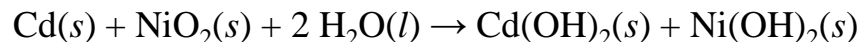


Sample Exercise 20.1 Identifying Oxidizing and Reducing Agents

The nickel-cadmium (nicad) battery, a rechargeable “dry cell” used in battery-operated devices, uses the following redox reaction to generate electricity:

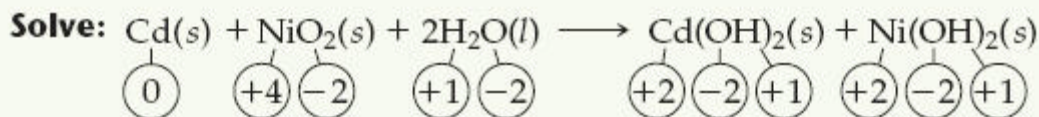


Identify the substances that are oxidized and reduced, and indicate which is the oxidizing agent and which is the reducing agent.

Solution

Analyze: We are given a redox equation and asked to identify the substance oxidized and the substance reduced and to label one as the oxidizing agent and the other as the reducing agent.

Plan: First, we assign oxidation states, or numbers, to all the atoms in the reaction and determine the elements that are changing oxidation state. Second, we apply the definitions of oxidation and reduction.



Cd increases in oxidation state from 0 to +2, and Ni decreases from +4 to +2.

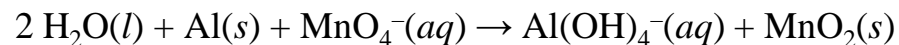
Because the Cd atom increases in oxidation state, it is oxidized (loses electrons) and therefore serves as the reducing agent. The Ni atom decreases in oxidation state as NiO_2 is converted into $\text{Ni}(\text{OH})_2$. Thus, NiO_2 is reduced (gains electrons) and therefore serves as the oxidizing agent.

Comment: A common mnemonic for remembering oxidation and reduction is “LEO the lion says GER”: *losing electrons is oxidation; gaining electrons is reduction.*

Sample Exercise 20.1 Identifying Oxidizing and Reducing Agents

Practice Exercise

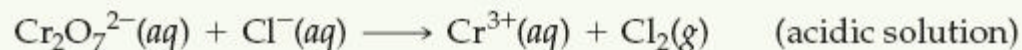
Identify the oxidizing and reducing agents in the oxidation-reduction reaction



Answer: $\text{Al}(s)$ is the reducing agent; $\text{MnO}_4^-(aq)$ is the oxidizing agent.

Sample Exercise 20.2 Balancing Redox Equations in Acidic Solution

Complete and balance this equation by the method of half-reactions:

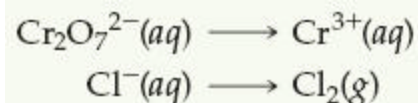


Solution

Analyze: We are given an incomplete, unbalanced (skeleton) equation for a redox reaction occurring in acidic solution and asked to complete and balance it.

Plan: We use the half-reaction procedure we just learned.

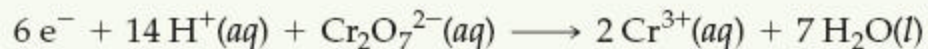
Solve: Step 1: We divide the equation into two half-reactions:



Step 2: We balance each half-reaction. In the first half-reaction the presence of one $\text{Cr}_2\text{O}_7^{2-}$ among the reactants requires two Cr^{3+} among the products. The seven oxygen atoms in $\text{Cr}_2\text{O}_7^{2-}$ are balanced by adding seven H_2O to the products. The 14 hydrogen atoms in 7 H_2O are then balanced by adding 14 H^{+} to the reactants:



We then balance the charge by adding electrons to the left side of the equation so that the total charge is the same on the two sides:



We can check this result by looking at the oxidation state changes. Each chromium atom goes from +6 to +3, gaining three electrons, and therefore the two Cr atoms in $\text{Cr}_2\text{O}_7^{2-}$ gains six electrons, in agreement with our half-reaction.

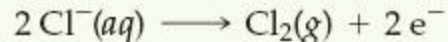
Sample Exercise 20.2 Balancing Redox Equations in Acidic Solution

Solution (continued)

In the second half-reaction, two Cl^- are required to balance one Cl_2 :

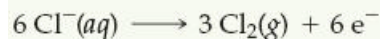


We add two electrons to the right side to attain charge balance:

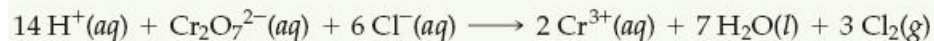


This result agrees with the oxidation state changes. Each chlorine atom goes from -1 to 0 , losing one electron, and therefore the two chlorine atoms lose two electrons.

Step 3: We equalize the number of electrons transferred in the two half-reactions. To do so, we multiply the Cl half-reaction by 3 so that the number of electrons gained in the Cr half-reaction (6) equals the number lost in the Cl half-reaction, allowing the electrons to cancel when the half-reactions are added:



Step 4: The equations are added to give the balanced equation:

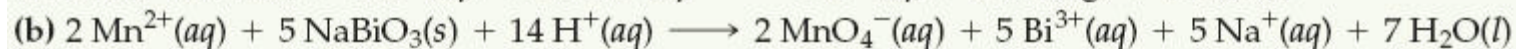
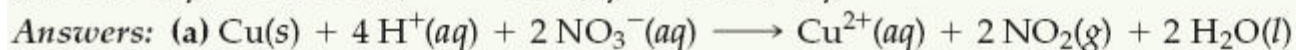
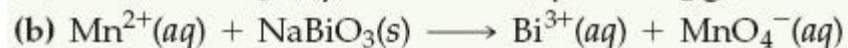


Step 5: There are equal numbers of atoms of each kind on the two sides of the equation (14 H , 2 Cr , 7 O , 6 Cl). In addition, the charge is the same on the two sides ($6+$). Thus, the equation is balanced.

Sample Exercise 20.2 Balancing Redox Equations in Acidic Solution

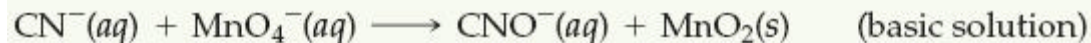
Practice Exercise

Complete and balance the following equations using the method of half-reactions. Both reactions occur in acidic solution.



