains} & \quad \text{PdCl}_2\text{aq}, \text{Cl}^-\text{aq}
\end{align*}
\]

20.33
**Analyze/Plan.** Follow the logic in Sample Exercise 20.6. **Solve.**

(a) \( \text{Cl}_2\text{(g)} \rightarrow 2\text{Cl}^-\text{(aq)} + 2e^- \) \( E_{\text{red}}^* = 1.359 \text{ V} \)
\( \text{I}_2\text{(s)} + 2e^- \rightarrow 2\text{I}^-\text{(aq)} \) \( E_{\text{red}}^* = 0.536 \text{ V} \)
\( E^* = 1.359 \text{ V} - 0.536 \text{ V} = 0.823 \text{ V} \)

(b) \( \text{Ni(s)} \rightarrow \text{Ni}^{2+}\text{(aq)} + 2e^- \) \( E_{\text{red}}^* = -0.28 \text{ V} \)
\( 2[\text{Ce}^{4+}\text{(aq)} + \text{Fe}^{3+}\text{(aq)}] \) \( E_{\text{red}}^* = 1.61 \text{ V} \)
\( E^* = 1.61 \text{ V} - (-0.28 \text{ V}) = 1.89 \text{ V} \)

(c) \( \text{Fe(s)} \rightarrow \text{Fe}^{2+}\text{(aq)} + 2e^- \) \( E_{\text{red}}^* = -0.440 \text{ V} \)
\( 2[\text{Fe}^{3+}\text{(aq)} + \text{Fe}^{2+}\text{(aq)}] \) \( E_{\text{red}}^* = 0.771 \text{ V} \)
\( E^* = 0.771 \text{ V} - (-0.440 \text{ V}) = 1.211 \text{ V} \)

(d) \( 3[\text{Ca(s)} \rightarrow \text{Ca}^{2+}\text{(aq)} + 2e^- ] \) \( E_{\text{red}}^* = -2.87 \text{ V} \)
\( 2[\text{AI}^{3+}\text{(aq)} + 3e^- \rightarrow \text{AI(s)}] \) \( E_{\text{red}}^* = -1.66 \text{ V} \)
\( E^* = -1.66 \text{ V} - (-2.87 \text{ V})] = 1.21 \text{ V} \)

20.34
(a) \( \text{F}_2\text{(g)} + 2e^- \rightarrow 2\text{F}^-\text{(aq)} \) \( E_{\text{red}}^* = 2.87 \text{ V} \)
\( \text{H}_2\text{(g)} \rightarrow 2\text{H}^+\text{(aq)} + 2e^- \) \( E_{\text{red}}^* = 0.00 \text{ V} \)
\( E^* = 2.87 \text{ V} - 0.00 \text{ V} = 2.87 \text{ V} \)

(b) \( \text{Cu(s)} \rightarrow \text{Cu}^{2+}\text{(aq)} + 2e^- \) \( E_{\text{red}}^* = 0.337 \text{ V} \)
\( \text{Ba}^{2+}\text{(aq)} + 2e^- \rightarrow \text{Ba(s)} \) \( E_{\text{red}}^* = -2.90 \text{ V} \)
\( E^* = -2.90 \text{ V} - (0.337 \text{ V}) = -3.24 \text{ V} \)
Solutions to Exercises

20.35 Analyze/Plan. Given four half-reactions, find \( E^{\circ} \) from Appendix E and combine them to obtain a desired \( E^{\circ}_{\text{cell}} \). (a) The largest \( E^{\circ}_{\text{cell}} \) will combine the half-reaction with the most positive \( E^{\circ} \) as the cathode reaction and the one with the most negative \( E^{\circ} \) as the anode reaction. (b) The smallest positive \( E^{\circ}_{\text{cell}} \) will combine two half-reactions whose \( E^{\circ} \) values are closest in magnitude and sign. Solve.

(a)
\[
\begin{align*}
3\text{Ag}^{+(aq)} + \text{I}^{-} &\rightarrow \text{Ag(s)} \quad E^{\circ} = 0.799 \\
\text{Cr(s)} &\rightarrow \text{Cr}^{3+}(aq) + 3\text{e}^- \quad E^{\circ} = -0.74 \\
3\text{Ag}^{+(aq)} + \text{Cr(s)} &\rightarrow 3\text{Ag(s)} + \text{Cr}^{3+}(aq) \quad E^{\circ} = 0.799 - (-0.74) = 1.54 \text{ V}
\end{align*}
\]

(b) Two of the combinations have essentially equal \( E^{\circ} \) values.
\[
\begin{align*}
2\text{Ag}^{+(aq)} + \text{Cu(s)} &\rightarrow 2\text{Ag(s)} + \text{Cu}^{2+}(aq) \quad E^{\circ} = 0.799 \text{ V} - 0.337 \text{ V} = 0.462 \text{ V} \\
3\text{Ni}^{2+}(aq) + 2\text{e}^- &\rightarrow 3\text{Ni(s)} \quad E^{\circ} = -0.28 \text{ V} \\
2\text{Cr(s)} &\rightarrow \text{Cr}^{3+}(aq) + 3\text{e}^- \quad E^{\circ} = -0.74 \text{ V} \\
3\text{Ni}^{2+}(aq) + 2\text{Cr(s)} &\rightarrow 3\text{Ni(s)} + 2\text{Cr}^{3+}(aq) \quad E^{\circ} = -0.28 \text{ V} - (-0.74) = 0.46 \text{ V}
\end{align*}
\]

20.36 (a) \[
\begin{align*}
2\text{Au(s)} + 4\text{Br}^-(aq) &\rightarrow \text{AuBr}_4^-(aq) + 3\text{e}^- \quad E^{\circ} = -0.858 \text{ V} \\
3[2\text{e}^- + \text{IO}_3^-(aq) + \text{H}_2\text{O}(l) &\rightarrow \text{I}^-(aq) + 2\text{OH}^-(aq)] \quad E^{\circ} = 0.49 \text{ V} \\
2\text{Au(s)} + 8\text{Br}^-(aq) + 3\text{IO}_3^-(aq) + 3\text{H}_2\text{O}(l) &\rightarrow 2\text{AuBr}_4^-(aq) + 3\text{I}^-(aq) + 6\text{OH}^-(aq) \\
E^{\circ} = 0.49 - (-0.858) = 1.35 \text{ V}
\end{align*}
\]

(b) \[
\begin{align*}
2\text{Eu}^{2+}(aq) &\rightarrow \text{Eu}^{3+}(aq) + \text{e}^- \quad E^{\circ} = -0.43 \text{ V} \\
\text{Sn}^{2+}(aq) + 2\text{e}^- &\rightarrow \text{Sn(s)} \quad E^{\circ} = -0.14 \text{ V} \\
2\text{Eu}^{3+}(aq) + \text{Sn}^{2+}(aq) &\rightarrow 2\text{Eu}^{2+}(aq) + \text{Sn(s)} \quad E^{\circ} = -0.14 - (-0.43) = 0.29 \text{ V}
\end{align*}
\]

20.37 Analyze/Plan. Given the description of a voltaic cell, answer questions about this cell. Combine ideas in Sample Exercises 20.4 and 20.7. The reduction half-reactions are:
\[
\begin{align*}
\text{Cu}^{2+}(aq) + 2\text{e}^- &\rightarrow \text{Cu(s)} \quad E^{\circ} = 0.337 \text{ V} \\
\text{Sn}^{2+}(aq) + 2\text{e}^- &\rightarrow \text{Sn(s)} \quad E^{\circ} = -0.136 \text{ V}
\end{align*}
\]

Solve.
20.38
(a) The two half-reactions are:
\[
Pb^{2+}(aq) + 2e^- \rightarrow Pb(s) \quad E^\circ = -0.126 \text{ V}
\]
\[
Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq) \quad E^\circ = 1.359 \text{ V}
\]
Because \(E^\circ\) for the reduction of \(Cl_2\) is higher, the reduction of \(Cl_2\) occurs at the Pt cathode. The Pb electrode is the anode.
(b) The Pb anode loses mass as \(Pb^{2+}(aq)\) is produced.
(c) \(Cl_2(g) + Pb(s) \rightarrow Pb^{2+}(aq) + 2Cl^-(aq)\)
(d) \(E^\circ = 1.359 \text{ V} - (-0.126 \text{ V}) = 1.485 \text{ V}\)

**Strengths of Oxidizing and Reducing Agents**

20.39 *Analyze/Plan.* Follow the logic in Sample Exercise 20.8. In each case, choose the half-reaction with the more positive reduction potential and with the given substance on the left. *Solve.*
(a) \(Cl_2(g) (1.359 \text{ V} vs. 1.065 \text{ V})\)
(b) \(Ni^{2+}(aq) (-0.28 \text{ V} vs. -0.403 \text{ V})\)
(c) \(BrO_3^-(aq) (1.52 \text{ V} vs. 1.195 \text{ V})\)
(d) \(O_3(g) (2.07 \text{ V} vs. 1.776 \text{ V})\)

20.40 The more readily a substance is oxidized, the stronger it is as a reducing agent. In each case choose the half-reaction with the more negative reduction potential and the given substance on the right.
(a) \(Mg(s) (-2.37 \text{ V} vs. -0.440 \text{ V})\)
(b) \(Ca(s) (-2.87 \text{ V} vs. -1.66 \text{ V})\)
(c) \(H_2(g, \text{ acidic}) (0.000 \text{ V} vs. 0.141 \text{ V})\)
(d) \(H_2C_2O_4(aq) (-0.49 \text{ V} vs. 0.17 \text{ V})\)

20.41 *Analyze/Plan.* If the substance is on the left of a reduction half-reaction, it will be an oxidant; if it is on the right, it will be a reductant. The sign and magnitude of the \(E^\circ_{\text{red}}\) determines whether it is strong or weak. *Solve.*
(a) \(Cl_2(aq): \text{ strong oxidant (on the left, } E^\circ_{\text{red}} = 1.359 \text{ V} \)\)
(b) \(MnO_4^-(aq, \text{ acidic}): \text{ strong oxidant (on the left, } E^\circ_{\text{red}} = 1.51 \text{ V} \)\)
(c) \( \text{Ba(s): strong reductant (on the right, } E_{\text{red}}^\text{r} = -2.90 \text{ V)} \)

(d) \( \text{Zn(s): reductant (on the right, } E_{\text{red}}^\text{r} = -0.763 \text{ V)} \)

20.42 If the substance is on the left of a reduction half-reaction, it will be an oxidant; if it is on the right, it will be a reductant. The sign and magnitude of the \( E_{\text{red}} \) determine whether it is strong or weak.

(a) \( \text{Na(s): strong reductant (on the right, } E_{\text{red}}^\text{r} = -2.71 \text{ V)} \)

(b) \( \text{O}_3(\text{g): strong oxidant (on the left, } E_{\text{red}}^\text{r} = 2.07 \text{ V)} \)

(c) \( \text{Ce}^{3+}(\text{aq): very weak reductant (on the right, } E_{\text{red}}^\text{r} = 1.61 \text{ V)} \)

(d) \( \text{Sn}^{2+}(\text{aq): reductant (on the right, } E_{\text{red}}^\text{r} = 0.154 \text{ V)} \) or weak oxidant (on the left, \(-0.136 \text{ V)} \)

20.43 \textit{Analyze/Plan.} Follow the logic in Sample Exercise 20.8. \textit{Solve.}

(a) Arranged in order of increasing strength as oxidizing agents (and increasing reduction potential):
\[ \text{Cu}^{2+}(\text{aq}) < \text{O}_3(\text{g}) < \text{Cr}_2\text{O}_7^{2-}(\text{aq}) < \text{Cl}_2(\text{g}) < \text{H}_2\text{O}_2(\text{aq}) \]

(b) Arranged in order of increasing strength as reducing agents (and decreasing reduction potential):
\[ \text{H}_2\text{O}_2(\text{aq}) < \text{I}^- (\text{aq}) < \text{Sn}^{2+}(\text{aq}) < \text{Zn(s)} < \text{Al(s)} \]

20.44 (a) The strongest oxidizing agent is the species most readily reduced, as evidenced by a large, positive reduction potential. That species is \( \text{H}_2\text{O}_2 \). The weakest oxidizing agent is the species that least readily accepts an electron. We expect that it will be very difficult to reduce \( \text{Zn(s)} \); indeed, \( \text{Zn(s)} \) acts as a comparatively strong reducing agent. No potential is listed for reduction of \( \text{Zn(s)} \), but we can safely assume that it is less readily reduced than any of the other species present.

