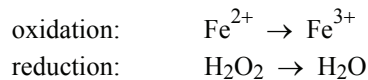


CHAPTER 19

ELECTROCHEMISTRY

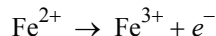
19.1 We follow the steps are described in detail in Section 19.1 of the text.

(a) The problem is given in ionic form, so combining Steps 1 and 2, the half-reactions are:

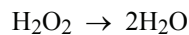


Step 3: We balance each half-reaction for number and type of atoms and charges.

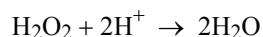
The *oxidation half-reaction* is already balanced for Fe atoms. There are three net positive charges on the right and two net positive charges on the left, we add one electrons to the right side to balance the charge.



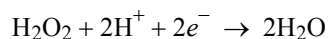
Reduction half-reaction: we add one H₂O to the right-hand side of the equation to balance the O atoms.



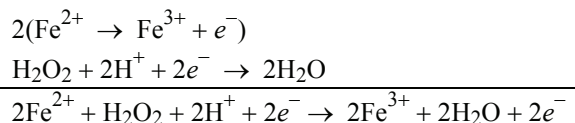
To balance the H atoms, we add 2H⁺ to the left-hand side.



There are two net positive charges on the left, so we add two electrons to the same side to balance the charge.



Step 4: We now add the oxidation and reduction half-reactions to give the overall reaction. In order to equalize the number of electrons, we need to multiply the oxidation half-reaction by 2.



The electrons on both sides cancel, and we are left with the balanced net ionic equation in acidic medium.



(b) The problem is given in ionic form, so combining Steps 1 and 2, the half-reactions are:



Step 3: We balance each half-reaction for number and type of atoms and charges.

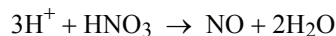
The *oxidation half-reaction* is already balanced for Cu atoms. There are two net positive charges on the right, so we add two electrons to the right side to balance the charge.



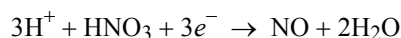
Reduction half-reaction: we add two H₂O to the right-hand side of the equation to balance the O atoms.



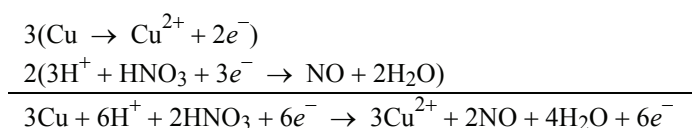
To balance the H atoms, we add 3H⁺ to the left-hand side.



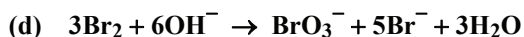
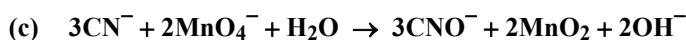
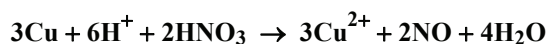
There are three net positive charges on the left, so we add three electrons to the same side to balance the charge.



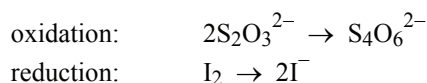
Step 4: We now add the oxidation and reduction half-reactions to give the overall reaction. In order to equalize the number of electrons, we need to multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2.



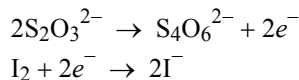
The electrons on both sides cancel, and we are left with the balanced net ionic equation in acidic medium.



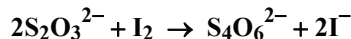
(e) Half-reactions balanced for S and I:



Both half-reactions are already balanced for O, so we balance charge with electrons



The electron count is the same on both sides. We add the equations, canceling electrons, to obtain the balanced equation.

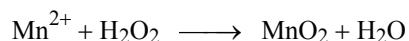


19.2 Strategy: We follow the procedure for balancing redox reactions presented in Section 19.1 of the text.

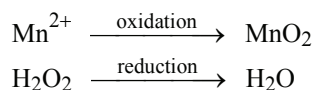
Solution:

(a)

Step 1: The unbalanced equation is given in the problem.

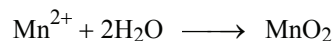


Step 2: The two half-reactions are:

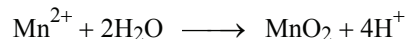


Step 3: We balance each half-reaction for number and type of atoms and charges.

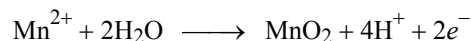
The *oxidation half-reaction* is already balanced for Mn atoms. To balance the O atoms, we add two water molecules on the left side.



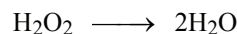
To balance the H atoms, we add 4H^+ to the right-hand side.



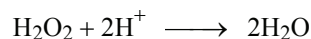
There are four net positive charges on the right and two net positive charge on the left, we add two electrons to the right side to balance the charge.



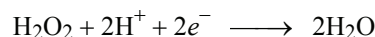
Reduction half-reaction: we add one H_2O to the right-hand side of the equation to balance the O atoms.



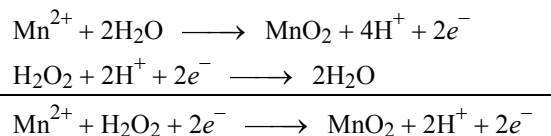
To balance the H atoms, we add 2H^+ to the left-hand side.



