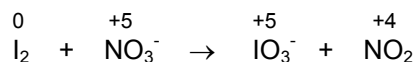

20. ELECTROCHEMISTRY

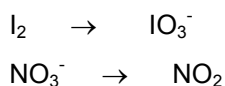
■ Solutions to Exercises

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.

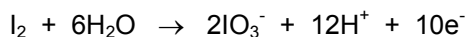
20.1 Assign oxidation numbers to the skeleton equation (Step 1).



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).



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



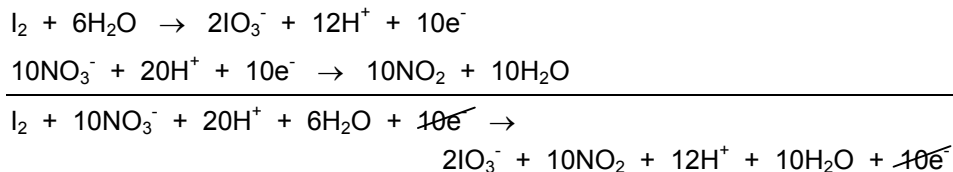
The reduction half-reaction is balanced in N (Step 3a). Add one H_2O to the right side to balance O atoms (Step 3b), and add two H^+ ion to the left side to balance H atoms. Finally, add one electron to the left side to balance the charge (Step 3d).

(continued)

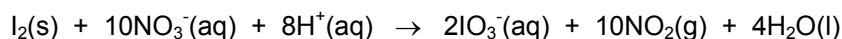
The balanced reduction half-reaction is



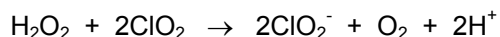
Multiply the reduction half-reaction by five so that, when added, the electrons cancel (Step 4a).



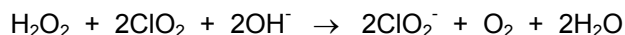
Simplify the equation by canceling the twelve H^+ and six H_2O that appear on both sides. The coefficients do not need to be reduced (Step 4b). The net ionic equation is



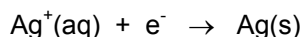
20.2 After balancing the equation as if it were in acid solution, you obtain the following:



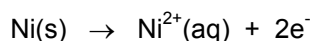
Add two OH^- to both sides of the equation (Step 5), and replace the two H^+ and two OH^- on the right side with two H_2O . No further cancellation is required. The balanced equation for the reaction in basic solution is



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

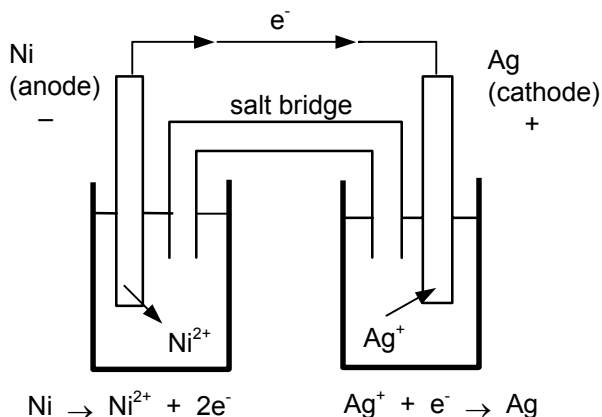


The nickel electrode (anode) is where oxidation occurs. The half-reaction is



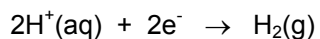
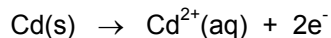
(continued)

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:

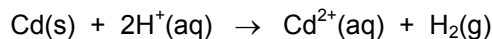


20.4 The notation for the cell is $\text{Zn(s)}|\text{Zn}^{2+}(\text{aq})||\text{H}^+(\text{aq})|\text{H}_2(\text{g})|\text{Pt(s)}$.

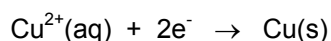
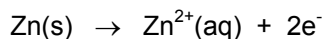
20.5 The half-cell reactions are



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



20.6 The half-reactions are



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

$$w_{\text{max}} = -nFE_{\text{cell}} = -2 \times 9.65 \times 10^4 \text{ C} \times 1.10 \text{ V} = -2.123 \times 10^5 \text{ V}\cdot\text{C} = -2.12 \times 10^5 \text{ J}$$

For 6.54 g of zinc metal, the maximum work is

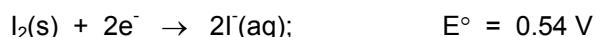
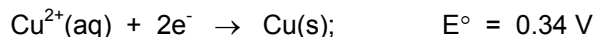
$$6.54 \text{ g Zn} \times \frac{1 \text{ mol Zn}}{65.39 \text{ g Zn}} \times \frac{-2.123 \times 10^5 \text{ J}}{1 \text{ mol Zn}} = -2.123 \times 10^4 = -2.12 \times 10^4 \text{ J}$$

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



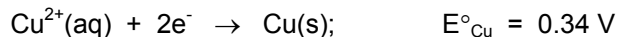
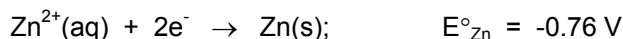
The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so NO_3^- is the stronger oxidizing agent.

- 20.8 In this reaction, Cu^{2+} is the oxidizing agent on the left side; I_2 is the oxidizing reagent on the right side. The corresponding standard electrode potentials are

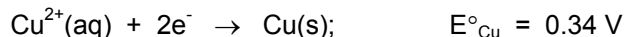
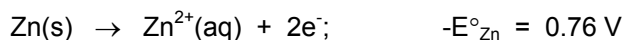


The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so I_2 is the stronger oxidizing agent. The reaction is nonspontaneous as written.

- 20.9 The reduction half-reactions and standard electrode potentials are



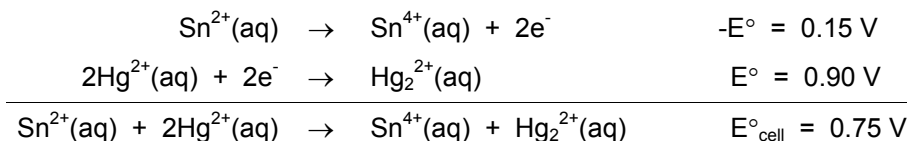
Reverse the first half-reaction and its half-cell potential to obtain



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

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

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



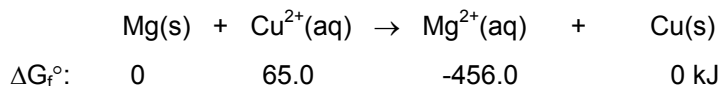
(continued)

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

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

Thus, the standard free-energy change is $-1.4 \times 10^2 \text{ kJ}$.

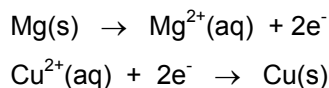
20.11 Write the equation with ΔG_f° 's beneath each substance.



Hence,

$$\begin{aligned} \Delta G^\circ &= \sum n\Delta G_f^\circ(\text{products}) - \sum m\Delta G_f^\circ(\text{reactants}) \\ &= [(-456.0) - 65.0] \text{ kJ} = -521.0 \text{ kJ} = -5.210 \times 10^5 \text{ J} \end{aligned}$$

Obtain n by splitting the reaction into half-reactions.



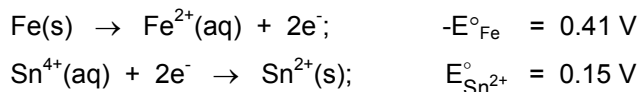
Each half-reaction involves two electrons, so n equals two. Therefore,

$$\begin{aligned} \Delta G^\circ &= -nFE^\circ_{\text{cell}} \\ -5.210 \times 10^5 \text{ J} &= -2 \times 9.65 \times 10^4 \text{ C} \times E^\circ_{\text{cell}} \end{aligned}$$

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

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

20.12 The half-reactions and standard electrode potentials are



The standard emf for the cell is

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

(continued)

Note that n equals two. Substitute into the equation relating E° and K . Also $K = K_c$.

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

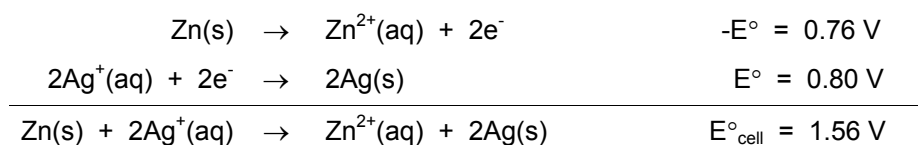
Solving for K_c , you get

$$\log K_c = 18.91$$

Take the antilog of both sides:

$$K_c = \text{antilog}(18.91) = 8.1 \times 10^{18} = 10^{19}$$

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



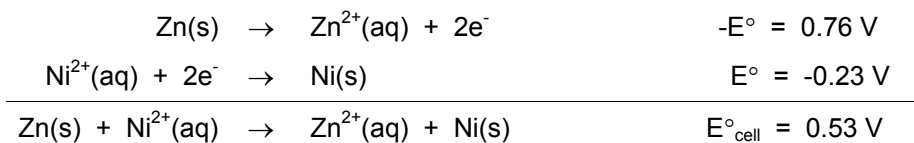
Note that n equals two. The reaction quotient is

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} = \frac{0.200}{(0.00200)^2} = 5.00 \times 10^4$$

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

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.0592}{n} \log Q \\ &= 1.56 - \frac{0.0592}{2} \log (5.00 \times 10^4) \\ &= 1.56 - 0.13909 = 1.4209 = 1.42 \text{ V} \end{aligned}$$

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



Note that n equals two. The standard emf is 0.53 V, and the emf is 0.34 V, so the Nernst equation becomes

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log Q$$

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

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

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]} = \text{antilog}(6.418) = 2.623 \times 10^6$$

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

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

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

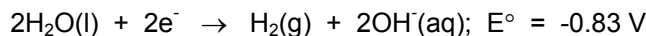
- 20.15 a. The cathode reaction is $\text{K}^+(\text{l}) + \text{e}^- \rightarrow \text{K(l)}$.

The anode reaction is $2\text{Cl}^-(\text{l}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$.

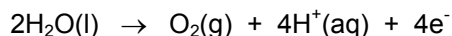
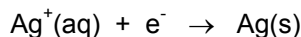
- b. The cathode reaction is $\text{K}^+(\text{l}) + \text{e}^- \rightarrow \text{K(l)}$.

The anode reaction is $4\text{OH}^-(\text{aq}) \rightarrow \text{O}_2(\text{g}) + 2\text{H}_2\text{O(g)} + 4\text{e}^-$.

- 20.16 The species you should consider for half-reactions are Ag^+ and H_2O . Two possible cathode reactions are



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



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

$$0.365 \text{ g Ag} \times \frac{1 \text{ mol Ag}}{107.9 \text{ g}} \times \frac{1 \text{ mol e}^-}{1 \text{ mol Ag}} \times \frac{9.65 \times 10^4 \text{ C}}{1 \text{ mol e}^-} = 326.4 \text{ C}$$

The time lapse, 216 min, equals $1.296 \times 10^3 \text{ s}$. Thus,

$$\text{Current} = \frac{\text{charge}}{\text{time}} = \frac{326.4 \text{ C}}{1.296 \times 10^3 \text{ s}} = 2.5188 \times 10^{-2} = 2.52 \times 10^{-2} \text{ A}$$

- 20.18 When the current flows for $1.85 \times 10^4 \text{ s}$, 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_2 . Hence,

$$\begin{aligned} 1.045 \times 10^3 \text{ C} \times \frac{1 \text{ mol e}^-}{9.65 \times 10^4 \text{ C}} \times \frac{1 \text{ mol O}_2}{4 \text{ mol e}^-} \times \frac{32.00 \text{ g O}_2}{1 \text{ mol O}_2} \\ = 0.08665 = 0.0866 \text{ g O}_2 \end{aligned}$$

■ 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 $E^\circ = 0.00 \text{ V}$, the H_2/H^+ half-reaction must have a voltage of $E^\circ = -0.54 \text{ V}$ 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 half-reaction.
- 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 ΔG° is negative.
- b. In order to reduce E_{cell} , change the concentrations in a way that increases the value of Q , where

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

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

- 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

- 20.1 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 $9.65 \times 10^4 \text{ C}$, or $9.65 \times 10^4 \text{ J/V}$.

- 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 $\text{H}^+/\text{H}_2(\text{g})$ 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° 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:

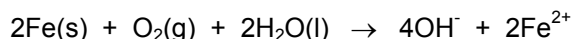
$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

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

Combining these two equations gives

$$\ln K = \frac{nFE^\circ_{\text{cell}}}{RT}$$

- 20.9 The first step in the corrosion of iron is



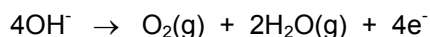
The Nernst equation for this reaction is

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

If the pH increases, the $[\text{OH}^-]$ increases, and thus E_{cell} becomes more negative (this predicts the reaction becomes less spontaneous). If the pH decreases, the $[\text{OH}^-]$ 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 $\text{MnO}_2(\text{s})$ to $\text{Mn}_2\text{O}_3(\text{s})$ 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



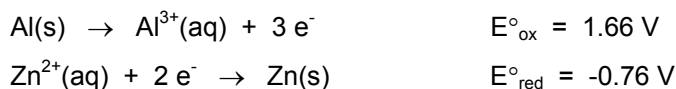
- 20.17 The reason different products are obtained is that water instead of Na^+ is reduced at the cathode during the electrolysis of aqueous NaCl. This is because water has a more positive E° (smaller decomposition voltage). At the anode, water instead of chloride ion is oxidized because water has a less positive E° (smaller decomposition voltage).
- 20.18 The Nernst equation for the electrode reaction of $2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$ is

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

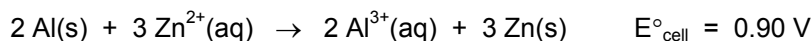
This equation implies that E increases as $[\text{Cl}^-]$ increases. For a sufficiently large $[\text{Cl}^-]$, Cl^- will be more readily oxidized than the water solvent.