(b) The strongest reducing agent is the species most easily oxidized (the largest negative reduction potential). \( \text{Zn, } E_{\text{red}}^\text{r} = -0.76 \text{ V, is the strongest reducing agent and } F^- , E_{\text{red}}^\text{r} = 2.87 \text{ V, is the weakest.} \)

20.45 \textit{Analyze/Plan.} In order to reduce \( \text{Eu}^{3+} \) to \( \text{Eu}^{2+} \), we need an oxidizing agent, one of the reduced species from Table 20.1 or Appendix E. It must have a greater tendency to be oxidized than \( \text{Eu}^{3+} \) has to be reduced. That is, \( E_{\text{red}}^\text{r} \) must be more negative than \(-0.43 \text{ V).} \)
\textit{Solve.}

Any of the reduced species in Table 20.1 or Appendix E from a half-reaction with a reduction potential more negative than \(-0.43 \text{ V will reduce } \text{Eu}^{3+} \) to \( \text{Eu}^{2+} \). From the list of possible reductants in the exercise, \( \text{Al} \text{ and } \text{H}_2\text{C}_2\text{O}_4 \) will reduce \( \text{Eu}^{3+} \) to \( \text{Eu}^{2+} \).

\textit{Free Energy and Redox Reactions}

20.46 Any oxidized species from Table 20.1 or Appendix E with a reduction potential greater than \( 0.59 \text{ V will oxidize } \text{RuO}_4^{2-} \) to \( \text{RuO}_4^- \). From the list of possible oxidants in the exercise, \( \text{Cr}_2\text{O}_7^{2-}(\text{aq}) \) and \( \text{ClO}^- (\text{aq}) \) will oxidize \( \text{RuO}_4^{2-} \) to \( \text{RuO}_4^- \).
20.47 Analyze/Plan. In each reaction, Fe$^{2+}$ → Fe$^{3+}$ will be the oxidation half-reaction and one of the other given half-reactions will be the reduction half-reaction. Follow the logic in Sample Exercise 20.10 to calculate $E^\circ$ and $\Delta G^\circ$ for each reaction. Solve.

(a) $2\text{Fe}^{2+}(aq) + \text{S}_2\text{O}_8^{2-}(aq) + 4\text{H}^+(aq) \rightarrow 2\text{Fe}^{3+}(aq) + 2\text{H}_2\text{SO}_4(aq)$

$$E^\circ = 0.60 \text{ V} - 0.77 \text{ V} = -0.17 \text{ V}$$

$2\text{Fe}^{2+}(aq) + \text{N}_2\text{O}(aq) + 2\text{H}^+(aq) \rightarrow 2\text{Fe}^{3+}(aq) + \text{N}_2(g) + \text{H}_2\text{O}(l)$

$$E^\circ = -1.77 \text{ V} - 0.77 \text{ V} = -2.54 \text{ V}$$

$\text{Fe}^{2+}(aq) + \text{VO}_2^+(aq) + 2\text{H}^+(aq) \rightarrow \text{Fe}^{3+}(aq) + \text{VO}_2^+(aq) + \text{H}_2\text{O}(l)$

$$E^\circ = 1.00 \text{ V} - 0.77 \text{ V} = +0.23 \text{ V}$$

(b) $\Delta G^\circ = -nF E^\circ$

For the first reaction,

$$\Delta G^\circ = -2 \text{ mol} \times \frac{96,500 \text{ J}}{1 \text{ V} \cdot \text{mol}} \times (-0.17 \text{ V}) = 3.281 \times 10^4 \text{ J} = 33 \text{ kJ}$$

For the second reaction,

$$\Delta G^\circ = -2(96,500)(-2.54) = 4.902 \times 10^5 \text{ J} = 4.90 \times 10^2 \text{ kJ}$$

For the third reaction,

$$\Delta G^\circ = 1(96,500)(0.23) = -2.22 \times 10^4 \text{ J} = -22 \text{ kJ}$$

(c) $\Delta G^\circ = -RT \ln K$; $\ln K = -\Delta G^\circ/RT$; $K = e^{-\Delta G^\circ/RT}$

For the first reaction,

$$\ln K = \frac{-3.281 \times 10^4}{(8.314 \text{ J/mol.K})(298 \text{ K})} = -13.243 \approx -13; K = e^{-13.243} = 1.78 \times 10^{-6} = 2 \times 10^{-6}$$

[Convert In to log; the number of decimal places in the log is the number of sig figs in the result.]

For the second reaction,

$$\ln K = \frac{-4.902 \times 10^5}{8.314 \text{ J/mol.K X 298 K}} = -197.86 \approx -198; K = e^{-198} = 1.23 \times 10^{-86} = 1 \times 10^{-86}$$

For the third reaction,

$$\ln K = \frac{-(-2.22 \times 10^4)}{8.314 \text{ J/mol.K X 298 K}} = 9.058 = 9; K = e^{9.058} = 7.77 \times 10^3 = 8 \times 10^3$$

Check. The equilibrium constants calculated here are indicators of equilibrium position, but are not particularly precise numerical values.

20.48 (a) $2\Gamma(aq) \rightarrow I_2(s) + 2e^-$

$$E^\circ_{\text{red}} = 0.536 \text{ V}$$

$\text{Hg}_2^{2+}(aq) + 2e^- \rightarrow 2\text{Hg(l)}$

$$E^\circ_{\text{red}} = 0.789 \text{ V}$$

$2\Gamma(aq) + \text{Hg}_2^{2+}(aq) \rightarrow I_2(s) + 2\text{Hg(l)}$

$$E^\circ = 0.789 - 0.536 = 0.253 \text{ V}$$

$$\Delta G^\circ = -nF E^\circ = -2 \text{ mol} e^- \times \frac{96.5 \text{ kJ}}{\text{V} \cdot \text{mol} e^-} \times 0.253 \text{ V} = -48.829 \text{ kJ} = -48.8 \text{ kJ}$$

$$\ln K = \frac{-(4.8829 \times 10^4)}{(8.314 \text{ J/mol.K})(298 \text{ K})} = 19.708 \approx 19.7; K = e^{19.7} = 3.61 \times 10^8 = 3.6 \times 10^8$$
Solutions to Exercises

(b) \[ 3\text{Cu}^+(aq) \rightarrow \text{Cu}^{2+}(aq) + 1e^- \quad E_{\text{red}}^\circ = 0.153 \text{ V} \]
\[ \text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3e^- \rightarrow \text{NO}(g) + \text{H}_2\text{O}(l) \quad E_{\text{red}}^\circ = 0.96 \text{ V} \]
\[ 3\text{Cu}^+(aq) + \text{NO}_3^-(aq) + 4\text{H}^+(aq) \rightarrow 3\text{Cu}^{2+}(aq) + \text{NO}(g) + 2\text{H}_2\text{O}(l) \]

E° = 0.96 - 0.153 = 0.81 V; \[ \Delta G^\circ = -3(96.5)(0.81) = -2.345 \times 10^2 \text{ kJ} = -2.3 \times 10^5 \text{ J} \]

\[ \ln K = \frac{-(2.345 \times 10^2 \text{ J})}{(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} = 94.65 = 95; \quad K = e^{95} \approx 1.3 \times 10^{41} = 10^{41} \]

(c) \[ 2[\text{Cr(OH)}_2(s) + 5\text{OH}^-(aq) \rightarrow \text{CrO}_4^{2-}(aq) + 4\text{H}_2\text{O}(l) + 3e^-] \quad E_{\text{red}}^\circ = -0.13 \text{ V} \]
\[ 3[\text{ClO}^-(aq) + \text{H}_2\text{O}(l) + 2e^- \rightarrow \text{Cl}^-(aq) + 2\text{OH}^-(aq)] \quad E_{\text{red}}^\circ = 0.89 \text{ V} \]
\[ 2\text{Cr(OH)}_2(s) + 3\text{ClO}^-(aq) + 4\text{OH}^-(aq) \rightarrow 2\text{CrO}_4^{2-}(aq) + 3\text{Cl}^-(aq) + 5\text{H}_2\text{O}(l) \]

E° = 0.89 - (-0.13) = 1.02 V; \[ \Delta G^\circ = -6(96.5)(1.02) = -590.58 \text{ kJ} = -5.91 \times 10^5 \text{ J} \]

\[ \ln K = \frac{-(5.9058 \times 10^5 \text{ J})}{(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} = 238.37 = 238; \quad K = 3.3 \times 10^{103} = 10^{103} \]

This is an unimaginably large number.

20.49 Analyze/Plan. Given K, calculate \( \Delta G^\circ \) and E°. Reverse the logic in Sample Exercise 20.10.

According to Equation [19.22], \( \Delta G^\circ = -RT \ln K \). According to Equation [20.12],
\( \Delta G^\circ = -nF E^\circ \), \( E^\circ = -\Delta G^\circ /nF \). Solve.

\[ K = 1.5 \times 10^{-4} \]
\[ \Delta G^\circ = -RT \ln K = -(8.314 \text{ J/mol}\cdot\text{K})(298) \ln (1.5 \times 10^{-4}) = 2.181 \times 10^4 \text{ J} = 21.8 \text{ kJ} \]
\[ E^\circ = -\Delta G^\circ /nF; \quad n = 2; \quad F = 96.5 \text{ kJ/mol e}^- \]
\[ E^\circ = \frac{-21.81 \text{ kJ}}{2 \text{ mol e}^- \times 96.5 \text{ kJ/V mol e}^-} = -0.113 \text{ V} \]

Check. The unit of \( \Delta G^\circ \) is actually kJ/mol, which means kJ per ‘mole of reaction’, or for the reaction as written. Since we don’t have a specific reaction, we interpret the unit as referring to the overall reaction.

20.50 \[ K = 3.7 \times 10^6; \quad \Delta G^\circ = -RT \ln K; \quad E^\circ = -\Delta G^\circ /nF; \quad n = 1; \quad T = 298 \text{ K} \]
\[ \Delta G^\circ = -8.314 \text{ J/molK} \times 298 \text{ K} \times \ln (3.7 \times 10^6) = -3.747 \times 10^4 \text{ J} = -37.5 \text{ kJ} \]
\[ E^\circ = -\Delta G^\circ /nF = \left( \frac{-37.47 \text{ kJ}}{1 \text{ e}^- \times 96.5 \text{ kJ/V mol e}^-} \right) = 0.388 \text{ V} \]

20.51 Analyze. Given \( E_{\text{red}}^\circ \) values for half reactions, calculate the value of K for a given redox reaction.

Plan. Combine the relationships involving \( E^\circ \), \( \Delta G^\circ \) and K to get a direct relationship between \( E^\circ \) and K. For each reaction, calculate \( E^\circ \) from \( E_{\text{red}}^\circ \), then apply the relationship to calculate K.