Sample Exercise 20.3 Balancing Redox Equations in Basic Solution

Complete and balance this equation for a redox reaction that takes place in basic solution:

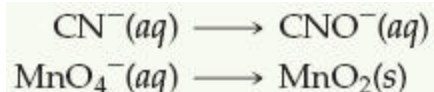


Solution

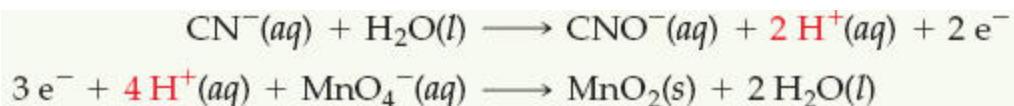
Analyze: We are given an incomplete equation for a basic redox reaction and asked to balance it.

Plan: We go through the first steps of our procedure as if the reaction were occurring in acidic solution. We then add the appropriate number of OH^- ions to each side of the equation, combining H^+ and OH^- to form H_2O . We complete the process by simplifying the equation.

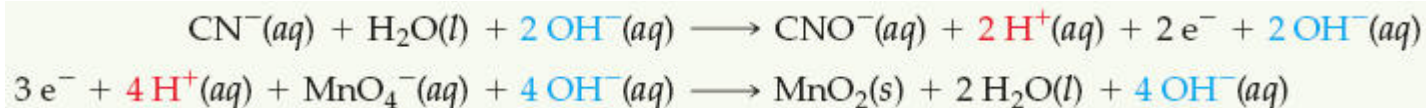
Solve: Step 1: We write the incomplete, unbalanced half-reactions:



Step 2: We balance each half-reaction as if it took place in acidic solution. The H^+ ions are set in red for emphasis:



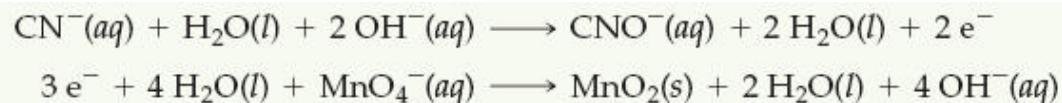
Now we need to take into account that the reaction occurs in basic solution, adding OH^- to both sides of both half-reactions to neutralize H^+ . The OH^- ions are set in blue for emphasis.



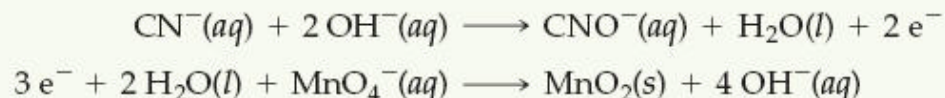
Sample Exercise 20.3 Balancing Redox Equations in Basic Solution

Solution (continued)

We now “neutralize” H^+ and OH^- by forming H_2O when they are on the same side of either half-reaction:

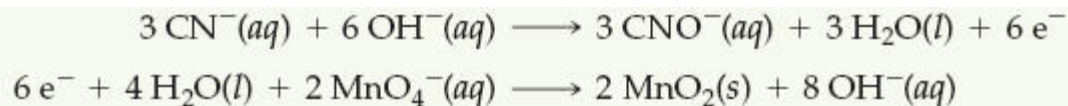


Next, we cancel water molecules that appear as both reactants and products:



Both half-reactions are now balanced. You can check the atoms and the overall charge.

Step 3: Now we multiply the cyanide half-reaction through by 3, which will give 6 electrons on the product side; and multiply the permanganate half-reaction through by 2, which will give 6 electrons on the reactant side:



Step 4: Now we can add the two half-reactions together and simplify by canceling species that appear as both reactants and products:



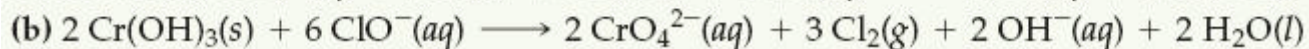
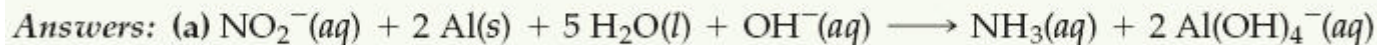
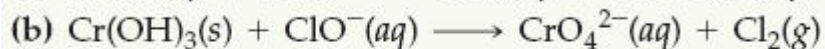
Step 5: Check that the atoms and charges are balanced.

There are 3 C, 3 N, 2 H, 9 O, 2 Mn, and a charge of 5– on both sides of the equation.

Sample Exercise 20.3 Balancing Redox Equations in Basic Solution

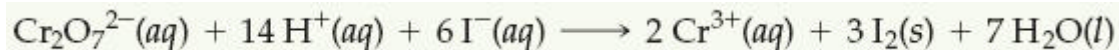
Practice Exercise

Complete and balance the following equations for oxidation-reduction reactions that occur in basic solution:



Sample Exercise 20.4 Describing a Voltaic Cell

The oxidation-reduction reaction



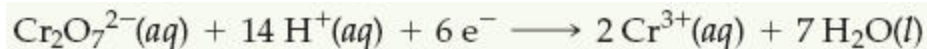
is spontaneous. A solution containing $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 is poured into one beaker, and a solution of KI is poured into another. A salt bridge is used to join the beakers. A metallic conductor that will not react with either solution (such as platinum foil) is suspended in each solution, and the two conductors are connected with wires through a voltmeter or some other device to detect an electric current. The resultant voltaic cell generates an electric current. Indicate the reaction occurring at the anode, the reaction at the cathode, the direction of electron migration, the direction of ion migration, and the signs of the electrodes.

Solution

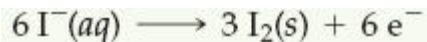
Analyze: We are given the equation for a spontaneous reaction that takes place in a voltaic cell and a description of how the cell is constructed. We are asked to write the half-reactions occurring at the anode and at the cathode, as well as the directions of electron and ion movements and the signs assigned to the electrodes.

Plan: Our first step is to divide the chemical equation into half-reactions so that we can identify the oxidation and the reduction processes. We then use the definitions of anode and cathode and the other terminology summarized in Figure 20.6.

Solve: In one half-reaction, $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ is converted into $\text{Cr}^{3+}(\text{aq})$. Starting with these ions and then completing and balancing the half-reaction, we have



In the other half-reaction, $\text{I}^-(\text{aq})$ is converted to $\text{I}_2(\text{s})$:



Sample Exercise 20.4 Describing a Voltaic Cell

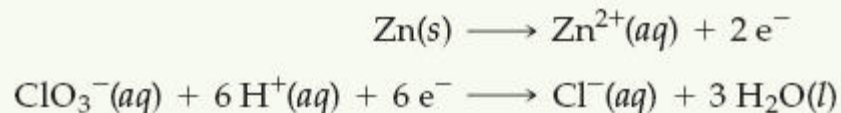
Solution (continued)

Now we can use the summary in Figure 20.6 to help us describe the voltaic cell. The first half-reaction is the reduction process (electrons on the reactant side of the equation). By definition, the reduction process occurs at the cathode. The second half-reaction is the oxidation process (electrons on the product side of the equation), which occurs at the anode.