■ Answers to Conceptual Problems

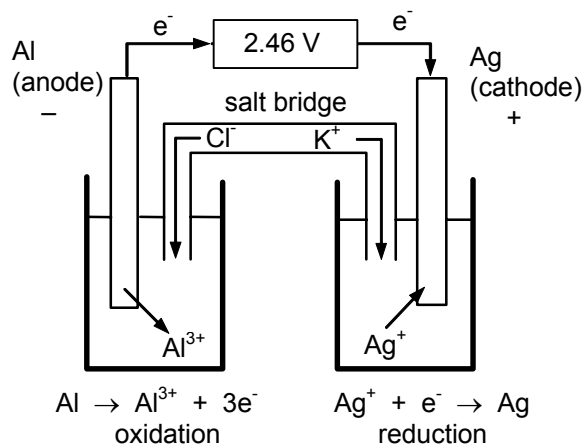
- 20.19 a. Since there is no species present to donate or accept electrons other than zinc, you would expect no change.
- b. Since there is no species present to donate or accept electrons other than copper, you would expect no change.
- c. According to the table of standard reduction potentials, the Cu^{2+} would undergo reduction, and the Zn would undergo oxidation. You would expect the Zn strip to dissolve as it becomes Zn^{2+} , the blue color of the solution to fade as the Cu^{2+} becomes Cu, and solid copper precipitate to form.
- d. According to the table of standard reduction potentials, since Zn^{2+} 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 $\text{Zn}^{2+}|\text{Zn}$ cathode with a voltage of -0.76 V , and an $\text{Al}|\text{Al}^{3+}$ anode with a voltage of 1.66 V . The appropriate half-reactions are



The overall balanced reaction and cell potential is



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



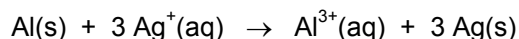
d. The cell emf is determined as follows.



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.80 \text{ V} - (-1.66 \text{ V}) = 2.46 \text{ V}$$

g. The species undergoing oxidation is $\text{Al}(\text{s})$, and the species undergoing reduction is $\text{Ag}^+(\text{aq})$.

h. The balanced overall reaction is



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

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log Q$$

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

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

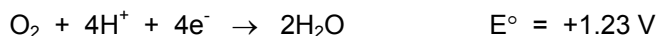
If $Q > 1$, $\log Q$ is positive, and the net result will be a decrease in cell potential and a decrease in the intensity of light. If $Q < 1$, $\log Q$ is negative, and the net result will be an increase in cell potential and an increase in the intensity of light.

(continued)

At the start, both $[\text{Zn}^{2+}]$ and $[\text{Cu}^{2+}]$ are 1.0 M, so $Q = 1$, and $\log Q = 0$, so $E_{\text{cell}} = E^{\circ}_{\text{cell}}$.

- If more $\text{CuSO}_4(\text{s})$ is dissolved in the CuSO_4 solution, $[\text{Cu}^{2+}]$ would be greater than one, so $Q < 1$. The effect is to increase the intensity of light.
- If more $\text{Zn}(\text{NO}_3)_2(\text{s})$ is dissolved in the $\text{Zn}(\text{NO}_3)_2$ solution, $[\text{Zn}^{2+}]$ would be greater than one, so $Q > 1$. The effect is to decrease the intensity of light.
- If H_2O is added to the CuSO_4 solution, $[\text{Cu}^{2+}]$ would be less than one, so $Q > 1$. The effect is to decrease the intensity of light.
- 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:



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.

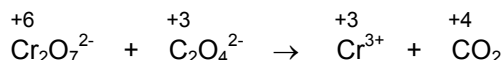
The density of the reducing agent is the next most important consideration. Hydrogen, the element with the lowest density, should certainly be considered. It does have some drawbacks, however. Because it is a gas, some method of storage needs to be developed. Liquid storage and metal hydride storage 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

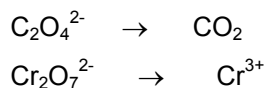
Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multiple-step problems, intermediate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



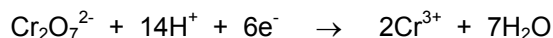
Separate into two incomplete half-reactions (Step 2). Note that carbon is oxidized (increases in oxidation number), and chromium is reduced (decreases in oxidation number).



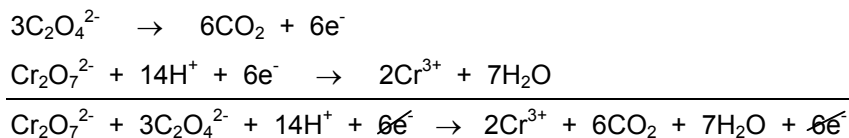
Balance each half-reaction separately. The oxidation half-reaction is not balanced in C, so place a two in front of CO_2 (Step 3a). Finally, add two electrons to the right side to balance the charge (Step 3d). The balanced oxidation half-reaction is



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

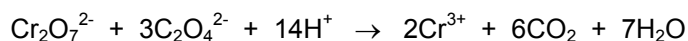


Multiply the oxidation half-reaction by three so that, when added, the electrons cancel (Step 4a).



(continued)

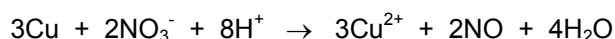
The equation does not need to be simplified any further (Step 4b). The net ionic equation is



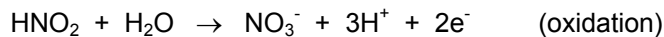
b. The two balanced half-reactions are



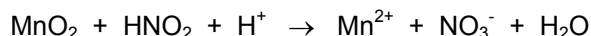
Multiply the oxidation half-reaction by three and the reduction half-reaction by four, and then add together. Cancel the six electrons from each side. No further simplification is needed. The balanced equation is



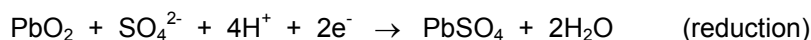
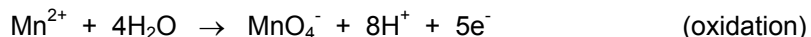
c. The two balanced half-reactions are



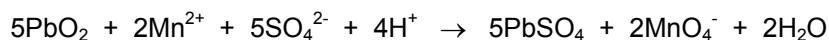
Add the two half-reactions together and cancel the two electrons from each side. Also, cancel three H^+ and one H_2O from each side. The balanced equation is



d. The two balanced half-reactions are

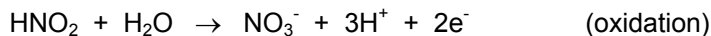


Multiply the oxidation half-reaction by two and the reduction half-reaction by five, and then add together. Cancel the ten electrons from each side. Also, cancel sixteen H^+ and eight H_2O from each side. The balanced equation is

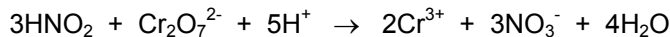


(continued)

e. The two balanced half-reactions are

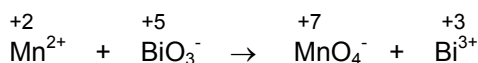


Multiply the oxidation half-reaction by three, and then add together. Cancel the six electrons from each side. Also, cancel nine H^+ and three H_2O from each side. The balanced equation is

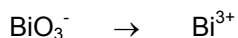
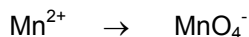


20.30 In balancing oxidation-reduction reactions in acid, the four steps in the text will be followed. For part a, each step is shown. For the other parts only a summary is shown.

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



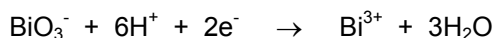
Separate into two incomplete half-reactions (Step 2). Note that manganese is oxidized (increases in oxidation number), and bismuth is reduced (decreases in oxidation number).



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

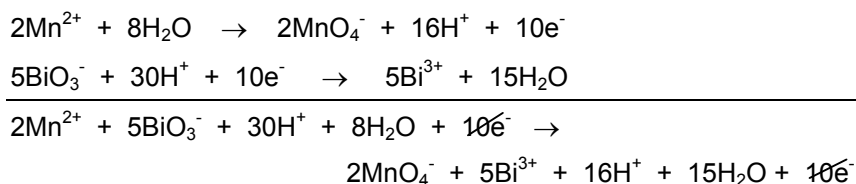


For the reduction half-reaction, add three H_2O to the right side to balance O atoms (Step 3b), and add six H^+ ion to the left side to balance H atoms (step 3c). Finally, add two electrons to the left side to balance the charge (Step 3d). The balanced reduction half-reaction is

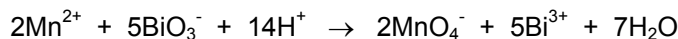


Multiply the oxidation half-reaction by two and the reduction half-reaction by five, so that, when added, the electrons cancel (Step 4a).

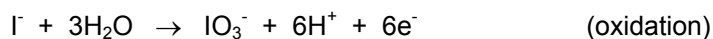
(continued)



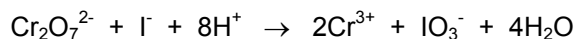
The equation can be further simplified by canceling sixteen H^+ and eight H_2O from each side (Step 4b). The net ionic equation is



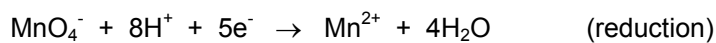
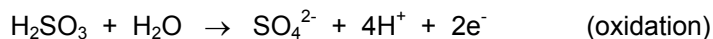
b. The two balanced half-reactions are



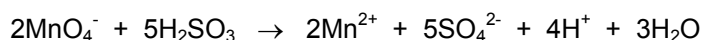
Add the two half-reactions together, and cancel the six electrons from each side. Also, cancel six H^+ and three H_2O from each side. The balanced equation is



c. The two balanced half-reactions are



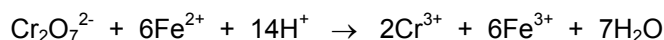
Multiply the oxidation half-reaction by five and the reduction half-reaction by two, and then add together. Cancel the ten electrons from each side. Also, cancel sixteen H^+ and five H_2O from each side. The balanced equation is



d. The two balanced half-reactions are

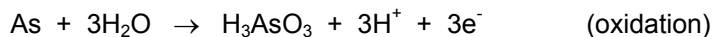


Multiply the oxidation half-reaction by six, and then add together. Cancel the six electrons from each side. The balanced equation is

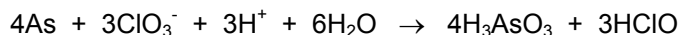


(continued)

e. The two balanced half-reactions are

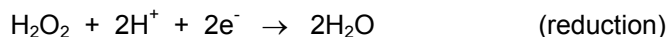
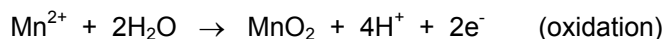


Multiply the oxidation half-reaction by four and the reduction half-reaction by three, and then add together. Cancel the twelve electrons from each side. Also, cancel twelve H^+ and six H_2O from each side. The balanced equation is

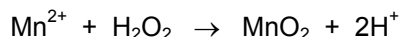


20.31 In balancing oxidation-reduction reactions in basic solution, it will first be balanced as if it were in acidic solution; then the extra two steps in the text will be followed.

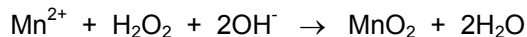
a. The two balanced half-reactions are



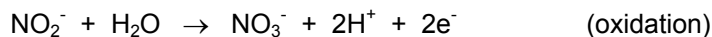
Add the two half-reactions together, and cancel the two electrons from each side. Also, cancel two H^+ and two H_2O from each side. The balanced equation in acidic solution is



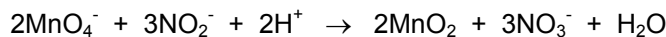
Now add two OH^- to each side (Step 5). Simplify by combining the H^+ and OH^- to give H_2O . No further simplification is required (Step 6). The balanced equation in basic solution is



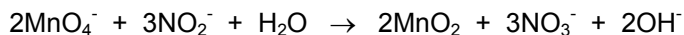
b. The two balanced half-reactions are



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^+ and six H_2O from each side. The balanced equation in acidic solution is

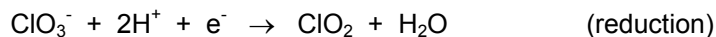
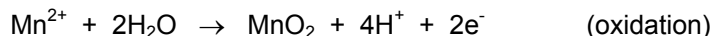


Now add two OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O . Then cancel one H_2O from each side. The balanced equation in basic solution is

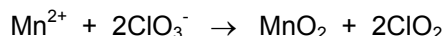


(continued)

c. The two balanced half-reactions are

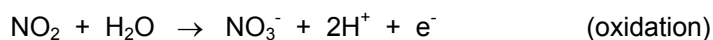


Multiply the reduction half-reaction by two and then add together. Cancel the two electrons from each side. Also, cancel four H^+ and two H_2O from each side. The balanced equation in acidic solution is

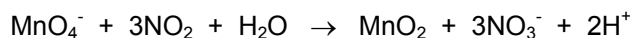


Since there are no H^+ on either side, no further simplification is needed. The balanced equation in basic solution is identical to the balanced equation in acidic solution.

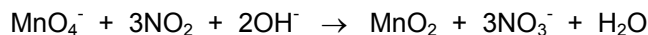
d. The two balanced half-reactions are



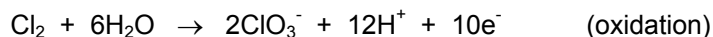
Multiply the oxidation half-reaction by three and then add together. Cancel the three electrons from each side. Also, cancel four H^+ and two H_2O from each side. The balanced equation in acidic solution is



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



e. The two balanced half-reactions are



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

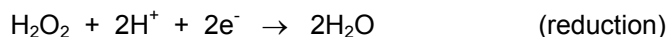
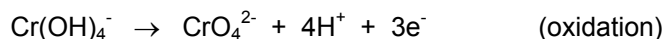


Now add six OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O . Then cancel three H_2O from each side. The balanced equation in basic solution is

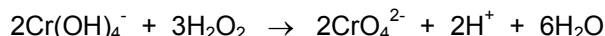


20.32 In balancing oxidation-reduction reactions in basic solution, it will first be balanced as if it were in acidic solution, then the extra two steps in the text will be followed.

a. The two balanced half-reactions are



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^+ from each side. The balanced equation in acidic solution is



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

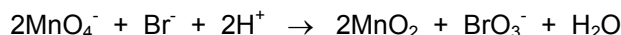


b. The two balanced half-reactions are

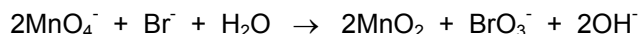


Multiply the reduction half-reaction by two, and then add together. Cancel the six electrons from each side. Also, cancel six H^+ and three H_2O from each side.

