# 20. ELECTROCHEMISTRY

### ■ Solutions to Exercises

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multiple-step problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

20.1 Assign oxidation numbers to the skeleton equation (Step 1).

Separate into two incomplete half-reactions (Step 2). Note that iodine is oxidized (increases in oxidation number), and nitrogen is reduced (decreases in oxidation number).

$$I_2 \rightarrow IO_3^ NO_3^- \rightarrow NO_2^-$$

Balance each half-reaction separately. The oxidation half-reaction is not balanced in I, so place a two in front of  $IO_3^-$  (Step 3a). Then add six  $H_2O$ 's to the left side to balance O atoms (Step 3b), and add twelve  $H^+$  ions to the right side to balance H atoms (Step 3c). Finally, add ten electrons to the right side to balance the charge (Step 3d). The balanced oxidation half-reaction is

$$I_2 + 6H_2O \rightarrow 2IO_3^- + 12H^+ + 10e^-$$

The reduction half-reaction is balanced in N (Step 3a). Add one  $H_2O$  to the right side to balance O atoms (Step 3b), and add two  $H^+$  ion to the left side to balance H atoms. Finally, add one electron to the left side to balance the charge (Step 3d).

The balanced reduction half-reaction is

$$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$$

Multiply the reduction half-reaction by five so that, when added, the electrons cancel (Step 4a).

$$I_2 + 6H_2O \rightarrow 2IO_3^- + 12H^+ + 10e^ 10NO_3^- + 20H^+ + 10e^- \rightarrow 10NO_2 + 10H_2O$$
 $I_2 + 10NO_3^- + 20H^+ + 6H_2O + 10e^- \rightarrow$ 
 $2IO_3^- + 10NO_2 + 12H^+ + 10H_2O + 10e^-$ 

Simplify the equation by canceling the twelve  $H^+$  and six  $H_2O$  that appear on both sides. The coefficients do not need to be reduced (Step 4b). The net ionic equation is

$$I_2(s) + 10NO_3^-(aq) + 8H^+(aq) \rightarrow 2IO_3^-(aq) + 10NO_2(g) + 4H_2O(l)$$

20.2 After balancing the equation as if it were in acid solution, you obtain the following:

$$H_2O_2 + 2CIO_2 \rightarrow 2CIO_2 + O_2 + 2H^+$$

Add two  $OH^-$  to both sides of the equation (Step 5), and replace the two  $H^+$  and two  $OH^-$  on the right side with two  $H_2O$ . No further cancellation is required. The balanced equation for the reaction in basic solution is

$$H_2O_2 + 2CIO_2 + 2OH^- \rightarrow 2CIO_2^- + O_2 + 2H_2O$$

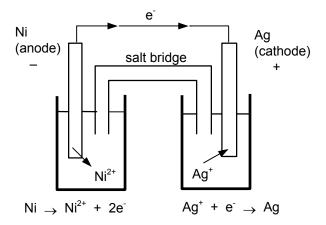
20.3 Silver ion is reduced at the silver electrode (cathode). The half-reaction is

$$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$$

The nickel electrode (anode) is where oxidation occurs. The half-reaction is

$$Ni(s) \rightarrow Ni^{2+}(aq) + 2e^{-}$$

Electron flow in the external circuit is from the nickel electrode (anode) to the silver electrode (cathode). Positive ions will flow in the solution portion of the circuit opposite to the direction of the electrons. A sketch of the cell is given below:



- 20.4 The notation for the cell is  $Zn(s)|Zn^{2+}(aq)||H^{+}(aq)|H_{2}(g)|Pt(s)$ .
- 20.5 The half-cell reactions are

Cd(s) 
$$\rightarrow$$
 Cd<sup>2+</sup>(aq) + 2e<sup>-</sup>  
2H<sup>+</sup>(aq) + 2e<sup>-</sup>  $\rightarrow$  H<sub>2</sub>(g)

Summing the half-cell reactions gives the overall cell reaction.

$$Cd(s) + 2H^{+}(aq) \rightarrow Cd^{2+}(aq) + H_{2}(g)$$

20.6 The half-reactions are

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$$
  
 $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ 

n equals two, and the maximum work for the reaction as written is

$$W_{max}$$
 = -nFE<sub>cell</sub> = -2 x 9.65 x 10<sup>4</sup> C x 1.10 V = -2.1 $\underline{2}$ 3 x 10<sup>5</sup> V•C = -2.12 x 10<sup>5</sup> J

For 6.54 g of zinc metal, the maximum work is

6.54 g Zn x 
$$\frac{1 \text{ mol Zn}}{65.39 \text{ g Zn}}$$
 x  $\frac{-2.123 \times 10^5 \text{ J}}{1 \text{ mol Zn}}$  =  $-2.123 \times 10^4$  =  $-2.12 \times 10^4$  J

20.7 The half-reactions and corresponding electrode potentials are as follows

$$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$$
 0.80 V  $NO_{3}^{-}(aq) + 4H^{+}(aq) + 4e^{-} \rightarrow NO(q) + 2H_{2}O(l)$  0.96 V

The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so NO<sub>3</sub> is the stronger oxidizing agent.

20.8 In this reaction, Cu<sup>2+</sup> is the oxidizing agent on the left side; I<sub>2</sub> is the oxidizing reagent on the right side. The corresponding standard electrode potentials are

$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s);$$
  $E^{\circ} = 0.34 \text{ V}$   $I_{2}(s) + 2e^{-} \rightarrow 2I^{-}(aq);$   $E^{\circ} = 0.54 \text{ V}$ 

The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so  $I_2$  is the stronger oxidizing agent. The reaction is nonspontaneous as written.

20.9 The reduction half-reactions and standard electrode potentials are

$$Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s);$$
  $E^{\circ}_{Zn} = -0.76 \text{ V}$   
 $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s);$   $E^{\circ}_{Cu} = 0.34 \text{ V}$ 

Reverse the first half-reaction and its half-cell potential to obtain

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-};$$
  $-E^{\circ}_{Zn} = 0.76 \text{ V}$   $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s);$   $E^{\circ}_{Cu} = 0.34 \text{ V}$ 

Obtain the cell emf by adding the half-cell potentials.

$$E^{\circ}_{cell} = E^{\circ}_{Cu} - E^{\circ}_{Zn} = 0.34 \text{ V} + 0.76 \text{ V} = 1.10 \text{ V}$$

20.10 The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$$Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^{-}$$
  $-E^{\circ} = 0.15 \text{ V}$   
 $2Hg^{2+}(aq) + 2e^{-} \rightarrow Hg_{2}^{2+}(aq)$   $E^{\circ} = 0.90 \text{ V}$   
 $Sn^{2+}(aq) + 2Hg^{2+}(aq) \rightarrow Sn^{4+}(aq) + Hg_{2}^{2+}(aq)$   $E^{\circ}_{cell} = 0.75 \text{ V}$ 

Note that each half-reaction involves two electrons; hence n equals two. Also,  $E^{\circ}_{cell}$  equals 0.75 V, and the faraday constant, F, is 9.65 x  $10^4$  C. Therefore,

$$\Delta G^{\circ} = -nFE^{\circ}_{rell} = -2 \times 9.65 \times 10^{4} \text{ C} \times 0.75 \text{ V} = -1.4475 \times 10^{5} \text{ J} = -1.4 \times 10^{5} \text{ J}$$

Thus, the standard free-energy change is -1.4 x 10<sup>2</sup> kJ.

20.11 Write the equation with  $\Delta G_f^{\circ}$ 's beneath each substance.

Hence,

$$\Delta G^{\circ} = \Sigma n \Delta G_{f}^{\circ} (products) - \Sigma m \Delta G_{f}^{\circ} (reactants)$$
$$= [(-456.0) - 65.0] \text{ kJ} = -521.0 \text{ kJ} = -5.210 \text{ x } 10^{5} \text{ J}$$

Obtain n by splitting the reaction into half-reactions.

$$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^{-}$$
  
 $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ 

Each half-reaction involves two electrons, so n equals two. Therefore,

$$\Delta G^{\circ} = -nFE^{\circ}_{cell}$$
  
-5.210 x 10<sup>5</sup> J = -2 x 9.65 x 10<sup>4</sup> C x  $E^{\circ}_{cell}$ 

Rearrange and solve for  $E^{\circ}_{cell}$ . Recall that  $J = C \cdot V$ .

$$E^{\circ}_{cell} = \frac{-5.210 \times 10^5 \text{ J}}{-2 \times 9.65 \times 10^4 \text{ C}} = 2.6994 = 2.70 \text{ V}$$

20.12 The half-reactions and standard electrode potentials are

Fe(s) 
$$\rightarrow$$
 Fe<sup>2+</sup>(aq) + 2e<sup>-</sup>; -E°<sub>Fe</sub> = 0.41 V  
Sn<sup>4+</sup>(aq) + 2e<sup>-</sup>  $\rightarrow$  Sn<sup>2+</sup>(s); E°<sub>Sn<sup>2+</sup></sub> = 0.15 V

The standard emf for the cell is

$$E^{\circ}_{cell} = E^{\circ}_{Fe} - E^{\circ}_{Sn^{2+}} = 0.41 \text{ V} + 0.15 \text{ V} = 0.56 \text{ V}$$

Note that n equals two. Substitute into the equation relating  $E^{\circ}$  and K. Also K =  $K_c$ .

$$0.56 \text{ V} = \frac{0.0592}{2} \log K_c$$

Solving for K<sub>c</sub>, you get

$$\log K_c = 18.91$$

Take the antilog of both sides:

$$K_c$$
 = antilog (18.91) = 8.1 x 10<sup>18</sup> = 10<sup>19</sup>

20.13 The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$$
  $-E^{\circ} = 0.76 \text{ V}$ 
 $2Ag^{+}(aq) + 2e^{-} \rightarrow 2Ag(s)$   $E^{\circ} = 0.80 \text{ V}$ 
 $Zn(s) + 2Ag^{+}(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$   $E^{\circ}_{cell} = 1.56 \text{ V}$ 

Note that n equals two. The reaction quotient is

$$Q = \frac{[Zn^{2+}]}{[Ag^+]^2} = \frac{0.200}{(0.00200)^2} = 5.0\underline{0} \times 10^4$$

The standard emf is 1.56 V, so the Nernst equation becomes

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592}{n} \log Q$$

$$= 1.56 - \frac{0.0592}{2} \log (5.00 \times 10^{4})$$

$$= 1.56 - 0.13909 = 1.4209 = 1.42 \text{ V}$$

20.14 The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$$
  $-E^{\circ} = 0.76 \text{ V}$ 
 $Ni^{2+}(aq) + 2e^{-} \rightarrow Ni(s)$   $E^{\circ} = -0.23 \text{ V}$ 
 $Zn(s) + Ni^{2+}(aq) \rightarrow Zn^{2+}(aq) + Ni(s)$   $E^{\circ}_{cell} = 0.53 \text{ V}$ 

Note that n equals two. The standard emf is  $0.53~\rm{V}$ , and the emf is  $0.34~\rm{V}$ , so the Nernst equation becomes

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592}{n} \log Q$$

$$0.34 \text{ V} = 0.53 \text{ V} - \frac{0.0592}{2} \log Q$$

Rearrange and solve for log Q

$$\log Q = \frac{2}{0.0592} \times (0.53 - 0.34) = 6.418$$

Take the antilog of both sides

Q = 
$$\frac{[Zn^{2+}]}{[Ni^{2+}]}$$
 = antilog (6.418) =  $\underline{2}$ .623 x 10<sup>6</sup>

Substitute in  $[Zn^{2+}]$  = 1.00 M and solve for  $[Ni^{2+}]$ .

$$\frac{1.00 \text{ M}}{[\text{Ni}^{2+}]} = 2.624 \times 10^6$$

$$[Ni^{2+}] = 3.81 \times 10^{-7} = 4 \times 10^{-7} M$$

20.15 a. The cathode reaction is  $K^+(I) + e^- \rightarrow K(I)$ .

The anode reaction is  $2Cl^{-}(l) \rightarrow Cl_{2}(g) + 2e^{-}$ .

b. The cathode reaction is  $K^+(I) + e^- \rightarrow K(I)$ .

The anode reaction is  $4OH^{-}(aq) \rightarrow O_2(g) + 2H_2O(g) + 4e^{-}$ .

20.16 The species you should consider for half-reactions are Ag<sup>+</sup> and H<sub>2</sub>O. Two possible cathode reactions are

$$Ag^{+}(aq) + e^{-} \rightarrow Ag(s); E^{\circ} = 0.80 \text{ V}$$
  
 $2H_{2}O(I) + 2e^{-} \rightarrow H_{2}(g) + 2OH^{-}(aq); E^{\circ} = -0.83 \text{ V}$ 

Because the silver electrode potential is larger than the reduction potential of water,  $Ag^{\dagger}$  is reduced. The only possible anode reaction is the oxidation of water. The expected half-reactions are

$$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$$
  
 $2H_{2}O(I) \rightarrow O_{2}(g) + 4H^{+}(aq) + 4e^{-}$ 

20.17 The conversion of grams of silver to coulombs required to deposit this amount of silver is

0.365 g Ag x 
$$\frac{1 \text{ mol Ag}}{107.9 \text{ g}}$$
 x  $\frac{1 \text{ mol e}^{-}}{1 \text{ mol Ag}}$  x  $\frac{9.65 \times 10^{4} \text{ C}}{1 \text{ mol e}^{-}}$  =  $32\underline{6}.4 \text{ C}$ 

The time lapse, 216 min, equals  $1.2\underline{9}6 \times 10^3$  s. Thus,

Current = 
$$\frac{\text{charge}}{\text{time}}$$
 =  $\frac{326.4 \text{ C}}{1.296 \text{ x } 10^4 \text{ s}}$  =  $2.5\underline{1}88 \text{ x } 10^{-2}$  =  $2.52 \text{ x } 10^{-2} \text{ A}$ 

20.18 When the current flows for 1.85 x 10<sup>4</sup> s, the amount of charge is

$$0.0565 \text{ A} \times 1.85 \times 10^4 \text{ s} = 1.045 \times 10^3 \text{ C}$$

Note that four moles of electrons are equivalent to one mol of O<sub>2</sub>. Hence,

$$1.045 \times 10^{3} \text{ C} \times \frac{1 \text{ mol e}^{-}}{9.65 \times 10^{4} \text{ C}} \times \frac{1 \text{ mol O}_{2}}{4 \text{ mol e}^{-}} \times \frac{32.00 \text{ g O}_{2}}{1 \text{ mol O}_{2}}$$

$$= 0.086\underline{6}5 = 0.0866 \text{ g O}_{2}$$

## ■ Answers to Concept Checks

20.1 No sustainable current would flow. The wire does not contain mobile positively and negatively charged species necessary to balance the accumulation of charges in each of the half cells.

- 20.2 a. Standard reduction potentials are measured against some arbitrarily chosen standard reference half-reaction. Only differences in potentials can be measured. A voltaic cell made from  $H_2$  and  $I_2$  and corresponding solutions will have the same voltage regardless of the choice of the reference cell. If the  $I_2/I^-$  half-reaction is assigned a value of  $E^\circ$  = 0.00 V, the  $H_2/H^+$  half-reaction must have a voltage of  $E^\circ$  = -0.54 V to keep the overall voltage the same.
  - b. The voltage of a voltaic cell made from Cu and Zn and corresponding solutions will have the same measured voltage regardless of the choice of the reference halfreaction.
  - c. The calculated voltage is 1.10 V and is the same either way.
- 20.3 a. Using the standard reduction potentials in Table 20.1, you see the voltage for this cell is positive, which suggests △G° is negative.
  - b. In order to reduce  $E_{\text{cell}}$ , change the concentrations in a way that increases the value of Q, where

$$Q = \frac{[Fe^{2+}]}{[Cu^{2+}]}$$

For example:  $Fe(s)|Fe^{2+}(1.10 \text{ M})||Cu^{2+}(0.50 \text{ M})|Cu(s)$ 

20.4 Many of the ions contained in seawater have very high reduction potentials—higher than Fe(s). This means spontaneous electrochemical reactions will occur with the Fe(s) causing the iron to form ions and go into solution while, at the same time, the ions in the sea will be reduced and plate out on the surface of the iron.

## Answers to Review Questions

- A voltaic cell is an electrochemical cell in which a spontaneous reaction generates an electric current (energy). An electrolytic cell is an electrochemical cell that requires electrical current (energy) to drive a nonspontaneous reaction to the right.
- 20.2 In both the voltaic and electrolytic cells, the cathode is the electrode at which reduction occurs, and the anode is the electrode at which oxidation occurs.
- 20.3 The SI unit of electrical potential is the volt (V).
- 20.4 The faraday (F) is the magnitude of charge on one mole of electrons; it equals 9.65 x 10<sup>4</sup> C. or 9.65 x 10<sup>4</sup> J/V.

- 20.5 It is necessary to measure the voltage of a voltaic cell when no current is flowing because the cell voltage exhibits its maximum value only when no current flows. Even if the current flows just for the time of measurement, the voltage drops enough so that what is measured is significantly less than the maximum.
- 20.6 Standard electrode potentials are defined relative to a standard electrode potential of zero volts (0.00, 0.000 V, etc.) for the  $H^{+}/H_{2}(g)$  electrode. Because the cell emf is measured using the hydrogen electrode at standard conditions and a second electrode at standard conditions, the cell emf equals the  $E^{\circ}$  of the half-reaction at the second electrode.
- 20.7 The SI unit of energy equals joules equals coulombs x volts.
- 20.8 The mathematical relationships are as follows:

$$\Delta G^{\circ} = -nFE^{\circ}_{cell}$$

$$\Delta G^{\circ} = -RT \ln K$$

Combining these two equations gives

$$\ln K = \frac{nFE_{cell}^{\circ}}{RT}$$

20.9 The first step in the corrosion of iron is

$$2Fe(s) + O_2(g) + 2H_2O(I) \rightarrow 4OH^- + 2Fe^{2+}$$

The Nernst equation for this reaction is

$$E_{cell} = E_{cell}^{\circ} - \frac{0.0592}{4} \log [OH]^{4} [Fe^{2+}]^{2}$$

If the pH increases, the [OH] increases, and thus  $E_{cell}$  becomes more negative (this predicts the reaction becomes less spontaneous). If the pH decreases, the [OH] decreases, and thus  $E_{cell}$  becomes more positive (this predicts the reaction becomes more spontaneous).

20.10 The zinc-carbon cell has a zinc can as the anode; the cathode is a graphite rod surrounded by a paste of manganese dioxide and carbon black. Around this is a second paste of ammonium and zinc chlorides. The electrode reactions involve oxidation of zinc metal to zinc(II) ion and reduction of  $MnO_2(s)$  to  $Mn_2O_3(s)$  at the cathode. The lead storage battery consists of a spongy lead anode and a lead dioxide cathode, both immersed in aqueous sulfuric acid. At the anode, the lead is oxidized to lead sulfate; at the cathode, lead dioxide is reduced to lead sulfate.