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Solve. \( \Delta G^\circ = -nF\varepsilon^\circ, \Delta G^\circ = -RT \ln K; \ln K = 2.303 \log K \)

\[
- \varepsilon^\circ = -RT \ln K, \varepsilon^\circ = \frac{RT}{nF} \ln K = \frac{2.303RT}{nF} \log K
\]

From Equation [20.15] and [20.16], \( 2.303 \frac{RT}{nF} = 0.0592 \).

\[
\varepsilon^\circ = \frac{0.0592}{n} \log K; \log K = \frac{n\varepsilon^\circ}{0.0592}; K = 10^{\log K}
\]

(a) \( \varepsilon^\circ = -0.28 - (-0.440) = 0.16 \text{ V}, n = 2 (\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}) \)

\[
\log K = \frac{2(0.16)}{0.0592} = 5.4054 = 5.4; K = 2.54 \times 10^5 = 3 \times 10^5
\]

(b) \( \varepsilon^\circ = 0 - (-0.277) = 0.277 \text{ V}; n = 2 (2\text{H}^+ + 2e^- \rightarrow \text{H}_2) \)

\[
\log K = \frac{2(0.277)}{0.0592} = 9.358 = 9.36; K = 2.3 \times 10^9
\]

(c) \( \varepsilon^\circ = 1.51 - 1.065 = 0.445 = 0.45 \text{ V}; n = 10 (2\text{MnO}_4^- + 10e^- \rightarrow 2\text{Mn}^{2+}) \)

\[
\log K = \frac{10(0.445)}{0.0592} = 75.169 = 75; K = 1.5 \times 10^{75} = 10^{75}
\]

Check. Note that small differences in \( \varepsilon^\circ \) values lead to large changes in the magnitude of \( K \). Sig fig rules limit precision of \( K \) values; using \( \log \) instead of \( \ln \) leads to more sig figs in the \( K \) value. This result is strictly numerical and does not indicate any greater precision in the data.

\[
20.52 \quad \varepsilon^\circ = \frac{0.0592 \text{ V}}{n} \log K; \log K = \frac{n\varepsilon^\circ}{0.0592 \text{ V}}. \text{ See Solution 20.51 for a more complete explanation.}
\]

(a) \( \varepsilon^\circ = 1.00 \text{ V} - 0.799 \text{ V} = 0.201 = 0.20 \text{ V}; n = 1 (\text{VO}_2^+ + e^- \rightarrow \text{VO}^2+) \)

\[
\log K = \frac{1(0.210 \text{ V})}{0.0592 \text{ V}} = 3.3953 = 3.40; K = 2.48 \times 10^3 = 2.5 \times 10^3
\]

Note: The correctly balanced chemical equation for this reaction is

\[ \text{VO}_2^+(aq) + 2\text{H}^+(aq) + \text{Ag}(s) \rightarrow 2\text{VO}^2+(aq) + \text{H}_2\text{O}(l) + \text{Ag}^+(aq), \text{for which } n = 1. \]

(b) \( \varepsilon^\circ = 1.61 \text{ V} - 0.32 \text{ V} = 1.29 \text{ V}; n = 3 (3\text{Ce}^{4+} + 3e^- \rightarrow 3\text{Ce}^{3+}) \)

\[
\log K = \frac{3(1.29)}{0.0592} = 65.372 = 65.4; K = 2.35 \times 10^{65} = 2 \times 10^{65}
\]

(c) \( \varepsilon^\circ = 0.36 \text{ V} - (-0.23 \text{ V}) = 0.59 \text{ V}; n = 4 (4\text{Fe(CN)}_6^{3-} + 4e^- \rightarrow 4\text{Fe(CN)}_6^{4-}) \)

\[
\log K = \frac{4(0.59)}{0.0592} = 39.865 = 40; K = 7.3 \times 10^{39} = 10^{40}
\]

20.53 \( \quad \text{Analyze/Plan.} \quad \varepsilon^\circ = \frac{0.0592 \text{ V}}{n} \log K. \text{ See Solution 20.51 for a more complete development.} \)

\[
\log K = \frac{-n\varepsilon^\circ}{0.0592 \text{ V}}. \quad \text{Solve.}
\]

(a) \( \log K = \frac{1(0.177 \text{ V})}{0.0592 \text{ V}} = 2.9899 = 2.99; K = 9.8 \times 10^2 \)
20.54

E° = \frac{0.0592 \text{ V}}{n} \log K; \quad n = \frac{0.0592 \text{ V}}{E°} \log K. \quad \text{See Solution 20.51 for a more complete development.}

n = \frac{0.0592 \text{ V}}{0.17 \text{ V}} \log (5.5 \times 10^5); \quad n = 2

Cell EMF under Nonstandard Conditions

20.55 (a) The Nernst equation is applicable when the components of an electrochemical cell are at nonstandard conditions.

(b) \( Q = 1 \) if all reactants and products are at standard conditions.

(c) If concentration of reactants increases, \( Q \) decreases, and \( E \) increases.

20.56 (a) No. As the spontaneous chemical reaction of the voltaic cell proceeds, the concentrations of products increase and the concentrations of reactants decrease, so standard conditions are not maintained.

(b) Yes. The Nernst equation is applicable to cell EMF at nonstandard conditions, so it must be applicable at temperatures other than 298 K. There are two terms in the Nernst Equation. First, values of \( E^o \) at temperatures other than 298 K are required. Then, in the form of Equation [20.14], there is a variable for \( T \) in the second term. In the short-hand form of Equation [20.16], the value 0.0592 assumes 298 K. A different coefficient would apply to cells at temperatures other than 298 K.

(c) If concentration of products increases, \( Q \) increases, and \( E \) decreases.

20.57 Analyze/Plan. Given a circumstance, determine its effect on cell emf. Each circumstance changes the value of \( Q \). An increase in \( Q \) reduces emf; a decrease in \( Q \) increases emf.

Solve.

\[ \text{Zn(s) + 2H}^+(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{H}_2(g); \quad E = E^o - \frac{0.0592}{n} \log Q; \quad Q = \left[ \frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2} \right] \]

(a) \( P_{H_2} \) increases, \( Q \) increases, \( E \) decreases

(b) \([\text{Zn}^{2+}]\) increases, \( Q \) increases, \( E \) decreases

(c) \([\text{H}^+]\) decreases, \( Q \) increases, \( E \) decreases

(d) No effect; does not appear in the Nernst equation

20.58 \( \text{Al(s) + 3Ag}^+(aq) \rightarrow \text{Al}^{3+}(aq) + 3\text{Ag(s); \quad E = E^o - \frac{0.0592}{n} \log Q; \quad Q = \left[ \frac{[\text{Al}^{3+}]}{[\text{Ag}^+]^3} \right]} \]

Any change that causes the reaction to be less spontaneous (that causes \( Q \) to increase and ultimately shifts the equilibrium to the left) will result in a less positive value for \( E \).
(a) Increases $E$ by decreasing $[A{1}^{3-}]$ on the right side of the equation, which decreases $Q$.

(b) No effect; the "concentrations" of pure solids and liquids do not influence the value of $K$ for a heterogeneous equilibrium.

(c) No effect; the concentration of $Ag^+$ and the value of $Q$ are unchanged.

(d) Decreases $E$; forming $AgCl(s)$ decreases the concentration of $Ag^+$, which increases $Q$.

20.59 Analyze/Plan. Follow the logic in Sample Exercise 20.11. Solve.

(a) $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s) \quad E^{\circ}_{red} = -0.28 \ V$

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \quad E^{\circ}_{red} = -0.763 \ V$

$Ni^{2+}(aq) + Zn(s) \rightarrow Ni(s) + Zn^{2+}(aq) \quad E^\circ = -0.28 - (-0.763) = 0.483 = 0.48 \ V$

(b) $E = E^\circ - \frac{0.0592}{n} \log \left( \frac{[Zn^{2+}]}{[Ni^{2+}]} \right) \quad n = 2$

$E = 0.483 - \frac{0.0592}{2} \log \left( \frac{0.100}{3.00} \right) = 0.483 - \frac{0.0592}{2} \log (0.0333)$

$E = 0.483 - \frac{0.0592}{2} (-1.477) = 0.483 + 0.0437 = 0.527 = 0.53 \ V$

(c) $E = 0.483 - \frac{0.0592}{2} \log \left( \frac{0.900}{0.200} \right) = 0.483 - 0.0193 = 0.464 = 0.46 \ V$

20.60 (a) $3[Ce^{4+}(aq) + 1e^- \rightarrow Ce^{3+}(aq)] \quad E^{\circ}_{red} = 1.61 \ V$

$Cr(s) \rightarrow Cr^{3+}(aq) + 3e^- \quad E^{\circ}_{red} = -0.74 \ V$

$3Ce^{4+}(aq) + Cr(s) \rightarrow 3Ce^{3+}(aq) + Cr^{3+}(aq) \quad E^{\circ} = 1.61 - (-0.74) = 2.35 \ V$

(b) $E = E^\circ - \frac{0.0592}{n} \log \left( \frac{[Ce^{3+}]^3}{[Ce^{4+}]^3} \right) \quad n = 3$

$E = 2.35 - \frac{0.0592}{3} \log \left( \frac{0.010}{(2.0)^3} \right) = 2.35 - \frac{0.0592}{3} \log (1.250 \times 10^{-9})$

$E = 2.35 - \frac{0.0592}{3} (-8.903) = 2.35 + 0.176 = 2.53 \ V$

(c) $E = 2.35 - \frac{0.0592}{3} \log \left( \frac{0.85^3}{0.35^3} \right) = 2.35 - 0.0244 = 2.33 \ V$

20.61 Analyze/Plan. Follow the logic in Sample Exercise 20.11. Solve.

(a) $4[Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + 1e^-] \quad E^{\circ}_{red} = 0.771 \ V$

$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) \quad E^{\circ}_{red} = 1.23 \ V$

$4Fe^{2+}(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Fe^{3+}(aq) + 2H_2O(l) \quad E^{\circ} = 1.23 - 0.771 = 0.459 = 0.46 \ V$
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(b) \[ E = E^\circ - \frac{0.0592}{n} \log \left( \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]^4} \right) \]
\[ Q = \frac{[\text{Zn}^{2+}, \text{dilute}]}{[\text{Zn}^{2+}, \text{conc.}]} \]
\[ E = 0.459 \text{ V} - \frac{0.0592}{4} \log \left( \frac{(0.010)^4}{(1.3)^4 (3.2 \times 10^{-4})^4 (0.50)} \right) = 0.459 - \frac{0.0592}{4} \log (7.0 \times 10^5) \]
\[ E = 0.459 - \frac{0.0592}{4} (5.845) = 0.459 - 0.0865 = 0.3725 \text{ V} \]

20.62 (a) \[ 2[\text{Fe}^{3+} (aq) + 1 \text{ e}^- \rightarrow \text{Fe}^{2+} (aq)] \]
\[ \text{H}_2(g) \rightarrow 2\text{H}^+ (aq) + 2\text{e}^- \]
\[ 2\text{Fe}^{3+} (aq) + \text{H}_2(g) \rightarrow 2\text{Fe}^{2+} (aq) + 2\text{H}^+ (aq) \]
\[ E^\circ = 0.771 \text{ V} \]
\[ E_{\text{red}} = 0.000 \text{ V} \]
\[ E^\circ = 0.771 - 0.000 = 0.771 \text{ V} \]

(b) \[ E = E^\circ - \frac{0.0592}{n} \log \left( \frac{[\text{Fe}^{2+}]^2 [\text{H}^+]^2}{[\text{Fe}^{3+}]^2 [\text{H}^+]^2} \right) \]
\[ [\text{H}^+] = 10^{-pH} = 1.0 \times 10^{-5}, n = 2 \]
\[ E = 0.771 - \frac{0.0592}{2} \log \left( \frac{(0.0010)^2 (1.0 \times 10^{-5})^2}{(1.50)^2 (0.50)} \right) = 0.771 - \frac{0.0592}{2} \log (8.9 \times 10^{-17}) \]
\[ E = 0.771 - \frac{0.0592 (-16.05)}{2} = 0.771 + 0.4751 = 1.246 \text{ V} \]

20.63 Analyze/Plan. We are given a concentration cell with Zn electrodes. Use the definition of a concentration cell in Section 20.6 to answer the stated questions. Use Equation [20.16] to calculate the cell emf. For a concentration cell, \( Q = [\text{dilute}] / [\text{concentrated}] \). Solve.

(a) The compartment with the more dilute solution will be the anode. That is, the compartment with \([\text{Zn}^{2+}] = 1.00 \times 10^{-2} \text{ M}\) is the anode.

(b) Since the oxidation half-reaction is the opposite of the reduction half-reaction, \( E^\circ \) is zero.

(c) \[ E = E^\circ - \frac{0.0592}{n} \log Q; Q = [\text{Zn}^{2+}, \text{dilute}] / [\text{Zn}^{2+}, \text{conc.}] \]
\[ E = 0 - \frac{0.0592}{2} \log \left( \frac{1.00 \times 10^{-5}}{1.8} \right) = 0.0668 \text{ V} \]

(d) In the anode compartment, Zn(s) \( \rightarrow \) Zn\(^{2+}\)(aq), so \([\text{Zn}^{2+}]\) increases from \(1.00 \times 10^{-2} \text{ M}\). In the cathode compartment, Zn\(^{2+}\)(aq) \( \rightarrow \) Zn(s), so \([\text{Zn}^{2+}]\) decreases from 1.8 M.