The I^- ions are the source of electrons, and the $\text{Cr}_2\text{O}_7^{2-}$ ions accept the electrons. Hence, the electrons flow through the external circuit from the electrode immersed in the KI solution (the anode) to the electrode immersed in the $\text{K}_2\text{Cr}_2\text{O}_7\text{--H}_2\text{SO}_4$ solution (the cathode). The electrodes themselves do not react in any way; they merely provide a means of transferring electrons from or to the solutions. The cations move through the solutions toward the cathode, and the anions move toward the anode. The anode (from which the electrons move) is the negative electrode, and the cathode (toward which the electrons move) is the positive electrode.

Practice Exercise

The two half-reactions in a voltaic cell are

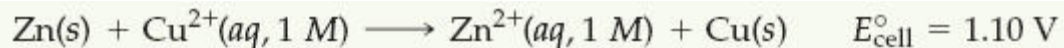


(a) Indicate which reaction occurs at the anode and which at the cathode. (b) Which electrode is consumed in the cell reaction? (c) Which electrode is positive?

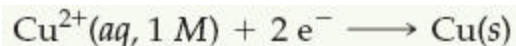
Answers: (a) The first reaction occurs at the anode and the second reaction at the cathode. (b) The anode (Zn) is consumed in the cell reaction. (c) The cathode is positive.

Sample Exercise 20.5 Calculating E°_{red} from E°_{cell}

For the Zn–Cu²⁺ voltaic cell shown in Figure 20.5, we have



Given that the standard reduction potential of Zn²⁺ to Zn(s) is -0.76 V , calculate the E°_{red} for the reduction of Cu²⁺ to Cu:



Solution

Analyze: We are given E°_{cell} and E°_{red} for Zn²⁺ and asked to calculate E°_{red} for Cu²⁺.

Plan: In the voltaic cell, Zn is oxidized and is therefore the anode. Thus, the given E°_{red} for Zn²⁺ is E°_{red} (anode). Because Cu²⁺ is reduced, it is in the cathode half-cell. Thus, the unknown reduction potential for Cu²⁺ is E°_{red} (cathode). Knowing E°_{cell} and E°_{red} (anode), we can use Equation 20.8 to solve for E°_{red} (cathode).

Solve:

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{red}}(\text{cathode}) - E^\circ_{\text{red}}(\text{anode}) \\ 1.10 \text{ V} &= E^\circ_{\text{red}}(\text{cathode}) - (-0.76 \text{ V}) \\ E^\circ_{\text{red}}(\text{cathode}) &= 1.10 \text{ V} - 0.76 \text{ V} = 0.34 \text{ V} \end{aligned}$$

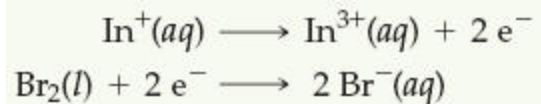
Check: This standard reduction potential agrees with the one listed in Table 20.1.

Comment: The standard reduction potential for Cu²⁺ can be represented as $E^\circ_{\text{Cu}^{2+}} = 0.34 \text{ V}$, and that for Zn²⁺ as $E^\circ_{\text{Zn}^{2+}} = -0.76 \text{ V}$. The subscript identifies the ion that is reduced in the reduction half-reaction.

Sample Exercise 20.5 Calculating E°_{red} from E°_{cell}

Practice Exercise

A voltaic cell is based on the half-reactions

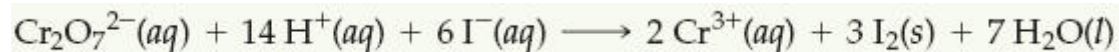


The standard emf for this cell is 1.46 V. Using the data in Table 20.1, calculate E°_{red} for the reduction of In^{3+} to In^+ .

Answer: -0.40 V

Sample Exercise 20.6 Calculating E°_{cell} from E°_{red}

Using the standard reduction potentials listed in Table 20.1, calculate the standard emf for the voltaic cell described in Sample Exercise 20.4, which is based on the reaction

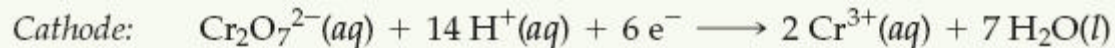


Solution

Analyze: We are given the equation for a redox reaction and asked to use data in Table 20.1 to calculate the standard emf (standard potential) for the associated voltaic cell.

Plan: Our first step is to identify the half-reactions that occur at the cathode and the anode, which we did in Sample Exercise 20.4. Then we can use data from Table 20.1 and Equation 20.8 to calculate the standard emf.

Solve: The half-reactions are



According to Table 20.1, the standard reduction potential for the reduction of $\text{Cr}_2\text{O}_7^{2-}$ to Cr^{3+} is +1.33 V, and the standard reduction potential for the reduction of I_2 to I^- (the reverse of the oxidation half-reaction) is +0.54 V. We then use these values in Equation 20.8.

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}}(\text{cathode}) - E^\circ_{\text{red}}(\text{anode}) = 1.33 \text{ V} - 0.54 \text{ V} = 0.79 \text{ V}$$

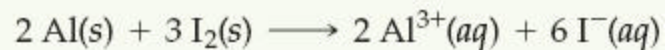
Although we must multiply the iodide half-reaction at the anode by 3 to obtain a balanced equation for the reaction, the value of E°_{red} is *not* multiplied by 3. As we have noted, the standard reduction potential is an intensive property, so it is independent of the specific stoichiometric coefficients.

Check: The cell potential, 0.79 V, is a positive number. As noted earlier, a voltaic cell must have a positive emf in order to operate.

Sample Exercise 20.6 Calculating E°_{cell} from E°_{red}

Practice Exercise

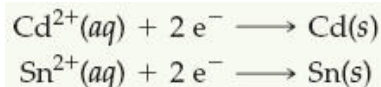
Using data in Table 20.1, calculate the standard emf for a cell that employs the following overall cell reaction:



Answer: $0.54 \text{ V} - (-1.66 \text{ V}) = 2.20 \text{ V}$

Sample Exercise 20.7 Determining Half-Reactions at electrodes and Calculating Cell EMF

A voltaic cell is based on the following two standard half-reactions:



By using the data in Appendix E, determine (a) the half-reactions that occur at the cathode and the anode, and (b) the standard cell potential.