- 20.11 A fuel cell is essentially a battery that does not use up its electrodes. Instead, it operates with a continuous supply of reactants (fuel). An example is the hydrogen-oxygen fuel cell in which oxygen is reduced at one electrode to the hydroxide ion, and hydrogen is oxidized at the other electrode to water (H in the +1 oxidation state). Such a cell produces electrical energy in a spacecraft for long periods of time.
- 20.12 During the rusting of iron, one end of a drop of water exposed to air acts as one electrode of a voltaic cell; at this electrode, an oxygen molecule is reduced by four electrons to four hydroxide ions. Oxidation of metallic iron to iron(II) ion at the center of the drop of water supplies the electrons, and the center serves as the other electrode of the voltaic cell. Thus, electrons flow from the center of the drop through the iron to the end of the drop.
- 20.13 When iron or steel is connected to an active metal such as zinc, a voltaic cell is formed with zinc as the anode and iron as the cathode. Any type of moisture forms the electrolyte solution, and the zinc metal is then oxidized to zinc(II) ion in preference to the oxidation of iron metal. Oxygen is reduced at the cathode to hydroxide ions. If iron or steel is exposed to oxygen while connected to a less active metal such as tin, a voltaic cell is formed with iron as the anode and tin as the cathode, and iron is oxidized to iron(II) ion rather than tin being oxidized to tin(II) ion. Thus, exposed iron corrodes rapidly in a tin can. Fortunately, as long as the iron is covered by the tin, it cannot corrode.
- 20.14 The addition of an ionic species such as strongly ionized sulfuric acid facilitates the passage of current through the solution.
- 20.15 Sodium metal can be prepared by electrolysis of molten sodium chloride.
- 20.16 The anode reaction in the electrolysis of molten potassium hydroxide is

$$4OH^{-} \rightarrow O_2(g) + 2H_2O(g) + 4e^{-}$$

- 20.17 The reason different products are obtained is that water instead of Na<sup>+</sup> is reduced at the cathode during the electrolysis of aqueous NaCl. This is because water has a more positive E° (smaller decomposition voltage). At the anode, water instead of chloride ion is oxidized because water has a less positive E° (smaller decomposition voltage).
- 20.18 The Nernst equation for the electrode reaction of  $2Cl(aq) \rightarrow Cl_2(g) + 2e^{-i}s$

E = -1.36 V - 
$$\frac{0.0592}{2} \log \frac{1 \text{ atm}}{[\text{Cl}^-]^2}$$
 = -1.36 V + 0.0592 log [Cl]

This equation implies that E increases as [Cl] increases. For a sufficiently large [Cl], Cl will be more readily oxidized than the water solvent.

## Answers to Conceptual Problems

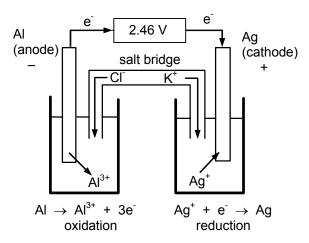
- 20.19 a. Since there is no species present to donate or accept electrons other than zinc, you would expect no change.
  - b. Since there is no species present to donate or accept electrons other than copper, you would expect no change.
  - c. According to the table of standard reduction potentials, the Cu<sup>2+</sup> would undergo reduction, and the Zn would undergo oxidation. You would expect the Zn strip to dissolve as it becomes Zn<sup>2+</sup>, the blue color of the solution to fade as the Cu<sup>2+</sup> becomes Cu, and solid copper precipitate to form.
  - d. According to the table of standard reduction potentials, since Zn<sup>2+</sup> cannot oxidize Cu, you would expect no change.
- 20.20 You could construct the battery by hooking together, in series, five individual cells, each with  $E^{\circ} = 1.20 \text{ V}$ .
- 20.21 The Zn is a sacrificial electrode that keeps the hull from undergoing oxidation by the dissolved ions in sea water. Zn works because it is more easily oxidized than Fe.
- 20.22 When an electrochemical reaction reaches equilibrium,  $E_{cell}$  equals 0, which means no current will flow, and nothing will happen when you turn on the flashlight. This is typically what has occurred when you have a dead battery.
- 20.23 Since there is more zinc present, the oxidation-reduction reactions in the battery will run for a longer period of time. This assumes zinc is the limiting reactant.
- 20.24 Any metal that has a more negative standard reduction potential (Mg, Al, etc.) could be used, keeping in mind that group IA metals that fall into this category are too reactive to be of practical use.
- 20.25 One possible combination using two metals is a cell constructed from a Zn<sup>2+</sup>|Zn cathode with a voltage of -0.76 V, and an Al|Al<sup>3+</sup> anode with a voltage of 1.66 V. The appropriate half-reactions are

Al(s) 
$$\to$$
 Al<sup>3+</sup>(aq) + 3 e<sup>-</sup>  $E^{\circ}_{ox}$  = 1.66 V  
Zn<sup>2+</sup>(aq) + 2 e<sup>-</sup>  $\to$  Zn(s)  $E^{\circ}_{red}$  = -0.76 V

The overall balanced reaction and cell potential is

$$2 \text{ Al(s)} + 3 \text{ Zn}^{2+}(\text{aq}) \rightarrow 2 \text{ Al}^{3+}(\text{aq}) + 3 \text{ Zn(s)}$$
  $\text{E}^{\circ}_{\text{cell}} = 0.90 \text{ V}$ 

20.26 (parts a to f) The completed diagram with all parts labeled is shown below.



d. The cell emf is determined as follows.

$$Al^{3+}(aq) + 3 e^{-} \rightarrow Al(s)$$
  $E^{\circ}_{red} = 1.66 \text{ V}$   
 $Ag^{+}(aq) e^{-} \rightarrow Ag(s)$   $E^{\circ}_{red} = 0.80 \text{ V}$   
 $E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode} = 0.80 \text{ V} - (-1.66 \text{ V}) = 2.46 \text{ V}$ 

- g. The species undergoing oxidation is Al(s), and the species undergoing reduction is  $Ag^{\dagger}(aq)$ .
- h. The balanced overall reaction is

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

20.27 The effect of the various changes on the intensity of the light can be determined using the Nernst equation,

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592}{n} \log Q$$

For this reaction,  $E^{\circ}$  = 1.10 V, n = 2, and Q is the reaction quotient.

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

If Q > 1, log Q is positive, and the net result will be a decrease in cell potential and a decrease in the intensity of light. If Q < 1, log Q is negative, and the net result will be an increase in cell potential and an increase in the intensity of light.

At the start, both  $[Zn^{2+}]$  and  $[Cu^{2+}]$  are 1.0 M, so Q = 1, and  $[Cu^{2+}]$ 

- a. If more  $CuSO_4(s)$  is dissolved in the  $CuSO_4$  solution,  $[Cu^{2^+}]$  would be greater than one, so Q < 1. The effect is to increase the intensity of light.
- b. If more  $Zn(NO_3)_2(s)$  is dissolved in the  $Zn(NO_3)_2$  solution,  $[Zn^{2+}]$  would be greater than one, so Q > 1. The effect is to decrease the intensity of light.
- c. If  $H_2O$  is added to the  $CuSO_4$  solution,  $[Cu^{2+}]$  would be less than one, so Q > 1. The effect is to decrease the intensity of light.
- d. If the salt bridge is removed, the circuit would not be complete, and the cell potential would be zero. No current would flow.
- 20.28 The most important consideration in battery design is the spontaneity of the cell reaction since this determines the cell voltage. The half-reactions for the reduction of oxygen gas given in Appendix I are:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^ E^\circ = +0.40 \text{ V}$$
  
 $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$   $E^\circ = +1.23 \text{ V}$ 

These represent the reduction of oxygen under basic and under acidic conditions. Thus, in basic solution, we would require an oxidation half-reaction (anode half-reaction) with a potential greater than -0.40 V to obtain a spontaneous reaction.

The density of the reducing agent is the next most important consideration. Hydrogen, the element with the lowest density, should certainly be considered. It does have some drawbacks, however. Because it is a gas, some method of storage needs to be developed. Liquid storage and metal hydride storage have been investigated. Storage of liquid hydrogen presents problems of safety and weight. Storage of hydrogen as a hydride is used in nickel-hydride cells presently available for portable computers, cellular phones, etc. (These batteries are rechargeable, but do not use oxygen.) The metal hydride obviously adds weight to the battery. Other elements you might consider are Na, Li, Al, K, Ca, and Zn, which have favorable power-to-mass ratios. Lithium and sodium might present some disposal problems since they are very reactive metals. Batteries using aluminum with atmospheric oxygen are available.

### ■ Solutions to Practice Problems

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multiple-step problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

- 20.29 In balancing oxidation-reduction reactions in acid, the four steps in the text will be followed. For part a, each step is shown. For the other parts, only a summary is shown.
  - a. Assign oxidation numbers to the skeleton equation (Step 1).

$$^{+6}$$
  $^{+3}$   $^{+3}$   $^{+3}$   $^{+4}$   $^{+2}$   $^{-2$ 

Separate into two incomplete half-reactions (Step 2). Note that carbon is oxidized (increases in oxidation number), and chromium is reduced (decreases in oxidation number).

$$C_2O_4^{2-} \rightarrow CO_2$$
 $Cr_2O_7^{2-} \rightarrow Cr^{3+}$ 

Balance each half-reaction separately. The oxidation half-reaction is not balanced in C, so place a two in front of  $CO_2$  (Step 3a). Finally, add two electrons to the right side to balance the charge (Step 3d). The balanced oxidation half-reaction is

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^{-}$$

The reduction half-reaction is not balanced in Cr, so place a two in front of  $Cr^{3+}$  (Step 3a). Add seven  $H_2O$  to the right side to balance O atoms (Step 3b), and add fourteen  $H^+$  ion to the left side to balance H atoms (step 3c). Finally, add six electrons to the left side to balance the charge (Step 3d). The balanced reduction half-reaction is

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

Multiply the oxidation half-reaction by three so that, when added, the electrons cancel (Step 4a).

The equation does not need to be simplified any further (Step 4b). The net ionic equation is

$$Cr_2O_7^{2-} + 3C_2O_4^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 6CO_2 + 7H_2O$$

b. The two balanced half-reactions are

Cu 
$$\rightarrow$$
 Cu<sup>2+</sup> + 2e<sup>-</sup> (oxidation)  
NO<sub>3</sub><sup>-</sup> + 4H<sup>+</sup> + 3e<sup>-</sup>  $\rightarrow$  NO + 2H<sub>2</sub>O (reduction)

Multiply the oxidation half-reaction by three and the reduction half-reaction by four, and then add together. Cancel the six electrons from each side. No further simplification is needed. The balanced equation is

$$3Cu + 2NO_3^- + 8H^+ \rightarrow 3Cu^{2+} + 2NO + 4H_2O$$

c. The two balanced half-reactions are

$$HNO_2 + H_2O \rightarrow NO_3^- + 3H^+ + 2e^-$$
 (oxidation)  
 $MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$  (reduction)

Add the two half-reactions together and cancel the two electrons from each side. Also, cancel three  $H^+$  and one  $H_2O$  from each side. The balanced equation is

$$MnO_2 + HNO_2 + H^{\dagger} \rightarrow Mn^{2+} + NO_3^{-} + H_2O$$

d. The two balanced half-reactions are

$$Mn^{2^{+}} + 4H_{2}O \rightarrow MnO_{4}^{-} + 8H^{+} + 5e^{-}$$
 (oxidation)  
 $PbO_{2} + SO_{4}^{2^{-}} + 4H^{+} + 2e^{-} \rightarrow PbSO_{4} + 2H_{2}O$  (reduction)

Multiply the oxidation half-reaction by two and the reduction half-reaction by five, and then add together. Cancel the ten electrons from each side. Also, cancel sixteen  $H^{+}$  and eight  $H_{2}O$  from each side. The balanced equation is

$$5PbO_2 + 2Mn^{2+} + 5SO_4^{2-} + 4H^+ \rightarrow 5PbSO_4 + 2MnO_4^{-} + 2H_2O_4^{-}$$

e. The two balanced half-reactions are

$$HNO_2 + H_2O \rightarrow NO_3^- + 3H^+ + 2e^-$$
 (oxidation)  
 $Cr_2O_7^{-2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$  (reduction)

Multiply the oxidation half-reaction by three, and then add together. Cancel the six electrons from each side. Also, cancel nine  $H^+$  and three  $H_2O$  from each side. The balanced equation is

$$3HNO_2 + Cr_2O_7^{2-} + 5H^+ \rightarrow 2Cr^{3+} + 3NO_3^{-} + 4H_2O$$

- 20.30 In balancing oxidation-reduction reactions in acid, the four steps in the text will be followed. For part a, each step is shown. For the other parts only a summary is shown.
  - a. Assign oxidation numbers to the skeleton equation (Step 1).

$$^{+2}$$
  $^{+5}$   $^{+7}$   $^{+3}$   $Mn^{2^{+}}$   $^{+}$   $BiO_{3}^{-}$   $\rightarrow$   $MnO_{4}^{-}$   $^{+}$   $Bi^{3^{+}}$ 

Separate into two incomplete half-reactions (Step 2). Note that manganese is oxidized (increases in oxidation number), and bismuth is reduced (decreases in oxidation number).

$$\text{Mn}^{2^+} \rightarrow \text{MnO}_4^-$$
  
 $\text{BiO}_3 \rightarrow \text{Bi}^{3^+}$ 

Balance each half-reaction separately. For the oxidation half-reaction, add four  $H_2O$  to the left side to balance O atoms (Step 3b), and add eight  $H^+$  ion to the right side to balance H atoms (step 3c). Finally, add five electrons to the right side to balance the charge (Step 3d). The balanced oxidation half-reaction is

$$Mn^{2+} + 4H_2O \rightarrow MnO_4^- + 8H^+ + 5e^-$$

For the reduction half-reaction, add three  $H_2O$  to the right side to balance O atoms (Step 3b), and add six  $H^+$  ion to the left side to balance H atoms (step 3c). Finally, add two electrons to the left side to balance the charge (Step 3d). The balanced reduction half-reaction is

$$BiO_3^- + 6H^+ + 2e^- \rightarrow Bi^{3+} + 3H_2O$$

Multiply the oxidation half-reaction by two and the reduction half-reaction by five, so that, when added, the electrons cancel (Step 4a).

$$2Mn^{2^{+}} + 8H_{2}O \rightarrow 2MnO_{4}^{-} + 16H^{+} + 10e^{-}$$
 $5BiO_{3}^{-} + 30H^{+} + 10e^{-} \rightarrow 5Bi^{3^{+}} + 15H_{2}O$ 
 $2Mn^{2^{+}} + 5BiO_{3}^{-} + 30H^{+} + 8H_{2}O + 10e^{-} \rightarrow$ 
 $2MnO_{4}^{-} + 5Bi^{3^{+}} + 16H^{+} + 15H_{2}O + 10e^{-}$ 

The equation can be further simplified by canceling sixteen H<sup>+</sup> and eight H<sub>2</sub>O from each side (Step 4b). The net ionic equation is

$$2Mn^{2+} + 5BiO_3^- + 14H^+ \rightarrow 2MnO_4^- + 5Bi^{3+} + 7H_2O$$

b. The two balanced half-reactions are

$$I^{-} + 3H_{2}O \rightarrow IO_{3}^{-} + 6H^{+} + 6e^{-}$$
 (oxidation)  
 $Cr_{2}O_{7}^{2-} + 14H^{+} + 6e^{-} \rightarrow 2Cr^{3+} + 7H_{2}O$  (reduction)

Add the two half-reactions together, and cancel the six electrons from each side. Also, cancel six  $H^{+}$  and three  $H_{2}O$  from each side. The balanced equation is

$$Cr_2O_7^{2-} + I^- + 8H^+ \rightarrow 2Cr^{3+} + IO_3^- + 4H_2O$$

c. The two balanced half-reactions are

$$H_2SO_3 + H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$$
 (oxidation)  
 $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$  (reduction)

Multiply the oxidation half-reaction by five and the reduction half-reaction by two, and then add together. Cancel the ten electrons from each side. Also, cancel sixteen  $H^{+}$  and five  $H_{2}O$  from each side. The balanced equation is

$$2MnO_4^- + 5H_2SO_3 \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+ + 3H_2O$$

d. The two balanced half-reactions are

$$Fe^{2^{+}} \rightarrow Fe^{3^{+}} + e^{-}$$
 (oxidation)  
 $Cr_{2}O_{7}^{2^{-}} + 14H^{+} + 6e^{-} \rightarrow 2Cr^{3^{+}} + 7H_{2}O$  (reduction)

Multiply the oxidation half-reaction by six, and then add together. Cancel the six electrons from each side. The balanced equation is

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

e. The two balanced half-reactions are

As + 
$$3H_2O \rightarrow H_3AsO_3 + 3H^+ + 3e^-$$
 (oxidation)  
 $CIO_3^- + 5H^+ + 4e^- \rightarrow HCIO + 2H_2O$  (reduction)

Multiply the oxidation half-reaction by four and the reduction half-reaction by three, and then add together. Cancel the twelve electrons from each side. Also, cancel twelve  $H^{+}$  and six  $H_{2}O$  from each side. The balanced equation is

$$4As + 3CIO_3 + 3H^+ + 6H_2O \rightarrow 4H_3AsO_3 + 3HCIO$$

- 20.31 In balancing oxidation-reduction reactions in basic solution, it will first be balanced as if it were in acidic solution; then the extra two steps in the text will be followed.
  - a. The two balanced half-reactions are

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^-$$
 (oxidation)  
 $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$  (reduction)

Add the two half-reactions together, and cancel the two electrons from each side. Also, cancel two  $H^{\dagger}$  and two  $H_2O$  from each side. The balanced equation in acidic solution is

$$Mn^{2+} + H_2O_2 \rightarrow MnO_2 + 2H^+$$

Now add two  $OH^-$  to each side (Step 5). Simplify by combining the  $H^+$  and  $OH^-$  to give  $H_2O$ . No further simplification is required (Step 6). The balanced equation in basic solution is

$$Mn^{2+} + H_2O_2 + 2OH^{-} \rightarrow MnO_2 + 2H_2O$$

b. The two balanced half-reactions are

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$$
 (oxidation)  
 $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$  (reduction)

Multiply the oxidation half-reaction by three and the reduction half-reaction by two, and then add together. Cancel the six electrons from each side. Also, cancel twelve  $H^{\dagger}$  and six  $H_2O$  from each side. The balanced equation in acidic solution is

$$2MnO_4^- + 3NO_2^- + 2H^+ \rightarrow 2MnO_2 + 3NO_3^- + H_2O$$

Now add two OH<sup>-</sup> to each side. Simplify by combining the H<sup>+</sup> and OH<sup>-</sup> to give H<sub>2</sub>O. Then cancel one H<sub>2</sub>O from each side. The balanced equation in basic solution is

$$2MnO_4$$
 +  $3NO_2$  +  $H_2O \rightarrow 2MnO_2$  +  $3NO_3$  +  $2OH$  (continued)

c. The two balanced half-reactions are

$$Mn^{2^+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^-$$
 (oxidation)  
 $CIO_3^- + 2H^+ + e^- \rightarrow CIO_2 + H_2O$  (reduction)