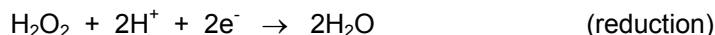
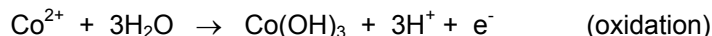
The balanced equation in acidic solution is



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



c. The two balanced half-reactions are



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

(continued)

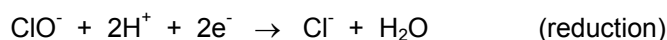
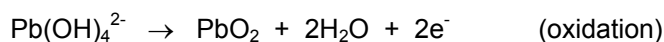
The balanced equation in acidic solution is



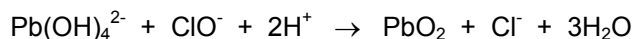
Now add four OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O . Then cancel four H_2O on each side. The balanced equation in basic solution is



d. The two balanced half-reactions are



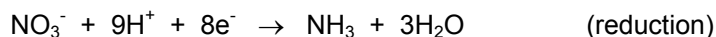
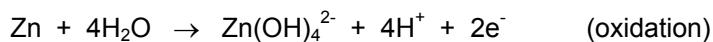
Add the two half-reactions together, and cancel the two electrons from each side. The balanced equation in acidic solution is



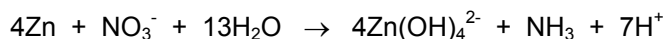
Now add two OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O . Then cancel two H_2O on each side. The balanced equation in basic solution is



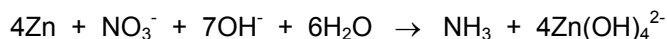
e. The two balanced half-reactions are



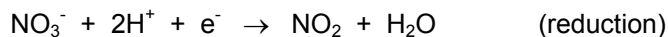
Multiply the oxidation half-reaction by four, and then add together. Cancel the eight electrons from each side. Also, cancel nine H^+ and three H_2O from each side. The balanced equation in acidic solution is



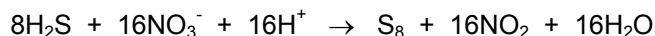
Now add seven OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O . Then cancel seven H_2O on each side. The balanced equation in basic solution is



20.33 a. The two balanced half-reactions are



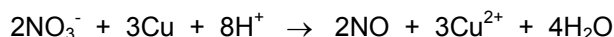
Multiply the reduction half-reaction by sixteen, and then add together. Cancel the sixteen electrons and sixteen H^+ from each side. The balanced equation is



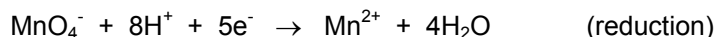
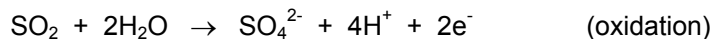
b. The two balanced half-reactions are



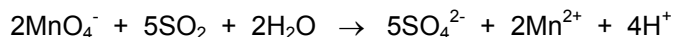
Multiply the oxidation half-reaction by three and the reduction half-reaction by two, and then add together. Cancel the six electrons from each side. The balanced equation is



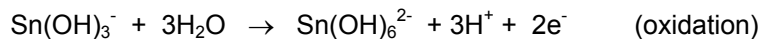
c. The two balanced half-reactions are



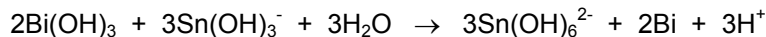
Multiply the oxidation half-reaction by five and the reduction half-reaction by two, and then add together. Cancel the ten electrons from each side. Also, cancel sixteen H^+ and eight H_2O from each side. The balanced equation is



d. The two balanced half-reactions are



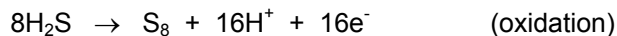
Multiply the oxidation half-reaction by three and the reduction half-reaction by two, and then add together. Cancel the six electrons from each side. Also, cancel six H^+ and six H_2O from each side. The balanced equation in acidic solution is



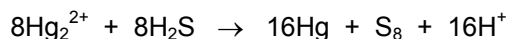
Now add three OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O . Then cancel three H_2O on each side. The balanced equation in basic solution is



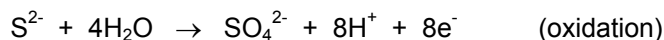
20.34 a. The two balanced half-reactions are



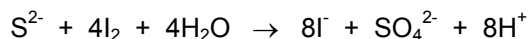
Multiply the reduction half-reaction by eight, and then add together. Cancel the sixteen electrons from each side. The balanced equation in acidic solution is



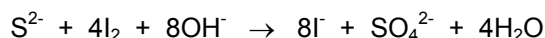
b. The two balanced half-reactions are



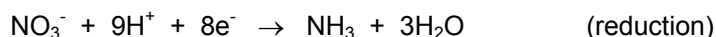
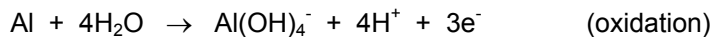
Multiply the reduction half-reaction by four, and then add together. Cancel the eight electrons from each side. The balanced equation in acidic solution is



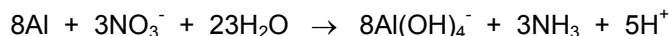
Now add eight OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O . Then cancel four H_2O on each side. The balanced equation in basic solution is



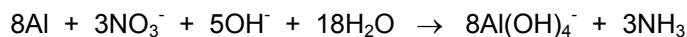
c. The two balanced half-reactions are



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^+ and nine H_2O from each side. The balanced equation in acidic solution is



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

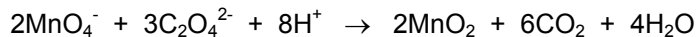


(continued)

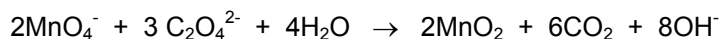
d. The two balanced half-reactions are



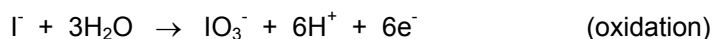
Multiply the oxidation half-reaction by three and the reduction half-reaction by two, and then add together. Cancel the six electrons from each side. The balanced equation in acidic solution is



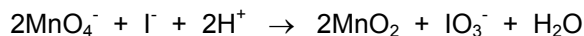
Now add eight OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O . Then cancel four H_2O on each side. The balanced equation in basic solution is



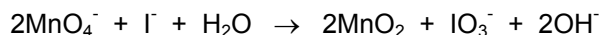
20.35 a. The two balanced half-reactions are



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_2O from each side. The balanced equation in acidic solution is



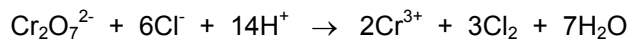
Now add two OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O . Then cancel one H_2O on each side. The balanced equation in basic solution is



b. The two balanced half-reactions are

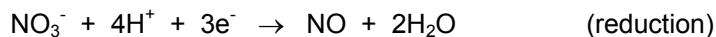
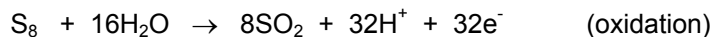


Multiply the oxidation half-reaction by three, and then add together. Cancel the six electrons from each side. The balanced equation is

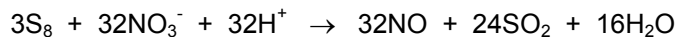


(continued)

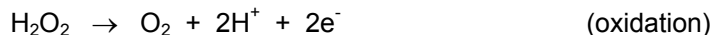
c. The two balanced half-reactions are



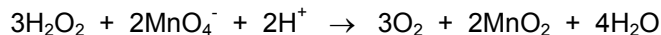
Multiply the oxidation half-reaction by three and the reduction half-reaction by thirty two, and then add together. Cancel the ninety six electrons from each side. Also, cancel ninety six H^+ and forty eight H_2O from each side. The balanced equation is



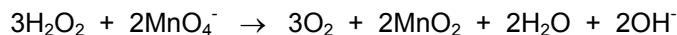
d. The two balanced half-reactions are



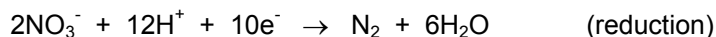
Multiply the oxidation half-reaction by three and the reduction half-reaction by two, and then add together. Cancel the six electrons from each side. Also, cancel six H^+ from each side. The balanced equation in acidic solution is



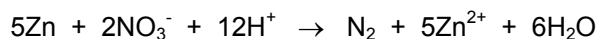
Now add two OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O . Then cancel two H_2O on each side. The balanced equation in basic solution is



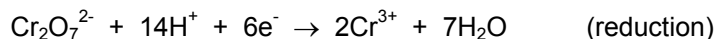
e. The two balanced half-reactions are



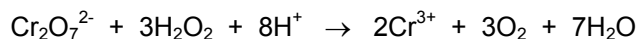
Multiply the oxidation half-reaction by five, and then add together. Cancel the ten electrons from each side. The balanced equation is



20.36 a. The two balanced half-reactions are

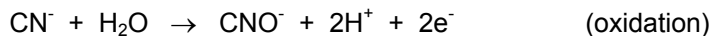


Multiply the oxidation half-reaction by three, and then add together. Cancel the six electrons from each side. Also, cancel six H^+ from each side. The balanced equation is

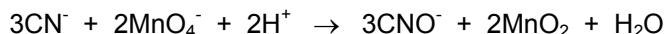


(continued)

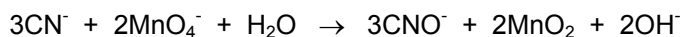
b. The two balanced half-reactions are



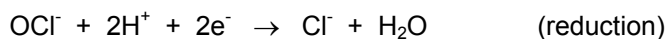
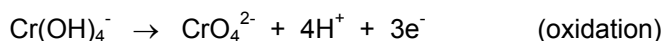
Multiply the oxidation half-reaction by three and the reduction half-reaction by two, and then add together. Cancel the six electrons from each side. Also, cancel six H^+ and three H_2O from each side. The balanced equation in acidic solution is



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



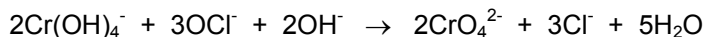
c. The two balanced half-reactions are



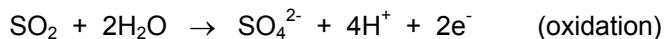
Multiply the oxidation half-reaction by two and the reduction half-reaction by three, and then add together. Cancel the six electrons from each side. Also, cancel six H^+ from each side. The balanced equation in acidic solution is



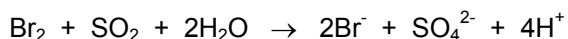
Now add two OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O . Then combine the H_2O on the right side into a single term. The balanced equation in basic solution is



d. The two balanced half-reactions are

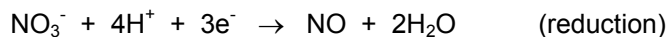
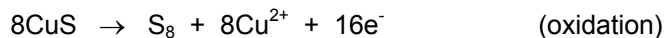


Add the two half-reactions together. Cancel the two electrons from each side. The balanced equation is

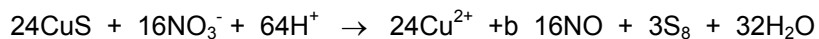


(continued)

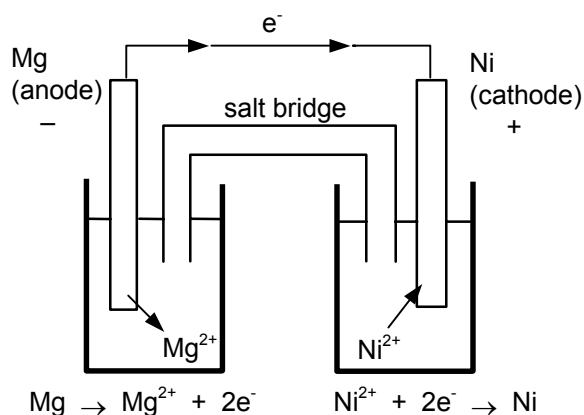
e. The two balanced half-reactions are



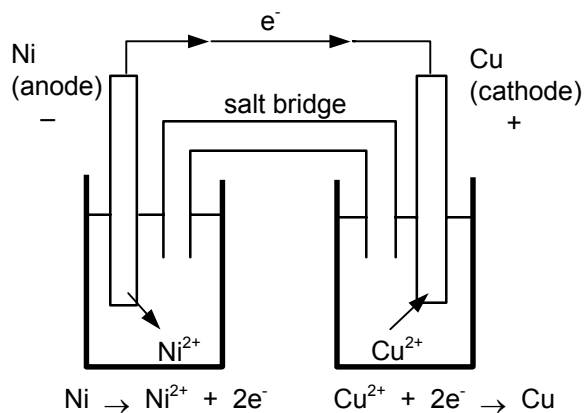
Multiply the oxidation half-reaction by three and the reduction half-reaction by sixteen, and then add together. Cancel the forty eight electrons from each side. The balanced equation is



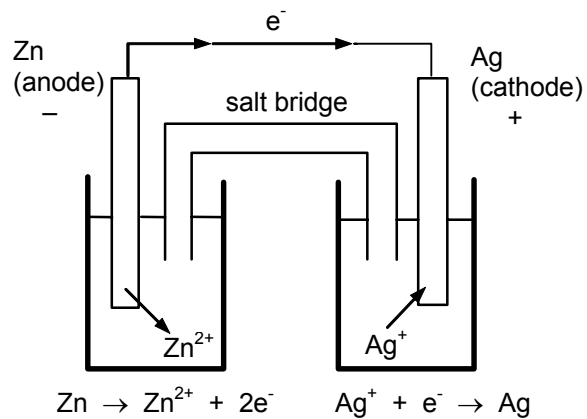
20.37 Sketch of the cell:



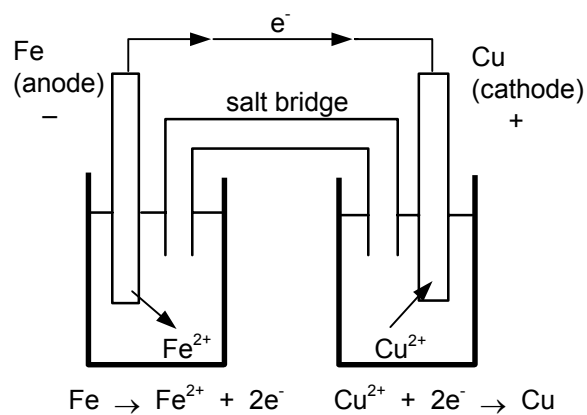
20.38 Sketch of the cell:



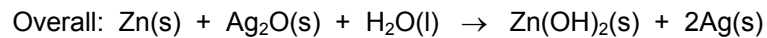
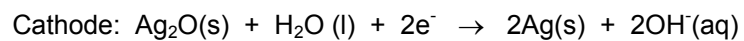
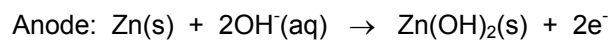
20.39 Sketch of the cell:



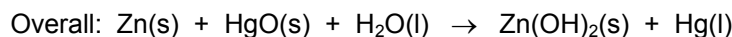
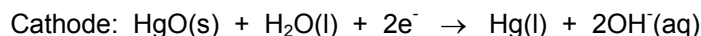
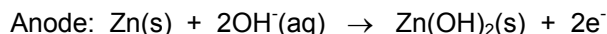
20.40 Sketch of the cell:



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



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



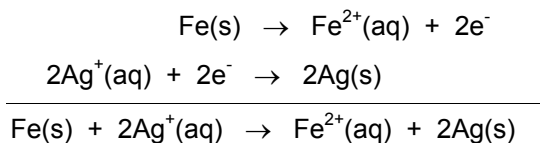
20.43 Because of its less negative E° , Pb^{2+} is reduced at the cathode and is written on the right; Ni(s) is oxidized at the anode and is written first, at the left, in the cell notation. The notation is $\text{Ni(s)}|\text{Ni}^{2+}(\text{aq})||\text{Pb}^{2+}(\text{aq})|\text{Pb(s)}$.