Solution

Analyze: We have to look up E°_{red} for two half-reactions and use these values to predict the cathode and anode of the cell and to calculate its standard cell potential, E°_{cell} .

Plan: The cathode will have the reduction with the more positive E°_{red} value. The anode will have the less positive E°_{red} . To write the half-reaction at the anode, we reverse the half-reaction written for the reduction, so that the half-reaction is written as an oxidation.

Solve:

(a) According to Appendix E, $E^{\circ}_{\text{red}}(\text{Cd}^{2+}/\text{Cd}) = -0.403 \text{ V}$ and $E^{\circ}_{\text{red}}(\text{Sn}^{2+}/\text{Sn}) = -0.136 \text{ V}$. The standard reduction potential for Sn^{2+} is more positive (less negative) than that for Cd^{2+} ; hence, the reduction of Sn^{2+} is the reaction that occurs at the cathode.



The anode reaction therefore is the loss of electrons by Cd.



(b) The cell potential is given by Equation 20.8.

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}}(\text{cathode}) - E^{\circ}_{\text{red}}(\text{anode}) = (-0.136 \text{ V}) - (-0.403 \text{ V}) = 0.267 \text{ V}$$

Sample Exercise 20.7 Determining Half-Reactions at electrodes and Calculating Cell EMF

Solution (continued)

Notice that it is unimportant that the E°_{red} values of both half-reactions are negative; the negative values merely indicate how these reductions compare to the reference reaction, the reduction of $\text{H}^+(\text{aq})$.

Check: The cell potential is positive, as it must be for a voltaic cell.

Practice Exercise

A voltaic cell is based on a Co^{2+}/Co half-cell and an AgCl/Ag half-cell.

(a) What half-reaction occurs at the anode? (b) What is the standard cell potential?

Answer: (a) $\text{Co} \rightarrow \text{Co}^{2+} + 2 \text{e}^-$; (b) $+0.499 \text{ V}$

Sample Exercise 20.8 Determining the Relative Strengths of Oxidizing Agents

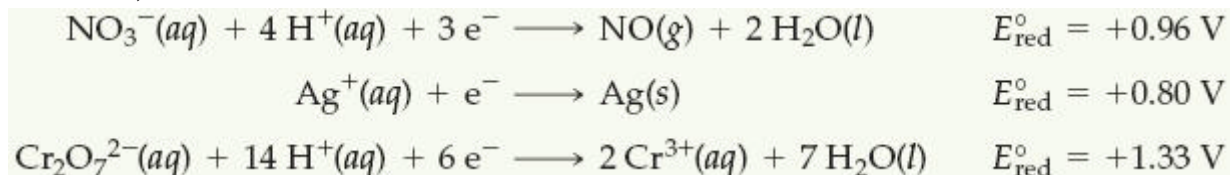
Using Table 20.1, rank the following ions in order of increasing strength as oxidizing agents: $\text{NO}_3^-(aq)$, $\text{Ag}^+(aq)$, $\text{Cr}_2\text{O}_7^{2-}(aq)$.

Solution

Analyze: We are given several ions and asked to rank their abilities to act as oxidizing agents.

Plan: The more readily an ion is reduced (the more positive its E°_{red} value), the stronger it is as an oxidizing agent.

Solve: From Table 20.1, we have



Because the standard reduction potential of $\text{Cr}_2\text{O}_7^{2-}$ is the most positive, $\text{Cr}_2\text{O}_7^{2-}$ is the strongest oxidizing agent of the three. The rank order is $\text{Ag}^+ < \text{NO}_3^- < \text{Cr}_2\text{O}_7^{2-}$.

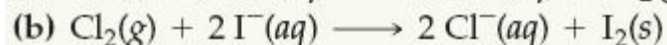
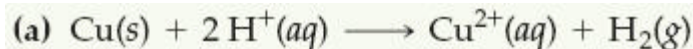
Practice Exercise

Using Table 20.1, rank the following species from the strongest to the weakest reducing agent: $\text{I}^-(aq)$, $\text{Fe}(s)$, $\text{Al}(s)$.

Answer: $\text{Al}(s) > \text{Fe}(s) > \text{I}^-(aq)$

Sample Exercise 20.9 Spontaneous or Not?

Using standard reduction potentials in Table 20.1, determine whether the following reactions are spontaneous under standard conditions.



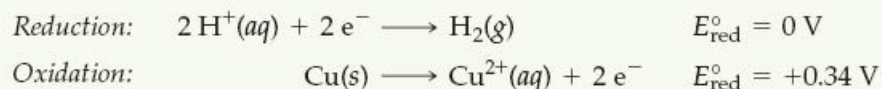
Solution

Analyze: We are given two equations and must determine whether each is spontaneous.

Plan: To determine whether a redox reaction is spontaneous under standard conditions, we first need to write its reduction and oxidation half-reactions. We can then use the standard reduction potentials and Equation 20.10 to calculate the standard emf, E° , for the reaction. If a reaction is spontaneous, its standard emf must be a positive number.

Solve:

(a) In this reaction Cu is oxidized to Cu^{2+} and H^+ is reduced to H_2 . The corresponding half-reactions and associated standard reduction potentials are



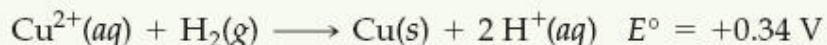
Notice that for the oxidation, we use the standard reduction potential from Table 20.1 for the reduction of Cu^{2+} to Cu. We now calculate E° by using Equation 20.10:

$$\begin{aligned} E^\circ &= E^\circ_{\text{red}} (\text{reduction process}) - E^\circ_{\text{red}} (\text{oxidation process}) \\ &= (0 \text{ V}) - (0.34 \text{ V}) = -0.34 \text{ V} \end{aligned}$$

Sample Exercise 20.9 Spontaneous or Not?

Solution (continued)

Because E° is negative, the reaction is not spontaneous in the direction written. Copper metal does not react with acids in this fashion. The reverse reaction, however, *is* spontaneous and would have an E° of +0.34V.



Cu^{2+} can be reduced by H_2 .

(b) We follow a procedure analogous to that in (a):



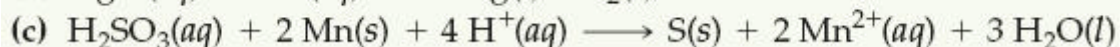
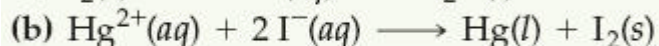
$$E^\circ = (1.36 \text{ V}) - (0.54 \text{ V}) = +0.82 \text{ V}$$

In this case

Because the value of E° is positive, this reaction is spontaneous and could be used to build a voltaic cell.