Multiply the reduction half-reaction by two and then add together. Cancel the two electrons from each side. Also, cancel four  $H^{+}$  and two  $H_{2}O$  from each side. The balanced equation in acidic solution is

$$Mn^{2+} + 2CIO_3^- \rightarrow MnO_2 + 2CIO_2$$

Since there are no H<sup>+</sup> on either side, no further simplification is needed. The balanced equation in basic solution is identical to the balanced equation in acidic solution.

d. The two balanced half-reactions are

$$NO_2 + H_2O \rightarrow NO_3^- + 2H^+ + e^-$$
 (oxidation)  
 $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$  (reduction)

Multiply the oxidation half-reaction by three and then add together. Cancel the three electrons from each side. Also, cancel four  $H^{\dagger}$  and two  $H_2O$  from each side. The balanced equation in acidic solution is

$$MnO_4^- + 3NO_2 + H_2O \rightarrow MnO_2 + 3NO_3^- + 2H^+$$

Now add two OH<sup>-</sup> to each side. Simplify by combining the H<sup>+</sup> and OH<sup>-</sup> to give H<sub>2</sub>O. Then cancel one H<sub>2</sub>O from each side. The balanced equation in basic solution is

$$MnO_4^- + 3NO_2 + 2OH^- \rightarrow MnO_2 + 3NO_3^- + H_2O$$

e. The two balanced half-reactions are

$$Cl_2 + 6H_2O \rightarrow 2ClO_3^- + 12H^+ + 10e^-$$
 (oxidation)  
 $Cl_2 + 2e^- \rightarrow 2Cl^-$  (reduction)

Multiply the reduction half-reaction by five and then add together. Cancel the ten electrons from each side. Also, divide all the coefficients by two. The balanced equation in acidic solution is

$$3Cl_2 + 3H_2O \rightarrow 5Cl^- + ClO_3^- + 6H^+$$

Now add six  $OH^-$  to each side. Simplify by combining the  $H^+$  and  $OH^-$  to give  $H_2O$ . Then cancel three  $H_2O$  from each side. The balanced equation in basic solution is

$$3Cl_2 + 6OH^- \rightarrow 5Cl^- + ClO_3^- + 3H_2O$$

- 20.32 In balancing oxidation-reduction reactions in basic solution, it will first be balanced as if it were in acidic solution, then the extra two steps in the text will be followed.
  - a. The two balanced half-reactions are

$$Cr(OH)_4^- \rightarrow CrO_4^{2^-} + 4H^+ + 3e^-$$
 (oxidation)  
 $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$  (reduction)

Multiply the oxidation half-reaction by two and the reduction half-reaction by three, and then add together. Cancel the six electrons from each side. Also, cancel six H<sup>+</sup> from each side. The balanced equation in acidic solution is

$$2Cr(OH)_4^- + 3H_2O_2 \rightarrow 2CrO_4^{-2-} + 2H^+ + 6H_2O_1^-$$

Now add two  $OH^-$  to each side. Simplify by combining the  $H^+$  and  $OH^-$  to give  $H_2O$ . Then combine the  $H_2O$  on the right side into one term. The balanced equation in basic solution is

$$2Cr(OH)_4^- + 3H_2O_2 + 2OH^- \rightarrow 2CrO_4^{2-} + 8H_2O$$

b. The two balanced half-reactions are

$$Br^{-} + 3H_{2}O \rightarrow BrO_{3}^{-} + 6H^{+} + 6e^{-}$$
 (oxidation)  
 $MnO_{4}^{-} + 4H^{+} + 3e^{-} \rightarrow MnO_{2} + 2H_{2}O$  (reduction)

Multiply the reduction half-reaction by two, and then add together. Cancel the six electrons from each side. Also, cancel six  $H^{+}$  and three  $H_{2}O$  from each side.

The balanced equation in acidic solution is

$$2MnO_4$$
 + Br +  $2H^+$   $\rightarrow$   $2MnO_2$  +  $BrO_3$  +  $H_2O$ 

Now add two OH<sup>-</sup> to each side. Simplify by combining the H<sup>+</sup> and OH<sup>-</sup> to give H<sub>2</sub>O. Then cancel one H<sub>2</sub>O on each side. The balanced equation in basic solution is

$$2MnO_4$$
 +  $Br^-$  +  $H_2O \rightarrow 2MnO_2$  +  $BrO_3$  +  $2OH^-$ 

c. The two balanced half-reactions are

$$Co^{2^+} + 3H_2O \rightarrow Co(OH)_3 + 3H^+ + e^-$$
 (oxidation)  
 $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$  (reduction)

Multiply the oxidation half-reaction by two, and then add together. Cancel the two electrons from each side. Also, cancel two  $H^{\dagger}$  and two  $H_2O$  from each side.

The balanced equation in acidic solution is

$$2Co^{2+} + H_2O_2 + 4H_2O \rightarrow 2Co(OH)_3 + 4H^+$$

Now add four OH<sup>-</sup> to each side. Simplify by combining the H<sup>+</sup> and OH<sup>-</sup> to give H<sub>2</sub>O. Then cancel four H<sub>2</sub>O on each side. The balanced equation in basic solution is

$$2Co^{2+} + H_2O_2 + 4OH^- \rightarrow 2Co(OH)_3$$

d. The two balanced half-reactions are

$$Pb(OH)_4^{2-} \rightarrow PbO_2 + 2H_2O + 2e^-$$
 (oxidation)  
 $CIO^- + 2H^+ + 2e^- \rightarrow CI^- + H_2O$  (reduction)

Add the two half-reactions together, and cancel the two electrons from each side. The balanced equation in acidic solution is

$$Pb(OH)_4^{2-} + CIO^{-} + 2H^{+} \rightarrow PbO_2 + CI^{-} + 3H_2O$$

Now add two  $OH^-$  to each side. Simplify by combining the  $H^+$  and  $OH^-$  to give  $H_2O$ . Then cancel two  $H_2O$  on each side. The balanced equation in basic solution is

$$Pb(OH)_4^{2-} + CIO^- \rightarrow PbO_2 + CI^- + 2OH^- + H_2O$$

e. The two balanced half-reactions are

$$Zn + 4H_2O \rightarrow Zn(OH)_4^{2^-} + 4H^+ + 2e^-$$
 (oxidation)  
 $NO_3^- + 9H^+ + 8e^- \rightarrow NH_3 + 3H_2O$  (reduction)

Multiply the oxidation half-reaction by four, and then add together. Cancel the eight electrons from each side. Also, cancel nine  $H^{\dagger}$  and three  $H_2O$  from each side. The balanced equation in acidic solution is

$$4Zn + NO_3^- + 13H_2O \rightarrow 4Zn(OH)_4^{2-} + NH_3 + 7H^+$$

Now add seven  $OH^-$  to each side. Simplify by combining the  $H^+$  and  $OH^-$  to give  $H_2O$ . Then cancel seven  $H_2O$  on each side. The balanced equation in basic solution is

$$4Zn + NO_3^- + 7OH^- + 6H_2O \rightarrow NH_3 + 4Zn(OH)_4^{2-}$$

20.33 a. The two balanced half-reactions are

$$8H_2S \rightarrow S_8 + 16H^+ + 16e^-$$
 (oxidation)  
 $NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$  (reduction)

Multiply the reduction half-reaction by sixteen, and then add together. Cancel the sixteen electrons and sixteen H<sup>+</sup> from each side. The balanced equation is

$$8H_2S + 16NO_3^- + 16H_2^+ \rightarrow S_8 + 16NO_2 + 16H_2O_3^-$$

b. The two balanced half-reactions are

Cu 
$$\rightarrow$$
 Cu<sup>2+</sup> + 2e<sup>-</sup> (oxidation)  
NO<sub>3</sub><sup>-</sup> + 4H<sup>+</sup> + 3e<sup>-</sup>  $\rightarrow$  NO + 2H<sub>2</sub>O (reduction)

Multiply the oxidation half-reaction by three and the reduction half-reaction by two, and then add together. Cancel the six electrons from each side. The balanced equation is

$$2NO_3^- + 3Cu + 8H^+ \rightarrow 2NO + 3Cu^{2+} + 4H_2O$$

c. The two balanced half-reactions are

$$SO_2 + 2H_2O \rightarrow SO_4^{2^-} + 4H^+ + 2e^-$$
 (oxidation)  
 $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2^+} + 4H_2O$  (reduction)

Multiply the oxidation half-reaction by five and the reduction half-reaction by two, and then add together. Cancel the ten electrons from each side. Also, cancel sixteen  $H^{+}$  and eight  $H_{2}O$  from each side. The balanced equation is

$$2MnO_4^- + 5SO_2 + 2H_2O \rightarrow 5SO_4^{2-} + 2Mn^{2+} + 4H^+$$

d. The two balanced half-reactions are

$$Sn(OH)_3^- + 3H_2O \rightarrow Sn(OH)_6^{2-} + 3H^+ + 2e^-$$
 (oxidation)  
 $Bi(OH)_3 + 3H^+ + 3e^- \rightarrow Bi + 3H_2O$  (reduction)

Multiply the oxidation half-reaction by three and the reduction half-reaction by two, and then add together. Cancel the six electrons from each side. Also, cancel six  $H^+$  and six  $H_2O$  from each side. The balanced equation in acidic solution is

$$2Bi(OH)_3 + 3Sn(OH)_3^- + 3H_2O \rightarrow 3Sn(OH)_6^{2-} + 2Bi + 3H^+$$

Now add three  $OH^-$  to each side. Simplify by combining the  $H^+$  and  $OH^-$  to give  $H_2O$ . Then cancel three  $H_2O$  on each side. The balanced equation in basic solution is

$$2Bi(OH)_3 + 3Sn(OH)_3^- + 3OH^- \rightarrow 3Sn(OH)_6^{2-} + 2Bi$$

#### 20.34 a. The two balanced half-reactions are

$$8H_2S \rightarrow S_8 + 16H^+ + 16e^-$$
 (oxidation)  
 $Hg_2^{2+} + 2e^- \rightarrow 2Hg$  (reduction)

Multiply the reduction half-reaction by eight, and then add together. Cancel the sixteen electrons from each side. The balanced equation in acidic solution is

$$8Hg_2^{2+} + 8H_2S \rightarrow 16Hg + S_8 + 16H^+$$

#### b. The two balanced half-reactions are

$$S^{2-} + 4H_2O \rightarrow SO_4^{2-} + 8H^+ + 8e^-$$
 (oxidation)  
 $I_2 + 2e^- \rightarrow 2I^-$  (reduction)

Multiply the reduction half-reaction by four, and then add together. Cancel the eight electrons from each side. The balanced equation in acidic solution is

$$S^{2-} + 4I_2 + 4H_2O \rightarrow 8I^- + SO_4^{2-} + 8H^+$$

Now add eight OH<sup>-</sup> to each side. Simplify by combining the H<sup>+</sup> and OH<sup>-</sup> to give H<sub>2</sub>O. Then cancel four H<sub>2</sub>O on each side. The balanced equation in basic solution is

$$S^{2-} + 4I_2 + 8OH^- \rightarrow 8I^- + SO_4^{2-} + 4H_2O$$

#### c. The two balanced half-reactions are

AI + 
$$4H_2O \rightarrow AI(OH)_4^- + 4H^+ + 3e^-$$
 (oxidation)  
 $NO_3^- + 9H^+ + 8e^- \rightarrow NH_3 + 3H_2O$  (reduction)

Multiply the oxidation half-reaction by eight and the reduction half-reaction by three, and then add together. Cancel the twenty four electrons from each side. Also, cancel twenty seven  $H^{\dagger}$  and nine  $H_2O$  from each side. The balanced equation in acidic solution is

$$8AI + 3NO_3^- + 23H_2O \rightarrow 8AI(OH)_4^- + 3NH_3^- + 5H_3^+$$

Now add five  $OH^-$  to each side. Simplify by combining the  $H^+$  and  $OH^-$  to give  $H_2O$ . Then cancel five  $H_2O$  on each side. The balanced equation in basic solution is

$$8AI + 3NO_3^- + 5OH^- + 18H_2O \rightarrow 8AI(OH)_4^- + 3NH_3$$

d. The two balanced half-reactions are

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$$
 (oxidation)  
 $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$  (reduction)

Multiply the oxidation half-reaction by three and the reduction half-reaction by two, and then add together. Cancel the six electrons from each side. The balanced equation in acidic solution is

$$2MnO_4^- + 3C_2O_4^{2-} + 8H^+ \rightarrow 2MnO_2 + 6CO_2 + 4H_2O$$

Now add eight OH<sup>-</sup> to each side. Simplify by combining the H<sup>+</sup> and OH<sup>-</sup> to give H<sub>2</sub>O. Then cancel four H<sub>2</sub>O on each side. The balanced equation in basic solution is

$$2MnO_4^- + 3C_2O_4^{2-} + 4H_2O \rightarrow 2MnO_2 + 6CO_2 + 8OH^-$$

20.35 a. The two balanced half-reactions are

$$I^- + 3H_2O \rightarrow IO_3^- + 6H^+ + 6e^-$$
 (oxidation)  
 $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$  (reduction)

Multiply the reduction half-reaction by two, and then add together. Cancel the six electrons from each side. Also, cancel six  $H^{+}$  and three  $H_{2}O$  from each side. The balanced equation in acidic solution is

$$2MnO_4^- + I^- + 2H^+ \rightarrow 2MnO_2 + IO_3^- + H_2O$$

Now add two OH<sup>-</sup> to each side. Simplify by combining the H<sup>+</sup> and OH<sup>-</sup> to give H<sub>2</sub>O. Then cancel one H<sub>2</sub>O on each side. The balanced equation in basic solution is

$$2MnO_4$$
 +  $I$  +  $H_2O$   $\rightarrow$   $2MnO_2$  +  $IO_3$  +  $2OH$ 

b. The two balanced half-reactions are

$$2Cl^- \rightarrow Cl_2 + 2e^-$$
 (oxidation)  
 $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$  (reduction)

Multiply the oxidation half-reaction by three, and then add together. Cancel the six electrons from each side. The balanced equation is

$$Cr_2O_7^{2-} + 6Cl^- + 14H^+ \rightarrow 2Cr^{3+} + 3Cl_2 + 7H_2O$$

c. The two balanced half-reactions are

$$S_8 + 16H_2O \rightarrow 8SO_2 + 32H^{+} + 32e^{-}$$
 (oxidation)  
 $NO_3^{-} + 4H^{+} + 3e^{-} \rightarrow NO + 2H_2O$  (reduction)

Multiply the oxidation half-reaction by three and the reduction half-reaction by thirty two, and then add together. Cancel the ninety six electrons from each side. Also, cancel ninety six H<sup>+</sup> and forty eight H<sub>2</sub>O from each side. The balanced equation is

$$3S_8 + 32NO_3^- + 32H^+ \rightarrow 32NO + 24SO_2 + 16H_2O$$

d. The two balanced half-reactions are

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$$
 (oxidation)  
 $MnO_4 + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$  (reduction)

Multiply the oxidation half-reaction by three and the reduction half-reaction by two, and then add together. Cancel the six electrons from each side. Also, cancel six H<sup>+</sup> from each side. The balanced equation in acidic solution is

$$3H_2O_2 + 2MnO_4^- + 2H^+ \rightarrow 3O_2 + 2MnO_2 + 4H_2O_4$$

Now add two OH<sup>-</sup> to each side. Simplify by combining the H<sup>+</sup> and OH<sup>-</sup> to give H<sub>2</sub>O. Then cancel two H<sub>2</sub>O on each side. The balanced equation in basic solution is

$$3H_2O_2 + 2MnO_4 \rightarrow 3O_2 + 2MnO_2 + 2H_2O + 2OH^2$$

e. The two balanced half-reactions are

$$Zn \rightarrow Zn^{2+} + 2e^{-}$$
 (oxidation)  
 $2NO_3^{-} + 12H^{+} + 10e^{-} \rightarrow N_2 + 6H_2O$  (reduction)

Multiply the oxidation half-reaction by five, and then add together. Cancel the ten electrons from each side. The balanced equation is

$$5Zn + 2NO_3^- + 12H^+ \rightarrow N_2 + 5Zn^{2+} + 6H_2O$$

20.36 a. The two balanced half-reactions are

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$$
 (oxidation)  
 $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$  (reduction)

Multiply the oxidation half-reaction by three, and then add together. Cancel the six electrons from each side. Also, cancel six  $H^{\dagger}$  from each side. The balanced equation is

$$Cr_2O_7^{2-} + 3H_2O_2 + 8H^+ \rightarrow 2Cr^{3+} + 3O_2 + 7H_2O$$
 (continued)

b. The two balanced half-reactions are

$$CN^{-} + H_2O \rightarrow CNO^{-} + 2H^{+} + 2e^{-}$$
 (oxidation)  
 $MnO_4^{-} + 4H^{+} + 3e^{-} \rightarrow MnO_2 + 2H_2O$  (reduction)

Multiply the oxidation half-reaction by three and the reduction half-reaction by two, and then add together. Cancel the six electrons from each side. Also, cancel six H<sup>+</sup> and three H<sub>2</sub>O from each side. The balanced equation in acidic solution is

$$3CN^{-} + 2MnO_{4}^{-} + 2H^{+} \rightarrow 3CNO^{-} + 2MnO_{2} + H_{2}O$$

Now add two OH<sup>-</sup> to each side. Simplify by combining the H<sup>+</sup> and OH<sup>-</sup> to give H<sub>2</sub>O. Then, cancel one H<sub>2</sub>O on each side. The balanced equation in basic solution is

$$3CN^{-} + 2MnO_{4}^{-} + H_{2}O \rightarrow 3CNO^{-} + 2MnO_{2} + 2OH^{-}$$

c. The two balanced half-reactions are

$$Cr(OH)_4^- \rightarrow CrO_4^{2^-} + 4H^+ + 3e^-$$
 (oxidation)  
 $OCI^- + 2H^+ + 2e^- \rightarrow CI^- + H_2O$  (reduction)

Multiply the oxidation half-reaction by two and the reduction half-reaction by three, and then add together. Cancel the six electrons from each side. Also, cancel six H<sup>+</sup> from each side. The balanced equation in acidic solution is

$$2Cr(OH)_4^- + 3OCl^- \rightarrow 2CrO_4^{2-} + 3Cl^- + 3H_2O + 2H^+$$

Now add two  $OH^-$  to each side. Simplify by combining the  $H^+$  and  $OH^-$  to give  $H_2O$ . Then combine the  $H_2O$  on the right side into a single term. The balanced equation in basic solution is

$$2Cr(OH)_{4}^{-} + 3OCI^{-} + 2OH^{-} \rightarrow 2CrO_{4}^{2-} + 3CI^{-} + 5H_{2}O$$

d. The two balanced half-reactions are

$$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$$
 (oxidation)  
 $Br_2 + 2e^- \rightarrow 2Br^-$  (reduction)