20.64 (a) The compartment with 0.0150 M Cl\(^-\) (aq) is the cathode.

(b) \( E^\circ = 0 \text{ V} \)

(c) \[ E = E^\circ - \frac{0.0592}{n} \log Q; Q = [\text{Cl}^-, \text{dilute}] / [\text{Cl}^-, \text{conc.}] \]
\[ E = 0 - \frac{0.0592}{1} \log \left( \frac{0.0150}{2.55} \right) = -0.13204 = -0.1320 \text{ V} \]

(d) In the anode compartment, [Cl\(^-\)] will decrease from 2.55 M. In the cathode, [Cl\(^-\)] will increase from 0.0150 M.

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\[ E = E^0 - \frac{0.0592}{2} \log \frac{[Pb^2+]}{[Zn^{2+}]} \; E^0 = 0.0 \; V \Rightarrow (-0.763 \; V) = 0.763 \; V \]

\[ 0.684 = 0.763 - \frac{0.0592}{2} \times (\log [Pb^2+] [Zn^{2+}] - 2 \log [H^+]) \]

\[ = 0.763 - \frac{0.0592}{2} \times (-0.5686 - 2 \log [H^+]) \]

\[ 0.684 = 0.763 + 0.0168 + 0.0592 \log [H^+]; \log [H^+] = \frac{0.684 - 0.0168 - 0.763}{0.0592} \]

\[ \log [H^+] = -1.6188 = -1.6; [H^+] = 0.0241 = 0.02 \; M; \; pH = 1.6 \]

20.66 (a) \[ E^0 = -0.136 \; V \Rightarrow (-0.126 \; V) = -0.010 \; V; \; n = 2 \]

\[ 0.22 = -0.010 - \frac{0.0592}{2} \log \frac{[Pb^{2+}]}{[Sn^{2+}]} = -0.010 - \frac{0.0592}{2} \log \frac{[Pb^{2+}]}{1.00} \]

\[ \log [Pb^{2+}] = \frac{-0.23 (2)}{0.0592} = -7.770 = -7.8; [Pb^{2+}] = 1.7 \times 10^{-8} = 2 \times 10^{-8} \; M \]

(b) For PbSO₄(s), Ksp = [Pb²⁺][SO₄²⁻] = (1.0)(1.7 \times 10^{-8}) = 1.7 \times 10^{-8}

Batteries and Fuel Cells

20.67 (a) The emf of a battery decreases as it is used. This happens because the concentrations of products increase and the concentrations of reactants decrease. According to the Nernst equation, these changes increase Q and decrease Ecell.

(b) The major difference between AA- and D-size batteries is the amount of reactants present. The additional reactants in a D-size battery enable it to provide power for a longer time.

20.68 First, H₂O is a reactant in the cathodic half-reaction, so it must be present in some form. Additionally, liquid water enhances mobility of the hydroxide ion in the alkaline battery. OH⁻ is produced in the cathode compartment and consumed in the anode compartment. It must be available at all points where Zn(s) is being oxidized. If the Zn(s) near the separator is mostly reacted, OH⁻ must diffuse through the gel until it reaches fresh Zn(s). A small amount of H₂O(l) mobilizes OH⁻ so that redox can continue until reactants throughout the battery are depleted.

20.69 Analyze/Plan. Given mass of a reactant (Pb), calculate mass of product (PbO₂). This is a stoichiometry problem; we need the balanced equation for the chemical reaction that occurs in the lead-acid battery. Then, g Pb → mol Pb → mol PbO₂ → g PbO₂. Solve.

The overall cell reaction (Equation [20.19]) is:

\[ Pb(s) + PbO_2(s) + 2H^+ (aq) + 2HSO_4^- (aq) → 2PbSO_4(s) + 2H_2O(l) \]

\[ 402 \; g \; Pb \times \frac{1 \; mol \; Pb}{207.2 \; g \; Pb} \times \frac{1 \; mol \; PbO_2}{1 \; mol \; Pb} \times \frac{239.2 \; g \; PbO_2}{1 \; mol \; PbO_2} = 464 \; g \; PbO_2 \]
20.70 The overall cell reaction is:

\[ 2\text{MnO}_2(s) + \text{Zn}(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{MnO(OH)}(s) + \text{Zn(OH)}_2(s) \]

\[ 12.6\text{ g Zn} \times \frac{1 \text{ mol Zn}}{65.39 \text{ g Zn}} \times \frac{2 \text{ mol MnO}_2}{1 \text{ mol Zn}} \times \frac{86.94 \text{ g MnO}_2}{1 \text{ mol MnO}_2} = 33.5 \text{ g MnO}_2 \text{ reduced} \]

20.71 **Analyze/Plan.** We are given a redox reaction and asked to write half-reactions, calculate \( E^* \), and indicate whether Li(s) is the anode or cathode. Determine which reactant is oxidized and which is reduced. Separate into half-reactions, find \( E_{\text{red}}^* \) for the half-reactions from Appendix E and calculate \( E^* \). Solve.

(a) Li(s) is oxidized at the anode.

(b) \( \text{Ag}_2\text{CrO}_4(s) + 2e^- \rightarrow 2\text{Ag}(s) + \text{CrO}_4^{2-}(aq) \) \( E_{\text{red}}^* = 0.446 \text{ V} \)

\[ 2[\text{Li}(s) \rightarrow \text{Li}^+(aq) + e^-] \] \( E_{\text{red}}^* = -3.05 \text{ V} \)

\[ \text{Ag}_2\text{CrO}_4(s) + 2\text{Li}(s) \rightarrow 2\text{Ag}(s) + \text{CrO}_4^{2-}(aq) + 2\text{Li}^+(aq) \]

\[ E^* = 0.446 \text{ V} - (-3.05 \text{ V}) = 3.496 = 3.50 \text{ V} \]

(c) The emf of the battery, 3.5 V, is exactly the standard cell potential calculated in part (b).

(d) For this battery at ambient conditions, \( E \approx E^* \), so \( \log Q \approx 0 \). This makes sense because all reactants and products in the battery are solids and thus present in their standard states. Assuming that \( E^* \) is relatively constant with temperature, the value of the second term in the Nernst equation is \( \approx 0 \) at 37°C, and \( E = 3.5 \text{ V} \).

20.72 (a) \( \text{HgO(s)} + \text{Zn(s)} \rightarrow \text{Hg(l)} + \text{ZnO(s)} \)

(b) \[ E_{\text{cell}}^* = E_{\text{red}}^* \text{ (cathode)} - E_{\text{red}}^* \text{ (anode)} \]

\[ E_{\text{red}}^* \text{ (anode)} = E_{\text{red}}^* - E_{\text{cell}}^* = 0.098 - 1.35 = -1.25 \text{ V} \]

(c) \( E_{\text{red}}^* \) is different from \( \text{Zn}^{2+} (aq) + 2e^- \rightarrow \text{Zn}(s) (-0.76 \text{ V}) \) because in the battery the process happens in the presence of base and \( \text{Zn}^{2+} \) is stabilized as \( \text{ZnO(s)} \). Stabilization of a reactant in a half-reaction decreases the driving force, so \( E_{\text{red}}^* \) is more negative.

20.73 **Analyze/Plan.** (a) Consider the function of Zn in an alkaline battery. What effect would it have on the redox reaction and cell emf if Cd replaces Zn? (b) Both batteries contain Ni. What is the difference in environmental impact between Cd and the metal hydride? Solve.

(a) \( E_{\text{red}}^* \) for Cd (-0.40 V) is less negative than \( E_{\text{red}}^* \) for Zn (-0.76 V), so \( E_{\text{cell}}^* \) will have a smaller (less positive) value.

(b) NiMH batteries use an alloy such as \( \text{ZnNi}_2 \) as the anode material. This eliminates the use and concomitant disposal problems associated with Cd, a toxic heavy metal.

20.74 (a) The alkali metal Li has much greater metallic character than Zn, Cd, Pb or Ni. The reduction potential for Li is thus more negative, leading to greater overall
cell emf for the battery. Also, Li is less dense than the other metals, so greater
total energy for a battery can be achieved for a given total mass of material. One
disadvantage is that Li is very reactive and the cell reactions are difficult to
control.

(b) Li has a much smaller molar mass (6.94 g/mol) than Ni (58.69 g/mol). A Li-ion
battery can have many more charge-carrying particles than a Ni-based battery
with the same mass. That is, Li-ion batteries have a greater energy density than Ni-
based batteries.

20.75 The main advantage of a H₂-O₂ fuel cell over an alkaline battery is that the fuel cell is
not a closed system. Fuel, H₂, and oxidant, O₂ are continuously supplied to the fuel
cell, so that it can produce electrical current for a time limited only by the amount of
available fuel. An alkaline battery contains a finite amount of reactant and produces
current only until the reactants are spent, or reach equilibrium.

Alkaline batteries are much more convenient, because they are self-contained. Fuel cells
require a means to acquire and store volatile and explosive H₂(g). Disposal of spent
alkaline batteries, which contain zinc and manganese solids, is much more problematic.
H₂-O₂ fuel cells produce only H₂O(l), which is not a disposal problem.

20.76 No. The fuel in a fuel cell must be fluid, either gas or liquid. Because fuel must be
continuously supplied to the fuel cell, it must be capable of flow; the fuel cannot be
solid.

Corrosion

20.77 Analyze/Plan. (a) Decide which reactant is oxidized and which is reduced. Write the
balanced half-reactions and assign the appropriate one as anode and cathode. (b) Write
the balanced half-reaction for Fe²⁺(aq) → Fe₃O₃ • 3H₂O. Use the reduction half-
reaction from part (a) to obtain the overall reaction. Solve.

(a) anode: Fe(s) → Fe²⁺(aq) + 2e⁻
cathode: O₂(g) + 4H⁺(aq) + 4e⁻ → 2H₂O(l)

(b) 2Fe²⁺(aq) + 6H₂O(l) → Fe₃O₃ • 3H₂O(s) + 6H⁺(aq) + 2e⁻
O₂(g) + 4H⁺(aq) + 4e⁻ → 2H₂O(l)

(Multiply the oxidation half-reaction by two to balance electrons and obtain the
overall balanced reaction.)

20.78 (a) Calculate E°cell for the given reactants at standard conditions.

O₂(g) + 4H⁺(aq) + 4 e⁻ → 2H₂O(l) \hspace{1cm} E°_\text{red} = 1.23 \text{ V}

2[\text{Cu(s)} → \text{Cu}^{2+}(aq) + 2e⁻] \hspace{1cm} E°_\text{red} = 0.337 \text{ V}

2\text{Cu(s)} + \text{O}_2(g) + 4\text{H}⁺(aq) → 2\text{Cu}^{2+}(aq) + 2\text{H}_2\text{O}(l) \hspace{1cm} E° = 1.23 - 0.337 = 0.89 \text{ V}

At standard conditions with O₂(g) and H⁺(aq) present, the oxidation of Cu(s) has
a positive E° value and is spontaneous. Cu(s) will oxidize (corrode) in air in the
presence of acid.
(b) Fe\(^{2+}\) has a more negative reduction potential (-0.440 V) than Cu\(^{2+}\) (+0.337 V), so Fe(s) is more readily oxidized than Cu(s). If the two metals are in contact, Fe(s) would act as a sacrificial anode and oxidize (corrode) in preference to Cu(s); this would weaken the iron support skeleton of the statue. The teflon spacers prevent contact between the two metals and insure that the iron skeleton doesn’t corrode when the Cu(s) skin comes in contact with atmospheric O\(_2\)(g) and H\(^+\)(aq).

20.79 (a) A "sacrificial anode" is a metal that is oxidized in preference to another when the two metals are coupled in an electrochemical cell; the sacrificial anode has a more negative \(E_{\text{red}}^\circ\) than the other metal. In this case, Mg acts as a sacrificial anode because it is oxidized in preference to the pipe metal; it is sacrificed to preserve the pipe.

(b) \(E_{\text{red}}^\circ\) for Mg\(^{2+}\) is -2.37 V, more negative than most metals present in pipes, including Fe (\(E_{\text{red}}^\circ = -0.44\) V) and Zn (\(E_{\text{red}}^\circ = -0.763\) V).