Practice Exercise

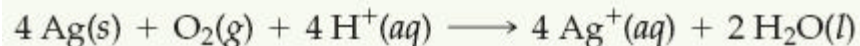
Using the standard reduction potentials listed in Appendix E, determine which of the following reactions are spontaneous under standard conditions:



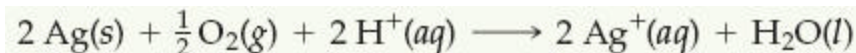
Answer: Reactions (b) and (c) are spontaneous.

Sample Exercise 20.10 Determining ΔG° and K

(a) Use the standard reduction potentials listed in Table 20.1 to calculate the standard free-energy change, ΔG° , and the equilibrium constant, K , at 298 K for the reaction



(b) Suppose the reaction in part (a) was written



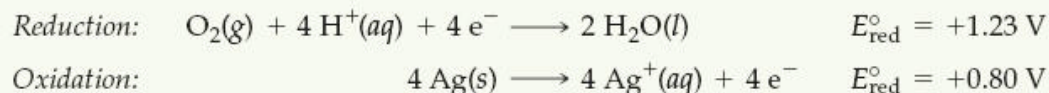
What are the values of E° , ΔG° , and K when the reaction is written in this way?

Solution

Analyze: We are asked to determine ΔG° and K for a redox reaction, using standard reduction potentials.

Plan: We use the data in Table 20.1 and Equation 20.10 to determine E° for the reaction and then use in E° Equation 20.12 to calculate ΔG° . We will then use Equation 19.17, $\Delta G^\circ = -RT \ln K$, to calculate K .

(a) We first calculate E° by breaking the equation into two half-reactions, as we did in Sample Exercise 20.9, and then obtain E°_{red} values from Table 20.1 (or Appendix E):



Even though the second half-reaction has 4 Ag, we use the E°_{red} value directly from Table 20.1 because emf is an intensive property.

Using Equation 20.10, we have

The half-reactions show the transfer of four electrons. Thus, for this reaction $n = 4$. We now use Equation 20.12 to calculate ΔG° :

$$\begin{aligned} E^\circ &= (1.23 \text{ V}) - (0.80 \text{ V}) = 0.43 \text{ V} \\ \Delta G^\circ &= -nFE^\circ \\ &= -(4)(96,485 \text{ J/V}\cdot\text{mol})(+0.43 \text{ V}) \\ &= -1.7 \times 10^5 \text{ J/mol} = -170 \text{ kJ/mol} \end{aligned}$$

The positive value of E° leads to a negative value of ΔG° .

Sample Exercise 20.10 Determining ΔG° and K

Solution (continued)

Now we need to calculate the equilibrium constant, K , using $\Delta G^\circ = -RT \ln K$. Because ΔG° is a large negative number, which means the reaction is thermodynamically very favorable, we expect K to be large.

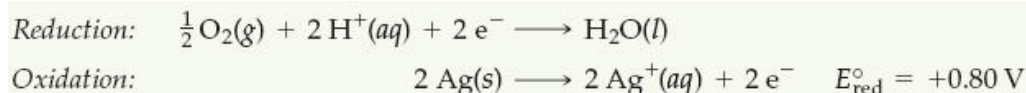
$$\begin{aligned}\Delta G^\circ &= -RT \ln K \\ -1.7 \times 10^5 \text{ J/mol} &= -(8.314 \text{ J/K mol})(298 \text{ K}) \ln K \\ \ln K &= \frac{-1.7 \times 10^5 \text{ J/mol}}{-(8.314 \text{ J/K mol})(298 \text{ K})} \\ \ln K &= 69 \\ K &= 9 \times 10^{29}\end{aligned}$$

K is indeed very large! This means that we expect silver metal to oxidize in acidic aqueous environments, in air, to Ag^+ . Notice that the voltage calculated for the reaction was 0.43 V, which is easy to measure. Directly measuring such a large equilibrium constant by measuring reactant and product concentrations at equilibrium, on the other hand, would be very difficult.

(b) The overall equation is the same as that in part (a), multiplied by $\frac{1}{2}$. The half reactions are

The values of E°_{red} are the same as they were in part (a); they are not changed by multiplying the half-reactions by $\frac{1}{2}$. Thus, E° has the same value as in part (a):

Notice, though, that the value of n has changed to $n = 2$, which is $\frac{1}{2}$ the value in part (a). Thus, ΔG° is half as large as in part (a).



$$E^\circ = +0.43 \text{ V}$$

$$\begin{aligned}\Delta G^\circ &= -(2)(96,485 \text{ J/V}\cdot\text{mol})(+0.43 \text{ V}) = -83 \text{ k J/mol} \\ -8.3 \times 10^4 \text{ J/mol} &= -(8.314 \text{ J/K mol})(298 \text{ K}) \ln K \\ K &= 4 \times 10^{14}\end{aligned}$$

Now we can calculate K as before:

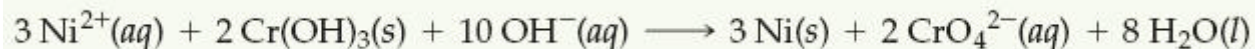
Sample Exercise 20.10 Determining ΔG° and K

Solution (continued)

Comment: E° is an *intensive* quantity, so multiplying a chemical equation by a certain factor will not affect the value of E° . Multiplying an equation will change the value of n , however, and hence the value of ΔG° . The change in free energy, in units of J/mol of reaction as written, is an *extensive* quantity. The equilibrium constant is also an extensive quantity.

Practice Exercise

For the reaction



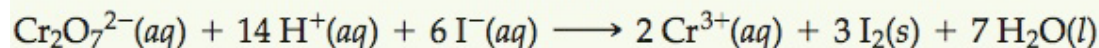
(a) What is the value of n ? (b) Use the data in Appendix E to calculate ΔG° . (c) Calculate K at $T = 298 \text{ K}$.

Answers: (a) 6, (b) +87 kJ/mol, (c) $K = 6 \times 10^{-16}$

Sample Exercise 20.11 Voltaic Cell EMF under Nonstandard Conditions

Calculate the emf at 298 K generated by the cell described in Sample Exercise 20.4

When $[\text{Cr}_2\text{O}_7^{2-}] = 2.0 \text{ M}$, $[\text{H}^+] = 1.0 \text{ M}$, $[\text{I}^-] = 1.0 \text{ M}$, and $[\text{Cr}^{3+}] = 1.0 \times 10^{-5} \text{ M}$.