Add the two half-reactions together. Cancel the two electrons from each side. The balanced equation is

$$Br_2 + SO_2 + 2H_2O \rightarrow 2Br^- + SO_4^{-2} + 4H^+$$

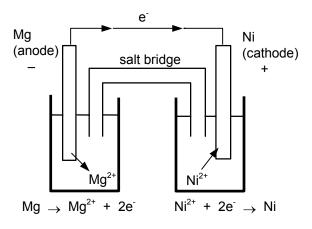
#### e. The two balanced half-reactions are

$$8CuS \rightarrow S_8 + 8Cu^{2+} + 16e^{-}$$
 (oxidation)  
 $NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$  (reduction)

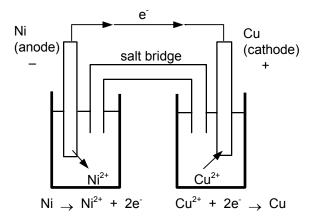
Multiply the oxidation half-reaction by three and the reduction half-reaction by sixteen, and then add together. Cancel the forty eight electrons from each side. The balanced equation is

24CuS + 
$$16NO_3$$
 +  $64H$   $\rightarrow$  24Cu<sup>2+</sup> +b  $16NO$  +  $3S_8$  +  $32H_2O$ 

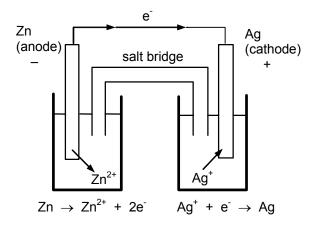
#### 20.37 Sketch of the cell:



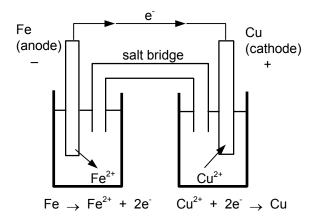
#### 20.38 Sketch of the cell:



#### 20.39 Sketch of the cell:



#### 20.40 Sketch of the cell:



#### 20.41 The electrode half-reactions and the overall cell reaction are

Anode:  $Zn(s) + 2OH(aq) \rightarrow Zn(OH)_2(s) + 2e^{-s}$ 

Cathode:  $Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq)$ 

Overall:  $Zn(s) + Ag_2O(s) + H_2O(l) \rightarrow Zn(OH)_2(s) + 2Ag(s)$ 

20.42 The electrode half-reactions and the overall cell reaction are

Anode: 
$$Zn(s) + 2OH^{-}(aq) \rightarrow Zn(OH)_{2}(s) + 2e^{-}$$

Cathode: 
$$HgO(s) + H_2O(l) + 2e^- \rightarrow Hg(l) + 2OH(aq)$$

Overall: 
$$Zn(s) + HgO(s) + H_2O(l) \rightarrow Zn(OH)_2(s) + Hg(l)$$

- 20.43 Because of its less negative E°, Pb<sup>2+</sup> is reduced at the cathode and is written on the right; Ni(s) is oxidized at the anode and is written first, at the left, in the cell notation. The notation is Ni(s)|Ni<sup>2+</sup>(aq)||Pb(s).
- 20.44 Because of its less negative  $E^{\circ}$ ,  $H^{+}$  is reduced at the cathode and is written on the right; Al(s) is oxidized at the anode and is written first, at the left, in the cell notation. The notation is Al(s)|A|<sup>3+</sup>(aq)||H<sup>+</sup>(aq)||H<sub>2</sub>(g)||Pt.
- 20.45 Because of its less negative  $E^{\circ}$ ,  $H^{+}$  is reduced at the cathode and is written on the right; Ni(s) is oxidized at the anode and is written first, at the left, in the cell notation. The notation is Ni(s)|Ni<sup>2+</sup>(1 M)||H<sup>+</sup>(1 M)|H<sub>2</sub>(g)|Pt.
- 20.46 Because of its less negative  $E^{\circ}$ ,  $Fe^{2^{+}}$  is reduced at the cathode and is written on the right; Zn(s) is oxidized at the anode and is written first, at the left, in the cell notation. The notation is  $Zn(s)|Zn^{2^{+}}(0.40 \text{ M})||Fe^{3^{+}}(0.30 \text{ M})|Fe(s)$ .
- 20.47 The Fe(s), on the left, is the reducing agent. The Ag<sup>+</sup>, on the right, is the oxidizing agent, gaining just one electron. Multiplying its half-reaction by two to equalize the numbers of electrons and writing both half-reactions gives the overall cell reaction:

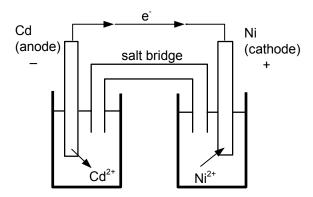
$$Fe(s) \rightarrow Fe^{2^{+}}(aq) + 2e^{-}$$

$$2Ag^{+}(aq) + 2e^{-} \rightarrow 2Ag(s)$$

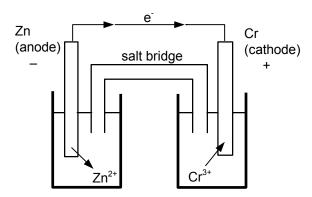
$$Fe(s) + 2Ag^{+}(aq) \rightarrow Fe^{2^{+}}(aq) + 2Ag(s)$$

20.48 The  $H_2(g)$ , on the left, is the reducing agent. The  $Br_2(I)$ , on the right, is the oxidizing agent. The half-reactions and the overall cell reaction are

20.49 The half-cell reactions, the overall cell reaction, and the sketch are



20.50 The half-cell reactions, the overall cell reaction, and the sketch are



#### 20.51 The half-cell reactions are

$$2Fe^{3+}(aq) + 2e^{-} \rightarrow 2Fe^{2+}(aq)$$
  
 $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ 

n equals two, and the maximum work for the reaction as written is

$$w_{\text{max}} = -nFE_{\text{cell}} = -2 \times 9.65 \times 10^4 \text{ C} \times 0.72 \text{ V} = -1.389 \times 10^5 \text{ C} \cdot \text{V}$$
  
= -1.389 x 10<sup>5</sup> J

Because this is the work obtained by reduction of two mol of Fe<sup>3+</sup>, the work for one mol is

$$w_{max} = (-1.389 \times 10^5 \text{ J})/2 \text{ mol} = -6.945 \times 10^4 = -6.9 \times 10^4 \text{ J} = -69 \text{ kJ}$$

#### 20.52 The half-cell reactions are

$$Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$$
  
 $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ 

n equals two, and the maximum work for the reaction as written is

$$w_{\text{max}} = -nFE_{\text{cell}} = -2 \times 9.65 \times 10^{-4} \text{ C} \times 0.853 \text{ V} = -1.646 \times 10^5 \text{ C} \cdot \text{V}$$
  
= -1.646 x 10<sup>5</sup> J

For 20.0 g of zinc, the maximum work is

20.0 g Zn x 
$$\frac{1 \text{ mol Zn}}{65.39 \text{ g Zn}}$$
 x  $\frac{-1.646 \times 10^5 \text{ J}}{1 \text{ mol Zn}}$  =  $-5.0344 \times 10^4$  = =  $-5.03 \times 10^4 \text{ J}$ 

#### 20.53 The half-cell reactions are

$$2Ag^{+}(aq) + 2e^{-} \rightarrow 2Ag(s)$$
  
Ni(s)  $\rightarrow$  Ni<sup>2+</sup>(aq) + 2e<sup>-</sup>

n equals two, and the maximum work for the reaction as written is

$$w_{max} = -nFE_{cell} = -2 \times 9.65 \times 10^4 C \times 0.97 V = -1.87 \times 10^5 C \cdot V$$
  
=  $-1.87 \times 10^5 J$ 

For 30.0 g of nickel, the maximum work is

30.0 g Ni x 
$$\frac{1 \text{ mol Ni}}{58.69 \text{ g Ni}}$$
 x  $\frac{-1.87 \times 10^5 \text{ J}}{1 \text{ mol Ni}}$  =  $-9.\underline{5}6 \times 10^4 \text{ J}$  =  $-96 \text{ kJ}$ 

20.54 The half-cell reactions are

$$3O_2(g) + 12H^+ + 12e^- \rightarrow 6H_2O(I)$$
  
 $4AI(s) \rightarrow 4AI^{3+}(aq) + 12e^-$ 

n equals twelve, and the maximum work for the reaction as written is

$$w_{\text{max}} = -nFE_{\text{cell}} = -(12)(9.65 \times 10^4 \text{ C})(1.15 \text{ V}) = -1.331 \times 10^6 \text{ C} \cdot \text{V}$$
  
= -1.331 x 10<sup>6</sup> J

For 50.0 g of aluminum, the maximum work is

50.0 g x 
$$\frac{1 \text{ mol Al}}{26.98 \text{ g Al}}$$
 x  $\frac{-1.331 \times 10^6 \text{ J}}{4 \text{ mol Al}}$  = -6.1 $\frac{6}{9}$  x 10<sup>5</sup> = = -6.17 x 10<sup>5</sup> J

20.55 The half-reactions and corresponding electrode potentials are as follows

$$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(I)$$
 0.96 V  $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(I)$  1.23 V  $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(I)$  1.49 V

The order by increasing oxidizing strength is  $NO_3(aq)$ ,  $O_2(g)$ ,  $MnO_4(aq)$ .

20.56 The half-reactions and corresponding electrode potentials are as follows

$$I_{2}(s) + 2e^{-} \rightarrow 2I^{-}(aq)$$
 0.54 V  
 $Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$  0.80 V  
 $MnO_{4}^{-}(aq) + 8H^{+}(aq) + 5e^{-} \rightarrow Mn^{2+}(aq) + 4H_{2}O(I)$  1.49 V

The order by increasing oxidizing strength is  $I_2(s)$ ,  $Ag^+(aq)$ ,  $MnO_4(aq)$ .

20.57 The half-reactions and corresponding electrode potentials are as follows

$$Zn^{2^{+}}(aq) + 2e^{-} \rightarrow Zn(s)$$
 -0.76 V  
 $Fe^{2^{+}}(aq) + 2e^{-} \rightarrow Fe(s)$  -0.41 V  
 $Cu^{2^{+}}(aq) + e^{-} \rightarrow Cu^{+}(aq)$  0.16 V

Zn(s) is the strongest, and Cu<sup>+</sup>(aq) is the weakest.

20.58 The half-reactions and corresponding electrode potentials are as follows

$$Sn^{4+}(aq) + 2e^{-} \rightarrow Sn^{2+}(aq)$$
 0.15 V  
 $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$  0.34 V  
 $I_{2}(s) + 2e^{-} \rightarrow 2I^{-}(aq)$  0.54 V

 $I_2(s)$  is the strongest and  $Sn^{4+}$  is the weakest.

20.59 a. In this reaction, Sn<sup>4+</sup> is the oxidizing agent on the left side; Fe<sup>3+</sup> is the oxidizing reagent on the right side. The corresponding standard electrode potentials are

$$Sn^{4+}(aq) + 2e^{-} \rightarrow Sn^{2+}(aq)$$
  $E^{\circ} = 0.15 \text{ V}$   
 $Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)$   $E^{\circ} = 0.77 \text{ V}$ 

The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so Fe<sup>3+</sup> is the stronger oxidizing agent. The reaction is nonspontaneous as written.

b. In this reaction, MnO<sub>4</sub> is the oxidizing agent on the left side; O<sub>2</sub> is the oxidizing reagent on the right side. The corresponding standard electrode potentials are

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(I)$$
  $E^\circ = 1.23 \text{ V}$   $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4 H_2O(I)$   $E^\circ = 1.49 \text{ V}$ 

The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so  $MnO_4^-$  is the stronger oxidizing agent. The reaction is spontaneous as written.

20.60 a. The reduction half-reactions and standard potentials are

Fe<sup>3+</sup>(aq) + e<sup>-</sup> 
$$\rightarrow$$
 Fe<sup>2+</sup>(aq) E° = 0.77 V  
Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>(aq) + 14H<sup>+</sup>(aq) + 6e<sup>-</sup>  $\rightarrow$  2Cr<sup>2+</sup>(aq) + 7H<sub>2</sub>O(I) E° = 1.33 V

The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so  $\text{Cr}_2\text{O}_7^{2^-}$  is the stronger oxidizing agent. Thus,  $\text{Cr}_2\text{O}_7^{2^-}$  will oxidize iron(II) ion in acidic solution under standard conditions.

b. The reduction half-reactions and standard electrode potentials are

$$Ni^{2^{+}}(aq) + 2e^{-} \rightarrow Ni(s)$$
  $E^{\circ} = -0.23 \text{ V}$   $Cu^{2^{+}}(aq) + 2e^{-} \rightarrow Cu(s)$   $E^{\circ} = 0.34 \text{ V}$ 

The stronger reducing agent is the one involved in the half-reaction with the smaller standard electrode potential, so Ni(s) is the stronger reducing agent. Thus, copper metal will not reduce Ni(II) ion spontaneously.

20.61 The reduction half-reactions and standard electrode potentials are

$$Br_2(I) + 2e^- \rightarrow 2Br^-(aq)$$
  $E^\circ = 1.07 \text{ V}$   $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$   $E^\circ = 1.36 \text{ V}$   $F_2(g) + 2e^- \rightarrow 2F^-(aq)$   $E^\circ = 2.87 \text{ V}$ 

From these, you see that the order of increasing oxidizing strength is  $Br_2$ ,  $Cl_2$ ,  $F_2$ . Therefore, chlorine gas will oxidize  $Br^-$  but will not oxidize  $F^-$ . The balanced equation for the reaction is

$$Cl_2(g) + 2Br(aq) \rightarrow 2Cl(aq) + Br_2(l)$$

20.62 The reduction half-reactions and standard electrode potentials are

$$Br_2(I) + 2e^- \rightarrow 2Br^-(aq)$$
  $E^\circ = 1.07 \text{ V}$   $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(I)$   $E^\circ = 1.33 \text{ V}$   $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(I)$   $E^\circ = 1.49 \text{ V}$ 

From these, you see that the order of increasing oxidizing strength is  $Br_2$ ,  $Cr_2O_7^{2-}$ ,  $MnO_4^-$ . Thus,  $Cr_2O_7^{2-}$  will oxidize  $Br^-$  but will not oxidize  $Mn^{2+}$ . The balanced equation for the reaction is

$$Cr_2O_7^{2-}(aq) + 6Br^{-}(aq) + 14H^{+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Br_2(I) + 7H_2O(I)$$

20.63 The half-reactions and standard electrode potentials are

$$Cr(s) \rightarrow Cr^{3+}(aq) + 3e^{-}$$
  $-E^{\circ}_{Cr} = 0.74 \text{ V}$   
 $Hg_2^{2+}(aq) + 2e^{-} \rightarrow 2Hg(I)$   $E^{\circ}_{Hg} = 0.80 \text{ V}$ 

Obtain the cell emf by adding the half-cell potentials.

$$E^{\circ}_{cell} = E^{\circ}_{Hq} - E^{\circ}_{Cr} = 0.80 \text{ V} + 0.74 \text{ V} = 1.54 \text{ V}$$

20.64 The half-reactions and standard electrode potentials are

$$Sn(s) \rightarrow Sn^{2+}(aq) + 2e^{-}$$
  $-E^{\circ}_{Sn} = 0.14 \text{ V}$   
 $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$   $E^{\circ}_{Cu} = 0.34 \text{ V}$ 

Obtain the cell emf by adding the half-cell potentials.

$$E^{\circ}_{cell} = E^{\circ}_{Cu} - E^{\circ}_{Sn} = 0.34 \text{ V} + 0.14 \text{ V} = 0.48 \text{ V}$$

20.65 The half-reactions and standard electrode potentials are

$$Cr(s) \rightarrow Cr^{3+}(aq) + 3e^{-}$$
  $-E^{\circ}_{Cr} = 0.74 \text{ V}$   
 $I_{2}(s) + 2e^{-} \rightarrow 2I^{-}(aq)$   $E^{\circ}_{I_{2}} = 0.54 \text{ V}$ 

Obtain the cell emf by adding the half-cell potentials.

$$E^{\circ}_{cell} = E^{\circ}_{Cr} - E^{\circ}_{I_2} = 0.54 \text{ V} + 0.74 \text{ V} = 1.28 \text{ V}$$

20.66 The half-reactions and standard electrode potentials are

$$Al(s) \rightarrow Al^{3+}(aq) + 3e^{-}$$
  $-E^{\circ}_{Al} = 1.66 \text{ V}$   $Hg_2^{2+}(aq) + 2e^{-} \rightarrow 2Hg(l)$   $E^{\circ}_{Hg} = 0.80 \text{ V}$ 

Obtain the cell emf by adding the half-cell potentials.

$$E^{\circ}_{cell} = E^{\circ}_{Hg} - E^{\circ}_{Al} = 0.80 \text{ V} + 1.66 \text{ V} = 2.46 \text{ V}$$

20.67 The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$$3Cu(s) \rightarrow 3Cu^{2+}(aq) + 6e^{-}$$
  $-E^{\circ} = -0.34 \text{ V}$   
 $2NO_3^{-}(aq) + 8H^{+}(aq) + 6e^{-} \rightarrow 2NO(g) + 4H_2O(l)$   $E^{\circ} = 0.96 \text{ V}$   
 $3Cu(s) + 2NO_3^{-}(aq) + 8H^{+}(aq) \rightarrow$   
 $3Cu^{2+}(aq) + 2NO(g) + 4H_2O(l)$   $E^{\circ}_{cell} = 0.62 \text{ V}$ 

Note that each half-reaction involves six electrons, hence n = 6. Therefore,

$$\Delta G^{\circ} = -nFE^{\circ}_{cell} = -6 \times 9.65 \times 10^{4} \, C \times 0.62 \, V = -3.58 \times 10^{5} \, J = -3.6 \times 10^{5} \, J$$

Thus, the standard free-energy change is -3.6 x 10<sup>2</sup> kJ.

20.68 The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$$4AI(s) \rightarrow 4AI^{3+}(aq) + 12e^{-}$$
  $-E^{\circ} = 1.66 \text{ V}$   
 $3O_2(g) + 12H^{+}(aq) + 12e^{-} \rightarrow 6H_2O(I)$   $E^{\circ} = 1.23 \text{ V}$   
 $4AI(s) + 3O_2(g) + 12H^{+}(aq) \rightarrow 4AI^{3+}(aq) + 6H_2O(I)$   $E^{\circ}_{cell} = 2.89 \text{ V}$ 

Note that each half-reaction involves twelve electrons, hence n = 12. Therefore,

$$\Delta G^{\circ} = -nFE^{\circ}_{cell} = -12 \times 9.65 \times 10^{4} \text{ C} \times 2.89 \text{ V} = -3.346 \times 10^{6} \text{ J} = -3.35 \times 10^{6} \text{ J}$$

Thus, the standard free-energy change is -3.35 x 10<sup>3</sup> kJ.