20.80 No. To afford cathodic protection, a metal must be more difficult to reduce (have a more negative reduction potential) than Fe\(^{2+}\). \(E_{\text{red}}^\circ\) Co\(^{2+}\) = -0.28 V, \(E_{\text{red}}^\circ\) Fe\(^{2+}\) = -0.44 V.

20.81 Analyze/Plan. Given the materials brass, composed of Zn and Cu, and galvanized steel, determine the possible spontaneous redox reactions that could occur when the materials come in contact. Calculate \(E^\circ\) values for these reactions.

Solve. The main metallic component of steel is Fe. Galvanized steel is steel plated with Zn. The three metals in question are Fe, Zn, and Cu; their \(E_{\text{red}}^\circ\) values are shown below.

- \(E_{\text{red}}^\circ\) Fe\(^{2+}\)(aq) = -0.440 V
- \(E_{\text{red}}^\circ\) Zn\(^{2+}\)(aq) = -0.763 V
- \(E_{\text{red}}^\circ\) Cu\(^{2+}\)(aq) = 0.337 V

Zn, with the most negative \(E_{\text{red}}^\circ\) value, can act as a sacrificial anode for either Fe or Cu. That is, Zn(s) will be preferentially oxidized when in contact with Fe(s) or Cu(s). For environmental corrosion, the oxidizing agent is usually O\(_2\)(g) in acidic solution, \(E_{\text{red}}^\circ = 1.23\) V. The pertinent reactions and their \(E^\circ\) values are:

- \(2\text{Zn}(s) + \text{O}_2(g) + 4\text{H}^+(aq) \rightarrow 2\text{Zn}^{2+}(aq) + 2\text{H}_2\text{O}(l)\)
  \(E^\circ = 1.23\) V - (-0.763 V) = 1.99 V
- \(2\text{Fe}(s) + \text{O}_2(g) + 4\text{H}^+(aq) \rightarrow 2\text{Fe}^{2+}(aq) + 2\text{H}_2\text{O}(l)\)
  \(E^\circ = 1.23\) V - (-0.440 V) = 1.67 V
- \(2\text{Cu}(s) + \text{O}_2(g) + 4\text{H}^+(aq) \rightarrow 2\text{Cu}^{2+}(aq) + 2\text{H}_2\text{O}(l)\)
  \(E^\circ = 1.23\) V - (0.337 V) = 0.893 V

Note, however, that Fe has a more negative \(E_{\text{red}}^\circ\) than Cu so when the two are in contact Fe acts as the sacrificial anode, and corrosion (of Fe) occurs preferentially. This is verified by the larger \(E^\circ\) value for the corrosion of Fe, 1.67 V, relative to the corrosion of Cu, 0.893 V. When the three metals Zn, Fe, and Cu are in contact, oxidation of Zn will happen first, followed by oxidation of Fe, and finally Cu.
20.82 The principal metallic component of steel is Fe. $E_{\text{red}}$ for Fe, -0.763 V, is more negative than that of Cu, 0.337 V. When the two are in contact, Fe acts as the sacrificial anode and corrodes (oxidizes) preferentially in the presence of $O_2(g)$.

$$2\text{Fe}(s) + O_2(g) + 4H^+(aq) \rightarrow 2\text{Fe}^{2+}(aq) + 2H_2O(l)$$

E° = 1.23 V - (-0.440 V) = 1.67 V

$$2\text{Cu}(s) + O_2(g) + 4H^+(aq) \rightarrow 2\text{Cu}^{2+}(aq) + 2H_2O(l)$$

E° = 1.23 V - (0.337 V) = 0.893 V

Both reactions are spontaneous, but the corrosion of Fe has the larger E° value and happens preferentially.

Electrolysis; Electrical Work

20.83 (a) Electrolysis is an electrochemical process driven by an outside energy source.

(b) Electrolysis reactions are, by definition, nonspontaneous.

(c) 2Cl⁻(l) → Cl₂(g) + 2e⁻

20.84 (a) An electrolytic cell is the vessel in which electrolysis occurs. It consists of a power source and two electrodes in a molten salt or aqueous solution.

(b) It is the cathode. In an electrolysis cell, as in a voltaic cell, electrons are consumed (via reduction) at the cathode. Electrons flow from the negative terminal of the voltage source and then to the cathode.

(c) A small amount of $H_2SO_4(aq)$ present during the electrolysis of water acts as a change carrier, or supporting electrolyte. This facilitates transfer of electrons through the solution and at the electrodes, speeding up the reaction. (Considering $H^+(aq)$ as the substance reduced at the cathode changes the details of the half-reactions, but not the overall E° for the electrolysis. $SO_4^{2-}(aq)$ cannot be oxidized.)

20.85 Analyze/Plan. Follow the logic in Sample Exercise 20.14, paying close attention to units. Coulombs = amps · s; since this is a 3e⁻ reduction, each mole of Cr(s) requires 3 Faradays. Solve.

(a) $7.60 \times 2.00 \times \frac{24 \text{ hr}}{1 \text{ d}} \times \frac{60 \text{ min}}{1 \text{ hr}} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{1 \text{ C}}{1 \text{ amp} \cdot \text{s}} \times \frac{1 \text{ F}}{96500 \text{ C}} \times \frac{1 \text{ mol Cr}}{3 \text{ F}} \times \frac{52.00 \text{ g Cr}}{1 \text{ mol Cr}} = 236 \text{ g Cr(s)}$

(b) $0.250 \text{ mol Cr} \times \frac{3 \text{ F}}{1 \text{ mol Cr}} \times \frac{96500 \text{ C}}{1 \text{ C}} \times \frac{1 \text{ amp} \cdot \text{s}}{8.00 \text{ hr}} \times \frac{1 \text{ hr}}{60 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} = 2.51 \text{ A}$

20.86 Coulombs = amps · s; since this is a 2e⁻ reduction, each mole of Mg(s) requires 2 Faradays.
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(a)  5.25 A × 2.50 d × \frac{24 \text{ hr}}{1 \text{ d}} × \frac{60 \text{ min}}{1 \text{ hr}} × \frac{60 \text{ s}}{1 \text{ min}} × \frac{1 \text{ C}}{1 \text{ amp}×\text{s}} × \frac{1 \text{ F}}{96,500 \text{ C}} × 1 \text{ mol Mg} × \frac{24.31 \text{ g Mg}}{1 \text{ mol Mg}} = 143 \text{ g Mg}

(b)  10.00 g Mg × \frac{24.31 \text{ g Mg}}{1 \text{ mol Mg}} × \frac{2 \text{ F}}{96,500 \text{ C}} × \frac{1 \text{ mol Mg}}{1 \text{ amp}×\text{s}} × \frac{1 \text{ min}}{60 \text{ s}} × \frac{1}{3.50 \text{ A}} = 378 \text{ min}

20.87 Analyze/Plan. Given a spontaneous chemical reaction, calculate the maximum possible work for a given amount of reactant at standard conditions. Separate the equation into half-reactions and calculate cell emf. Use Equation [20.19], \( w_{\text{max}} = -nFE \), to calculate maximum work. At standard conditions, \( E = E^0 \). Solve.

\[
\begin{align*}
I_2(s) + 2e^- & \rightarrow 2I^- (aq) \\
Sn(s) & \rightarrow Sn^{2+} (aq) + 2e^- \\
I_2(s) + Sn(s) & \rightarrow 2I^- (aq) + Sn^{2+} (aq)
\end{align*}
\]

\[
E_{\text{red}} = 0.536 \text{ V} \\
E_{\text{red}} = -0.136 \text{ V}
\]

\[
w_{\text{max}} = -2(96.5)(0.536) = -129.7 = -130 \text{ kJ/mol Sn}
\]

\[
\frac{129.7 \text{ kJ/mol Sn}}{75.0 \text{ g Sn}} × 75.0 \text{ g Sn} × \frac{1000 \text{ J}}{1 \text{ kJ}} = -8.19 × 10^4 \text{ J}
\]

Check. The (-) sign indicates that work is done by the cell.

20.88 For this cell at standard conditions, \( E^0 = 1.10 \text{ V} \).

\[
w_{\text{max}} = \Delta G^\circ = -nFE^0 = -2(96.5)(1.10) = -212.3 = -212 \text{ kJ/mol Cu}
\]

6.5 \times 10^3 \text{ A} \times 48 \text{ hr} \times \frac{3600 \text{ s}}{1 \text{ hr}} × \frac{1 \text{ C}}{1 \text{ amp}×\text{s}} × \frac{1 \text{ mol Li}}{96,500 \text{ C}} × \frac{1 \text{ F}}{1 \text{ F}} × \frac{6.94 \text{ g Li}}{1 \text{ mol Li}} × \frac{1 \text{ mol Li}}{0.85} = 3.961 × 10^5 = 4.0 × 10^5 \text{ g Li}

20.89 Analyze/Plan. Follow the logic in Sample Exercise 20.15, paying close attention to units. Solve.

(a)  7.5 \times 10^4 \text{ A} \times 24 \text{ hr} \times \frac{3600 \text{ s}}{1 \text{ hr}} × \frac{1 \text{ C}}{1 \text{ amp}×\text{s}} × \frac{1 \text{ F}}{96,500 \text{ C}} × \frac{1 \text{ mol Li}}{1 \text{ F}} × \frac{6.94 \text{ g Li}}{1 \text{ mol Li}} × \frac{1 \text{ mol Li}}{0.85} = 1.135 × 10^7

(b)  If the cell is 85% efficient, \( \frac{96,500 \text{ C}}{F} × \frac{1 \text{ F}}{0.85 \text{ mol}} = 1.135 × 10^5 \text{ C/mol Li required}

\[
\text{Energy} = 7.5 \text{ V} × \frac{1.135 × 10^5 \text{ C}}{\text{mol Li}} × \frac{1 \text{ F}}{1 \text{ C}×\text{V}} × \frac{1 \text{ kWh}}{3.6 × 10^6 \text{ J}} = 0.24 \text{ kWh/mol Li}
\]

20.90 (a)  6.5 \times 10^3 \text{ A} \times 48 \text{ hr} \times \frac{3600 \text{ s}}{1 \text{ hr}} × \frac{1 \text{ C}}{1 \text{ amp}×\text{s}} × \frac{1 \text{ F}}{96,500 \text{ C}} × \frac{1 \text{ mol Ca}}{2 \text{ F}} × \frac{40.08 \text{ g Ca}}{1 \text{ mol Ca}} × \frac{1 \text{ mol Ca}}{0.68} = 1.586 × 10^5 = 1.6 × 10^5 \text{ g Ca}

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(b) If the cell is 68% efficient, 
\[ \frac{96,500 \text{ C}}{F} \times \frac{2 \text{ F}}{0.68 \text{ mol Ca}} = 2.838 \times 10^5 \]

\[ = 2.8 \times 10^5 \text{ C/mol Ca required} \]

Energy = \[5.00 \text{ V} \times \frac{2.838 \times 10^5 \text{ C}}{\text{mol Ca}} \times \frac{1 \text{ kWh}}{3.6 \times 10^6 \text{ J}} = 0.3942 = 0.39 \text{ kWh} \]

Additional Exercises

20.91 (a) \[ \text{Ni}^{2+} \text{(aq) } + \text{e}^- \rightarrow \text{Ni(s)} \]
\[ \text{Ni}^2+ \text{(aq) } \rightarrow \text{Ni}^{2+} \text{(aq) } + \text{e}^- \]
\[ 2\text{Ni}^{2+} \text{(aq) } \rightarrow \text{Ni(s) } + \text{Ni}^{2+} \text{(aq)} \]

(b) \[ \text{MnO}_4^{-} \text{(aq) } + 4\text{H}^+ \text{(aq) } + 2\text{e}^- \rightarrow \text{MnO}_2 \text{(s) } + 2\text{H}_2\text{O(l)} \]

\[ 2[\text{MnO}_4^{-} \text{(aq) } \rightarrow \text{MnO}_2 \text{(aq) } + \text{e}^-] \]

\[ 3\text{MnO}_4^{-} \text{(aq) } + 4\text{H}^+ \text{(aq) } \rightarrow 2\text{MnO}_2 \text{(aq) } + \text{MnO}_2 \text{(s) } + 2\text{H}_2\text{O(l)} \]