Solution

Analyze: We are given a chemical equation for a voltaic cell and the concentrations of reactants and products under which it operates. We are asked to calculate the emf of the cell under these nonstandard conditions.

Plan: To calculate the emf of a cell under nonstandard conditions, we use the Nernst equation in the form of Equation 20.16.

Solve: We first calculate E° for the cell from standard reduction potentials (Table 20.1 or Appendix E). The standard emf for this reaction was calculated in Sample Exercise 20.6: $E^\circ = 0.79 \text{ V}$. As you will see if you refer back to that exercise, the balanced equation shows six electrons transferred from reducing agent to oxidizing agent, so $n = 6$. The reaction quotient, Q , is

$$Q = \frac{[\text{Cr}^{3+}]^2}{[\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^{14}[\text{I}^-]^6} = \frac{(1.0 \times 10^{-5})^2}{(2.0)(1.0)^{14}(1.0)^6} = 5.0 \times 10^{-11}$$

Using Equation 20.16, we have

$$\begin{aligned} E &= 0.79 \text{ V} - \frac{0.0592 \text{ V}}{6} \log(5.0 \times 10^{-11}) \\ &= 0.79 \text{ V} - \frac{0.0592 \text{ V}}{6} (-10.30) \\ &= 0.79 \text{ V} + 0.10 \text{ V} = 0.89 \text{ V} \end{aligned}$$

Sample Exercise 20.11 Voltaic Cell EMF under Nonstandard Conditions

Solution (continued)

Check: This result is qualitatively what we expect: Because the concentration of $\text{Cr}_2\text{O}_7^{2-}$ (a reactant) is greater than 1 M and the concentration of Cr^{3+} (a product) is less than 1 M , the emf is greater than E° . Q is about 10^{-10} , so $\log Q$ is about -10 . Thus, the correction to E° is about $0.06 \times (10)/6$, which is 0.1, in agreement with the more detailed calculation.

Practice Exercise

Calculate the emf generated by the cell described in the practice exercise accompanying Sample Exercise 20.6 when $[\text{Al}^{3+}] = 4.0 \times 10^{-3}M$ and $[\text{I}^-] = 0.010M$.

Answer: $E = +2.36 \text{ V}$

Sample Exercise 20.12 Calculating Concentrations in a Voltaic Cell

If the voltage of a Zn–H⁺ cell (like that in Figure 20.11) is 0.45 V at 25 °C when [Zn²⁺] = 1.0 M and P_{H_2} = 1.0 atm, what is the concentration of H⁺?

Solution

Analyze: We are given a description of a voltaic cell, its emf, and the concentrations of all reactants and products except H⁺, which we are asked to calculate.

Plan: First, we write the equation for the cell reaction and use standard reduction potentials from Table 20.1 to calculate E° for the reaction. After determining the value of n from our reaction equation, we solve the Nernst equation for Q . Finally, we use the equation for the cell reaction to write an expression for Q that contains [H⁺] to determine [H⁺].

Sample Exercise 20.12 Calculating Concentrations in a Voltaic Cell

Solution (continued)

Solve: The cell reaction is

The standard emf is

Because each Zn atom loses two electrons,
Using Equation 20.16, we can solve for Q :

Q has the form of the equilibrium constant
for the reaction

Solving for $[\text{H}^+]$, we have



$$E^\circ = E^\circ_{\text{red}} (\text{reduction}) - E^\circ_{\text{red}} (\text{oxidation})$$

$$= 0 \text{ V} - (-0.76 \text{ V}) = +0.76 \text{ V}$$

$$n = 2$$

$$0.45 \text{ V} = 0.76 \text{ V} - \frac{0.0592 \text{ V}}{2} \log Q$$

$$\log Q = (0.76 \text{ V} - 0.45 \text{ V}) \left(\frac{2}{0.0592 \text{ V}} \right) = 10.5$$

$$Q = 10^{10.5} = 3 \times 10^{10}$$

$$Q = \frac{[\text{Zn}^{2+}]P_{\text{H}_2}}{[\text{H}^+]^2} = \frac{(1.0)(1.0)}{[\text{H}^+]^2} = 3 \times 10^{10}$$

$$[\text{H}^+]^2 = \frac{1.0}{3 \times 10^{10}} = 3 \times 10^{-11}$$

$$[\text{H}^+] = \sqrt{3 \times 10^{-11}} = 6 \times 10^{-6} \text{ M}$$

Comment: A voltaic cell whose cell reaction involves H^+ can be used to measure $[\text{H}^+]$ or pH. A pH meter is a specially designed voltaic cell with a voltmeter calibrated to read pH directly. (Section 16.4)

Practice Exercise

What is the pH of the solution in the cathode compartment of the cell pictured in Figure 20.11 when $P_{\text{H}_2} = 1.0$ atm, $[\text{Zn}^{2+}]$ in the anode compartment is 0.10 M , and cell emf is 0.542 V ?

Answer: pH = 4.23 (using data from Appendix E to obtain E° to three significant figures)

Sample Exercise 20.13 Determining pH Using a Concentration Cell

A voltaic cell is constructed with two hydrogen electrodes. Electrode 1 has $P_{\text{H}_2} = 1.00$ atm and an unknown concentration of $\text{H}^+(aq)$. Electrode 2 is a standard hydrogen electrode ($[\text{H}^+] = 1.00\text{M}$, $P_{\text{H}_2} = 1.00$ atm). At 298 K the measured cell voltage is 0.211 V, and the electrical current is observed to flow from electrode 1 through the external circuit to electrode 2. Calculate $[\text{H}^+]$ for the solution at electrode 1. What is its pH?

Solution

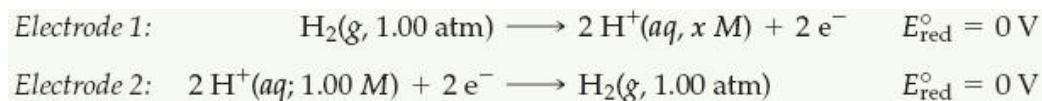
Analyze: We are given the voltage of a concentration cell and the direction in which the current flows. We also have the concentrations of all reactants and products except for $[\text{H}^+]$ in half-cell 1, which is our unknown.

Plan: We can use the Nernst equation to determine Q and then use Q to calculate the unknown concentration. Because this is a concentration cell, $E^\circ_{\text{cell}} = 0$ V.