20.69 The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

Note that each half-reaction involves two electrons, hence n = 2. Therefore,

$$\Delta G^{\circ}$$
 = -nFE $^{\circ}_{cell}$  = -2 x 9.65 x 10 $^{4}$  C x 0.82 V = -1.58 x 10 $^{5}$  J = -1.6 x 10 $^{5}$  J

Thus, the standard free-energy change is -1.6 x 10<sup>2</sup> kJ.

20.70 The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$$Na(s) \rightarrow Na^{+}(aq) + e^{-}$$
  $-E^{\circ} = 2.71 \text{ V}$ 
 $1/2Br_{2}(g) + e^{-} \rightarrow Br^{-}(aq)$   $E^{\circ} = 1.07 \text{ V}$ 
 $Na(s) + 1/2Br_{2}(g) \rightarrow Na^{+}(aq) + Br^{-}(aq)$   $E^{\circ}_{cell} = 3.78 \text{ V}$ 

Note that each half-reaction involves one electron, hence n = 1. Therefore,

$$\Delta G^{\circ} = -nFE^{\circ}_{cell} = -1 \times 9.65 \times 10^{4} \, C \times 3.78 \, V = -3.647 \times 10^{5} \, J = -3.65 \times 10^{5} \, J$$

Thus, the standard free-energy change is -365 kJ.

20.71 Write the equation with  $\Delta G_f^{\circ}$ 's beneath each substance.

Mg(s) + 
$$2Ag^{+}(aq)$$
 → Mg<sup>2+</sup>(aq) +  $2Ag(s)$   
 $\Delta G_{f}^{\circ}$ : 0 2 x 77.111 -456.01 0 kJ

Hence,

$$\Delta G^{\circ} = \Sigma n \Delta G_f^{\circ} (products) - \Sigma m \Delta G_f^{\circ} (reactants)$$
  
= [-456.01 - 2 x 77.111] kJ = -610.23 kJ = -6.1023 x 10<sup>5</sup> J

Obtain n by splitting the reaction into half-reactions.

$$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^{-}$$
  
 $2Ag^{+}(aq) + 2e^{-} \rightarrow 2Ag(s)$ 

Each half-reaction involves two electrons, so n = 2. Therefore,

$$\Delta G^{\circ} = -nFE^{\circ}_{cell}$$
  
-6.1023 x 10<sup>5</sup> J = -2 x 9.65 x 10<sup>4</sup> C x  $E^{\circ}_{cell}$ 

Rearrange and solve for  $E^{\circ}_{cell}$ . Recall that  $J = C \cdot V$ .

$$E_{cell}^{\circ} = \frac{-6.1023 \times 10^5 \text{ J}}{-2 \times 9.65 \times 10^4 \text{ C}} = 3.1618 = 3.16 \text{ V}$$

20.72 Write the equation with  $\Delta G_f^{\circ}$ 's beneath each substance.

$$2 \text{Al(s)} \ + \ 3 \text{Cu}^{2+} (\text{aq}) \ \rightarrow \ 2 \text{Al}^{3+} (\text{aq}) \ + \ 3 \text{Cu(s)}$$
 
$$\Delta G_f^{\circ} \colon \quad 0 \qquad 3 \times 64.98 \qquad 2 \times (-481.2) \qquad 0 \text{ kJ}$$

Hence,

$$\Delta G^{\circ} = \Sigma n \Delta G_{f}^{\circ} (products) - \Sigma m \Delta G_{f}^{\circ} (reactants)$$
  
= [2 x -481.2 - 3 x 64.98] kJ = -1.157.34 kJ = -1.15734 x 10<sup>6</sup> J

Obtain n by splitting the reaction into half-reactions.

$$2AI(s) \rightarrow 2AI^{3+}(aq) + 3e^{-}$$
  
 $3Cu^{2+}(aq) + 3e^{-} \rightarrow 3Cu(s)$ 

Each half-reaction involves three electrons, so n = 3. Therefore,

$$\Delta G^{\circ} = -nFE^{\circ}_{cell}$$
  
-1.15734 x 10<sup>6</sup> J = -3 x 9.65 x 10<sup>4</sup> C x  $E^{\circ}_{cell}$ 

Rearrange and solve for  $E^{\circ}_{cell}$ . Recall that  $J = C \cdot V$ .

$$E^{\circ}_{cell} = \frac{-1.15734 \times 10^6 \text{ J}}{-3 \times 9.65 \times 10^4 \text{ C}} = 1.9988 = 2.00 \text{ V}$$

20.73 Write the equation with  $\Delta G_f^{\circ}$ 's beneath each substance:

$$PbO_{2}(s) + 2HSO_{4}^{-}(aq) + 2H^{+}(aq) + Pb(s) \rightarrow 2PbSO_{4}(s) + 2H_{2}O(l)$$
 
$$\Delta G_{f}^{\circ}: -189.2 \quad 2(-752.87) \quad 0 \quad 0 \quad 2(-811.24) \quad 2(-237.192) \text{ kJ}$$

Hence,

$$\Delta G^{\circ}$$
 = [2 x -811.24 + 2 x -237.192 - -189.2 - 2 x -752.87] kJ  
= -401.924 kJ = -4.0192 x 10<sup>5</sup> J

Obtain n by splitting the reaction into half-reactions.

Each half-reaction involves two electrons, so n = 2. Therefore,

$$\Delta G^{\circ} = -nFE^{\circ}_{cell}$$

$$-4.0192 \times 10^5 \text{ J} = -2 \times 9.65 \times 10^4 \text{ C} \times \text{E}^{\circ}_{\text{cell}}$$

Rearrange and solve for  $E^{\circ}_{cell}$ . Recall that  $J = C \cdot V$ .

$$E^{\circ}_{cell} = \frac{-4.0192 \times 10^5 \text{ J}}{-2 \times 9.65 \times 10^4 \text{ C}} = 2.0825 = 2.08 \text{ V}$$

20.74 Write the equation with  $\Delta G_f^{\circ}$ 's beneath each substance:

$$5H_2C_2O_4(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 10CO_2(g) + 8H_2O(I) + 2Mn^{2+}(aq)$$
  
 $\Delta G_f^{\circ}$ : 5(-698) 2(-425.1) 0 10(-394.4) 8(-237.1) 2(-223) kJ

Hence,

$$\Delta G^{\circ}$$
 = [10(-394.4) + 8(-237.1) + 2(-223) - 5(-698) - 2(-425.1)] kJ  
= -1946.6 kJ = -1.9466 x 10<sup>6</sup> J

Obtain n by splitting the reaction into half-reactions.

$$5H_2C_2O_4(aq) \rightarrow 10CO_2(g) + 10H^+(aq) + 10e^-$$
  
 $2MnO_4^-(aq) + 16H^+(aq) + 10e^- \rightarrow 2Mn^{2+}(aq) + 8H_2O(l)$ 

Each half-reaction involves ten electrons, so n = 10. Therefore,

$$\Delta G^{\circ} = -nFE^{\circ}_{cell}$$

$$-1.9466 \times 10^6 \text{ J} = -10 \times 9.65 \times 10^4 \text{ C} \times \text{E}^{\circ}_{\text{cell}}$$

Rearrange and solve for  $E^{\circ}_{cell}$ . Recall that  $J = C \cdot V$ .

$$E^{\circ}_{cell} = \frac{-1.9466 \times 10^6 \text{ J}}{-10 \times 9.65 \times 10^4 \text{ C}} = 2.0\underline{1}72 = 2.02 \text{ V}$$

20.75 The half-reactions and standard electrode potentials are

Cu(s) 
$$\rightarrow$$
 Cu<sup>2+</sup>(aq) + 2e<sup>-</sup> -E°<sub>Cu</sub> = -0.34 V  
2Fe<sup>3+</sup>(aq) + 2e<sup>-</sup>  $\rightarrow$  2Fe<sup>2+</sup>(aq)  $E^{\circ}_{Fe^{3+}}$  = 0.77 V

The standard emf for the cell is

$$E^{\circ}_{cell} = E^{\circ}_{Fe^{3+}} - E^{\circ}_{Cu} = 0.77 \text{ V} - 0.34 \text{ V} = 0.43 \text{ V}$$

Note that n = 2. Substitute into the equation relating  $E^{\circ}$  and K. Note that K =  $K_c$ .

$$0.43 \text{ V} = \frac{0.0592}{2} \log K_c$$

Solving for K<sub>c</sub>, you get

$$\log K_c = 14.52$$

Take the antilog of both sides:

$$K_c$$
 = antilog (14.52) = 3.4 x 10<sup>14</sup> = 10<sup>14</sup>

20.76 The half-reactions and standard electrode potentials are

$$2 \text{Hg(I)} \rightarrow \text{Hg}_2^{2+}(\text{aq}) + 2 \text{e}^ -\text{E}^{\circ}_{\text{Hg}} = -0.80 \text{ V}$$
  $\text{Sn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Sn(s)}$   $\text{E}^{\circ}_{\text{Sn}^{2+}} = -0.14 \text{ V}$ 

The standard emf for the cell is

$$E^{\circ}_{cell}$$
 =  $E^{\circ}_{Sn^{2+}}$  -  $E^{\circ}_{Hg}$  = -0.14 V - 0.80 V = -0.94 V

Note that n = 2. Substitute into the equation relating  $E^{\circ}$  and K. Note that  $K = K_c$ .

$$-0.94 \text{ V} = \frac{0.0592}{2} \log K_c$$

Solving for K<sub>c</sub>, you get

$$\log K_c = -31.756$$

Take the antilog of both sides:

$$K_c$$
 = antilog (-31.756) = 1.75 x 10<sup>-32</sup> = 10<sup>-32</sup>

20.77 The half-reactions and standard electrode potentials are

$$Cu^{+}(aq) \rightarrow Cu^{2+}(aq) + e^{-}$$
  $-E^{\circ} = -0.16 \text{ V}$   
 $Cu^{+}(aq) + e^{-} \rightarrow Cu(s)$   $E^{\circ} = 0.52 \text{ V}$ 

The standard emf for the cell is

$$E^{\circ}_{cell} = 0.52 \text{ V} - 0.16 \text{ V} = 0.36 \text{ V}$$

Note that n equals 1. Substitute into the equation relating  $E^\circ$  and K. Note that K equals  $K_c$ .

$$0.36 \text{ V} = \frac{0.0592}{1} \log K_c$$

Solving for K<sub>c</sub>, you get

$$\log K_c = 6.081$$

Take the antilog of both sides:

$$K_c$$
 = antilog (6.081) = 1.2 x 10<sup>6</sup> = 1 x 10<sup>6</sup>

20.78 The half-reactions and standard electrode potentials are

$$CIO_2^-(aq) + 2OH^-(aq) \rightarrow CIO_3^-(aq) + H_2O(I) + 2e^- - E^\circ = -0.35 \text{ V}$$
  
 $CIO_4^-(aq) + H_2O(I) + 2e^- \rightarrow CIO_3^-(aq) + 2OH^-(aq)$   $E^\circ = 0.17 \text{ V}$ 

The standard emf for the cell is

$$E^{\circ}_{cell} = 0.17 \text{ V} - 0.35 \text{ V} = -0.18 \text{ V}$$

Note that n equals two. Substitute into the equation relating  $E^\circ$  and K. Note that K equals  $K_{\rm c}.$ 

$$-0.18 \text{ V} = \frac{0.0592}{2} \log K_c$$

Solving for K<sub>c</sub>, you get

$$log K_c = -6.081$$

Take the antilog of both sides:

$$K_c = antilog (-6.081) = 8.29 \times 10^{-7} = 8 \times 10^{-7}$$

20.79 The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$$2Cr(s) \rightarrow 2Cr^{3+}(aq) + 6e^{-} - E^{\circ} = 0.74 \text{ V}$$

$$3Ni^{2+}(aq) + 6e^{-} \rightarrow 3Ni(s) \qquad E^{\circ} = -0.23 \text{ V}$$

$$2Cr(s) + 3Ni^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Ni(s) \qquad E^{\circ}_{cell} = 0.51 \text{ V}$$

Note that n equals six. The reaction quotient is

$$Q = \frac{[Cr^{3+}]^2}{[Ni^{2+}]^3} = \frac{(1.0 \times 10^{-3})^2}{(1.5)^3} = 2.962 \times 10^{-7}$$

The standard emf is 0.51 V, so the Nernst equation becomes

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592}{n} \log Q$$

$$= 0.51 - \frac{0.0592}{6} \log (2.962 \times 10^{-7})$$

$$= 0.51 - (-0.06441) = 0.574 = 0.57 \text{ V}$$

20.80 The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$$Ni(s) \rightarrow Ni^{2+}(aq) + 2e^{-}$$
  $-E^{\circ} = 0.23 \text{ V}$ 

$$\frac{Sn^{2+}(aq) + 2e^{-} \rightarrow Sn(s)}{Ni(s) + Sn^{2+}(aq) \rightarrow Ni^{2+}(aq) + Sn(s)}$$
 $E^{\circ}_{cell} = 0.09 \text{ V}$ 

Note that n equals two. The reaction quotient is

$$Q = \frac{[Ni^{2+}]}{[Sn^{2+}]} = \frac{1.0}{1.0 \times 10^{-4}} = 1.\underline{0}0 \times 10^{4}$$

The standard emf is 0.09 V, so the Nernst equation becomes

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592}{n} \log Q$$

$$= 0.09 - \frac{0.0592}{2} \log (1.00 \times 10^{4})$$

$$= 0.09 \text{ V} - (0.1184 \text{ V}) = -0.0284 = -0.03 \text{ V}$$

20.81 The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$$10Br^{-}(aq) \rightarrow 5Br_{2}(I) + 10e^{-} \qquad -E^{\circ} = 1.07 \text{ V}$$

$$\frac{2MnO_{4}^{-}(aq) + 16H^{+}(aq) + 10e^{-} \rightarrow 2Mn^{2+}(aq) + 8H_{2}O(I)}{2MnO_{4}^{-}(aq) + 10Br^{-}(aq) + 16H^{+}(aq) \rightarrow}$$

$$2Mn^{2+}(aq) + 5Br_{2}(I) + 8H_{2}O(I)$$

$$E^{\circ}_{cell} = 0.42 \text{ V}$$

Note that n equals ten. The reaction quotient is

$$Q = \frac{[Mn^{2+}]^2}{[MnO_4^{2-}]^2[Br^-]^{10}[H^+]^{16}} = \frac{(0.15)^2}{(0.010)^2(0.010)^{10}(1.0)^{16}} = 2.\underline{2}5 \times 10^{22}$$

The standard emf is 0.09 V, so the Nernst equation becomes

$$E_{cell} = E_{cell}^{\circ} - \frac{0.0592}{n} \log Q = 0.42 - \frac{0.0592}{10} \log (2.25 \times 10^{22})$$
  
= 0.42 - (0.1323) = 0.2876 = 0.29 V

20.82 The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$$6l^{-}(aq) \rightarrow 3l_{2}(l) + 6e^{-} \qquad -E^{\circ} = -0.54 \text{ V}$$

$$Cr_{2}O_{7}^{2-}(aq) + 14H^{+}(aq) + 6e^{-} \rightarrow 2Cr^{3+}(aq) + 7H_{2}O(l) \qquad E^{\circ} = 1.33 \text{ V}$$

$$Cr_{2}O_{7}^{2-}(aq) + 6l^{-}(aq) + 14H^{+}(aq) \rightarrow$$

$$2Cr^{3+}(aq) + 3l_{2}(s) + 7H_{2}O(l) \qquad E^{\circ}_{cell} = 0.79 \text{ V}$$

Note that n equals six. The reaction quotient is

$$Q = \frac{[Cr^{3+}]^2}{[Cr_2Q_7^{2-}][\Gamma]^6[H^+]^{14}} = \frac{(0.40)^2}{(0.020)(0.015)^6(0.50)^{14}} = 1.\underline{1}507 \times 10^{16}$$

The standard emf is 0.79 V, so the Nernst equation becomes

$$E_{cell} = E_{cell}^{\circ} - \frac{0.0592}{n} \log Q = 0.79 - \frac{0.0592}{6} \log (1.1507 \times 10^{16})$$
  
= 0.79 - (0.1584) = 0.6315 = 0.63 V

## 20.83 The overall reaction is

$$Cd(s) + Ni^{2+}(aq) \rightarrow Cd^{2+}(aq) + Ni(s)$$

Note that n equals two. The reaction quotient is

$$Q = \frac{[Cd^{2+}]}{[Ni^{2+}]} = \frac{[Cd^{2+}]}{1.0} = [Cd^{+}]$$

The standard emf is 0.170 V, and the emf is 0.240 V, so the Nernst equation becomes

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592}{n} \log Q$$

$$0.240 = 0.170 - \frac{0.0592}{2} \log Q$$

Rearrange and solve for log Q

$$\log Q = \frac{2}{0.0592} \times (0.240 - 0.170) = -2.3648$$

Take the antilog of both sides

Q = 
$$[Cd^{2+}]$$
 = antilog (-2.3648) =  $\underline{4}.31 \times 10^{-3}$  = 0.004 M

The Cd<sup>2+</sup> concentration is 0.004 M.

## 20.84 The overall reaction is

$$Zn(s) + 2H^{+}(aq) \rightarrow Zn^{2+}(aq) + H_{2}(q)$$

Note that n equals two. The reaction quotient is

$$Q = \frac{[Zn^{2+}] \times P_{H_2}}{[H^+]^2} = \frac{(1.0)(1.0)}{[H^+]^2} = \frac{1}{[H^+]^2}$$

The standard emf is equal to the standard oxidation potential for Zn, which is 0.76 V. The emf is 0.475 V, so the Nernst equation becomes

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592}{n} \log Q$$

$$0.475 = 0.76 - \frac{0.0592}{2} \log Q$$

Rearrange and solve for log Q

$$\log Q = \frac{2}{0.0592} \times (0.475 - 0.76) = 9.628$$

Use the properties of logs to simplify log Q as follows:

$$\log Q = \log \frac{1}{[H^+]^2} = \log [H^+]^{-2} = -2 \log [H^+] = 2(-\log [H^+]) = 2 \times pH$$

Therefore

$$log Q = 2 x pH = 9.628$$

$$pH = 9.628 \div 2 = 4.814 = 4.8$$

20.85 a. The cathode reaction is  $Ca^{2+}(I) + 2e^{-} \rightarrow Ca(I)$ .

The anode reaction is  $S^{2}(I) \rightarrow S(I) + 2e^{-}$ .

b. The cathode reaction is  $Cs^{+}(I) + e^{-} \rightarrow Cs(I)$ .

The anode reaction is  $4OH^{-}(I) \rightarrow O_2(g) + 2H_2O(g) + 4e^{-}$ .

20.86 a. The cathode reaction is  $Mg^{2+}(I) + 2e^{-} \rightarrow Mg(I)$ .

The anode reaction is  $2Br(I) \rightarrow Br_2(I) + 2e^{-}$ .

b. The cathode reaction is  $Ca^{2+}(I) + 2e^{-} \rightarrow Ca(I)$ .