(c) \[ \text{H}_2\text{SO}_3 \text{(aq) } + 4\text{H}^+ \text{(aq) } + 4\text{e}^- \rightarrow \text{S(s) } + 3\text{H}_2\text{O(l)} \]

\[ 2[\text{H}_2\text{SO}_3 \text{(aq) } + \text{H}_2\text{O(l)} \rightarrow \text{HSO}_4^{-} \text{(aq) } + 3\text{H}^+ \text{(aq) } + 2\text{e}^-] \]

\[ 3\text{H}_2\text{SO}_3 \text{(aq) } \rightarrow \text{S(s) } + 2\text{HSO}_4^{-} \text{(aq) } + 2\text{H}^+ \text{(aq) } + \text{H}_2\text{O(l)} \]

(d) \[ \text{Cl}_2 \text{(aq) } + 2\text{H}_2\text{O(l)} \rightarrow 2\text{ClO}^- \text{(aq) } + 4\text{H}^+ \text{(aq) } + 2\text{e}^- \]

\[ 4\text{OH}^- \text{(aq) } + 4\text{OH}^- \text{(aq) } \rightarrow 2\text{ClO}^- \text{(aq) } + 2\text{H}_2\text{O(l)} + 2\text{e}^- \]

\[ \text{Cl}_2 \text{(aq) } + 2\text{e}^- \rightarrow 2\text{Cl}^- \text{(aq) } \]

\[ 1/2[2\text{Cl}_2 \text{(aq) } + 4\text{OH}^- \text{(aq) } \rightarrow 2\text{Cl}^- \text{(aq) } + 2\text{ClO}^- \text{(aq) } + 2\text{H}_2\text{O(l)}] \]

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

20.92 (a)

\[ \text{Anode } (-) \quad \text{Cathode } (+) \]

\[ \text{e}^- \quad \text{e}^- \]

\[ \text{V} \]

\[ \text{Salt Bridge} \]

\[ \text{Pt} \quad \text{Fe}^{2+}, \text{Fe}^{3+} \quad \text{H}^+ \quad \text{MnO}_4^- \quad \text{Mn}^{2+} \]

\[ \text{anions} \quad \text{cations} \]

(b) 573
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(c) \( \text{MnO}_4^- (aq) + 8H^+ (aq) + 5e^- \rightarrow \text{Mn}^{2+} (aq) + 4H_2O(l) \) \( E'_{\text{red}} = 1.51 \text{ V} \)
\[ 5[\text{Fe}^{2+} (aq) \rightarrow \text{Fe}^{3+} (aq) + e^-] \] \( \text{E}^{o} = 0.771 \text{ V} \)
\[ E' = E^{o} - 0.0592 \frac{\log [\text{Fe}^{3+}] [\text{Mn}^{2+}]}{5[\text{MnO}_4^-] [H^+]^6] \text{; pH} = 0.0, [H^+] = 1.0 \]
\[ E = 0.74 \text{ V} - 0.0592 \frac{\log (2.5 \times 10^{-4})(0.010)}{5(1.50)(1.0)^6} = 0.74 \text{ V} + 0.01 \text{ V} = 0.75 \text{ V} \]

20.93 (a) \[ \text{Anode} \rightarrow \text{Cathode} \]
\[ \text{Fe(s)} \rightarrow \text{Fe}^{2+} (aq) + 2e^- \]
\[ 2\text{Ag}^+ (aq) + 2e^- \rightarrow 2\text{Ag(s)} \]
\[ \text{Fe(s)} + 2\text{Ag}^+ (aq) \rightarrow \text{Fe}^{2+} (aq) + 2\text{Ag(s)} \]

(b) \[ \text{Zn(s)} \rightarrow \text{Zn}^{2+} (s) + 2e^- \]
\[ 2\text{H}^+ (aq) + 2e^- \rightarrow \text{H}_2 (g) \]
\[ \text{Zn(s)} + 2\text{H}^+ (aq) \rightarrow \text{Zn}^{2+} (aq) + \text{H}_2 (g) \]

(c) \[ \text{Cu}^{2+} || \text{ClO}_3^- , \text{Cl}^- \text{Pt} \]
Here, both the oxidized and reduced forms of the cathode solution are in the same phase, so we separate them by a comma, and then indicate an inert electrode.

\[ \text{Anode} (-) \rightarrow \text{Cathode} (+) \]

20.94 We need in each case to determine whether \( E' \) is positive (spontaneous) or negative (nonspontaneous).
Solutions to Exercises

(a) \[ \text{I}_2(\text{aq}) + 2e^- \rightarrow 2\text{I}^- (\text{aq}) \quad E^\text{red} = -0.536 \text{ V} \]

\[ \text{Sn}(\text{aq}) \rightarrow \text{Sn}^{2+}(\text{aq}) + 2e^- \quad E^\text{red} = -0.136 \text{ V} \]

\[ \text{Sn}(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow \text{Sn}^{2+}(\text{aq}) + 2\text{I}^- (\text{aq}) \quad E^\circ = 0.536 - (-0.136) = 0.672 \text{ V, spontaneous} \]

(b) \[ \text{Ni}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Ni}(\text{aq}) \quad E^\text{red} = -0.28 \text{ V} \]

\[ 2\text{I}^- (\text{aq}) \rightarrow \text{I}_2(\text{aq}) + 2e^- \quad E^\text{red} = 0.536 \text{ V} \]

\[ \text{Ni}^{2+}(\text{aq}) + 2\text{I}^- (\text{aq}) \rightarrow \text{Ni}(\text{aq}) + \text{I}_2(\text{aq}) \quad E^\circ = -0.28 - 0.536 = -0.82 \text{ V, nonspontaneous} \]

(c) \[ 2[\text{Ce}^{4+}(\text{aq}) + 1e^- \rightarrow \text{Ce}^{3+}(\text{aq})] \quad E^\text{red} = 1.61 \text{ V} \]

\[ \text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2e^- \quad E^\text{red} = -0.68 \text{ V} \]

\[ 2\text{Ce}^{4+}(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{Ce}^{3+}(\text{aq}) + \text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) \quad E^\circ = 1.61 - 0.68 = 0.93 \text{ V, spontaneous} \]

(d) \[ \text{Cu}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Cu}(\text{aq}) \quad E^\text{red} = 0.337 \text{ V} \]

\[ \text{Sn}^{2+}(\text{aq}) \rightarrow \text{Sn}^{4+}(\text{aq}) + 2e^- \quad E^\text{red} = -0.154 \text{ V} \]

\[ \text{Cu}^{2+}(\text{aq}) + \text{Sn}^{2+}(\text{aq}) \rightarrow \text{Cu}(\text{aq}) + \text{Sn}^{4+}(\text{aq}) \quad E^\circ = 0.337 - 1.54 = 0.183 \text{ V, spontaneous} \]

20.95 (a) The reduction potential for \( \text{O}_2(\text{g}) \) in the presence of acid is 1.23 V. \( \text{O}_2(\text{g}) \) cannot oxidize \( \text{Au}(\text{s}) \) to \( \text{Au}^{3+}(\text{aq}) \) or \( \text{Au}^{3+}(\text{aq}) \), even in the presence of acid.

(b) The possible oxidizing agents need a reduction potential greater than 1.50 V. These include \( \text{Co}^{3+}(\text{aq}) \), \( \text{F}_2(\text{g}) \), \( \text{H}_2\text{O}_2(\text{aq}) \), and \( \text{O}_3(\text{g}) \). Marginal oxidizing agents (those with reduction potential near 1.50 V) from Appendix E are \( \text{Br}_2(\text{aq}) \), \( \text{Ce}^{4+}(\text{aq}) \), \( \text{HClO}(\text{aq}) \), \( \text{MnO}_4^-(\text{aq}) \), and \( \text{PbO}_2(\text{s}) \).

(c) \[ 4\text{Au}(\text{s}) + 8\text{NaCN}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + \text{O}_3(\text{g}) \rightarrow 4\text{Na}[\text{Au(CN)}_2](\text{aq}) + 4\text{NaOH}(\text{aq}) \]

\[ \text{Au}(\text{s}) + 2\text{CN}^-(\text{aq}) \rightarrow \text{[Au(CN)}_2]^\text{-} + 1\text{e}^- \]

\[ \text{O}_3(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq}) \]

\( \text{Au}(\text{s}) \) is being oxidized and \( \text{O}_3(\text{g}) \) is being reduced.

(d) \[ 2[\text{Na}[\text{Au(CN)}_2](\text{aq}) + 1\text{e}^- \rightarrow \text{Au}(\text{s}) + 2\text{CN}^-(\text{aq}) + \text{Na}^+(\text{aq})] \]

\[ 2\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \quad 2[\text{Na}[\text{Zn}^{2+}(\text{aq})] + 2\text{Zn}(\text{s}) \rightarrow 2\text{Na}(\text{aq}) + \text{Zn}^{2+}(\text{aq}) + 2\text{Na}^+(\text{aq}) + 4\text{CN}^-(\text{aq}) \]

\( \text{Zn}(\text{s}) \) is being oxidized and \( \text{[Au(CN)}_2]^\text{-}(\text{aq}) \) is being reduced. While \( \text{OH}^-(\text{aq}) \) is not included in the redox reaction above, its presence in the reaction mixture probably causes \( \text{Zn(OH)}_2(\text{s}) \) to form as the product. This increases the driving force (and \( E^\circ \)) for the overall reaction.

20.96 (a) \[ 2[\text{Ag}^+(\text{aq}) + 1\text{e}^- \rightarrow \text{Ag}(\text{s})] \quad E^\text{red} = 0.80 \text{ V} \]

\[ \text{Ni}(\text{aq}) \rightarrow \text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \quad E^\text{red} = -0.28 \text{ V} \]

\[ 2\text{Ag}^+(\text{aq}) + \text{Ni}(\text{aq}) \rightarrow 2\text{Ag}(\text{s}) + \text{Ni}^{2+}(\text{aq}) \quad E^\circ = 0.80 - (-0.28) = 1.08 \text{ V} \]

(b) As the reaction proceeds, \( \text{Ni}^{2+}(\text{aq}) \) is produced, so \( [\text{Ni}^{2+}] \) increases as the cell operates.

(c) \[ E = E^\circ - \frac{0.0592}{n} \log K \]

\[ n = 1 \]

\[ K = 1.12 \]

\[ E = 0.80 - \frac{0.0592}{2} \log \left( \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2} \right) \]

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Solutions to Exercises

20.97 (a) 

\[ \frac{0.04(2)}{0.0592} = \log(0.0100) + \log([Ag^+])^2 \; \text{and} \; \log([Ag^+])^2 = \log(0.0100) + \frac{0.04(2)}{0.0592} \]

\( \log([Ag^+])^2 = -2.000 + 1.351 = -0.649; \; [Ag^+] = 0.255 \; \text{M}; \; [Ag^+] = 0.474 = 0.5 \; \text{M} \)

(Strictly speaking, \([E - E^0]\) having only one sig fig leads (after several steps) to the answer having only one sig fig. This is not a very precise or useful result.)

(b) Since the cell potential is negative at these concentration conditions, the cell would be spontaneous in the opposite direction and the inert electrode in the \(I_2/\text{I}^-\) compartment would be the anode; Cu(s) would be the cathode.

(c) No. At standard conditions the cell reaction is as written in part (a) and Cu(s) is the anode.