20.44 Because of its less negative E° , 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 $\text{Al(s)}|\text{Al}^{3+}(\text{aq})||\text{H}^+(\text{aq})|\text{H}_2(\text{g})|\text{Pt}$.

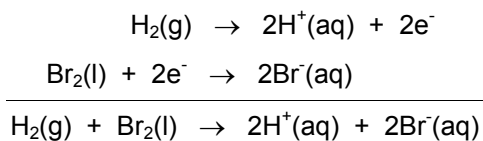
20.45 Because of its less negative E° , H^+ is reduced at the cathode and is written on the right; Ni(s) is oxidized at the anode and is written first, at the left, in the cell notation. The notation is $\text{Ni(s)}|\text{Ni}^{2+}(1\text{ M})||\text{H}^+(1\text{ M})|\text{H}_2(\text{g})|\text{Pt}$.

20.46 Because of its less negative E° , 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 $\text{Zn(s)}|\text{Zn}^{2+}(0.40\text{ M})||\text{Fe}^{3+}(0.30\text{ M})|\text{Fe(s)}$.

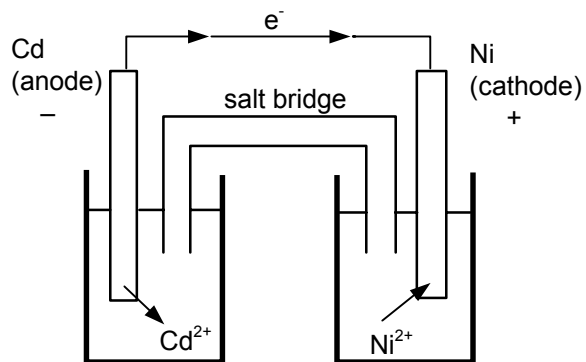
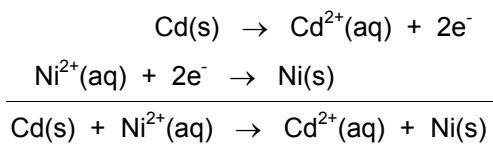
20.47 The Fe(s) , on the left, is the reducing agent. The Ag^+ , on the right, is the oxidizing agent, gaining just one electron. Multiplying its half-reaction by two to equalize the numbers of electrons and writing both half-reactions gives the overall cell reaction:



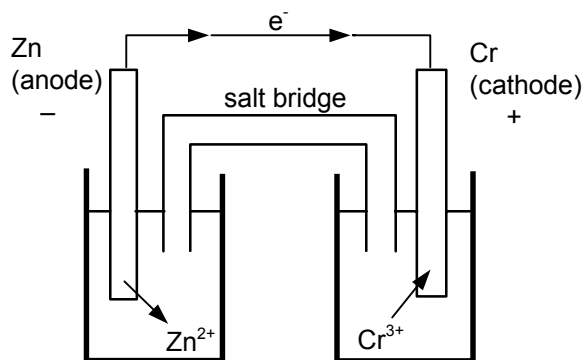
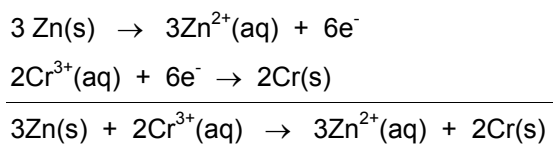
20.48 The $\text{H}_2(\text{g})$, on the left, is the reducing agent. The $\text{Br}_2(\text{l})$, on the right, is the oxidizing agent. The half-reactions and the overall cell reaction are



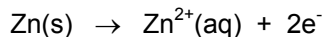
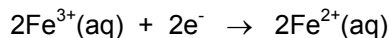
20.49 The half-cell reactions, the overall cell reaction, and the sketch are



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



20.51 The half-cell reactions are



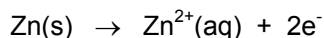
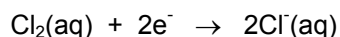
n equals two, and the maximum work for the reaction as written is

$$\begin{aligned} w_{\max} &= -nFE_{\text{cell}} = -2 \times 9.65 \times 10^4 \text{ C} \times 0.72 \text{ V} = -1.389 \times 10^5 \text{ C}\cdot\text{V} \\ &= -1.389 \times 10^5 \text{ J} \end{aligned}$$

Because this is the work obtained by reduction of two mol of Fe^{3+} , the work for one mol is

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

20.52 The half-cell reactions are



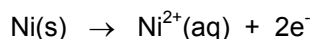
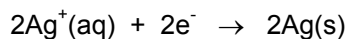
n equals two, and the maximum work for the reaction as written is

$$\begin{aligned} w_{\max} &= -nFE_{\text{cell}} = -2 \times 9.65 \times 10^4 \text{ C} \times 0.853 \text{ V} = -1.646 \times 10^5 \text{ C}\cdot\text{V} \\ &= -1.646 \times 10^5 \text{ J} \end{aligned}$$

For 20.0 g of zinc, the maximum work is

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

20.53 The half-cell reactions are



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

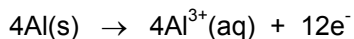
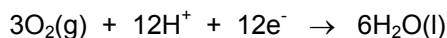
$$\begin{aligned} w_{\max} &= -nFE_{\text{cell}} = -2 \times 9.65 \times 10^4 \text{ C} \times 0.97 \text{ V} = -1.87 \times 10^5 \text{ C}\cdot\text{V} \\ &= -1.87 \times 10^5 \text{ J} \end{aligned}$$

(continued)

For 30.0 g of nickel, the maximum work is

$$30.0 \text{ g Ni} \times \frac{1 \text{ mol Ni}}{58.69 \text{ g Ni}} \times \frac{-1.87 \times 10^5 \text{ J}}{1 \text{ mol Ni}} = -9.56 \times 10^4 \text{ J} = -96 \text{ kJ}$$

20.54 The half-cell reactions are



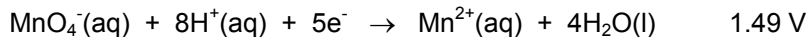
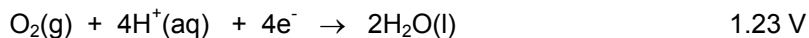
n equals twelve, and the maximum work for the reaction as written is

$$\begin{aligned} w_{\max} &= -nFE_{\text{cell}} = -(12)(9.65 \times 10^4 \text{ C})(1.15 \text{ V}) = -1.331 \times 10^6 \text{ C}\cdot\text{V} \\ &= -1.331 \times 10^6 \text{ J} \end{aligned}$$

For 50.0 g of aluminum, the maximum work is

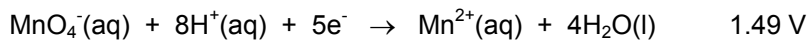
$$50.0 \text{ g} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \times \frac{-1.331 \times 10^6 \text{ J}}{4 \text{ mol Al}} = -6.169 \times 10^5 \text{ J} = -6.17 \times 10^5 \text{ J}$$

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



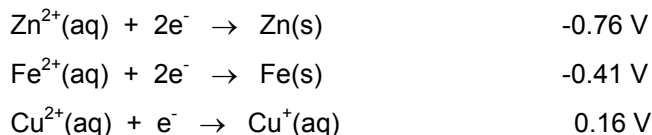
The order by increasing oxidizing strength is $\text{NO}_3^-(\text{aq})$, $\text{O}_2(\text{g})$, $\text{MnO}_4^-(\text{aq})$.

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



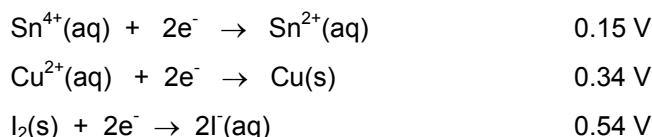
The order by increasing oxidizing strength is $\text{I}_2(\text{s})$, $\text{Ag}^+(\text{aq})$, $\text{MnO}_4^-(\text{aq})$.

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



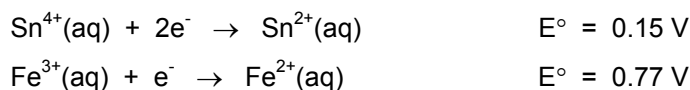
Zn(s) is the strongest, and $\text{Cu}^{+}(\text{aq})$ is the weakest.

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



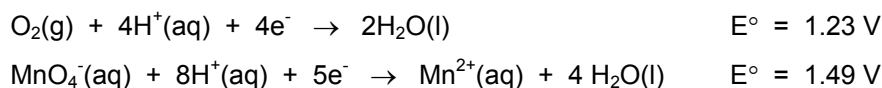
$\text{I}_2(\text{s})$ is the strongest and Sn^{4+} is the weakest.

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



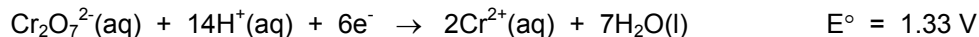
The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so Fe^{3+} is the stronger oxidizing agent. The reaction is nonspontaneous as written.

b. In this reaction, MnO_4^{-} is the oxidizing agent on the left side; O_2 is the oxidizing reagent on the right side. The corresponding standard electrode potentials are



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



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

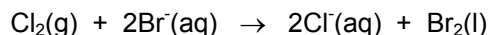


The stronger reducing agent is the one involved in the half-reaction with the smaller standard electrode potential, so Ni(s) is the stronger reducing agent. Thus, copper metal will not reduce Ni(II) ion spontaneously.

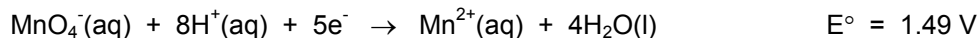
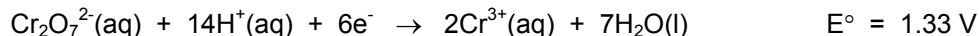
20.61 The reduction half-reactions and standard electrode potentials are



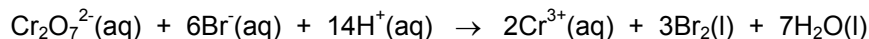
From these, you see that the order of increasing oxidizing strength is Br_2 , Cl_2 , F_2 . Therefore, chlorine gas will oxidize Br^{-} but will not oxidize F^{-} . The balanced equation for the reaction is



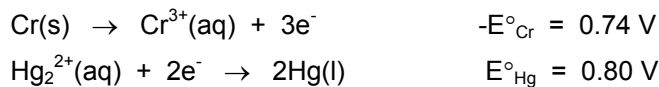
20.62 The reduction half-reactions and standard electrode potentials are



From these, you see that the order of increasing oxidizing strength is Br_2 , $\text{Cr}_2\text{O}_7^{2-}$, MnO_4^{-} . Thus, $\text{Cr}_2\text{O}_7^{2-}$ will oxidize Br^{-} but will not oxidize Mn^{2+} . The balanced equation for the reaction is



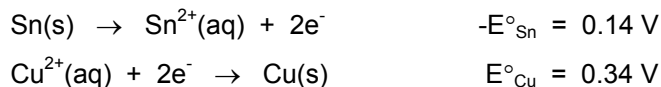
20.63 The half-reactions and standard electrode potentials are



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

$$E^\circ_{\text{cell}} = E^\circ_{\text{Hg}} - E^\circ_{\text{Cr}} = 0.80 \text{ V} + 0.74 \text{ V} = 1.54 \text{ V}$$

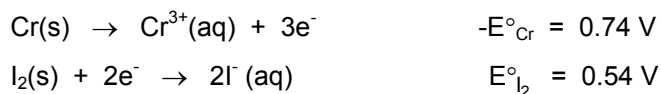
20.64 The half-reactions and standard electrode potentials are



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

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

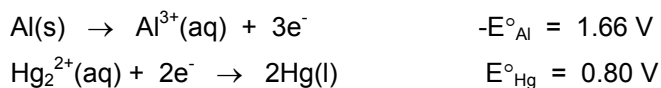
20.65 The half-reactions and standard electrode potentials are



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

$$E^\circ_{\text{cell}} = E^\circ_{\text{Cr}} - E^\circ_{\text{I}_2} = 0.54 \text{ V} + 0.74 \text{ V} = 1.28 \text{ V}$$

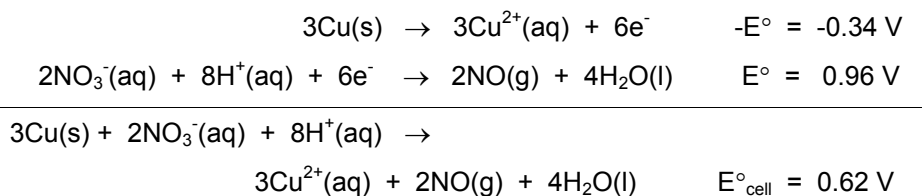
20.66 The half-reactions and standard electrode potentials are



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

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

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

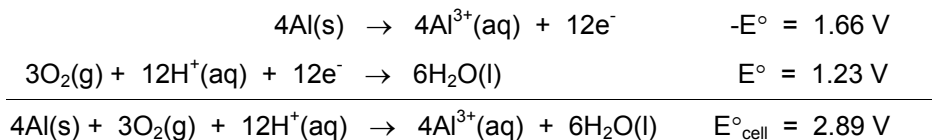


Note that each half-reaction involves six electrons, hence $n = 6$. Therefore,

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

Thus, the standard free-energy change is $-3.6 \times 10^2 \text{ kJ}$.

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

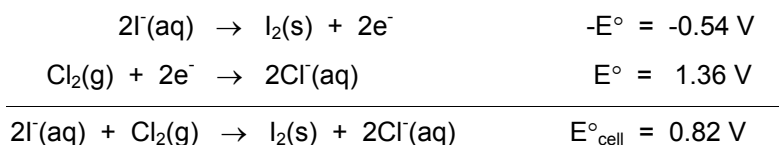


Note that each half-reaction involves twelve electrons, hence $n = 12$. Therefore,

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

Thus, the standard free-energy change is $-3.35 \times 10^3 \text{ kJ}$.