The anode reaction is  $4OH(I) \rightarrow O_2(g) + 2H_2O(g) + 4e^{-1}$ .

20.87 a. The species you should consider for half-reactions are  ${\rm Na}^{^+},\,{\rm SO_4}^{2^-},\,{\rm and}\,{\rm H_2O}.$  The possible cathode reactions are

$$Na^{+}(aq) + e^{-} \rightarrow Na(s)$$
  $E^{\circ} = -2.71 \text{ V}$ 

$$2H_2O(I) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$
  $E^\circ = -0.83 \text{ V}$ 

Because the electrode potential for H<sub>2</sub>O is larger (less negative), it is easier to reduce.

The possible anode reactions are

$$2H_2O(I) \rightarrow O_2(g) + 4H^+(aq) + 4e^ E^{\circ} = -1.23 \text{ V}$$
  
 $2SO_4^{2-}(aq) \rightarrow S_2O_4^{2-}(aq) + 2e^ E^{\circ} = -2.01 \text{ V}$ 

Because the electrode potential for H<sub>2</sub>O is less negative, it is easier to oxidize.

The expected half-reactions are

$$2H_2O(I) \rightarrow O_2(g) + 4H^+(aq) + 4e^ E^\circ = -1.23 \text{ V}$$
  
 $4H_2O(I) + 4e^- \rightarrow 2H_2(g) + 4OH^-(aq)$   $E^\circ = -0.83 \text{ V}$ 

The overall reaction is

$$2H_2O(I) \rightarrow 2H_2(g) + O_2(g)$$

b. The species you should consider for half-reactions are K<sup>+</sup>, Br<sup>-</sup>, and H<sub>2</sub>O. The possible cathode reactions are

$$K^{+}(aq) + e^{-} \rightarrow K(s)$$
  $E^{\circ} = -2.92 \text{ V}$   $2H_{2}O(I) + 2e^{-} \rightarrow H_{2}(g) + 2OH^{-}(aq)$   $E^{\circ} = -0.83 \text{ V}$ 

Because the electrode potential for  $H_2O$  is larger (less negative), it is easier to reduce. The possible anode reactions are

$$2H_2O(I) \rightarrow O_2(g) + 4H^+(aq) + 4e^ E^{\circ} = -1.23 \text{ V}$$
  
 $2Br^{\circ}(aq) \rightarrow Br_2(I) + 2e^ E^{\circ} = -1.07 \text{ V}$ 

Because the electrode potential for Br is less negative, it is easier to oxidize.

The expected half-reactions are

$$2Br^{-}(aq) \rightarrow Br_{2}(I) + 2e^{-}$$
  $E^{\circ} = -1.07 \text{ V}$   $2H_{2}O(I) + 2e^{-} \rightarrow H_{2}(g) + 2OH^{-}(aq)$   $E^{\circ} = -0.83 \text{ V}$ 

The overall reaction is

$$2Br^{-}(aq) + 2H_{2}O(I) \rightarrow Br_{2}(I) + H_{2}(g) + 2OH^{-}$$

20.88 a. The species you should consider for half-reactions are Cu<sup>2+</sup>, Cl<sup>-</sup>, and H<sub>2</sub>O. The possible cathode reactions are

$$Cu^{2^+}(aq) + 2e^- \rightarrow Cu(s)$$
  $E^{\circ} = 0.34 \text{ V}$   $2H_2O(I) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$   $E^{\circ} = -0.83 \text{ V}$ 

Because the electrode potential for Cu<sup>2+</sup> is larger (less negative), it is easier to reduce. The possible anode reactions are

$$2H_2O(I) \rightarrow O_2(g) + 4H^+(aq) + 4e^ E^{\circ} = -1.23 \text{ V}$$
  
 $2CI^{\circ}(aq) \rightarrow CI_2(g) + 2e^ E^{\circ} = -1.36 \text{ V}$ 

Because the electrode potential for H<sub>2</sub>O is less negative, it is easier to oxidize.

The expected half-reactions are

$$2H_2O(I) \rightarrow O_2(g) + 4H^+(aq) + 4e^ E^{\circ} = -1.23 \text{ V}$$
  $2Cu^{2+}(aq) + 4e^- \rightarrow 2Cu(s)$   $E^{\circ} = 0.34 \text{ V}$ 

The overall reaction is

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

b. The species you should consider for half-reactions are Cu<sup>2+</sup> and H<sub>2</sub>O. The possible cathode reactions are

$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$$
  $E^{\circ} = 0.34 \text{ V}$   $2H_2O(I) + 2e^{-} \rightarrow H_2(g) + 2OH^{-}(aq)$   $E^{\circ} = -0.83 \text{ V}$ 

Because the electrode potential for Cu<sup>2+</sup> is larger (less negative), it is easier to reduce. The anode reaction is

$$2H_2O(I) \rightarrow O_2(g) + 4H^+(ag) + 4e^- \qquad E^\circ = -1.23 \text{ V}$$

The expected half-reactions are

$$2H_2O(I) \rightarrow O_2(g) + 4H^+(aq) + 4e^ E^{\circ} = -1.23 \text{ V}$$
  
 $2Cu^{2+}(aq) + 4e^- \rightarrow 2Cu(s)$   $E^{\circ} = 0.34 \text{ V}$ 

The overall reaction is

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

20.89 The conversion of grams of aluminum (3.61 kg =  $3.61 \times 10^3$  g) to coulombs required to give this amount of aluminum is

$$3.61 \times 10^{3} \text{ g} \times \frac{1 \text{ mol Al}}{26.98 \text{ g}} \times \frac{3 \text{ mol e}^{-}}{1 \text{ mol Al}} \times \frac{9.65 \times 10^{4} \text{ C}}{1 \text{ mol e}^{-}}$$

$$= 3.87 \times 10^{7} = 3.87 \times 10^{7} \text{ C}$$

20.90 The conversion of grams of chlorine (1.18 kg =  $1.18 \times 10^3$  g) to coulombs required to produce this amount of chlorine is

1.18 x 10<sup>3</sup> g x 
$$\frac{1 \text{ mol Cl}_2}{70.91 \text{ g}}$$
 x  $\frac{2 \text{ mol e}^-}{1 \text{ mol Cl}_2}$  x  $\frac{9.65 \text{ x } 10^4 \text{ C}}{1 \text{ mol e}^-}$   
= 3.211 x 10<sup>6</sup> = 3.21 x 10<sup>6</sup> C

Using the current of 5.00 x 10<sup>2</sup> A, calculate the time in s:

Time = 
$$\frac{1 \text{ mol Cl}_2}{70.91 \text{ g}}$$
 =  $\frac{1 \text{ mol Cl}_2}{70.91 \text{ g}}$  =  $6.42 \times 10^3 \text{ s}$ 

20.91 The conversion of coulombs to grams of lithium is

$$5.00 \times 10^{3} \text{ C} \times \frac{1 \text{ mol e}^{-}}{9.65 \times 10^{4} \text{ C}} \times \frac{1 \text{ mol Li}}{1 \text{ mol e}^{-}} \times \frac{6.941 \text{ g Li}}{1 \text{ mol Li}} = 0.35\underline{9}6$$
  
= 0.360 g Li

20.92 The conversion of current and time into coulombs is (221 min = 1.326 x 10<sup>4</sup> s)

C = amp x sec = 
$$1.51 \text{ A} \times 1.326 \times 10^4 \text{ s} = 2.002 \times 10^4 \text{ C}$$

The conversion of coulombs to grams of cadmium is

$$2.002 \times 10^{4} \text{ C} \times \frac{1 \text{ mol e}^{-}}{9.65 \times 10^{4} \text{ C}} \times \frac{1 \text{ mol Cd}}{2 \text{ mol e}^{-}} \times \frac{112.4 \text{ g Cd}}{1 \text{ mol Cd}} = 11.\underline{6}6$$
  
= 11.7 g Cd

# **■** Solutions to General Problems

20.93 a. The half-reactions and net ionic equation are

$$3Fe(s) \rightarrow 3Fe^{2^{+}}(aq) + 6e^{-}$$

$$2NO_{3}^{-}(aq) + 8H^{+}(aq) + 6e^{-} \rightarrow 2NO(g) + 4H_{2}O(l)$$

$$3Fe(s) + 2NO_{3}^{-}(aq) + 8H^{+}(aq) \rightarrow 3Fe^{2^{+}}(aq) + 2NO(g) + 4H_{2}O(l)$$

b. The half-reactions and net ionic equation are

$$3Fe^{2^{+}}(aq) \rightarrow 3Fe^{3^{+}}(aq) + 3e^{-}$$

$$NO_{3}^{-}(aq) + 4H^{+}(aq) + 3e^{-} \rightarrow NO(g) + 2H_{2}O(l)$$

$$3Fe^{2^{+}}(aq) + NO_{3}^{-}(aq) + 4H^{+}(aq) \rightarrow 3Fe^{3^{+}}(aq) + NO(g) + 2H_{2}O(l)$$

c. Add the results from parts (a) and (b)

$$3Fe(s) + 2NO_3^{-}(aq) + 8H^{+}(aq) \rightarrow 3Fe^{2+}(aq) + 2NO(g) + 4H_2O(l)$$

$$3Fe^{2+}(aq) + NO_3^{-}(aq) + 4H^{+}(aq) \rightarrow 3Fe^{3+}(aq) + NO(g) + 2H_2O(l)$$

$$Fe(s) + NO_3^{-}(aq) + 4H^{+}(aq) \rightarrow Fe^{3+}(aq) + NO(g) + 2H_2O(l)$$

20.94 a. The half-reactions and net ionic equation are

$$3TI(s) \rightarrow 3TI^{+}(aq) + 3e^{-}$$

$$\frac{NO_{3}^{-}(aq) + 4H^{+}(aq) + 3e^{-}}{3TI(s) + NO_{3}^{-}(aq) + 4H^{+}(aq) \rightarrow 3TI^{+}(aq) + NO(g) + 2H_{2}O(I)}$$

b. The half-reactions and net ionic equation are

$$3TI^{+}(aq) \rightarrow 3TI^{3+}(aq) + 6e^{-}$$

$$2NO_{3}^{-}(aq) + 8H^{+}(aq) + 6e^{-} \rightarrow 2NO(g) + 4H_{2}O(I)$$

$$3TI^{+}(aq) + 2NO_{3}^{-}(aq) + 8H^{+}(aq) \rightarrow 3TI^{+}(aq) + 2NO(g) + 4H_{2}O(I)$$

c. Add the results from parts (a) and (b)

$$3TI(s) + NO_3^{-}(aq) + 4H^{+}(aq) \rightarrow 3TI^{+}(aq) + NO(g) + 2H_2O(I)$$
  
 $3TI^{+}(aq) + 2NO_3^{-}(aq) + 8H^{+}(aq) \rightarrow 3TI^{+}(aq) + 2NO(g) + 4H_2O(I)$   
 $TI(s) + NO_3^{-}(aq) + 4H^{+}(aq) \rightarrow TI^{3+}(aq) + NO(g) + 2H_2O(I)$ 

20.95 a. The two balanced half-reactions are

$$8S^{2-} \rightarrow S_8 + 16e^-$$
 (oxidation)  
 $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$  (reduction)

Multiply the oxidation half-reaction by three and the reduction half-reaction by sixteen, and then add together. Cancel the forty eight electrons from each side. The balanced equation in acidic solution is

$$16MnO_4^- + 24S^{2-} + 64H^+ \rightarrow 16MnO_2 + 3S_8 + 32H_2O$$

Now add sixty four  $OH^-$  to each side. Simplify by combining the  $H^+$  and  $OH^-$  to give  $H_2O$ . Then cancel thirty two  $H_2O$  on each side. The balanced equation in basic solution is

$$16MnO_{4}^{-}(aq) + 24S^{2-}(aq) + 32H_{2}O(I) \rightarrow 16MnO_{2}(aq) + 3S_{8}(aq) + 64OH^{-}(I)$$

b. The two balanced half-reactions are

$$HSO_3^- + H_2O \rightarrow SO_4^{2-} + 3H^+ + 2e^-$$
 (oxidation)  
 $IO_3^- + 6H^+ + 6e^- \rightarrow I^- + 3H_2O$  (reduction)

Multiply the oxidation half-reaction by three, and then add together. Cancel the six electrons from each side. Also, cancel six  $H^{\dagger}$  and three  $H_2O$  from each side. The balanced equation is

$$IO_3^-(aq) + 3HSO_3^-(aq) \rightarrow I^- + 3SO_4^{-2}(aq) + 3H^+(aq)$$

c. The two balanced half-reactions are

$$Fe(OH)_2 + H_2O \rightarrow Fe(OH)_3 + H^+ + e^-$$
 (oxidation)  
 $CrO_4^{2-} + 4H^+ + 3e^- \rightarrow Cr(OH)_4^-$  (reduction)

Multiply the oxidation half-reaction by three, and then add together. Cancel the three electrons and cancel three  $H^+$  from each side. The balanced equation in acidic solution is

$$CrO_4^{2-}(aq) + 3Fe(OH)_2(s) + H^+(aq) + 3H_2O(I) \rightarrow Cr(OH)_4^{-}(aq) + 3Fe(OH)_3(s)$$
(continued)

Now add one  $OH^-$  to each side. Simplify by combining the  $H^+$  and  $OH^-$  to give  $H_2O$ . Then, combine the  $H_2Os$  on the left side into a single term. The balanced equation in basic solution is

$$CrO_4^{2-}(aq) + 3Fe(OH)_2(aq) + 4H_2O(I) \rightarrow Cr(OH)_4^{-}(aq) + 3Fe(OH)_3(s) + OH^{-}(aq)$$

d. The two balanced half-reactions are

$$Cl_2 + 2H_2O \rightarrow 2ClO^- + 4H^+ + 2e^-$$
 (oxidation)  
 $Cl_2 + 2e^- \rightarrow 2Cl^-$  (reduction)

Add the two half-reactions together. Cancel the two electrons from each side. Divide all the coefficients by a factor of two. The balanced equation in acidic solution is

$$Cl_2 + H_2O \rightarrow Cl^- + ClO^- + 2H^+$$

Now add two  $OH^-$  to each side. Simplify by combining the  $H^+$  and  $OH^-$  to give  $H_2O$ . Then cancel one  $H_2O$  on each side. The balanced equation in basic solution is

$$Cl_2(aq) + 2OH^-(aq) \rightarrow Cl^-(aq) + ClO^-(aq) + H_2O(l)$$

20.96 a. The two balanced half-reactions are

$$8H_2S \rightarrow S_8 + 16H^+ + 16e^-$$
 (oxidation)  
 $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$  (reduction)

Multiply the oxidation half-reaction by five and the reduction half-reaction by sixteen, and then add together. Cancel the eighty electrons from each side. Also, cancel eighty  $\text{H}^{\dagger}$  from each side. The balanced equation is

$$16MnO_4^{-1}(aq) + 40H_2S(aq) + 48H^{+}(aq) \rightarrow 16Mn^{2+}(aq) + 5S_8(aq) + 64H_2O(l)$$

b. The two balanced half-reactions are

$$Zn \rightarrow Zn^{2+} + 2e^{-}$$
 (oxidation)  
 $2NO_3^- + 10H^+ + 8e^- \rightarrow N_2O + 5H_2O$  (reduction)

Multiply the oxidation half-reaction by four, and then add together. The balanced equation is

$$2NO_3^-(aq) + 4Zn(s) + 10H^+(aq) \rightarrow N_2O(g) + 4Zn^{2+}(aq) + 5H_2O(l)$$
 (continued)

c. The two balanced half-reactions are

$$MnO_4^{2-} \rightarrow MnO_4^{-} + e^{-}$$
 (oxidation)  
 $MnO_4^{2-} + 4H^+ + 2e^{-} \rightarrow MnO_2 + 2H_2O$  (reduction)

Multiply the oxidation half-reaction by two, and then add together. Cancel the two electrons from each side. Also, combine the  ${\rm MnO_4}^{2^-}$  on the left into a single term. The balanced equation in acidic solution is

$$3MnO_4^{2-} + 4H^+ \rightarrow MnO_2 + 2MnO_4^- + 2H_2O$$

Now add four OH<sup>-</sup> to each side. Simplify by combining the H<sup>+</sup> and OH<sup>-</sup> to give H<sub>2</sub>O. Then cancel two H<sub>2</sub>O on each side. The balanced equation in basic solution is

$$3MnO_4^{2-}(aq) + 2H_2O(I) \rightarrow MnO_2(s) + 2MnO_4^{-}(aq) + 4OH^{-}(aq)$$

d. The two balanced half-reactions are

$$Br_2 + 6H_2O \rightarrow 2BrO_3^- + 12H^+ + 10e^-$$
 (oxidation)  
 $Br_2 + 2e^- \rightarrow 2Br^-$  (reduction)

Multiply the reduction half-reaction by five, and then add together. Cancel the ten electrons from each side. Also, combine the  $Br_2$  on the left into a single term. The balanced equation in acidic solution is

$$3Br_2 + 3H_2O \rightarrow 5Br^- + BrO_3^- + 6H^+$$

Now add six  $OH^-$  to each side. Simplify by combining the  $H^+$  and  $OH^-$  to give  $H_2O$ . Then cancel three  $H_2O$  on each side. The balanced equation in basic solution is

$$3Br_2(aq) + 6OH(aq) \rightarrow 5Br(aq) + BrO_3(aq) + 3H_2O(l)$$

20.97 This reaction takes place in basic solution. The skeleton equation is

$$Fe(OH)_2(s) + O_2(g) \rightarrow Fe(OH)_3(s)$$

The two balanced half-reactions are

$$Fe(OH)_2 + H_2O \rightarrow Fe(OH)_3 + H^+ + e^-$$
 (oxidation)  
 $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$  (reduction)

Multiply the oxidation half-reaction by four, and then add together. Cancel the four electrons from each side. Also, cancel four  $H^+$  and two  $H_2O$  from each side. The balanced equation in acidic or in basic solution is

$$4Fe(OH)_2(s) + O_2(g) + 2H_2O(I) \rightarrow 4Fe(OH)_3(s)$$

20.98 This reaction takes place in basic solution. The skeleton equation is

$$SnO_2^{2-}(aq) + Bi^{3+}(aq) \rightarrow SnO_3^{2-}(aq) + Bi(s)$$

The two balanced half-reactions are

$$SnO_2^{2-} + H_2O \rightarrow SnO_3^{2-} + 2H^+ + 2e^-$$
 (oxidation)  
 $Bi^{3+} + 3e^- \rightarrow Bi$  (reduction)

Multiply the oxidation half-reaction by three and the reduction reaction by two, and then add together. Cancel the six electrons from each side. The balanced equation in acidic solution is

$$2Bi^{3+} + 3SnO_2^{2-} + 3H_2O \rightarrow 2Bi + 3SnO_3^{2-} + 6H^+$$

Now add six OH<sup>-</sup> to each side. Simplify by combining the H<sup>+</sup> and OH<sup>-</sup> to give H<sub>2</sub>O. Then cancel three H<sub>2</sub>O on each side. The balanced equation in basic solution is

$$2Bi^{3+}(aq) + 3SnO_2^{2-}(aq) + 6OH^{-}(aq) \rightarrow 2Bi(s) + 3SnO_3^{2-}(aq) + 3H_2O(l)$$

20.99 The cell notation is  $Ca(s)|Ca^{2+}(aq)||Cl^{-}(aq)||Cl_{2}(g)||Pt(s)|$ . The reactions are

Anode: Ca(s) 
$$\to$$
 Ca<sup>2+</sup>(aq) + 2e<sup>-</sup> -E° = 2.76 V  
Cathode: Cl<sub>2</sub>(g) + 2e<sup>-</sup>  $\to$  2Cl<sup>-</sup>(aq) E° = 1.36 V  
E° <sub>cell</sub> = 1.36 V + 2.76 V = 4.12 V

20.100 The cell notation is Mg(s)|Mg<sup>2+</sup>(aq)||Ag<sup>+</sup>(aq)||Ag(s). The reactions are

Anode: Mg(s) 
$$\to$$
 Mg<sup>2+</sup>(aq) + 2e<sup>-</sup> -E<sup>-</sup> = 2.38 V  
Cathode: Ag<sup>+</sup>(aq) + e<sup>-</sup>  $\to$  Ag(s) E<sup>-</sup> = 0.80 V  
E<sup>-</sup><sub>cell</sub> = 0.80 V + 2.38 V = 3.18 V

20.101a. In this reaction, Fe<sup>3+</sup> is the oxidizing agent on the left side; Ni<sup>2+</sup> is the oxidizing reagent on the right side. The corresponding standard electrode potentials are

$$Ni^{2+}(aq) + 2e^{-} \rightarrow Ni(s)$$
  $E^{\circ} = -0.23 \text{ V}$   
 $Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)$   $E^{\circ} = 0.77 \text{ V}$ 

The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so Fe<sup>3+</sup> is the stronger oxidizing agent. The oxidation of nickel by iron(III) is a spontaneous reaction.

b. In this reaction, Fe<sup>3+</sup> is the oxidizing agent on the left side; Sn<sup>4+</sup> is the oxidizing reagent on the right side. The corresponding standard electrode potentials are

$$Sn^{4+}(aq) + 2e^{-} \rightarrow Sn^{2+}(aq)$$
  $E^{\circ} = 0.15 \text{ V}$   
 $Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)$   $E^{\circ} = 0.77 \text{ V}$ 

The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so Fe<sup>3+</sup> is the stronger oxidizing agent. The oxidation of tin(II) by iron(III) is a spontaneous reaction.