Solve: Using the Nernst equation, we have

$$\begin{aligned}0.211 \text{ V} &= 0 - \frac{0.0592 \text{ V}}{2} \log Q \\ \log Q &= -(0.211 \text{ V}) \left(\frac{2}{0.0592 \text{ V}} \right) = -7.13 \\ Q &= 10^{-7.13} = 7.4 \times 10^{-8}\end{aligned}$$

Because electrons flow from electrode 1 to electrode 2, electrode 1 is the anode of the cell and electrode 2 is the cathode. The electrode reactions are therefore as follows, with the concentration of $\text{H}^+(aq)$ in electrode 1 represented with the unknown x :



Sample Exercise 20.13 Determining pH Using a Concentration Cell

Solution (continued)

Thus,

$$\begin{aligned} Q &= \frac{[\text{H}^+ (\text{electrode 1})]^2 P_{\text{H}_2} (\text{electrode 2})}{[\text{H}^+ (\text{electrode 2})]^2 P_{\text{H}_2} (\text{electrode 1})} \\ &= \frac{x^2(1.00)}{(1.00)^2(1.00)} = x^2 = 7.4 \times 10^{-8} \\ x &= \sqrt{7.4 \times 10^{-8}} = 2.7 \times 10^{-4} \\ [\text{H}^+] &= 2.7 \times 10^{-4} \text{ M} \\ \text{pH} &= -\log[\text{H}^+] = -\log(2.7 \times 10^{-4}) = 3.57 \end{aligned}$$

At electrode 1, therefore,

and the pH of the solution is

Comment: The concentration of H^+ at electrode 1 is lower than that in electrode 2, which is why electrode 1 is the anode of the cell: The oxidation of H_2 to $\text{H}^+(\text{aq})$ increases $[\text{H}^+]$ at electrode 1.

Practice Exercise

A concentration cell is constructed with two $\text{Zn}(\text{s})\text{--}\text{Zn}^{2+}(\text{aq})$ half-cells. The first half-cell has $[\text{Zn}^{2+}] = 1.35 \text{ M}$, and the second half cell has $[\text{Zn}^{2+}] = 3.75 \times 10^{-4} \text{ M}$. **(a)** Which half-cell is the anode of the cell? **(b)** What is the emf of the cell?

Answer: **(a)** the second half-cell, **(b)** 0.105 V

Sample Exercise 20.14 Relating Electrical Charge and Quantity of Electrolysis

Calculate the number of grams of aluminum produced in 1.00 h by the electrolysis of molten AlCl_3 if the electrical current is 10.0 A.

Solution

Analyze: We are told that AlCl_3 is electrolyzed to form Al and asked to calculate the number of grams of Al produced in 1.00 h with 10.0 A.

Plan: Figure 20.30 provides a road map of the problem. First, the product of the amperage and the time in seconds gives the number of coulombs of electrical charge being used (Equation 20.18). Second, the coulombs can be converted with the Faraday constant ($F = 96,485 \text{ C/mole electrons}$) to tell us the number of moles of electrons being supplied. Third, reduction of 1 mol of Al^{3+} to Al requires three moles of electrons. Hence we can use the number of moles of electrons to calculate the number of moles of Al metal it produces. Finally, we convert moles of Al into grams.

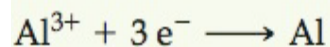
Solve: First, we calculate the coulombs of electrical charge that are passed into the electrolytic cell:

$$\text{Coulombs} = \text{amperes} \times \text{seconds} = (10.0 \text{ A})(1.00 \text{ h}) \frac{(3600 \text{ s})}{\text{h}} = 3.60 \times 10^4 \text{ C}$$

$$\text{Moles } e^- = (3.60 \times 10^4 \text{ C}) \left(\frac{1 \text{ mol } e^-}{96,485 \text{ C}} \right) = 0.373 \text{ mol } e^-$$

Second, we calculate the number of moles of electrons that pass into the cell:

Third, we relate the number of moles of electrons to the number of moles of aluminum being formed, using the half-reaction for the reduction of Al^{3+} :



Sample Exercise 20.14 Relating Electrical Charge and Quantity of Electrolysis

Solution Continued)

Thus, three moles of electrons ($3 F$ of electrical charge) are required to form 1 mol of Al:

$$\text{Moles Al} = (0.373 \text{ mol e}^-) \left(\frac{1 \text{ mol Al}}{3 \text{ mol e}^-} \right) = 0.124 \text{ mol Al}$$

Finally, we convert moles to grams:

$$\text{Grams Al} = (0.124 \text{ mol Al}) \left(\frac{27.0 \text{ g Al}}{1 \text{ mol Al}} \right) = 3.36 \text{ g Al}$$

Because each step involves a multiplication by a new factor, the steps can be combined into a single sequence of factors:

$$\text{Grams Al} = (3.60 \times 10^4 \text{ C}) \left(\frac{1 \text{ mole e}^-}{96,485 \text{ C}} \right) \left(\frac{1 \text{ mol Al}}{3 \text{ mol e}^-} \right) \left(\frac{27.0 \text{ g Al}}{1 \text{ mol Al}} \right) = 3.36 \text{ g Al}$$

Practice Exercise

(a) The half-reaction for formation of magnesium metal upon electrolysis of molten MgCl_2 is $\text{Mg}^{2+} + 2 \text{e}^- \rightarrow \text{Mg}$. Calculate the mass of magnesium formed upon passage of a current of 60.0 A for a period of $4.00 \times 10^3 \text{ s}$.

(b) How many seconds would be required to produce 50.0 g of Mg from MgCl_2 if the current is 100.0 A?

Answers: (a) 30.2 g of Mg, (b) $3.97 \times 10^3 \text{ s}$

Sample Exercise 20.15 Calculating Energy in Kilowatt-hours

Calculate the number of kilowatt-hours of electricity required to produce 1.0×10^3 kg of aluminum by electrolysis of Al^{3+} if the applied voltage is 4.50 V.

Solution

Analyze: We are given the mass of Al produced from and the applied voltage and asked to calculate the energy, in kilowatt-hours, required for the reduction.

Plan: From the mass of Al, we can calculate first the number of moles of Al and then the number of coulombs required to obtain that mass. We can then use Equation 20.20, $w = nFE_{\text{ext}}$, where nF is the total charge in coulombs and E_{ext} is the applied potential, 4.50 V.