(d) 

\[ E = E^0 + 0.0592 \log Q = 0.15 - \frac{0.0592}{2} \log [Cu^+]^2 [I^-]^2 \]

\[ E = +0.015 - \frac{0.0592}{2} \log (2.5)^2 (3.5)^2 = +0.015 - 0.056 = -0.041 \; \text{V} \]

20.98 Both \(E^0\) and \(K\) are related to \(\Delta G^\circ\). (See Solution 20.51.)

\[ \Delta G^\circ = -nFE^0; \; \Delta G^\circ = -RT \ln K \]

\[-nFE^0 = -RT \ln K, \; E^0 = \frac{RT}{nF} \ln K \]

In terms of base 10 logs, \(\ln K = 2.303 \log K\).

\[ E^0 = \frac{2.303 RT}{nF} \log K \]

From the development of the Nernst equation,

\[ \frac{2.303 RT}{F} = 0.0592, \; E^0 = \frac{0.0592}{n} \log K \]

20.99 Use the relationship developed in Solution 20.98 to calculate \(K\) from \(E^0\). Use data from Appendix E to calculate \(E^0\) for the disproportionation.

\[ \text{Cu}^+(aq) + \text{e}^- \rightarrow \text{Cu}(s) \quad \text{\(E^0_{\text{red}} = 0.521 \; \text{V}\)} \]

\[ \text{Cu}^+(aq) \rightarrow \text{Cu}^{2+}(aq) + \text{e}^- \quad \text{\(E^0_{\text{red}} = 0.153 \; \text{V}\)} \]

\[ 2\text{Cu}^+(aq) \rightarrow \text{Cu}(s) + \text{Cu}^{2+}(aq) \quad \text{\(E^0 = 0.521 \; \text{V} - 0.153 \; \text{V} = 0.368 \; \text{V}\)} \]

\[ E^0 = \frac{0.0592}{n} \log K, \; \log K = \frac{-nE^0}{0.0592} = \frac{1 \times 0.368}{0.0592} = 6.216 = 6.22 \]

\[ K = 10^{6.216} = 1.6 \times 10^6 \]
20.100  (a) False. For standard cell potentials derived from $E_{\text{red}}^{*}$ values listed in Appendix E, the maximum $E_{\text{cell}}$ value is 5.92 V. This reaction involves $F_{2}(g)$, the element with the largest positive $E_{\text{red}}^{*}$, and Li, the element with the most negative $E_{\text{red}}^{*}$. Other species stable in aqueous solution will have $E_{\text{cell}}^{*}$ values between these two limiting values, so other possible $E_{\text{cell}}^{*}$ values would be less than 5.92 V. Aqueous $E_{\text{cell}}^{*}$ values are not likely to exceed 5.92 V.

(b) False. The effect of concentration of voltage is given by the Nernst equation: $E = E^{0} - \frac{0.0592}{n} \log Q$, where $Q$ is the reaction quotient which incorporates concentrations. Clearly $E$ is not directly proportional to either individual concentrations or $Q$.

(c) True. Oxidizing agents are themselves reduced. The strength of an oxidizing agent is measured by the magnitude of its reduction potential, $E_{\text{red}}^{*}$.

20.101  (a) In discharge: Cd(s) + 2NiO(OH)(s) + 2H₂O(l) $\rightarrow$ Cd(OH)₂(s) + 2Ni(OH)₂(s)

In charging, the reverse reaction occurs.

(b) $E^{0} = 0.49 \text{ V} - (-0.76 \text{ V}) = 1.25 \text{ V}$

(c) The 1.25 V calculated in part (b) is the standard cell potential, $E^{0}$. The concentrations of reactants and products inside the battery are adjusted so that the cell output is greater than $E^{0}$. Note that most of the reactants and products are pure solids or liquids, which do not appear in the $Q$ expression. It must be $[\text{OH}^{-}]$ that is other than 1.0 M, producing an emf of 1.30 rather than 1.25.

(d) $E^{*} = \frac{0.0592}{n} \log K$; $\log K = \frac{nE^{0}}{0.0592}$

$\log K = \frac{2 \times 1.25}{0.0592} = 42.23 = 42.2$; $K = 1.7 \times 10^{42} = 2 \times 10^{42}$

20.102  The ship’s hull should be made negative. By keeping an excess of electrons in the metal of the ship, the tendency for iron to undergo oxidation, with release of electrons, is diminished. The ship, as a negatively charged “electrode,” becomes the site of reduction, rather than oxidation, in an electrolytic process.

20.103  It is well established that corrosion occurs most readily when the metal surface is in contact with water. Thus, moisture is a requirement for corrosion. Corrosion also occurs more readily in acid solution, because $O_{2}$ has a more positive reduction potential in the presence of $H^{+}(aq)$. $SO_{2}$ and its oxidation products dissolve in water to produce acidic solutions, which encourage corrosion. The anodic and cathodic reactions for the corrosion of Ni are:

$\text{Ni(s)} \rightarrow \text{Ni}^{2+}(aq) + 2e^{-}$  $E_{\text{red}}^{*} = -0.28 \text{ V}$

$O_{2}(g) + 4H^{+}(aq) + 4e^{-} \rightarrow 2H_{2}O(l)$  $E^{*} = 1.23 \text{ V}$

Nickel(II) oxide, NiO(s), can form by the dry air oxidation of Ni. This NiO coating serves to protect against further corrosion. However, NiO dissolves in acidic solutions such as those produced by $SO_{2}$ or $SO_{3}$, according to the reaction:

$\text{NiO(s)} + 2H^{+}(aq) \rightarrow \text{Ni}^{2+}(aq) + H_{2}O(l)$. This exposes Ni(s) to further wet corrosion.
20.104 A battery is a voltaic cell, so the cathode compartment contains the positive terminal of the battery. In the alkaline, Ni-Cd and NiMH batteries, \( \text{OH}^-\) (aq) is produced at the cathode. The wire that turns the indicator pink is in contact with \( \text{OH}^-\) (aq), so the rightmost wire is connected to the positive terminal of the battery. [The battery could not be a lead-acid battery because \( \text{OH}^-\) (aq) is not present in either compartment, so neither wire would turn the indicator pink.]

20.105 (a) Total volume of Cr = \(2.5 \times 10^{-4} \text{ m} \times 0.32 \text{ m}^2 = 8.0 \times 10^{-5} \text{ m}^3\)

\[
\text{mol Cr} = \frac{8.0 \times 10^{-5} \text{ m}^3 \times 10^2 \text{ cm}^3}{1 \text{ m}^3} \times \frac{7.20 \text{ g Cr}}{1 \text{ cm}^3} \times \frac{1 \text{ mol Cr}}{52.0 \text{ g Cr}} = 11.077
\]

\[
= 11 \text{ mol Cr}
\]

The electrode reaction is:

\[
\text{CrO}_4^{2-}(aq) + 4\text{H}_2\text{O}(l) + 6e^- \rightarrow \text{Cr}(s) + 8\text{OH}^-\) (aq)
\]

Coulombs required = 11.077 \text{ mol Cr} \times \frac{6 \text{ F}}{1 \text{ mol Cr}} \times \frac{96,500 \text{ C}}{1 \text{ F}} = 6.41 \times 10^6

\[
= 6.4 \times 10^6 \text{ C}
\]

(b) \(6.41 \times 10^6 \text{ C} \times \frac{1 \text{ amp} \times \text{s}}{1 \text{ C}} \times \frac{1}{10.0 \text{ s}} = 6.4 \times 10^5 \text{ amp}
\]

(c) If the cell is 65% efficient, \((6.41 \times 10^6 \text{ C}/0.65) = 9.867 \times 10^6 \text{ C} = 9.9 \times 10^6 \text{ C}\) are required to plate the bumper.

\[
6.0 \text{ V} \times 9.867 \times 10^6 \text{ C} \times \frac{1 \text{ kW h}}{1 \text{ C} \times \text{ V} \times \frac{1 \text{ J}}{3.6 \times 10^6}} = 16.445 = 16 \text{ kWh}
\]

20.106 (a) The work obtainable is given by the product of the voltage, which has units of \(\text{J/C}\), times the number of Coulombs of electricity produced:

\[
\text{w}_{\text{max}} = 300 \text{ amp} \times \text{hr} \times \frac{3600 \text{ s}}{1 \text{ hr}} \times \frac{1 \text{ C}}{1 \text{ amp} \times \text{s}} 
\times \frac{6 \text{ J}}{1 \text{ C} \times \text{V} \times \frac{1 \text{ kW h}}{3.6 \times 10^6}} = 1.8 \text{ kW h} = 2 \text{ kWh}
\]

(b) This maximum amount of work is never realized because some of the electrical energy is dissipated in overcoming the internal resistance of the battery, because the cell voltage does not remain constant as the reaction proceeds, and because the systems to which the electrical energy is delivered are not capable of completely converting electrical energy into work.

20.107 (a) 7 \( \times 10^8 \) mol \( \text{H}_2\) \times \(\frac{2 \text{ F}}{1 \text{ mol} \text{H}_2} \times \frac{96,500 \text{ C}}{1 \text{ F}} = 1.35 \times 10^{14} = 1 \times 10^{14} \text{ C}
\]

(b) 2\(\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4e^-\)  \(E^\circ_{\text{red}} = 1.23 \text{ V}\)

\[
\frac{2[2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g)]}{2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 2\text{H}_2(g)} \frac{E^\circ_{\text{red}} = 0 \text{ V}}{E^\circ = 0.00 - 1.23 = -1.23 \text{ V}}
\]

\(P_\text{H}_2 = 300 \text{ atm} = P_{\text{O}_2} + P_{\text{H}_2}\). Since \(\text{H}_2(g)\) and \(\text{O}_2(g)\) are generated in a 2:1 mole ratio, \(P_{\text{H}_2} = 200 \text{ atm}\) and \(P_{\text{O}_2} = 100 \text{ atm}\).
20.108 \[2[\text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3e^- \rightarrow \text{NO}(g) + 2\text{H}_2\text{O}(l)] \quad E^\circ_{\text{red}} = 0.96 \text{ V}\]
\[3\text{Cu}(s) \rightarrow \text{Cu}^{2+}(aq) + 2e^- \quad E^\circ_{\text{red}} = 0.34 \text{ V}\]
\[3\text{Cu}(s) + 2\text{NO}_3^-(aq) + 8\text{H}^+(aq) \rightarrow 3\text{Cu}^{2+}(aq) + 2\text{NO}(g) + 4\text{H}_2\text{O}(l) \quad E^\circ = 0.96 - 0.34 = 0.62 \text{ V}\]
\[2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g) \quad E^\circ = 0 \text{ V}\]
\[\text{Cu}(s) \rightarrow \text{Cu}^{2+}(aq) + 2e^- \quad E^\circ_{\text{red}} = 0.34 \text{ V}\]
\[\text{Cu}(s) + 2\text{H}^+(aq) \rightarrow \text{Cu}^{2+}(aq) + \text{H}_2(g) \quad E^\circ = 0 - 0.34 = -0.34 \text{ V}\]

The overall cell potential for the oxidation of Cu(s) by HNO₃ is positive and the reaction is spontaneous. The cell potential for the oxidation of Cu(s) by HCl is negative and the reaction is nonspontaneous. Note that in the reaction with HNO₃, it is NO₃⁻ that is reduced, not H⁺; Cl⁻ from HCl cannot be further reduced.

20.109 \[\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)\]
(a) The oxidation number of H₂(g) and N₂(g) is 0. The oxidation number of N in NH₃ is -3, H in NH₃ is +1. H₂ is being oxidized and N₂ is being reduced.
(b) Calculate \(\Delta G^\circ\) from \(\Delta G^\circ_{i}\) values in Appendix C. Use \(\Delta G^\circ = -RT \ln K\) to calculate K.
\[
\Delta G^\circ = 2\Delta G^\circ_{\text{NH}_3(g)} - \Delta G^\circ_{\text{N}_2(g)} - 3\Delta G^\circ_{\text{H}_2(g)}
\]
\[
\Delta G^\circ = 2(-16.66 \text{ kJ}) - 0 - 3(0) = -33.32 \text{ kJ}
\]
\[
\Delta G^\circ = -RT \ln K, \ln K = \frac{-\Delta G^\circ}{RT} = \frac{-(-33.32 \times 10^3 \text{ J})}{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} = 13.4487 = 13.45
\]
\[K = e^{13.4487} = 6.9 \times 10^5\]
(c) \(\Delta G^\circ = -nFE^\circ\), \(E^\circ = \frac{-\Delta G^\circ}{nF}\)
\[n = 7 \text{ N atoms change from 0 to } -3, \text{ or 6 H atoms change from 0 to } +1. \text{ Either way, } n = 6.
\]
\[E^\circ = \frac{-(-33.32 \text{ kJ})}{6 \times 96.5 \text{ kJ/V}} = 0.05755 \text{ V}\]
20.110 The redox reaction is: \( 2\text{Ag}^+(aq) + \text{H}_2(g) \rightarrow 2\text{Ag}(s) + 2\text{H}^+(aq) \). \( n = 2 \) for this reaction.

\[
E = E^\circ - \frac{0.0592}{n} \log \frac{[\text{H}^+]^2}{[\text{Ag}^+]^2 P_{\text{H}_2}}
\]

\([\text{H}^+]\) [in the cell is held essentially constant by the benzoate buffer.

\[
K_a = \frac{[\text{H}^+][\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} = \frac{0.10 \text{ M}}{0.050 \text{ M}} \times K_a = 2K_a
\]

Solve the Nernst expression for \([\text{H}^+]\) and calculate \( K_a \) and \( pK_a \) as shown above.

\[
1.030 \text{ V} = 0.799 \text{ V} - \frac{0.0592}{2} \log \frac{[\text{H}^+]^2}{(1.00)^2(1.00)}
\]

\[
0.231 = -2 \log [\text{H}^+] = -2 \log (10^{-x})
\]

\[
0.231 = -\log [\text{H}^+] = \text{pH}; \text{pH} = 3.902 = 10^{-3.902} = 1.253 \times 10^{-4} = 1.3 \times 10^{-4};
\]

\([\text{H}^+] = 2K_a, K_a = [\text{H}^+] / 2 = 6.265 \times 10^{-5} = 6.3 \times 10^{-5}; pK_a = 4.20
\]

Check. According to Appendix D, \( K_a \) for benzoic acid is \( 6.3 \times 10^{-5} \).