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

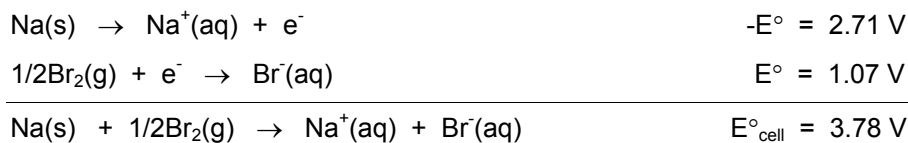


Note that each half-reaction involves two electrons, hence $n = 2$. Therefore,

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

Thus, the standard free-energy change is $-1.6 \times 10^2 \text{ kJ}$.

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

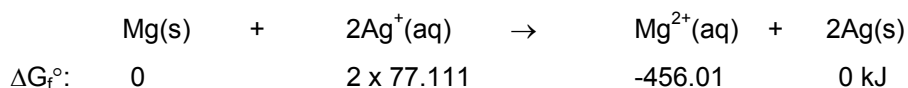


Note that each half-reaction involves one electron, hence $n = 1$. Therefore,

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

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

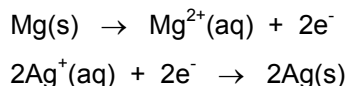
- 20.71 Write the equation with ΔG_f° 's beneath each substance.



Hence,

$$\begin{aligned}\Delta G^\circ &= \sum n\Delta G_f^\circ(\text{products}) - \sum m\Delta G_f^\circ(\text{reactants}) \\ &= [-456.01 - 2 \times 77.111] \text{ kJ} = -610.23 \text{ kJ} = -6.1023 \times 10^5 \text{ J}\end{aligned}$$

Obtain n by splitting the reaction into half-reactions.



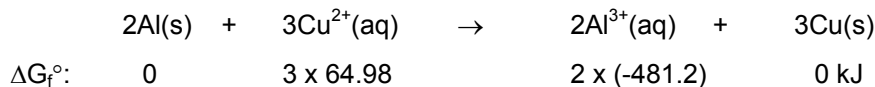
Each half-reaction involves two electrons, so $n = 2$. Therefore,

$$\begin{aligned}\Delta G^\circ &= -nFE^\circ_{\text{cell}} \\ -6.1023 \times 10^5 \text{ J} &= -2 \times 9.65 \times 10^4 \text{ C} \times E^\circ_{\text{cell}}\end{aligned}$$

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

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

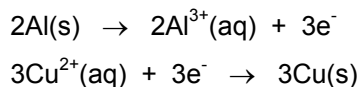
20.72 Write the equation with ΔG_f° 's beneath each substance.



Hence,

$$\begin{aligned}
 \Delta G^\circ &= \sum n \Delta G_f^\circ(\text{products}) - \sum m \Delta G_f^\circ(\text{reactants}) \\
 &= [2 \times -481.2 - 3 \times 64.98] \text{ kJ} = -1157.34 \text{ kJ} = -1.15734 \times 10^6 \text{ J}
 \end{aligned}$$

Obtain n by splitting the reaction into half-reactions.



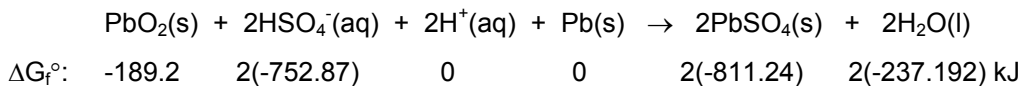
Each half-reaction involves three electrons, so $n = 3$. Therefore,

$$\begin{aligned}
 \Delta G^\circ &= -nFE^\circ_{\text{cell}} \\
 -1.15734 \times 10^6 \text{ J} &= -3 \times 9.65 \times 10^4 \text{ C} \times E^\circ_{\text{cell}}
 \end{aligned}$$

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

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

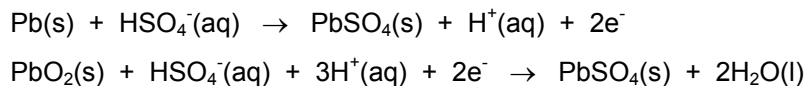
20.73 Write the equation with ΔG_f° 's beneath each substance:



Hence,

$$\begin{aligned}
 \Delta G^\circ &= [2 \times -811.24 + 2 \times -237.192 - -189.2 - 2 \times -752.87] \text{ kJ} \\
 &= -401.924 \text{ kJ} = -4.0192 \times 10^5 \text{ J}
 \end{aligned}$$

Obtain n by splitting the reaction into half-reactions.



(continued)

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

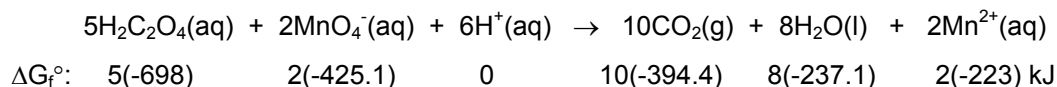
$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

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

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

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

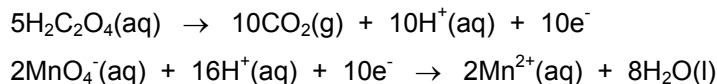
20.74 Write the equation with ΔG_f° 's beneath each substance:



Hence,

$$\begin{aligned}\Delta G^\circ &= [10(-394.4) + 8(-237.1) + 2(-223) - 5(-698) - 2(-425.1)] \text{ kJ} \\ &= -1946.6 \text{ kJ} = -1.9466 \times 10^6 \text{ J}\end{aligned}$$

Obtain n by splitting the reaction into half-reactions.



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

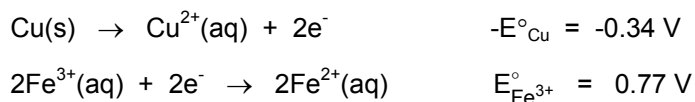
$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

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

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

$$E^\circ_{\text{cell}} = \frac{-1.9466 \times 10^6 \text{ J}}{-10 \times 9.65 \times 10^4 \text{ C}} = 2.0172 = 2.02 \text{ V}$$

20.75 The half-reactions and standard electrode potentials are



(continued)

The standard emf for the cell is

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

Note that $n = 2$. Substitute into the equation relating E° and K . Note that $K = K_c$.

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

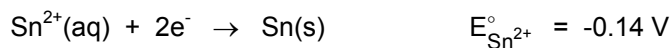
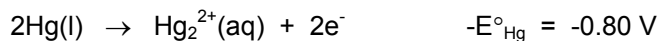
Solving for K_c , you get

$$\log K_c = 14.52$$

Take the antilog of both sides:

$$K_c = \text{antilog}(14.52) = 3.4 \times 10^{14} = 10^{14}$$

20.76 The half-reactions and standard electrode potentials are



The standard emf for the cell is

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

Note that $n = 2$. Substitute into the equation relating E° and K . Note that $K = K_c$.

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

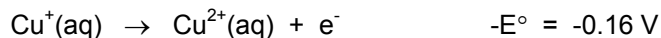
Solving for K_c , you get

$$\log K_c = -31.756$$

Take the antilog of both sides:

$$K_c = \text{antilog}(-31.756) = 1.75 \times 10^{-32} = 10^{-32}$$

20.77 The half-reactions and standard electrode potentials are



The standard emf for the cell is

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

Note that n equals 1. Substitute into the equation relating E° and K . Note that K equals K_c .

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

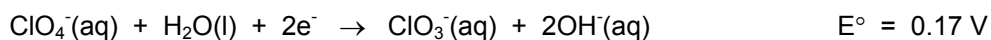
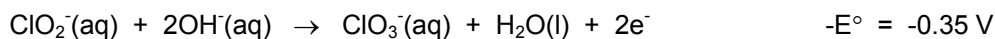
Solving for K_c , you get

$$\log K_c = 6.081$$

Take the antilog of both sides:

$$K_c = \text{antilog}(6.081) = 1.2 \times 10^6 = 1 \times 10^6$$

20.78 The half-reactions and standard electrode potentials are



The standard emf for the cell is

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

Note that n equals two. Substitute into the equation relating E° and K . Note that K equals K_c .

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

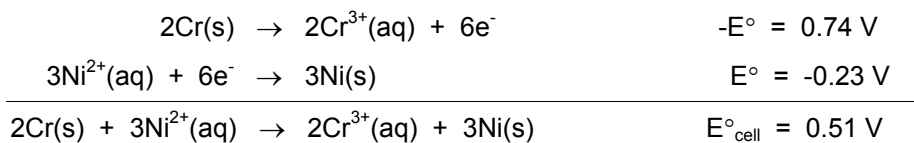
Solving for K_c , you get

$$\log K_c = -6.081$$

Take the antilog of both sides:

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

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



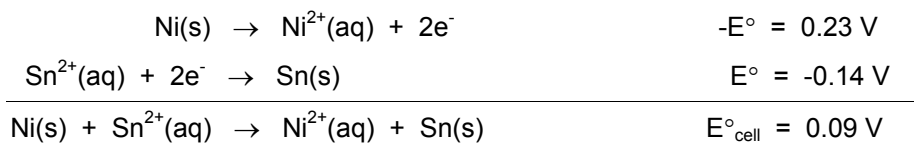
Note that n equals six. The reaction quotient is

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

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

$$\begin{aligned}
 E_{\text{cell}} &= E^{\circ}_{\text{cell}} - \frac{0.0592}{n} \log Q \\
 &= 0.51 - \frac{0.0592}{6} \log (2.962 \times 10^{-7}) \\
 &= 0.51 - (-0.06441) = 0.574 = 0.57 \text{ V}
 \end{aligned}$$

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



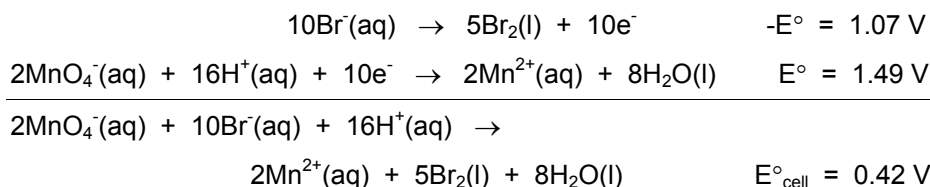
Note that n equals two. The reaction quotient is

$$Q = \frac{[\text{Ni}^{2+}]}{[\text{Sn}^{2+}]} = \frac{1.0}{1.0 \times 10^{-4}} = 1.00 \times 10^4$$

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

$$\begin{aligned}
 E_{\text{cell}} &= E^{\circ}_{\text{cell}} - \frac{0.0592}{n} \log Q \\
 &= 0.09 - \frac{0.0592}{2} \log (1.00 \times 10^4) \\
 &= 0.09 \text{ V} - (0.1184 \text{ V}) = -0.0284 = -0.03 \text{ V}
 \end{aligned}$$

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



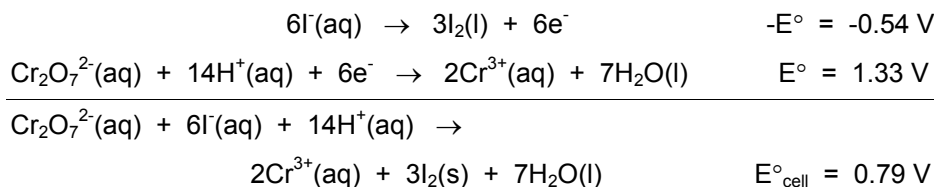
Note that n equals ten. The reaction quotient is

$$Q = \frac{[\text{Mn}^{2+}]^2}{[\text{MnO}_4^{2-}]^2 [\text{Br}^-]^{10} [\text{H}^+]^{16}} = \frac{(0.15)^2}{(0.010)^2 (0.010)^{10} (1.0)^{16}} = 2.25 \times 10^{22}$$

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

$$\begin{aligned}
 E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.0592}{n} \log Q = 0.42 - \frac{0.0592}{10} \log (2.25 \times 10^{22}) \\
 &= 0.42 - (0.1323) = 0.2876 = 0.29 \text{ V}
 \end{aligned}$$

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



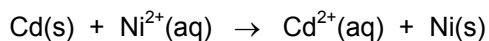
Note that n equals six. The reaction quotient is

$$Q = \frac{[\text{Cr}^{3+}]^2}{[\text{Cr}_2\text{O}_7^{2-}] [\text{I}^-]^6 [\text{H}^+]^{14}} = \frac{(0.40)^2}{(0.020)(0.015)^6 (0.50)^{14}} = 1.1507 \times 10^{16}$$

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

$$\begin{aligned}
 E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.0592}{n} \log Q = 0.79 - \frac{0.0592}{6} \log (1.1507 \times 10^{16}) \\
 &= 0.79 - (0.1584) = 0.6315 = 0.63 \text{ V}
 \end{aligned}$$

20.83 The overall reaction is



Note that n equals two. The reaction quotient is

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

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

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

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

Rearrange and solve for $\log Q$

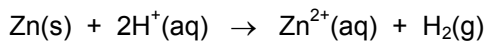
$$\log Q = \frac{2}{0.0592} \times (0.240 - 0.170) = -2.3648$$

Take the antilog of both sides

$$Q = [\text{Cd}^{2+}] = \text{antilog}(-2.3648) = 4.31 \times 10^{-3} = 0.004 \text{ M}$$

The Cd^{2+} concentration is 0.004 M.

20.84 The overall reaction is



Note that n equals two. The reaction quotient is

$$Q = \frac{[\text{Zn}^{2+}] \times P_{\text{H}_2}}{[\text{H}^{+}]^2} = \frac{(1.0)(1.0)}{[\text{H}^{+}]^2} = \frac{1}{[\text{H}^{+}]^2}$$

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

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

(continued)

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

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:

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

Therefore

$$\log Q = 2 \times \text{pH} = 9.628$$

$$\text{pH} = 9.628 \div 2 = 4.814 = 4.8$$

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

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

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

The anode reaction is $4\text{OH}^-(\text{l}) \rightarrow \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) + 4\text{e}^-$.

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

The anode reaction is $2\text{Br}^-(\text{l}) \rightarrow \text{Br}_2(\text{l}) + 2\text{e}^-$.

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

The anode reaction is $4\text{OH}^-(\text{l}) \rightarrow \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) + 4\text{e}^-$.

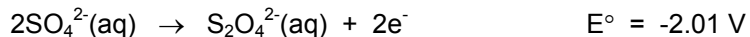
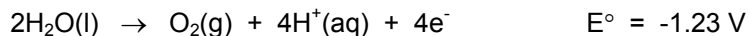
20.87 a. The species you should consider for half-reactions are Na^+ , SO_4^{2-} , and H_2O . The possible cathode reactions are



Because the electrode potential for H_2O is larger (less negative), it is easier to reduce.

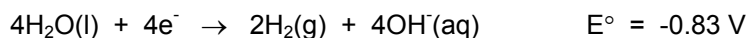
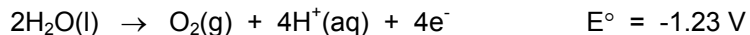
(continued)

The possible anode reactions are

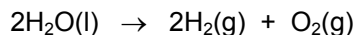


Because the electrode potential for H_2O is less negative, it is easier to oxidize.