Solve: First, we need to calculate nF , the number of coulombs required:

$$\begin{aligned}\text{Coulombs} &= (1.00 \times 10^3 \text{ kg Al}) \left(\frac{1000 \text{ g Al}}{1 \text{ kg Al}} \right) \left(\frac{1 \text{ mol Al}}{27.0 \text{ g Al}} \right) \left(\frac{3 \text{ mol e}^-}{1 \text{ mol Al}} \right) \left(\frac{96,485 \text{ C}}{1 \text{ mole e}^-} \right) \\ &= 1.07 \times 10^{10} \text{ C}\end{aligned}$$

We can now calculate w . In doing so, we must apply several conversion factors, including Equation 20.21, which gives the conversion between kilowatt-hours and joules:

$$\begin{aligned}\text{Kilowatt-hours} &= (1.07 \times 10^{10} \text{ C})(4.50 \text{ V}) \left(\frac{1 \text{ J}}{1 \text{ C} \cdot \text{V}} \right) \left(\frac{1 \text{ kWh}}{3.6 \times 10^6 \text{ J}} \right) \\ &= 1.34 \times 10^4 \text{ kWh}\end{aligned}$$

Comment: This quantity of energy does not include the energy used to mine, transport, and process the aluminum ore, and to keep the electrolysis bath molten during electrolysis. A typical electrolytic cell used to reduce aluminum ore to aluminum metal is only 40% efficient, with 60% of the electrical energy being dissipated as heat. It therefore requires approximately 33 kWh of electricity to produce 1 kg of aluminum. The aluminum industry consumes about 2% of the electrical energy generated in the United States. Because this energy is used mainly to reduce aluminum, recycling this metal saves large quantities of energy.

Sample Exercise 20.15 Calculating Energy in Kilowatt-hours

Practice Exercise

Calculate the number of kilowatt-hours of electricity required to produce 1.00 kg of Mg from electrolysis of molten MgCl_2 if the applied emf is 5.00 V. Assume that the process is 100% efficient.

Answer: 11.0 kWh

Sample Integrative Exercise Putting Concepts Together

The K_{sp} at 298 K for iron(II) fluoride is 2.4×10^{-6} . **(a)** Write a half-reaction that gives the likely products of the two-electron reduction of $\text{FeF}_2(s)$ in water. **(b)** Use the K_{sp} value and the standard reduction potential of $\text{Fe}^{2+}(aq)$ to calculate the standard reduction potential for the half-reaction in part (a). **(c)** Rationalize the difference in the reduction potential for the half-reaction in part (a) with that for $\text{Fe}^{2+}(aq)$.

Solution

Analyze: We are going to have to combine what we know about equilibrium constants and electrochemistry to obtain reduction potentials.

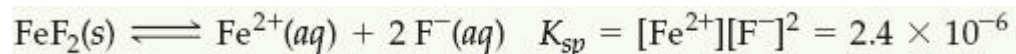
Plan: For (a) we need to determine which ion, Fe^{2+} or Fe , is more likely to be reduced by 2 electrons and write the overall reaction for $\text{FeF}_2 + 2 e^- \rightarrow ?$ For (b) we need to write the K_{sp} reaction and manipulate it to get E° for the reaction in (a). For (c) we need to see what we get for (a) and (b).

Solve:

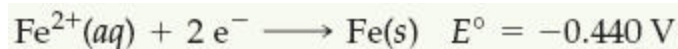
(a) Iron(II) fluoride is an ionic substance that consists of Fe^{2+} and F^- ions. We are asked to predict where two electrons could be added to FeF_2 . We can't envision adding the electrons to the F^- ions to form F^{2-} , so it seems likely that we could reduce the Fe^{2+} ions to $\text{Fe}(s)$. We therefore predict the half-reaction



(b) The K_{sp} value refers to the following equilibrium (Section 17.4):



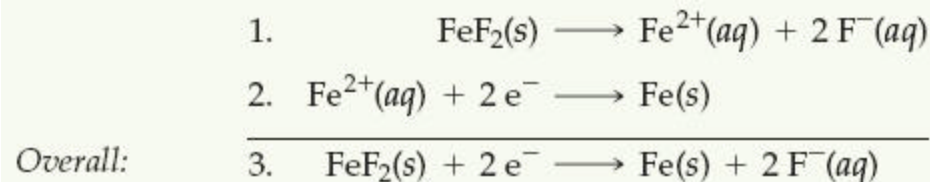
We were also asked to use the standard reduction potential of Fe^{2+} , whose half-reaction and standard voltage are listed in Appendix E:



Sample Integrative Exercise Putting Concepts Together

Solution (continued)

Recall that according to Hess's law, we can add reactions to get the one we want and we can add thermodynamic quantities like ΔH and ΔG to solve for the enthalpy or free energy of the reaction we want. (Section 5.6) In this case notice that if we add the K_{sp} reaction to the standard reduction half-reaction for Fe^{2+} , we get the half-reaction we want:



Reaction 3 is still a half-reaction, so we do see the free electrons. If we knew ΔG° for reactions 1 and 2, we could add them to get ΔG° for reaction 3. Recall that we can relate ΔG° to E° by $\Delta G^\circ = -nFE^\circ$ and to K by $\Delta G^\circ = -RT \ln K$. We know K for reaction 1; it is K_{sp} . We know E° for reaction 2. Therefore we can calculate ΔG° for reactions 1 and 2:

Reaction 1:

$$\Delta G^\circ = -RT \ln K = -(8.314 \text{ J/K mol})(298 \text{ K}) \ln(2.4 \times 10^{-6}) = 3.21 \times 10^4 \text{ J/mol}$$

Reaction 2:

$$\Delta G^\circ = -nFE^\circ = -(2 \text{ mol})(96,485 \text{ C/mol})(-0.440 \text{ J/C}) = 8.49 \times 10^4 \text{ J}$$

(Recall that 1 volt is 1 joule per coulomb.)

Then, ΔG° for reaction 3, the one we want, is $3.21 \times 10^4 \text{ J}$ (for one mole of FeF_2) $+ 8.49 \times 10^4 \text{ J}$ $= 1.17 \times 10^5 \text{ J}$. We can convert this to easily from the relationship $\Delta G^\circ = -nFE^\circ$:

$$1.17 \times 10^5 \text{ J} = -(2 \text{ mol})(96,485 \text{ C/mol}) E^\circ$$
$$E^\circ = -0.606 \text{ J/C} = -0.606 \text{ V.}$$

Sample Integrative Exercise Putting Concepts Together

Solution (continued)

(c) The standard reduction potential for FeF_2 (-0.606 V) is more negative than that for Fe^{2+} (-0.440 V), telling us that the reduction of FeF_2 is the less favorable process. When FeF_2 is reduced, we not only reduce the Fe^{2+} ions but also break up the ionic solid. Because this additional energy must be overcome, the reduction of FeF_2 is less favorable than the reduction of Fe^{2+} .