20.111 (a) The oxidation potential of \( \text{A} \) is equal in magnitude but opposite in sign to the reduction potential of \( \text{A}^+ \).

(b) \( \text{Li}(s) \) has the highest oxidation potential, \( \text{Au}(s) \) the lowest.

(c) The relationship is reasonable because both oxidation potential and ionization energy describe removing electrons from a substance. Ionization energy is a property of gas phase atoms or ions, while oxidation potential is a property of the bulk material.

20.112 (a) \( \text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3e^- \rightarrow \text{NO}(g) + 2\text{H}_2\text{O}(l) \) \( E^\circ = 0.96 \text{ V} \)

\[
\frac{\text{Au}(s) + \text{NO}_3^-(aq) + 4\text{H}^+(aq) \rightarrow \text{Au}^{3+}(aq) + 3e^-}{E^\circ = 1.498 \text{ V}}
\]

\[
E^0 = 0.96 - 1.498 = -0.54 \text{ V}; E^0 \text{ is negative, the reaction is not spontaneous.}
\]

(b) \( 3[2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g)] \) \( E^\circ = 0.000 \text{ V} \)

\[
\frac{2[\text{Au}(s) + 4\text{Cl}^-(aq) \rightarrow \text{AuCl}_4^-(aq) + 3e^-]}{E^\circ = 1.002 \text{ V}}
\]

\[
E^0 = 0.000 - 1.002 = -1.002 \text{ V}; E^0 \text{ is negative, the reaction is not spontaneous.}
\]

(c) \( \text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3e^- \rightarrow \text{NO}(g) + 2\text{H}_2\text{O}(l) \) \( E^\circ = 0.96 \text{ V} \)

\[
\frac{\text{Au}(s) + 4\text{Cl}^-(aq) \rightarrow \text{AuCl}_4^-(aq) + 3e^-}{E^\circ = 1.002 \text{ V}}
\]

\[
E^0 = 0.96 - 1.002 = -0.04 \text{ V}; E^0 \text{ is small but negative, the process is not spontaneous.}
\]
20.113 (a) 
\[
\begin{align*}
\text{Ag}^+(aq) + e^- &\rightarrow \text{Ag}(s) & E_{\text{red}} = 0.799 \text{ V} \\
\text{Fe}^{2+}(aq) &\rightarrow \text{Fe}^{3+}(aq) + e^- & E_{\text{red}} = 0.771 \text{ V}
\end{align*}
\]
\[
\text{Ag}^+(aq) + \text{Fe}^{2+}(aq) \rightarrow \text{Ag}(s) + \text{Fe}^{3+}(aq) &\rightarrow \text{Fe}^{2+}(aq) + \text{Ag}(s)
\]

(b) Ag\(^{+}(aq)\) is reduced at the cathode and Fe\(^{2+}(aq)\) is oxidized at the anode.

(c) \(\Delta G^o = -nFE\) = -(1)(96.5)(0.028) = -2.7 kJ

\[
\begin{align*}
\Delta S^o &= S^o \text{Ag}(s) + S^o \text{Fe}^{3+}(aq) - S^o \text{Ag}^+(aq) - S^o \text{Fe}^{2+}(aq) \\
&= 42.55 \text{ J} + 293.3 \text{ J} - 73.93 \text{ J} - 113.4 \text{ J} = 148.5 \text{ J}
\end{align*}
\]

\(\Delta G^o = \Delta H^o - T\Delta S^o\) Since \(\Delta S^o\) is positive, \(\Delta G^o\) will become more negative and \(E^o\) will become more positive as temperature is increased.

20.114 (a) \(\Delta H^o = 2\Delta H^o \text{H}_2\text{O}(l) - 2\Delta H^o \text{H}_2(g) - \Delta H^o \text{O}_2(g) = 2(-285.83) - 2(0) - 0 = -571.66 \text{ kJ}\)

\[
\begin{align*}
\Delta S^o &= 2S^o \text{H}_2\text{O}(l) - 2S^o \text{H}_2(g) - \Delta S^o \text{O}_2(g) \\
&= 2(69.91) - 2(130.58) - (205.0) = -326.34 \text{ J}
\end{align*}
\]

(b) Since \(\Delta S^o\) is negative, \(-T\Delta S^o\) is positive and the value of \(\Delta G\) will become more positive as \(T\) increases. The reaction will become nonspontaneous at a fairly low temperature, because the magnitude of \(\Delta S^o\) is large.

(c) \(\Delta G = w_{\text{max}}\). The larger the negative value of \(\Delta G\), the more work the system is capable of doing on the surroundings. As the magnitude of \(\Delta G\) decreases with increasing temperature, the usefulness of \(\text{H}_2\) as a fuel decreases.

(d) The combustion method increases the temperature of the system, which quickly decreases the magnitude of the work that can be done by the system. Even if the effect of temperature on this reaction could be controlled, only about 40% of the energy from any combustion can be converted to electrical energy, so combustion is intrinsically less efficient than direct production of electrical energy via a fuel cell.

20.115 First balance the equation:

\[
4\text{CyFe}^{3+}(aq) + \text{O}_2(g) + 4\text{H}^+(aq) \rightarrow 4\text{CyFe}^{3+}(aq) + 2\text{H}_2\text{O}(l); E = +0.60 \text{ V}; n = 4
\]

(a) From Equation [20.11] we can calculate \(\Delta G\) for the process under the conditions specified for the measured potential \(E\):

\[
\Delta G = -nFE = -(4 \text{ mol e}^-) \times \frac{96.5 \text{ kJ}}{1 \text{ V} \cdot \text{mol e}^-} 
\times (0.60 \text{ V}) = -231.6 = -232 \text{ kJ}
\]

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The moles of ATP synthesized per mole of O₂ is given by:

\[
\frac{231.6 \text{ kJ}}{37.7 \text{ kJ}} \times 1 \text{ mol ATP formed} \approx 6 \text{ mol ATP/mol O₂}
\]

20.116

\[
\begin{align*}
\text{AgSCN(s)} + e^- &\rightarrow \text{Ag(s)} + \text{SCN}^- (aq) & E_{\text{red}}^\circ &= 0.0895 \text{ V} \\
\text{Ag(s)} + \text{Ag}^- (aq) + e^- &\rightarrow \text{Ag}^+ (aq) + \text{SCN}^- (aq) & E_{\text{red}}^\circ &= 0.799 \text{ V} \\
\text{AgSCN(s)} &\rightarrow \text{Ag}^+ (aq) + \text{SCN}^- (aq) & E^\circ &= 0.0895 - 0.799 = -0.710 \text{ V}
\end{align*}
\]

\[
E^\circ = \frac{0.0592}{n} \log K_{sp}; \log K_{sp} = \frac{(-0.710)(1)}{0.0592} = -11.993 = -12.0
\]

\[
K_{sp} = 10^{-11.993} = 1.02 \times 10^{-12} = 1 \times 10^{-12}
\]

20.117

The reaction can be written as a sum of the steps:

\[
\begin{align*}
\text{Pb}^{2+}(aq) + 2e^- &\rightarrow \text{Pb}(s) & E_{\text{red}}^\circ &= -0.126 \text{ V} \\
\text{PbS(s)} &\rightarrow \text{Pb}^{2+}(aq) + S^{2-}(aq) & E^\circ &= ? \\
\text{PbS(s)} + 2e^- &\rightarrow \text{Pb}(s) + S^{2-}(aq) & E_{\text{red}}^\circ &= ?
\end{align*}
\]

"\(E^\circ\)" for the second step can be calculated from \(K_{sp}\).

\[
E^\circ = \frac{0.0592}{n} \log K_{sp} = \frac{0.0592}{2} \log (8.0 \times 10^{-28}) = \frac{0.0592}{2} (-27.10) = -0.802 \text{ V}
\]

\(E^\circ\) for the half-reaction = -0.126 V + (-0.802 V) = -0.928 V

Calculating an imaginary \(E^\circ\) for a nonredox process like step 2 may be a disturbing idea. Alternatively, one could calculate \(K\) for step 1 \((5.4 \times 10^{-5})\), \(K\) for the reaction in question \((K = K_1 \times K_{sp} = 4.4 \times 10^{-32})\) and then \(E^\circ\) for the half-reaction. The result is the same.

20.118

(a)

\[
\begin{array}{c}
\text{anode} \quad \overset{V}{\text{e}^-} \quad \text{cathode} \\
\text{H}_2(g), \text{1 atm} & \quad \text{e}^- \quad \text{H}_2(g), \text{1 atm}
\end{array}
\]

\[
\text{Anion movement} \\
\text{Porous separator}
\]

(b) \(2\text{H}^+(aq, 1 \text{ M}) + 2e^- \rightarrow \text{H}_2(g) \quad E_{\text{red}}^\circ = 0 \quad \text{H}_2(g) \rightarrow 2\text{H}^+(aq, 1 \text{ M}) + 2e^- \quad E_{\text{red}}^\circ = 0 \quad 2\text{H}^+(aq, 1 \text{ M}) + \text{H}_2(g) \rightarrow 2\text{H}^+(aq, 1 \text{ M}) + \text{H}_2(g) \quad E^\circ = 0
\]

(c) At standard conditions, [\text{H}^+] = 1 \text{ M}, \text{pH} = 0
Solutions to Exercises

20.119 The two half-reactions in the electrolysis of H₂O(l) are:

\[ \text{H₂O(l)} + 2e^- \rightarrow H_2(g) + 2OH^- \]

\[ 2\text{H₂O(l)} \rightarrow O_2(g) + 4H^+ + 4e^- \]

4 mol e^-/2 mol H₂(g) or 2 mol e^-/mol H₂(g)

Using partial pressures and the ideal-gas law, calculate the mol H₂(g) produced, and the current required to do so.

\[ P_H = P_H + P_{H_2O} \]

From Appendix B, P_{H_2O} at 25.5°C is approximately 24.5 torr.

\[ P_{H_2} = 768 \text{ torr} - 24.5 \text{ torr} = 743.5 \text{ torr} \]

\[ n = \frac{PV}{RT} = \frac{(743.5/760) \text{ atm} \times 0.0123 \text{ L}}{298.5 \text{ K} \times 0.08206 \text{ L atm/mol K}} = 4.912 \times 10^{-4} = 4.91 \times 10^{-4} \text{ mol H}_2 \]

\[ 4.912 \times 10^{-4} \text{ mol H}_2 \times \frac{2 \text{ mol e}^-}{1 \text{ mol H}_2} \times \frac{96,500 \text{ C}}{1 \text{ mol e}^-} \times \frac{1 \text{ amp} \times \text{s}}{60 \text{ s}} \times \frac{1 \text{ min}}{2.00 \text{ min}} = 0.790 \text{ amp} \]