The expected half-reactions are



The overall reaction is

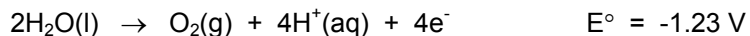


- b. The species you should consider for half-reactions are K^+ , Br^- , and H_2O . The possible cathode reactions are



Because the electrode potential for H_2O is larger (less negative), it is easier to reduce.

The possible anode reactions are

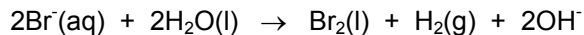


Because the electrode potential for Br^- is less negative, it is easier to oxidize.

The expected half-reactions are



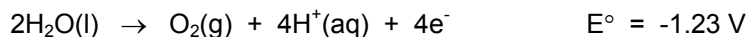
The overall reaction is



- 20.88 a. The species you should consider for half-reactions are Cu^{2+} , Cl^- , and H_2O . The possible cathode reactions are

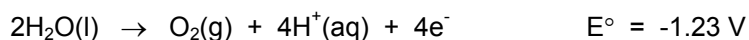


Because the electrode potential for Cu^{2+} is larger (less negative), it is easier to reduce. The possible anode reactions are

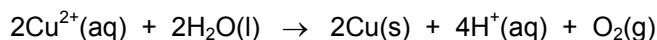


Because the electrode potential for H_2O is less negative, it is easier to oxidize.

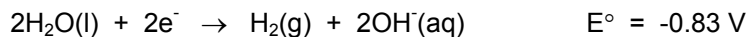
The expected half-reactions are



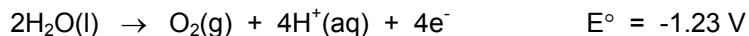
The overall reaction is



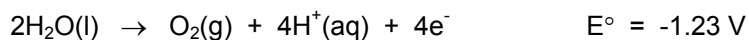
- b. The species you should consider for half-reactions are Cu^{2+} and H_2O . The possible cathode reactions are



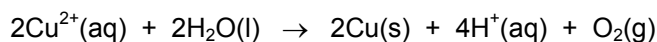
Because the electrode potential for Cu^{2+} is larger (less negative), it is easier to reduce. The anode reaction is



The expected half-reactions are



The overall reaction is



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

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

$$= 3.873 \times 10^7 = 3.87 \times 10^7 \text{ C}$$

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

$$1.18 \times 10^3 \text{ g} \times \frac{1 \text{ mol Cl}_2}{70.91 \text{ g}} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Cl}_2} \times \frac{9.65 \times 10^4 \text{ C}}{1 \text{ mol e}^-}$$

$$= 3.211 \times 10^6 = 3.21 \times 10^6 \text{ C}$$

Using the current of $5.00 \times 10^2 \text{ A}$, calculate the time in s:

$$\text{Time} = \frac{1 \text{ mol Cl}_2}{70.91 \text{ g}} = \frac{1 \text{ mol Cl}_2}{70.91 \text{ g}} = 6.423 \times 10^3 = 6.42 \times 10^3 \text{ s}$$

- 20.91 The conversion of coulombs to grams of lithium is

$$5.00 \times 10^3 \text{ C} \times \frac{1 \text{ mol e}^-}{9.65 \times 10^4 \text{ C}} \times \frac{1 \text{ mol Li}}{1 \text{ mol e}^-} \times \frac{6.941 \text{ g Li}}{1 \text{ mol Li}} = 0.3596$$

$$= 0.360 \text{ g Li}$$

- 20.92 The conversion of current and time into coulombs is ($221 \text{ min} = 1.326 \times 10^4 \text{ s}$)

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

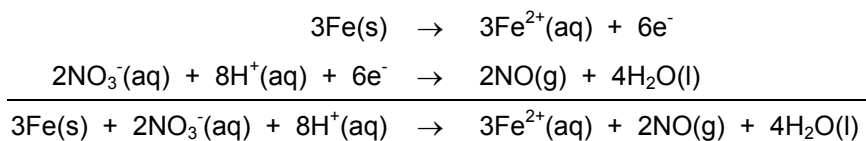
The conversion of coulombs to grams of cadmium is

$$2.002 \times 10^4 \text{ C} \times \frac{1 \text{ mol e}^-}{9.65 \times 10^4 \text{ C}} \times \frac{1 \text{ mol Cd}}{2 \text{ mol e}^-} \times \frac{112.4 \text{ g Cd}}{1 \text{ mol Cd}} = 11.66$$

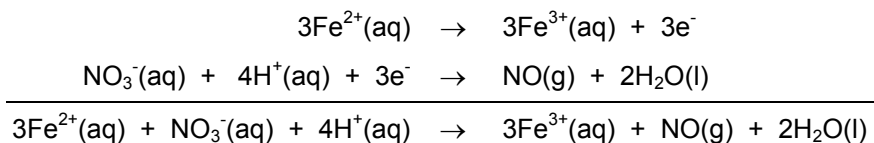
$$= 11.7 \text{ g Cd}$$

■ Solutions to General Problems

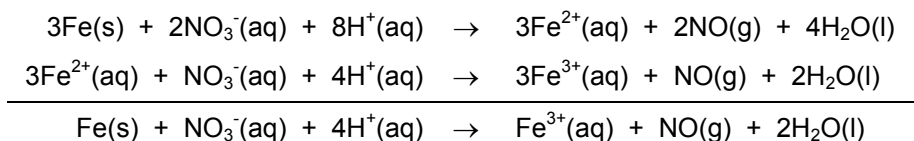
20.93 a. The half-reactions and net ionic equation are



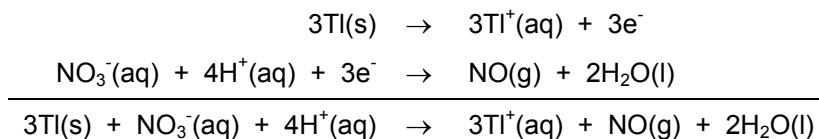
b. The half-reactions and net ionic equation are



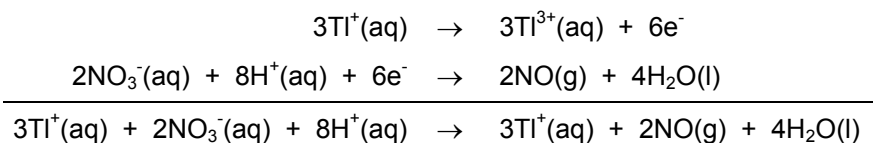
c. Add the results from parts (a) and (b)



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

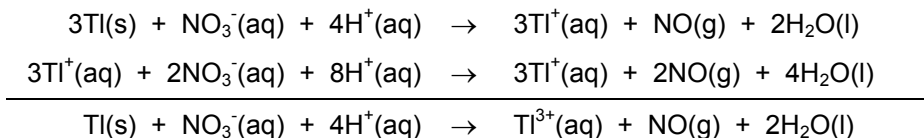


b. The half-reactions and net ionic equation are



(continued)

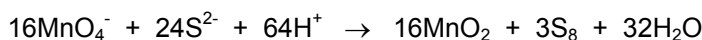
c. Add the results from parts (a) and (b)



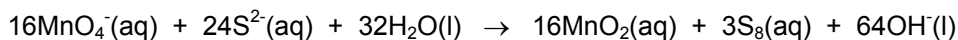
20.95 a. The two balanced half-reactions are



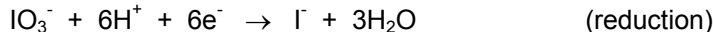
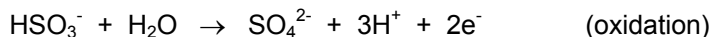
Multiply the oxidation half-reaction by three and the reduction half-reaction by sixteen, and then add together. Cancel the forty eight electrons from each side. The balanced equation in acidic solution is



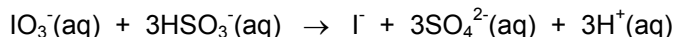
Now add sixty four OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O . Then cancel thirty two H_2O on each side. The balanced equation in basic solution is



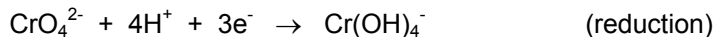
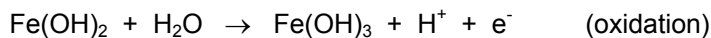
b. The two balanced half-reactions are



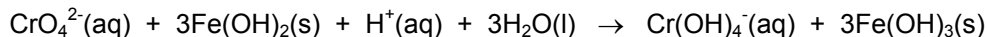
Multiply the oxidation half-reaction by three, and then add together. Cancel the six electrons from each side. Also, cancel six H^+ and three H_2O from each side. The balanced equation is



c. The two balanced half-reactions are

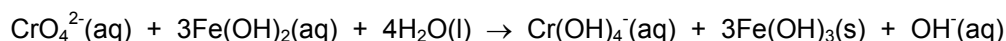


Multiply the oxidation half-reaction by three, and then add together. Cancel the three electrons and cancel three H^+ from each side. The balanced equation in acidic solution is

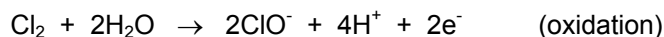


(continued)

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



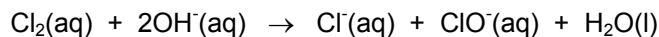
d. The two balanced half-reactions are



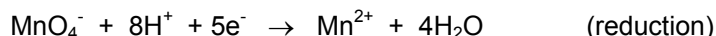
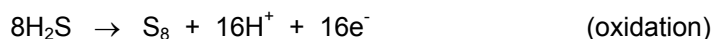
Add the two half-reactions together. Cancel the two electrons from each side. Divide all the coefficients by a factor of two. The balanced equation in acidic solution is



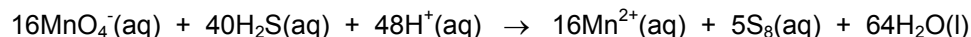
Now add two OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O . Then cancel one H_2O on each side. The balanced equation in basic solution is



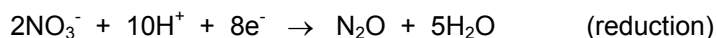
20.96 a. The two balanced half-reactions are



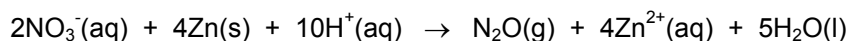
Multiply the oxidation half-reaction by five and the reduction half-reaction by sixteen, and then add together. Cancel the eighty electrons from each side. Also, cancel eighty H^+ from each side. The balanced equation is



b. The two balanced half-reactions are



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



(continued)

c. The two balanced half-reactions are



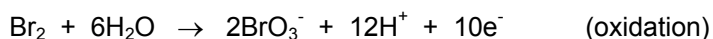
Multiply the oxidation half-reaction by two, and then add together. Cancel the two electrons from each side. Also, combine the MnO_4^{2-} on the left into a single term. The balanced equation in acidic solution is



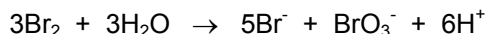
Now add four OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O . Then cancel two H_2O on each side. The balanced equation in basic solution is



d. The two balanced half-reactions are



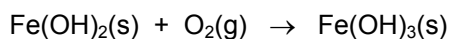
Multiply the reduction half-reaction by five, and then add together. Cancel the ten electrons from each side. Also, combine the Br_2 on the left into a single term. The balanced equation in acidic solution is



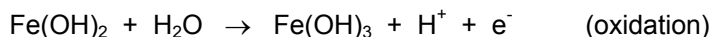
Now add six OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O . Then cancel three H_2O on each side. The balanced equation in basic solution is



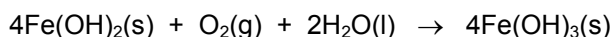
20.97 This reaction takes place in basic solution. The skeleton equation is



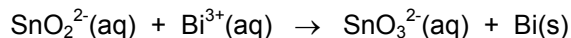
The two balanced half-reactions are



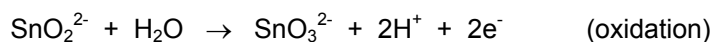
Multiply the oxidation half-reaction by four, and then add together. Cancel the four electrons from each side. Also, cancel four H^+ and two H_2O from each side. The balanced equation in acidic or in basic solution is



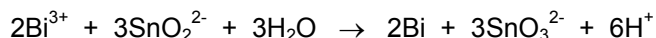
20.98 This reaction takes place in basic solution. The skeleton equation is



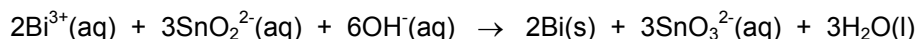
The two balanced half-reactions are



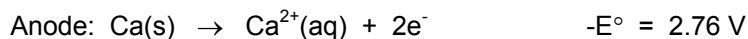
Multiply the oxidation half-reaction by three and the reduction reaction by two, and then add together. Cancel the six electrons from each side. The balanced equation in acidic solution is



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

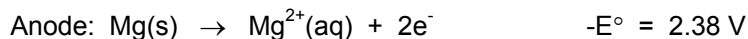


20.99 The cell notation is $\text{Ca}(\text{s})|\text{Ca}^{2+}(\text{aq})||\text{Cl}^-(\text{aq})|\text{Cl}_2(\text{g})|\text{Pt}(\text{s})$. The reactions are



$$E^\circ_{\text{cell}} = 1.36 \text{ V} + 2.76 \text{ V} = 4.12 \text{ V}$$

20.100 The cell notation is $\text{Mg}(\text{s})|\text{Mg}^{2+}(\text{aq})||\text{Ag}^+(\text{aq})|\text{Ag}(\text{s})$. The reactions are



$$E^\circ_{\text{cell}} = 0.80 \text{ V} + 2.38 \text{ V} = 3.18 \text{ V}$$

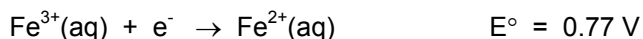
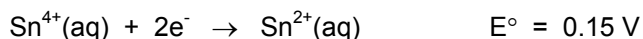
20.101 a. In this reaction, Fe^{3+} is the oxidizing agent on the left side; Ni^{2+} is the oxidizing reagent on the right side. The corresponding standard electrode potentials are



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

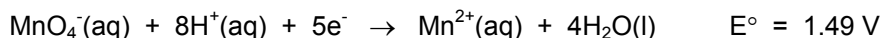
(continued)

- b. In this reaction, Fe^{3+} is the oxidizing agent on the left side; Sn^{4+} is the oxidizing reagent on the right side. The corresponding standard electrode potentials are



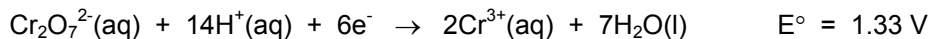
The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so Fe^{3+} is the stronger oxidizing agent. The oxidation of tin(II) by iron(III) is a spontaneous reaction.