20.102a. The half-reactions and the corresponding standard electrode potential values are

$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$$
  $E^\circ = 1.36 \text{ V}$   $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$   $E^\circ = 1.49 \text{ V}$ 

The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so  $MnO_4^-$  is the stronger oxidizing agent. The oxidation of chloride ion by permanganate ion is a spontaneous reaction.

b. The half-reactions and the corresponding standard electrode potential values are

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(I)$$
  $E^\circ = 1.33 \text{ V}$   $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$   $E^\circ = 1.36 \text{ V}$ 

The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so  $\text{Cl}_2$  is the stronger oxidizing agent. The oxidation of chloride ion by dichromate ion is not a spontaneous reaction.

20.103 The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

Note that n equals two. Next, use K<sub>sp</sub> to calculate [Pb<sup>2+</sup>].

$$[Pb^{2^{+}}] = \frac{K_{sp}}{[SO_4^{2^{-}}]} = \frac{1.7 \times 10^{-8}}{1.0} = 1.7 \times 10^{-8} M$$

The reaction quotient for the cell reaction is

$$Q = \frac{[Pb^{2+}] \times P_{H_2}}{[H^+]^2} = \frac{(1.7 \times 10^{-8})(1.0)}{(1.0)^2} = 1.7 \times 10^{-8}$$

The standard emf is 0.13 V , so the Nernst equation becomes

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592}{n} \log Q$$

$$E_{cell} = 0.13 \text{ V} - \frac{0.0592}{2} \log (1.7 \times 10^{-8})$$

$$= 0.13 \text{ V} - (-0.2299 \text{ V}) = 0.3599 = 0.36 \text{ V}$$

20.104 The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$$H_2(g) \rightarrow 2H^+(aq) + 2e^ -E^\circ = 0.00 \text{ V}$$
 $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$   $E^\circ = 0.80 \text{ V}$ 
 $H_2(g) + 2Ag^+(aq) \rightarrow 2H^+(aq) + 2Ag(s)$   $E^\circ_{cell} = 0.80 \text{ V}$ 

Note that n equals two. Next, use  $K_{sp}$  to calculate [Ag $^{+}$ ].

$$[Ag^{+}] = \frac{K_{sp}}{[C\Gamma]} = \frac{1.8 \times 10^{-10}}{1.0} = 1.8 \times 10^{-10} M$$

The reaction quotient for the cell reaction is

$$Q = \frac{[H^+]^2}{[Ag^+]^2 P_{H_2}} = \frac{(1.0)^2}{(1.8 \times 10^{-10})^2 (1.0)} = 3.\underline{0}86 \times 10^{19}$$

The standard emf is 0.80 V, so the Nernst equation becomes

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592}{n} \log Q$$

$$E_{cell} = 0.80 \text{ V} - \frac{0.0592}{2} \log (3.086 \times 10^{19})$$

$$= 0.80 \text{ V} - (0.5768 \text{ V}) = 0.2231 = 0.22 \text{ V}$$

20.105a. Note that  $E^{\circ}$  = 0.010 V and n equals two. Substitute into the equation relating  $E^{\circ}$  and K.

$$E^{\circ} = \frac{0.0592}{n} \log K$$

$$0.010 \text{ V} = \frac{0.0592}{2} \log \text{ K}$$

Solving for K, you get

$$\log K = 0.3378$$

Take the antilog of both sides:

$$K = K_c = antilog (0.3378) = 2.176 = 2.2$$

b. Substitute into the equilibrium expression using  $[Sn^{2+}] = x$ , and  $[Pb^{2+}] = 1.0 \text{ M} - x$ .

$$K_c = \frac{[Sn^{2+}]}{[Pb^{2+}]} = \frac{x}{1.0 - x} = 2.176$$

$$x = 0.6851 M$$

$$[Pb^{2+}] = 1.0 M - x = 0.3149 = 0.3 M$$

20.106a. Note that  $E^{\circ}$  = 0.030 V and n equals one. Substitute into the equation relating  $E^{\circ}$  and K.

$$E^{\circ} = \frac{0.0592}{n} \log K$$

$$0.030 \text{ V} = \frac{0.0592}{1} \log \text{ K}$$

Solving for K, you get

$$\log K = 0.5067$$

Take the antilog of both sides:

$$K = K_c = antilog (0.5067) = 3.211 = 3.2$$

b. After mixing equal volumes, the initial concentrations of  $Ag^+$  and  $Fe^{2^+}$  are 0.50 M. Substitute into the equilibrium expression using  $[Fe^{3^+}] = x$ , and  $[Ag^+] = [Fe^{2^+}] = 0.50$  M - x.

$$K_c = \frac{[Fe^{3+}]}{[Ag^+][Fe^{2+}]} = \frac{x}{(0.50 - x)^2} = 3.211$$

This equation can be rearranged to give the following quadratic equation.

$$3.211x^2 - 4.211x + 0.8029 = 0$$

$$x = \frac{-(-4.211) \pm \sqrt{(-4.211)^2 - 4(3.211)(0.8029)}}{2(3.211)} = 0.2314 \text{ M}$$

$$[Fe^{2+}] = 0.50 - x = 0.50 M - 0.2314 M = 0.2686 = 0.27 M$$

20.107a. The number of faradays is

1.0 mol Na<sup>+</sup> x 
$$\frac{1 \text{ mol e}^{-}}{1 \text{ mol Na}^{+}}$$
 x  $\frac{1 \text{ F}}{1 \text{ mol e}^{-}}$  = 1.0 F

The number of coulombs is

$$1.0 \text{ F x} = \frac{9.65 \times 10^4 \text{ C}}{1 \text{ F}} = 9.\underline{6}5 \times 10^4 = 9.7 \times 10^4 \text{ C}$$

b. The number of faradays is

1.0 mol Cu<sup>2+</sup> x 
$$\frac{2 \text{ mol e}^{-}}{1 \text{ mol Cu}^{2+}}$$
 x  $\frac{1 \text{ F}}{1 \text{ mol e}^{-}}$  = 2.0 F

The number of coulombs is

$$2.0 \text{ F x } \frac{9.65 \times 10^4 \text{ C}}{1 \text{ F}} = 1.9 \times 10^5 \text{ C}$$

c. The number of faradays is

1.0 g H<sub>2</sub>O x 
$$\frac{1 \text{ mol H}_2\text{O}}{18.01 \text{ g H}_2\text{O}}$$
 x  $\frac{2 \text{ mol e}^-}{1 \text{ mol H}_2\text{O}}$  x  $\frac{1 \text{ F}}{1 \text{ mol e}^-}$  = 0.11 F

The number of coulombs is

$$0.1110 \,\mathrm{F} \,\mathrm{x} \,\frac{9.65 \,\mathrm{x} \,10^4 \,\mathrm{C}}{1 \,\mathrm{F}} = 1.\underline{07} \,\mathrm{x} \,10^4 = 1.1 \,\mathrm{x} \,10^4 \,\mathrm{C}$$

d. The number of faradays is

1.0 g Cl<sup>-</sup> x 
$$\frac{1 \text{ mol Cl}^-}{35.45 \text{ g Cl}^-}$$
 x  $\frac{2 \text{ mol e}^-}{2 \text{ mol Cl}^-}$  x  $\frac{1 \text{ F}}{1 \text{ mol e}^-}$  = 0.028 F

The number of coulombs is

$$0.02820 \text{ F x} = \frac{9.65 \times 10^4 \text{ C}}{1 \text{ F}} = 2.722 \times 10^3 = 2.7 \times 10^3 \text{ C}$$

20.108a. The number of faradays is

1.0 mol Fe<sup>3+</sup> x 
$$\frac{1 \text{ mol e}^{-}}{1 \text{ mol Fe}^{3+}}$$
 x  $\frac{1 \text{ F}}{1 \text{ mol e}^{-}}$  = 1.0 F

The number of coulombs is

$$1.0 \text{ F x} = \frac{9.65 \times 10^4 \text{ C}}{1 \text{ F}} = 9.\underline{65} \times 10^4 = 9.7 \times 10^4 \text{ C}$$

b. The number of faradays is

1.0 mol Fe<sup>3+</sup> x 
$$\frac{3 \text{ mol e}^{-}}{1 \text{ mol Fe}^{3+}}$$
 x  $\frac{1 \text{ F}}{1 \text{ mol e}^{-}}$  = 3.0 F

The number of coulombs is

$$3.0 \text{ F x } \frac{9.65 \times 10^4 \text{ C}}{1 \text{ F}} = 2.895 \times 10^5 = 2.9 \times 10^5 \text{ C}$$

c. The number of faradays is

1.0 g Sn<sup>2+</sup> x 
$$\frac{1 \text{ mol Sn}^{2+}}{118.7 \text{ g Sn}^{2+}}$$
 x  $\frac{2 \text{ mol e}^{-}}{1 \text{ mol Sn}^{2+}}$  x  $\frac{1 \text{ F}}{1 \text{ mol e}^{-}}$  = 0.01684 = 0.017 F

The number of coulombs is

$$0.01684 \text{ F x} = \frac{9.65 \times 10^4 \text{ C}}{1 \text{ F}} = 1.62 \times 10^3 = 1.6 \times 10^3 \text{ C}$$

d. The number of faradays is

$$1.0 \text{ g Au}^{3+} \times \frac{1 \text{ mol Au}^{3+}}{197.0 \text{ g Au}^{3+}} \times \frac{3 \text{ mol e}^{-}}{1 \text{ mol Au}^{3+}} \times \frac{1 \text{ F}}{1 \text{ mol e}^{-}} = 0.01\underline{5}22 = 0.015 \text{ F}$$

The number of coulombs is

$$0.01522 \text{ F x} = \frac{9.65 \times 10^4 \text{ C}}{1 \text{ F}} = 1.469 \times 10^3 = 1.5 \times 10^3 \text{ C}$$

20.109 From the electrolysis information, calculate the total moles of I<sub>2</sub> formed

65.4 s x (10.5 x 10<sup>-3</sup> A) x 
$$\frac{1 \text{ C}}{1 \text{ A} \cdot \text{s}}$$
 x  $\frac{1 \text{ mol } \text{e}^{\text{-}}}{9.65 \text{ x } 10^{4} \text{ C}}$  x  $\frac{1 \text{ mol } \text{l}_{2}}{2 \text{ mol } \text{e}^{\text{-}}}$   
= 3.558 x 10<sup>-6</sup> mol l<sub>2</sub>

From the balanced equation

$$3.558 \times 10^{-6} \text{ mol } I_2 \times \frac{1 \text{ mol } H_3 \text{AsO}_3}{1 \text{ mol } I_2} \times \frac{1 \text{ mol As}}{1 \text{ mol } H_3 \text{AsO}_3} \times \frac{79.42 \text{ g As}}{1 \text{ mol As}}$$

$$= 2.8257 \times 10^{-4} = 2.83 \times 10^{-4} \text{ g As}$$

20.110 From the electrolysis information, calculate the total moles of OH<sup>-</sup> formed.

115 s x (15.6 x 10<sup>-3</sup> A) x 
$$\frac{1C}{1A \cdot s}$$
 x  $\frac{1 \text{ mol e}^{-}}{9.65 \text{ x } 10^{4} \text{ C}}$  x  $\frac{2 \text{ mol OH}^{-}}{2 \text{ mol e}^{-}}$   
= 1.859 x 10<sup>-5</sup> mol OH<sup>-</sup>

From the balanced equation

1.859 x 10<sup>-5</sup> mol OH<sup>-</sup> x 
$$\frac{1 \text{ mol HC}_3\text{H}_5\text{O}_3}{1 \text{ mol OH}^-}$$
 x  $\frac{90.08 \text{ g HC}_3\text{H}_5\text{O}_3}{1 \text{ mol HC}_3\text{H}_5\text{O}_3}$   
= 1.6745 x 10<sup>-3</sup> = 1.67 x 10<sup>-3</sup> g HC<sub>3</sub>H<sub>5</sub>O<sub>3</sub>

20.111a. The spontaneous chemical reaction and maximum cell potential are

Cd(s) → Cd<sup>2+</sup>(aq) + 2e<sup>-</sup> -E° = 0.40 V  

$$2Ag^{+}(aq) + 2e^{-}$$
 →  $2Ag(s)$  E° = 0.80 V  
Cd(s) +  $2Ag^{+}(aq)$  →  $2Ag(s) + Cd^{2+}(aq)$  E°<sub>cell</sub> = 1.20 V

- b. Addition of S<sup>2-</sup> would greatly decrease the Cd<sup>2+</sup>(aq) concentration and help shift the equilibrium to the right, thus forming more Ag.
- c. No effect. The size of the electrode makes no difference in the potential.

## 20.112a. The spontaneous chemical reaction and maximum cell potential are

$$Fe(s) \rightarrow Fe^{2^{+}}(aq) + 2e^{-} \qquad -E^{\circ} = 0.41 \text{ V}$$

$$Cu^{2^{+}}(aq) + 2e^{-} \rightarrow Cu(s) \qquad E^{\circ} = 0.34 \text{ V}$$

$$Fe(s) + Cu^{2^{+}}(aq) \rightarrow Cu(s) + Fe^{2^{+}}(aq) \qquad E^{\circ}_{cell} = 0.75 \text{ V}$$

- b. The Cu<sup>2+</sup>(aq) concentration is greatly decreased shifting the equilibrium to the left and thus forms less Cu.
- c. No effect. The size of the electrode makes no difference in the potential.

20.113 Anode: 
$$2H_2O(I) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$$

Cathode: 
$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$$

20.114 Anode: 
$$2Cl^{-}(aq) \rightarrow Cl_{2}(g) + 2e^{-}$$

Cathode: 
$$2H_2O(aq) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

20.115a. First, find the moles of silver.

$$2.48 \text{ g Ag x} \frac{1 \text{ mol Ag}}{107.9 \text{ g Ag}} = 0.022 \underline{9}8 \text{ mol Ag}$$

The number of coulombs is

0.02298 mol Ag x 
$$\frac{1 \text{ mol e}^{-}}{1 \text{ mol Ag}}$$
 x  $\frac{9.65 \times 10^{4} \text{ C}}{1 \text{ mol e}^{-}}$  =  $22\underline{1}8 \text{ C}$ 

Since amp x sec = coul, the number of seconds is

time = 
$$\frac{2218 \text{ C}}{1.50 \text{ amp}}$$
 =  $1.4\underline{7}8 \times 10^3 = 1.48 \times 10^3 \text{ s}$ 

b. For the same amount of current, the moles of Cr would be

2217 C x 
$$\frac{1 \text{ mol e}^{-}}{9.65 \times 10^{4} \text{ C}}$$
 x  $\frac{1 \text{ mol Cr}}{3 \text{ mol e}^{-}}$  x  $\frac{52.00 \text{ g Cr}}{1 \text{ mol Cr}}$   
= 0.3984 = 0.398 g

20.116a. First, find the moles of copper.

$$2.10 \text{ g Cu x } \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} = 0.033\underline{0}4 \text{ mol Cu}$$

The number of coulombs is

0.03304 mol Cu x 
$$\frac{2 \text{ mol e}^{-}}{1 \text{ mol Cu}}$$
 x  $\frac{9.65 \times 10^{4} \text{ C}}{1 \text{ mol e}^{-}}$  =  $63\underline{7}$ 7 C

Since amp x sec = coul, the number of seconds is

$$s = \frac{6377 \text{ C}}{1.25 \text{ amp}} = 5.10 \times 10^3 = 5.10 \times 10^3 \text{ s}$$

b. For the same amount of current, the moles of Ag would be

6377 C x 
$$\frac{1 \text{ mol e}^{-}}{9.65 \times 10^{4} \text{ C}}$$
 x  $\frac{1 \text{ mol Ag}}{1 \text{ mol e}^{-}}$  x  $\frac{107.9 \text{ g Ag}}{1 \text{ mol Ag}}$   
=  $7.1\underline{3}1$  =  $7.13 \text{ g}$ 

20.117a. Note that 3.50 hours = 12600 s, and the efficiency is 90.0 percent.

2.75 amp x 12600 s x 
$$\frac{1 \text{ F}}{9.65 \times 10^4 \text{ C}}$$
 x 0.900 = 0.3232 = 0.323 F

b. The moles of Au that were deposited is

mol Au = 21.221 g Au x 
$$\frac{1 \text{ mol Au}}{197.0 \text{ g}}$$
 = 0.107720 mol

Since 1 F = 1 mol e<sup>-</sup>, the ratio of moles of e<sup>-</sup> to moles Au is

$$\frac{\text{mol e}^{-}}{\text{mol Au}} = \frac{0.3232}{0.10772} = \frac{3.00}{1}$$

Thus, the ion must be Au<sup>3+</sup>. The reaction is

$$Au^{3+} + 3e^{-} \rightarrow Au$$

20.118a. Note that 1.90 hours = 6840 s, and the efficiency is 95.0 percent.