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



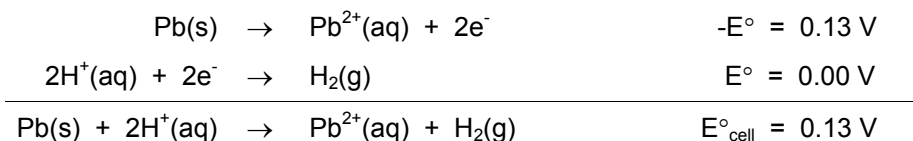
The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so MnO_4^- is the stronger oxidizing agent. The oxidation of chloride ion by permanganate ion is a spontaneous reaction.

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



The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so 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_{sp} to calculate $[\text{Pb}^{2+}]$.

$$[\text{Pb}^{2+}] = \frac{K_{\text{sp}}}{[\text{SO}_4^{2-}]} = \frac{1.7 \times 10^{-8}}{1.0} = 1.7 \times 10^{-8} \text{ M}$$

(continued)

The reaction quotient for the cell reaction is

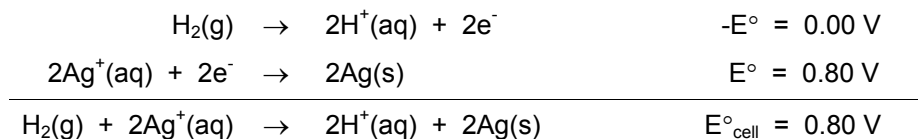
$$Q = \frac{[\text{Pb}^{2+}] \times P_{\text{H}_2}}{[\text{H}^+]^2} = \frac{(1.7 \times 10^{-8})(1.0)}{(1.0)^2} = 1.7 \times 10^{-8}$$

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

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log Q$$

$$\begin{aligned} E_{\text{cell}} &= 0.13 \text{ V} - \frac{0.0592}{2} \log (1.7 \times 10^{-8}) \\ &= 0.13 \text{ V} - (-0.2299 \text{ V}) = 0.3599 = 0.36 \text{ V} \end{aligned}$$

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



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

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

The reaction quotient for the cell reaction is

$$Q = \frac{[\text{H}^+]^2}{[\text{Ag}^+]^2 P_{\text{H}_2}} = \frac{(1.0)^2}{(1.8 \times 10^{-10})^2 (1.0)} = 3.086 \times 10^{19}$$

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

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log Q$$

$$\begin{aligned} E_{\text{cell}} &= 0.80 \text{ V} - \frac{0.0592}{2} \log (3.086 \times 10^{19}) \\ &= 0.80 \text{ V} - (0.5768 \text{ V}) = 0.2231 = 0.22 \text{ V} \end{aligned}$$

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

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

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

Solving for K , you get

$$\log K = 0.3378$$

Take the antilog of both sides:

$$K = K_c = \text{antilog}(0.3378) = 2.176 = 2.2$$

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

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

$$x = 0.6851 \text{ M}$$

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

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

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

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

Solving for K , you get

$$\log K = 0.5067$$

Take the antilog of both sides:

$$K = K_c = \text{antilog}(0.5067) = 3.211 = 3.2$$

(continued)

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

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

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

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

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

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

- 20.107 a. The number of faradays is

$$1.0 \text{ mol Na}^+ \times \frac{1 \text{ mol e}^-}{1 \text{ mol Na}^+} \times \frac{1 \text{ F}}{1 \text{ mol e}^-} = 1.0 \text{ F}$$

The number of coulombs is

$$1.0 \text{ F} \times \frac{9.65 \times 10^4 \text{ C}}{1 \text{ F}} = 9.65 \times 10^4 = 9.7 \times 10^4 \text{ C}$$

- b. The number of faradays is

$$1.0 \text{ mol Cu}^{2+} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Cu}^{2+}} \times \frac{1 \text{ F}}{1 \text{ mol e}^-} = 2.0 \text{ F}$$

The number of coulombs is

$$2.0 \text{ F} \times \frac{9.65 \times 10^4 \text{ C}}{1 \text{ F}} = 1.93 \times 10^5 = 1.9 \times 10^5 \text{ C}$$

(continued)

c. The number of faradays is

$$1.0 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.01 \text{ g H}_2\text{O}} \times \frac{2 \text{ mol e}^-}{1 \text{ mol H}_2\text{O}} \times \frac{1 \text{ F}}{1 \text{ mol e}^-} = 0.1110 = 0.11 \text{ F}$$

The number of coulombs is

$$0.1110 \text{ F} \times \frac{9.65 \times 10^4 \text{ C}}{1 \text{ F}} = 1.07 \times 10^4 = 1.1 \times 10^4 \text{ C}$$

d. The number of faradays is

$$1.0 \text{ g Cl}^- \times \frac{1 \text{ mol Cl}^-}{35.45 \text{ g Cl}^-} \times \frac{2 \text{ mol e}^-}{2 \text{ mol Cl}^-} \times \frac{1 \text{ F}}{1 \text{ mol e}^-} = 0.02820 = 0.028 \text{ F}$$

The number of coulombs is

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

20.108a. The number of faradays is

$$1.0 \text{ mol Fe}^{3+} \times \frac{1 \text{ mol e}^-}{1 \text{ mol Fe}^{3+}} \times \frac{1 \text{ F}}{1 \text{ mol e}^-} = 1.0 \text{ F}$$

The number of coulombs is

$$1.0 \text{ F} \times \frac{9.65 \times 10^4 \text{ C}}{1 \text{ F}} = 9.65 \times 10^4 = 9.7 \times 10^4 \text{ C}$$

b. The number of faradays is

$$1.0 \text{ mol Fe}^{3+} \times \frac{3 \text{ mol e}^-}{1 \text{ mol Fe}^{3+}} \times \frac{1 \text{ F}}{1 \text{ mol e}^-} = 3.0 \text{ F}$$

The number of coulombs is

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

(continued)

c. The number of faradays is

$$1.0 \text{ g Sn}^{2+} \times \frac{1 \text{ mol Sn}^{2+}}{118.7 \text{ g Sn}^{2+}} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Sn}^{2+}} \times \frac{1 \text{ F}}{1 \text{ mol e}^-} = 0.01684 = 0.017 \text{ F}$$

The number of coulombs is

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

d. The number of faradays is

$$1.0 \text{ g Au}^{3+} \times \frac{1 \text{ mol Au}^{3+}}{197.0 \text{ g Au}^{3+}} \times \frac{3 \text{ mol e}^-}{1 \text{ mol Au}^{3+}} \times \frac{1 \text{ F}}{1 \text{ mol e}^-} = 0.01522 = 0.015 \text{ F}$$

The number of coulombs is

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

20.109 From the electrolysis information, calculate the total moles of I_2 formed

$$\begin{aligned} 65.4 \text{ s} \times (10.5 \times 10^{-3} \text{ A}) \times \frac{1 \text{ C}}{1 \text{ A} \cdot \text{s}} \times \frac{1 \text{ mol e}^-}{9.65 \times 10^4 \text{ C}} \times \frac{1 \text{ mol I}_2}{2 \text{ mol e}^-} \\ = 3.558 \times 10^{-6} \text{ mol I}_2 \end{aligned}$$

From the balanced equation

$$\begin{aligned} 3.558 \times 10^{-6} \text{ mol I}_2 \times \frac{1 \text{ mol H}_3\text{AsO}_3}{1 \text{ mol I}_2} \times \frac{1 \text{ mol As}}{1 \text{ mol H}_3\text{AsO}_3} \times \frac{79.42 \text{ g As}}{1 \text{ mol As}} \\ = 2.8257 \times 10^{-4} = 2.83 \times 10^{-4} \text{ g As} \end{aligned}$$

20.110 From the electrolysis information, calculate the total moles of OH^- formed.

$$115 \text{ s} \times (15.6 \times 10^{-3} \text{ A}) \times \frac{1 \text{ C}}{1 \text{ A} \cdot \text{s}} \times \frac{1 \text{ mol e}^-}{9.65 \times 10^4 \text{ C}} \times \frac{2 \text{ mol OH}^-}{2 \text{ mol e}^-}$$

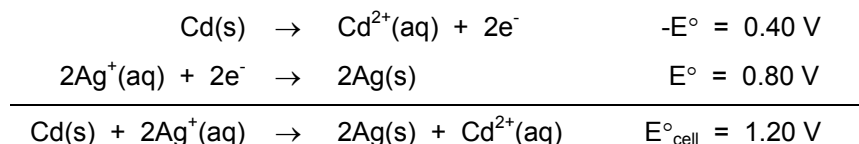
$$= 1.859 \times 10^{-5} \text{ mol OH}^-$$

From the balanced equation

$$1.859 \times 10^{-5} \text{ mol OH}^- \times \frac{1 \text{ mol HC}_3\text{H}_5\text{O}_3}{1 \text{ mol OH}^-} \times \frac{90.08 \text{ g HC}_3\text{H}_5\text{O}_3}{1 \text{ mol HC}_3\text{H}_5\text{O}_3}$$

$$= 1.6745 \times 10^{-3} = 1.67 \times 10^{-3} \text{ g HC}_3\text{H}_5\text{O}_3$$

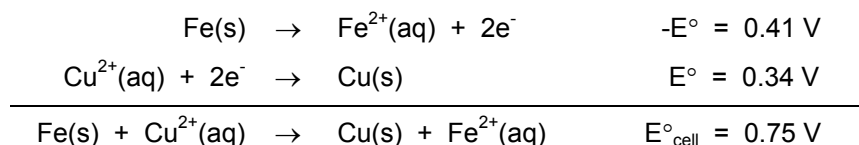
20.111 a. The spontaneous chemical reaction and maximum cell potential are



b. Addition of S^{2-} would greatly decrease the $\text{Cd}^{2+}(\text{aq})$ concentration and help shift the equilibrium to the right, thus forming more Ag.

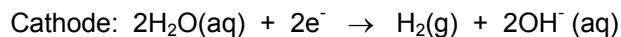
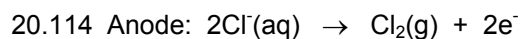
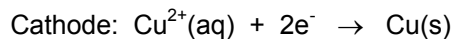
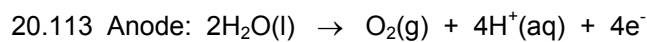
c. No effect. The size of the electrode makes no difference in the potential.

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



b. The $\text{Cu}^{2+}(\text{aq})$ 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.



20.115a. First, find the moles of silver.

$$2.48 \text{ g Ag} \times \frac{1 \text{ mol Ag}}{107.9 \text{ g Ag}} = 0.02298 \text{ mol Ag}$$

The number of coulombs is

$$0.02298 \text{ mol Ag} \times \frac{1 \text{ mol e}^-}{1 \text{ mol Ag}} \times \frac{9.65 \times 10^4 \text{ C}}{1 \text{ mol e}^-} = 2218 \text{ C}$$

Since $\text{amp} \times \text{sec} = \text{coul}$, the number of seconds is

$$\text{time} = \frac{2218 \text{ C}}{1.50 \text{ amp}} = 1.478 \times 10^3 = 1.48 \times 10^3 \text{ s}$$

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

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

20.116a. First, find the moles of copper.

$$2.10 \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} = 0.03304 \text{ mol Cu}$$

The number of coulombs is

$$0.03304 \text{ mol Cu} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Cu}} \times \frac{9.65 \times 10^4 \text{ C}}{1 \text{ mol e}^-} = 6377 \text{ C}$$

(continued)

Since $\text{amp} \times \text{sec} = \text{coul}$, the number of seconds is

$$s = \frac{6377 \text{ C}}{1.25 \text{ amp}} = 5.102 \times 10^3 = 5.10 \times 10^3 \text{ s}$$

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

$$\begin{aligned} 6377 \text{ C} \times \frac{1 \text{ mol e}^-}{9.65 \times 10^4 \text{ C}} \times \frac{1 \text{ mol Ag}}{1 \text{ mol e}^-} \times \frac{107.9 \text{ g Ag}}{1 \text{ mol Ag}} \\ = 7.131 = 7.13 \text{ g} \end{aligned}$$

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

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

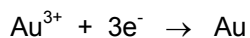
b. The moles of Au that were deposited is

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

Since $1 \text{ F} = 1 \text{ mol e}^-$, the ratio of moles of e^- 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^{3+} . The reaction is



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

$$2.50 \text{ amp} \times 6840 \text{ s} \times \frac{1 \text{ F}}{9.65 \times 10^4 \text{ C}} \times 0.950 = 0.1683 = 0.168 \text{ F}$$

(continued)

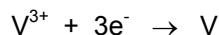
b. The moles of V that were deposited is

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

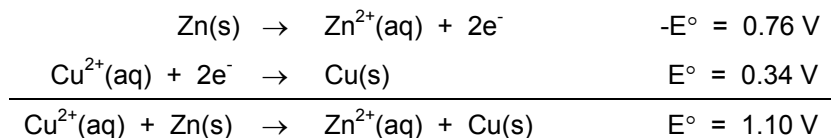
Since $1 \text{ F} = 1 \text{ mol e}^-$, the ratio of moles of e^- to moles V is

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

Thus, the ion must be V^{3+} . The reaction is



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



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

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

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

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

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

$$1.00 \text{ amp} \times 225 \text{ s} \times \frac{1 \text{ mol e}^-}{9.65 \times 10^4 \text{ C}} = 0.002332 \text{ mol e}^-$$

The moles of Cu deposited are

$$0.002332 \text{ mol e}^- \times \frac{1 \text{ mol Cu}}{2 \text{ mol e}^-} = 0.001166 \text{ mol Cu}$$

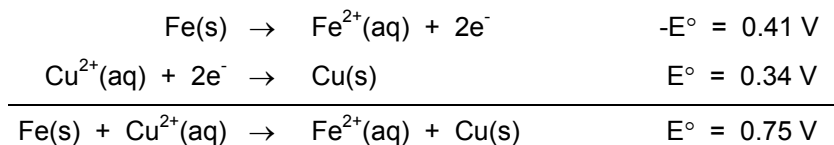
(continued)

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:



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

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

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

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

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

$$1.25 \text{ amp} \times 335 \text{ s} \times \frac{1 \text{ mol e}^-}{9.65 \times 10^4 \text{ C}} = 0.004339 \text{ mol e}^-$$

The moles of Cu deposited are

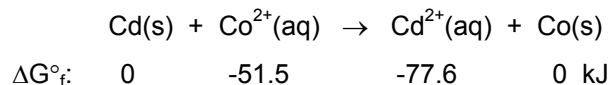
$$0.004339 \text{ mol e}^- \times \frac{1 \text{ mol Cu}}{2 \text{ mol e}^-} = 0.002170 \text{ mol}$$

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.