2.50 amp x 6840 s x 
$$\frac{1 \text{ F}}{9.65 \times 10^4 \text{ C}}$$
 x 0.950 = 0.168 F

b. The moles of V that were deposited is

mol V = 2.850 g V x 
$$\frac{1 \text{ mol V}}{50.94 \text{ g V}}$$
 = 0.055948 mol V

Since 1 F = 1 mol e, the ratio of moles of e to moles V is

$$\frac{\text{mol e}^{-}}{\text{mol V}} = \frac{0.1683}{0.055948} = \frac{3.00}{1}$$

Thus, the ion must be V<sup>3+</sup>. The reaction is

$$V^{3+} + 3e^{-} \rightarrow V$$

20.119a. The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$$
  $-E^{\circ} = 0.76 \text{ V}$ 

$$\frac{Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)}{Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s)}$$
  $E^{\circ} = 1.10 \text{ V}$ 

Use the Nernst equation to calculate the voltage of the cell.

$$E = E^{\circ} - \frac{0.0592}{n} \log Q = E^{\circ} - \frac{0.0592}{n} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Note that n equals two,  $[Zn^{2+}] = 0.200 \text{ M}$ , and  $[Cu^{2+}] = 0.0100 \text{ M}$ .

$$E^{\circ} = 1.10 \text{ V} - \frac{0.0592}{2} \log \frac{[0.200]}{[0.0100]}$$
  
= 1.10 V - 0.03851 V = 1.061 = 1.06 V

b. First, calculate the moles of electrons passing through the cell.

1.00 amp x 225 s x 
$$\frac{1 \text{ mol e}^{-}}{9.65 \times 10^{4} \text{ C}} = 0.0023\underline{3}2 \text{ mol e}^{-}$$

The moles of Cu deposited are

$$0.002332 \text{ mol e}^{-} \times \frac{1 \text{ mol Cu}}{2 \text{ mol e}^{-}} = 0.0011\underline{6}6 \text{ mol Cu}$$

The moles of Cu remaining in the 1.00 L of solution are

$$0.0100 - 0.001166 = 0.008834 = 0.0088 \, \text{mol}$$

Since the volume of the solution is 1.00 L, the molarity of  $Cu^{2+}$  is 0.0088 M.

20.120a. The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

Fe(s) 
$$\rightarrow$$
 Fe<sup>2+</sup>(aq) + 2e<sup>-</sup> -E° = 0.41 V  
Cu<sup>2+</sup>(aq) + 2e<sup>-</sup>  $\rightarrow$  Cu(s) E° = 0.34 V  
Fe(s) + Cu<sup>2+</sup>(aq)  $\rightarrow$  Fe<sup>2+</sup>(aq) + Cu(s) E° = 0.75 V

Use the Nernst equation to calculate the voltage of the cell.

$$E = E^{\circ} - \frac{0.0592}{n} \log Q = E^{\circ} - \frac{0.0592}{n} \log \frac{[Fe^{2+}]}{[Cu^{2+}]}$$

Note that n equals two,  $[Fe^{2+}] = 0.15 \text{ M}$ , and  $[Cu^{2+}] = 0.036 \text{ M}$ .

$$E^{\circ} = 0.75 \text{ V} - \frac{0.0592}{2} \log \frac{[0.15]}{[0.036]}$$
  
= 0.7316 = 0.73 V

b. First, calculate the moles of electrons passing through the cell.

1.25 amp x 335 s x 
$$\frac{1 \text{ mol e}^{-}}{9.65 \times 10^{4} \text{ C}} = 0.0043\underline{3}9 \text{ mol e}^{-}$$

The moles of Cu deposited are

$$0.004339 \text{ mol } e^{-} \times \frac{1 \text{ mol Cu}}{2 \text{ mol } e^{-}} = 0.0021 \underline{70} \text{ mol}$$

The moles of Cu remaining in the 1.00 L of solution are

$$0.036 - 0.002170 = 0.0338 = 0.034 \text{ mol}$$

Since the volume of the solution is 1.00 L, the molarity of  $Cu^{2+}$  is 0.034 M.

20.121a. Write the cell reaction with the  $\Delta G^{\circ}_{f}$ 's beneath

$$Cd(s) + Co^{2+}(aq) \rightarrow Cd^{2+}(aq) + Co(s)$$
  
 $\Delta G^{\circ}_{f}$ : 0 -51.5 -77.6 0 kJ

Hence,

$$\Delta G^{\circ} = \Sigma n \Delta G_f^{\circ} (products) - \Sigma m \Delta G_f^{\circ} (reactants)$$
  
= [-77.6 + 51.5] kJ = -26.1 kJ = -2.61 x 10<sup>4</sup> J

b. Next, determine the standard emf for the cell. Note that n equals two.

$$\Delta G^{\circ} = -nFE^{\circ}$$
  
-2.61 x 10<sup>4</sup> J = -2(9.65 x 10<sup>4</sup> C) x E°

Solve for E° to get

$$E^{\circ} = \frac{-2.61 \times 10^4 \text{ J}}{-2(9.65 \times 10^4 \text{ C})} = 0.1352 = 0.135 \text{ V}$$

The half-reactions and voltages are

$$Cd(s)$$
 →  $Cd^{2+}(aq) + 2e^{-}$   $-E^{\circ}_{ox} = 0.40 \text{ V}$   
 $Co^{2+}(aq) + 2e^{-}$  →  $Co(s)$   $E^{\circ}_{red} = ?$   
 $Cd(s) + Co^{2+}(aq)$  →  $Cd^{2+}(aq) + Co(s)$   $E^{\circ} = 0.1352 \text{ V}$ 

The cell emf is

$$E^{\circ} = E^{\circ}_{red} + (-E^{\circ}_{ox})$$
  
 $0.1352 \text{ V} = E^{\circ}_{red} + 0.40 \text{ V}$   
 $E^{\circ}_{red} = 0.1352 \text{ V} - 0.40 \text{ V} = -0.2647 = -0.26 \text{ V}$ 

20.122a. Write the cell reaction with the  $\Delta G^{\circ}_{f}$ 's beneath

$$2TI(s) + Pb^{2+}(aq) \rightarrow 2TI^{+}(aq) + Pb(s)$$
  
 $\Delta G^{\circ}_{f}$ : 0 -24.3 2(-32.4) 0 kJ

Hence,

$$\Delta G^{\circ} = [2(-32.4) - (-24.3)] \text{ kJ} = -40.5 \text{ kJ} = -4.05 \text{ x} \cdot 10^4 \text{ J}$$
 (continued)

b. Next, determine the standard emf for the cell. Note that n equals two.

$$\Delta G^{\circ} = -nFE^{\circ}$$
  
-4.05 x 10<sup>4</sup> J = -2(9.65 x 10<sup>4</sup> C) x E°

Solve for E° to get

$$E^{\circ} = \frac{-4.05 \times 10^4 \text{ J}}{-2(9.65 \times 10^4 \text{ C})} = 0.0.2098 = 0.210 \text{ V}$$

The half-reactions and voltages are

$$2TI(s) \rightarrow 2TI^{+}(aq) + 2e^{-}$$
  $-E^{\circ}_{ox} = E^{\circ}_{red}$   $Pb^{2+}(aq) + 2e^{-} \rightarrow Pb(s)$   $E^{\circ}_{red} = -0.13 \text{ V}$   $Cd(s) + Co^{2+}(aq) \rightarrow Cd^{2+}(aq) + Co(s)$   $E^{\circ} = 0.2098 \text{ V}$ 

The cell emf is

$$E^{\circ} = E^{\circ}_{red} + (-E^{\circ}_{ox})$$
  
 $0.2098 V = -13 V + E^{\circ}_{red}$   
 $E^{\circ}_{red} = 0.2098 V + 0.13 V = 0.3398 = 0.34 V$ 

## ■ Solutions to Cumulative-Skills Problems

20.123 The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$$3Zn(s) \rightarrow 3Zn^{2+}(aq) + 6e^{-} -E^{\circ} = 0.76 \text{ V}$$
  
 $2Cr^{3+}(aq) + 6e^{-} \rightarrow 2Cr(s)$   $E^{\circ} = -0.74 \text{ V}$   
 $2Cr^{3+}(aq) + 3Zn(s) \rightarrow 3Zn^{2+}(aq) + 2Cr(s)$   $E^{\circ} = 0.02 \text{ V}$ 

Note that n equals six. Therefore,

$$\Delta G^{\circ} = -nFE^{\circ} = -6(9.65 \times 10^{4} \text{ C})(0.02 \text{ V}) = -\underline{1}.158 \times 10^{4} \text{ J} = -\underline{1}1.58 \text{ kJ}$$
(continued)

Write the cell reaction with the  $\Delta H^{\circ}_{f}$ 's beneath

$$2Cr^{3^+}(aq) \ + \ 3Zn(s) \ \rightarrow \ 3Zn^{2^+}(aq) \ + \ 2Cr(s)$$
 
$$\Delta H^{\circ}_{f} : \quad 2(-1971) \qquad \qquad 3(-152.4) \qquad 0 \ \ kJ$$

Hence,

$$\Delta H^{\circ} = \Sigma n \Delta H_{f}^{\circ} (products) - \Sigma m \Delta H_{f}^{\circ} (reactants)$$
  
= [3(-152.4) - 2(-1971)] kJ = 3484.8 = 3485 kJ

Now calculate  $\Delta S^{\circ}$ .

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$
  
-11.58 kJ = 3484.8 kJ - 298 K x  $\Delta S^{\circ}$ 

Solving for  $\Delta S^{\circ}$  gives

$$\Delta S^{\circ} = \frac{3484.8 \text{ kJ} + 11.58 \text{ kJ}}{298 \text{ K}} = 11.7 \text{ kJ/K}$$

20.124 The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$$2Cr(s) \rightarrow 2Cr^{3+}(aq) + 6e^{-} -E^{\circ} = 0.74 \text{ V}$$
  
 $3Fe^{2+}(aq) + 6e^{-} \rightarrow 3Fe(s)$   $E^{\circ} = -0.41 \text{ V}$   
 $2Cr(s) + 3Fe^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Fe(s)$   $E^{\circ} = 0.33 \text{ V}$ 

Note that n equals six. Therefore,

$$\Delta G^{\circ} = -nFE^{\circ} = -6(9.65 \times 10^{4} \text{ C})(0.33 \text{ V}) = -1.9107 \times 10^{5} \text{ J} = -191.07 \text{ kJ}$$

Write the cell reaction with the  $\Delta H^{\circ}_{f}$ 's beneath

$$2Cr(s) + 3Fe^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Fe(s)$$
 
$$\Delta H^{\circ}_{f} : 0 \qquad 3(-87.9) \qquad 3(-1971) \qquad 0 \text{ kJ}$$

Hence.

$$\Delta H^{\circ} = \Sigma n \Delta H_{f}^{\circ} (products) - \Sigma m \Delta H_{f}^{\circ} (reactants)$$
  
= [3(-1971) - 3(-87.9] kJ = -3678.3 = -3678 kJ

Now calculate  $\Delta S^{\circ}$ .

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$
  
-191.07 kJ = -3678.3 kJ - 298 K x  $\Delta S^{\circ}$ 

Solving for  $\Delta S^{\circ}$  gives

$$\Delta S^{\circ} = \frac{-3678.3 \text{ kJ} + 191.07 \text{ kJ}}{298 \text{ K}} = -11.702 = -11.7 \text{ kJ/K}$$

20.125 The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

Now, convert the pH to [H<sup>+</sup>]

$$[H^{+}]$$
 = antilog (-3.60) = 2.51 x 10<sup>-4</sup> M

Under standard conditions [Br] = 1 M, and the pressure of  $O_2$  is one atm. Thus, substitute into the Nernst equation, where n equals four.

$$E = E^{\circ} - \frac{0.0592}{n} \log Q = E^{\circ} - \frac{0.0592}{n} \log \frac{1}{[H^{+}]^{4} [Br^{-}]^{4} \times P_{O_{2}}}$$

$$= 0.16 \text{ V} - \frac{0.0592}{4} \log \frac{1}{(2.51 \times 10^{-4})^{4}}$$

$$= 0.16 \text{ V} - 0.2131 \text{ V} = -0.0531 = -0.05 \text{ V}$$

Thus, the reaction is nonspontaneous at this [H<sup>+</sup>].

20.126 The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

Now, convert the pH to [H<sup>+</sup>]

$$[H^{+}]$$
 = antilog (-9.10) =  $7.943 \times 10^{-10} M$ 

Under standard conditions  $[{\rm Co}^{2^+}]$  and  $[{\rm Co}^{3^+}]$  = 1 M, and the partial pressures of  ${\rm O}_2$  and  ${\rm O}_3$  equals one atm. Thus, substitute into the Nernst equation, where n equals two.

E = E° - 
$$\frac{0.0592}{n} log Q = E° - \frac{0.0592}{n} log \frac{[Co^{3+}]^2 \times P_{O_2}}{[H^+]^2 [Co^{2+}]^4 \times P_{O_3}}$$
  
=  $0.25 V - \frac{0.0592}{2} log \frac{1}{(7.94 \times 10^{-10})^2}$   
=  $0.25 V - 0.26936 V = -0.01936 = -0.02 V$ 

Thus, the reaction is nonspontaneous at this [H<sup>+</sup>].

20.127 Use the K<sub>a</sub> to calculate [H+] for the buffer.

$$K_a = \frac{[H^+][OCN^-]}{[HOCN]} = 3.5 \times 10^{-4}$$

Rearrange, and solve for  $[H^{+}]$ , assuming [HOCN] and  $[OCN^{-}]$  remain constant in the buffer. Thus,  $[H^{+}] = K_a = 3.5 \times 10^{-4} M$ .

In Problem 20.123,  $E^{\circ}$  for this cell reaction was found to be 0.16 V. Under standard conditions [Br $^{-}$ ] = 1 M, and the pressure of  $O_2$  is one atm. Thus, substitute into the Nernst equation, where n equals four.

E = E° - 
$$\frac{0.0592}{n} log Q = E^{\circ} - \frac{0.0592}{n} log \frac{1}{[H^{+}]^{4} [Br^{-}]^{4} \times P_{O_{2}}}$$
  
=  $0.16 \text{ V} - \frac{0.0592}{4} log \frac{1}{(3.5 \times 10^{-4})^{4}}$   
=  $0.16 \text{ V} - 0.20459 \text{ V} = -0.04455 = -0.04 \text{ V}$ 

Thus, the reaction is nonspontaneous at this [H<sup>+</sup>].

20.128 Use the K<sub>a</sub> to calculate [H+] for the buffer.

$$K_a = \frac{[H^+][OC\Gamma]}{[HOCI]} = 3.5 \times 10^{-8}$$

Rearrange, and solve for  $[H^{+}]$  assuming [HOCI] and  $[OCI^{-}]$  remain constant in the buffer. Thus,  $[H^{+}] = K_a = 3.5 \times 10^{-8} M$ .

In Problem 20.124, E° for this cell reaction was found to be 0.25 V. Under standard conditions  $[\text{Co}^{2+}]$  and  $[\text{Co}^{3+}]$  = 1 M, and the partial pressures of  $O_2$  and  $O_3$  equals one atm. Thus, Substitute into the Nernst equation, where n equals two.

E = E° - 
$$\frac{0.0592}{n} log Q = E° - \frac{0.0592}{n} log \frac{[Co^{3+}]^2 \times P_{O_2}}{[H^+]^2 [Co^{2+}]^4 \times P_{O_3}}$$
  
=  $0.25 V - \frac{0.0592}{2} log \frac{1}{(3.5 \times 10^{-8})^2}$   
=  $0.25 V - 0.44139 V = -0.19139 = -0.19 V$ 

Thus, the reaction is nonspontaneous at this [H<sup>+</sup>].

20.129 The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$$H_2(g) \rightarrow 2H^+(aq) + 2e^ -E^\circ = -0.00 \text{ V}$$
  
 $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$   $E^\circ = 0.80 \text{ V}$   
 $H_2(g) + 2Ag^+(aq) \rightarrow 2H^+(aq) + 2Ag(s)$   $E^\circ = 0.80 \text{ V}$ 

The standard hydrogen electrode has  $[H^{\dagger}] = 1.0$  M and the pressure of  $H_2$  equals one atm. Substitute into the Nernst equation, where E = 0.45 V and n equals two.

$$E = E^{\circ} - \frac{0.0592}{n} \log Q = E^{\circ} - \frac{0.0592}{n} \log \frac{[H^{+}]^{2}}{[Ag^{+}]^{2} \times P_{H_{2}}}$$

$$0.45 \, V = 0.80 \, V - \frac{0.0592}{2} \log \frac{1}{[Ag^+]^2}$$

Using the properties of logs, rearrange to get

$$0.45 \text{ V} = 0.80 \text{ V} + 0.0592 \log[\text{Ag}^{\dagger}]$$

Solve for [Ag<sup>+</sup>]

$$log[Ag^{+}] = \frac{0.45 - 0.80}{0.0592} = -5.912$$

$$[Ag^{+}] = 10^{-5.912} = 1.224 \times 10^{-6} M$$

Finally, determine the solubility product, using [SCN] = 0.10 M

$$K_{sp} = [Ag^{+}][SCN^{-}] = (1.224 \times 10^{-6})(0.10) = \underline{1}.224 \times 10^{-7} = 1 \times 10^{-7}$$

20.130 The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

The standard hydrogen electrode has  $[H^{+}] = 1.0$  M and the pressure of  $H_2$  equals one atm. Substitute into the Nernst equation, where E = 0.268 V and n equals two.

$$E = E^{\circ} - \frac{0.0592}{n} \log Q = E^{\circ} - \frac{0.0592}{n} \log \frac{[H^{+}]^{2}}{[Hg_{2}^{2+}] \times P_{H_{2}}}$$

$$0.268 \text{ V} = 0.80 \text{ V} - \frac{0.0592}{2} \log \frac{1}{[\text{Hg}_2^{2+}]}$$

Using the properties of logs, rearrange to get

$$0.268 \text{ V} = 0.80 \text{ V} + \frac{0.0592}{2} \log[\text{Hg}_2^{2^+}]$$

Solve for [Hg<sub>2</sub><sup>2+</sup>]

$$\log[Hg_2^{2^+}] = \frac{2(0.268 - 0.80)}{0.0592} = 1\underline{7}.972$$

$$[Hg_2^{2+}] = 10^{-17.972} = 1.06 \times 10^{-18} M$$

Finally, determine the solubility product, using [Cl<sup>-</sup>] = 1.00 M

$$K_{so} = [Hg_2^{2+}][CI]^2 = (1.06 \times 10^{-18})(1.00)^2 = 1.06 \times 10^{-18} = 10^{-18}$$

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