20.121 a. Write the cell reaction with the ΔG_f° 's beneath



Hence,

$$\begin{aligned} \Delta G^\circ &= \sum n\Delta G_f^\circ(\text{products}) - \sum m\Delta G_f^\circ(\text{reactants}) \\ &= [-77.6 + 51.5] \text{ kJ} = -26.1 \text{ kJ} = -2.61 \times 10^4 \text{ J} \end{aligned}$$

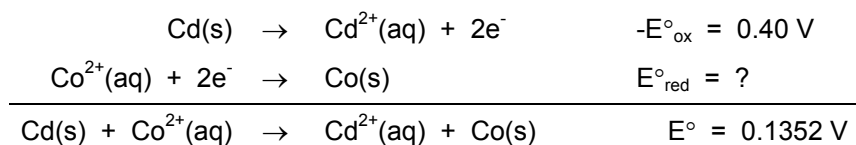
b. Next, determine the standard emf for the cell. Note that n equals two.

$$\begin{aligned} \Delta G^\circ &= -nFE^\circ \\ -2.61 \times 10^4 \text{ J} &= -2(9.65 \times 10^4 \text{ C}) \times E^\circ \end{aligned}$$

Solve for E° to get

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

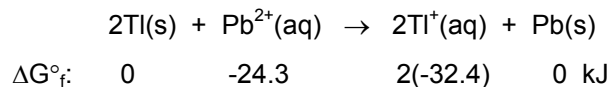
The half-reactions and voltages are



The cell emf is

$$\begin{aligned} E^\circ &= E^\circ_{\text{red}} + (-E^\circ_{\text{ox}}) \\ 0.1352 \text{ V} &= E^\circ_{\text{red}} + 0.40 \text{ V} \\ E^\circ_{\text{red}} &= 0.1352 \text{ V} - 0.40 \text{ V} = -0.2647 = -0.26 \text{ V} \end{aligned}$$

20.122 a. Write the cell reaction with the ΔG_f° 's beneath



Hence,

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

(continued)

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

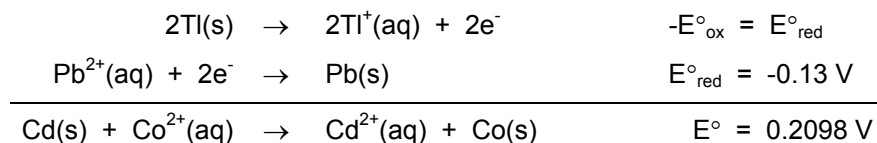
$$\Delta G^\circ = -nFE^\circ$$

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

Solve for E° to get

$$E^\circ = \frac{-4.05 \times 10^4 \text{ J}}{-2(9.65 \times 10^4 \text{ C})} = 0.02098 = 0.210 \text{ V}$$

The half-reactions and voltages are



The cell emf is

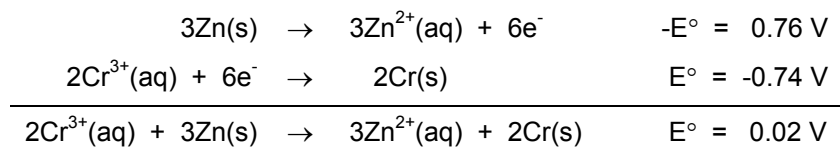
$$E^\circ = E^\circ_{\text{red}} + (-E^\circ_{\text{ox}})$$

$$0.2098 \text{ V} = -0.13 \text{ V} + E^\circ_{\text{red}}$$

$$E^\circ_{\text{red}} = 0.2098 \text{ V} + 0.13 \text{ V} = 0.3398 = 0.34 \text{ V}$$

■ Solutions to Cumulative-Skills Problems

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

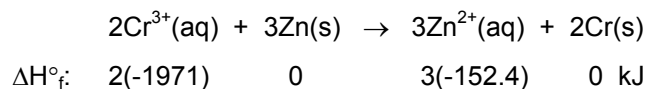


Note that n equals six. Therefore,

$$\Delta G^\circ = -nFE^\circ = -6(9.65 \times 10^4 \text{ C})(0.02 \text{ V}) = -1.158 \times 10^4 \text{ J} = -11.58 \text{ kJ}$$

(continued)

Write the cell reaction with the ΔH_f° 's beneath



Hence,

$$\begin{aligned}
 \Delta H^\circ &= \sum n\Delta H_f^\circ(\text{products}) - \sum m\Delta H_f^\circ(\text{reactants}) \\
 &= [3(-152.4) - 2(-1971)] \text{ kJ} = 3484.8 = 3485 \text{ kJ}
 \end{aligned}$$

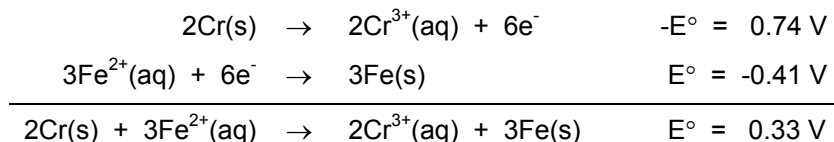
Now calculate ΔS° .

$$\begin{aligned}
 \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\
 -11.58 \text{ kJ} &= 3484.8 \text{ kJ} - 298 \text{ K} \times \Delta S^\circ
 \end{aligned}$$

Solving for ΔS° gives

$$\Delta S^\circ = \frac{3484.8 \text{ kJ} + 11.58 \text{ kJ}}{298 \text{ K}} = 11.73 = 11.7 \text{ kJ/K}$$

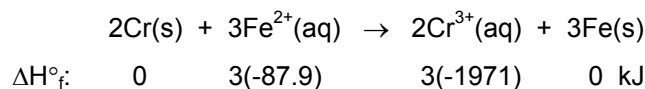
- 20.124 The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:



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 ΔH_f° 's beneath



Hence,

$$\begin{aligned}
 \Delta H^\circ &= \sum n\Delta H_f^\circ(\text{products}) - \sum m\Delta H_f^\circ(\text{reactants}) \\
 &= [3(-1971) - 3(-87.9)] \text{ kJ} = -3678.3 = -3678 \text{ kJ}
 \end{aligned}$$

(continued)

Now calculate ΔS° .

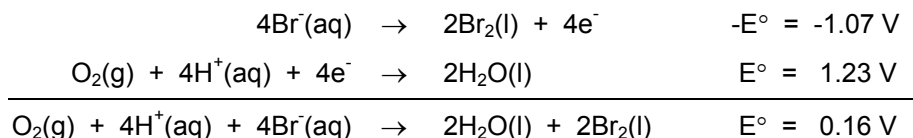
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$-191.07 \text{ kJ} = -3678.3 \text{ kJ} - 298 \text{ K} \times \Delta S^\circ$$

Solving for ΔS° 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 $[\text{H}^+]$

$$[\text{H}^+] = \text{antilog}(-3.60) = 2.51 \times 10^{-4} \text{ M}$$

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

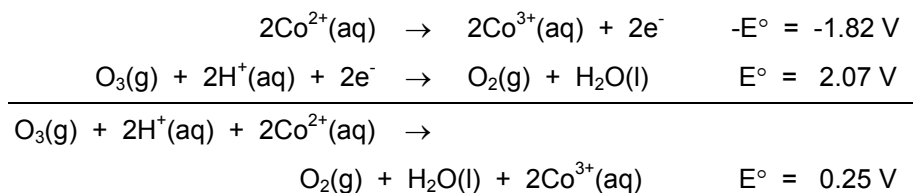
$$E = E^\circ - \frac{0.0592}{n} \log Q = E^\circ - \frac{0.0592}{n} \log \frac{1}{[\text{H}^+]^4 [\text{Br}^-]^4 \times P_{\text{O}_2}}$$

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

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

Thus, the reaction is nonspontaneous at this $[\text{H}^+]$.

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



(continued)

Now, convert the pH to $[H^+]$

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

Under standard conditions $[Co^{2+}]$ and $[Co^{3+}] = 1 \text{ M}$, and the partial pressures of O_2 and O_3 equals one atm. Thus, substitute into the Nernst equation, where n equals two.

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

Thus, the reaction is nonspontaneous at this $[H^+]$.

20.127 Use the K_a to calculate $[H^+]$ for the buffer.

$$K_a = \frac{[H^+][OCN^-]}{[HO CN]} = 3.5 \times 10^{-4}$$

Rearrange, and solve for $[H^+]$, assuming $[HO CN]$ and $[OCN^-]$ remain constant in the buffer. Thus, $[H^+] = K_a = 3.5 \times 10^{-4} \text{ M}$.

In Problem 20.123, E° for this cell reaction was found to be 0.16 V. Under standard conditions $[Br^-] = 1 \text{ M}$, and the pressure of O_2 is one atm. Thus, substitute into the Nernst equation, where n equals four.

$$\begin{aligned} E &= E^\circ - \frac{0.0592}{n} \log Q = E^\circ - \frac{0.0592}{n} \log \frac{1}{[H^+]^4 [Br^-]^4 \times P_{O_2}} \\ &= 0.16 \text{ V} - \frac{0.0592}{4} \log \frac{1}{(3.5 \times 10^{-4})^4} \\ &= 0.16 \text{ V} - 0.20459 \text{ V} = -0.04459 = -0.04 \text{ V} \end{aligned}$$

Thus, the reaction is nonspontaneous at this $[H^+]$.

20.128 Use the K_a to calculate $[H^+]$ for the buffer.

$$K_a = \frac{[H^+][OCl^-]}{[HOCl]} = 3.5 \times 10^{-8}$$

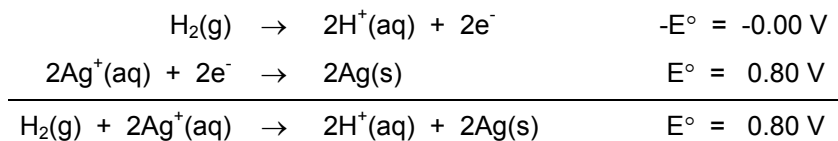
Rearrange, and solve for $[H^+]$ assuming $[HOCl]$ and $[OCl^-]$ remain constant in the buffer. Thus, $[H^+] = K_a = 3.5 \times 10^{-8} \text{ M}$.

In Problem 20.124, E° for this cell reaction was found to be 0.25 V. Under standard conditions $[Co^{2+}]$ and $[Co^{3+}] = 1 \text{ M}$, and the partial pressures of O_2 and O_3 equals one atm. Thus, Substitute into the Nernst equation, where n equals two.

$$\begin{aligned} E &= E^\circ - \frac{0.0592}{n} \log Q = E^\circ - \frac{0.0592}{n} \log \frac{[Co^{3+}]^2 \times P_{O_2}}{[H^+]^2 [Co^{2+}]^4 \times P_{O_3}} \\ &= 0.25 \text{ V} - \frac{0.0592}{2} \log \frac{1}{(3.5 \times 10^{-8})^2} \\ &= 0.25 \text{ V} - 0.44139 \text{ V} = -0.19139 = -0.19 \text{ V} \end{aligned}$$

Thus, the reaction is nonspontaneous at this $[H^+]$.

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



The standard hydrogen electrode has $[H^+] = 1.0 \text{ M}$ and the pressure of H_2 equals one atm. Substitute into the Nernst equation, where $E = 0.45 \text{ V}$ and n equals two.

$$\begin{aligned} E &= E^\circ - \frac{0.0592}{n} \log Q = E^\circ - \frac{0.0592}{n} \log \frac{[H^+]^2}{[Ag^+]^2 \times P_{H_2}} \\ 0.45 \text{ V} &= 0.80 \text{ V} - \frac{0.0592}{2} \log \frac{1}{[Ag^+]^2} \end{aligned}$$

Using the properties of logs, rearrange to get

$$0.45 \text{ V} = 0.80 \text{ V} + 0.0592 \log [Ag^+]$$

(continued)

Solve for $[\text{Ag}^+]$

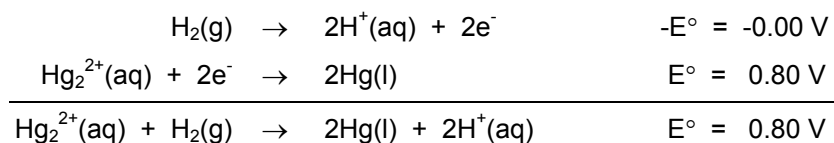
$$\log[\text{Ag}^+] = \frac{0.45 - 0.80}{0.0592} = -5.912$$

$$[\text{Ag}^+] = 10^{-5.912} = 1.224 \times 10^{-6} \text{ M}$$

Finally, determine the solubility product, using $[\text{SCN}^-] = 0.10 \text{ M}$

$$K_{\text{sp}} = [\text{Ag}^+][\text{SCN}^-] = (1.224 \times 10^{-6})(0.10) = 1.224 \times 10^{-7} = 1 \times 10^{-7}$$

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



The standard hydrogen electrode has $[\text{H}^+] = 1.0 \text{ M}$ and the pressure of H_2 equals one atm. Substitute into the Nernst equation, where $E = 0.268 \text{ V}$ and n equals two.

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

$$0.268 \text{ V} = 0.80 \text{ V} - \frac{0.0592}{2} \log \frac{1}{[\text{Hg}_2^{2+}]}$$

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 $[\text{Hg}_2^{2+}]$

$$\log[\text{Hg}_2^{2+}] = \frac{2(0.268 - 0.80)}{0.0592} = 17.972$$

$$[\text{Hg}_2^{2+}] = 10^{-17.972} = 1.06 \times 10^{-18} \text{ M}$$

Finally, determine the solubility product, using $[\text{Cl}^-] = 1.00 \text{ M}$

$$K_{\text{sp}} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = (1.06 \times 10^{-18})(1.00)^2 = 1.06 \times 10^{-18} = 10^{-18}$$

Filename: chapter20.doc
Directory: D:\hmco\chemistry\general\ebbing\general_chem\8e\instructors\
solutions_manual
Template: C:\Documents and Settings\willsoj\Application
Data\Microsoft\Templates\Normal.dot
Title: 19
Subject:
Author: David Bookin
Keywords:
Comments:
Creation Date: 7/21/2003 7:08 PM
Change Number: 39
Last Saved On: 12/6/2003 5:00 PM
Last Saved By: David Bookin
Total Editing Time: 226 Minutes
Last Printed On: 1/9/2004 3:43 PM
As of Last Complete Printing
Number of Pages: 72
Number of Words: 14,291 (approx.)
Number of Characters: 81,463 (approx.)