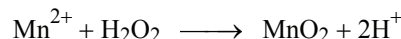
There are two net positive charges on the left, so we add two electrons to the same side to balance the charge.



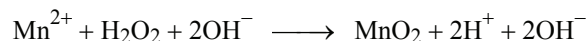
Step 4: We now add the oxidation and reduction half-reactions to give the overall reaction. Note that the number of electrons gained and lost is equal.



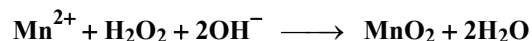
The electrons on both sides cancel, and we are left with the balanced net ionic equation in acidic medium.



Because the problem asks to balance the equation in basic medium, we add one OH^- to both sides for each H^+ and combine pairs of H^+ and OH^- on the same side of the arrow to form H_2O .

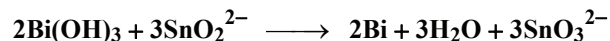


Combining the H^+ and OH^- to form water we obtain:

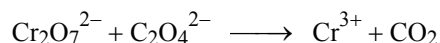
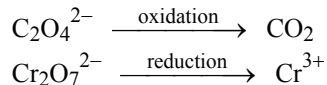
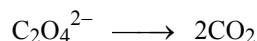


Step 5: Check to see that the equation is balanced by verifying that the equation has the same types and numbers of atoms and the same charges on both sides of the equation.

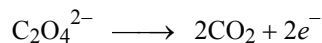
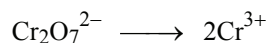
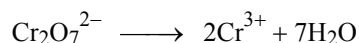
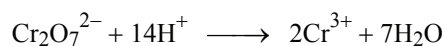
(b) This problem can be solved by the same methods used in part (a).



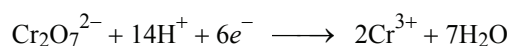
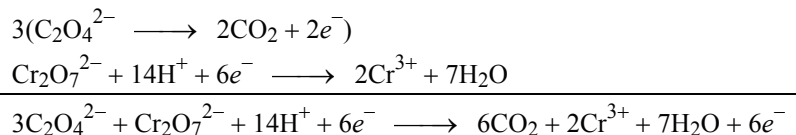
(c)

Step 1: The unbalanced equation is given in the problem.**Step 2:** The two half-reactions are:**Step 3:** We balance each half-reaction for number and type of atoms and charges.In the *oxidation half-reaction*, we first need to balance the C atoms.

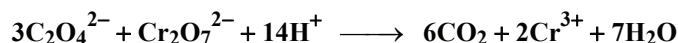
The O atoms are already balanced. There are two net negative charges on the left, so we add two electrons to the right to balance the charge.

In the *reduction half-reaction*, we first need to balance the Cr atoms.We add seven H₂O molecules on the right to balance the O atoms.To balance the H atoms, we add 14H⁺ to the left-hand side.

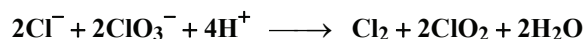
There are twelve net positive charges on the left and six net positive charges on the right. We add six electrons on the left to balance the charge.

**Step 4:** We now add the oxidation and reduction half-reactions to give the overall reaction. In order to equalize the number of electrons, we need to multiply the oxidation half-reaction by 3.

The electrons on both sides cancel, and we are left with the balanced net ionic equation in acidic medium.

**Step 5:** Check to see that the equation is balanced by verifying that the equation has the same types and numbers of atoms and the same charges on both sides of the equation.

(d) This problem can be solved by the same methods used in part (c).



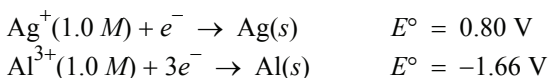
19.11	<u>Half-reaction</u>	<u>$E^\circ(\text{V})$</u>
	$\text{Mg}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Mg}(\text{s})$	-2.37
	$\text{Cu}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Cu}(\text{s})$	+0.34

The overall equation is: $\text{Mg}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Mg}^{2+}(\text{aq}) + \text{Cu}(\text{s})$

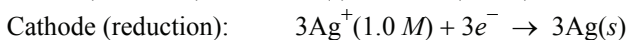
$$E^\circ = 0.34 \text{ V} - (-2.37 \text{ V}) = \mathbf{2.71 \text{ V}}$$

19.12 Strategy: At first, it may not be clear how to assign the electrodes in the galvanic cell. From Table 19.1 of the text, we write the standard reduction potentials of Al and Ag and apply the diagonal rule to determine which is the anode and which is the cathode.

Solution: The standard reduction potentials are:



Applying the diagonal rule, we see that Ag^+ will oxidize Al.



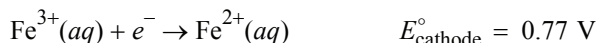
Note that in order to balance the overall equation, we multiplied the reduction of Ag^+ by 3. We can do so because, as an intensive property, E° is not affected by this procedure. We find the emf of the cell using Equation (19.1) and Table 19.1 of the text.

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = E_{\text{Ag}^+/\text{Ag}}^\circ - E_{\text{Al}^{3+}/\text{Al}}^\circ$$

$$E_{\text{cell}}^\circ = 0.80 \text{ V} - (-1.66 \text{ V}) = \mathbf{+2.46 \text{ V}}$$

Check: The positive value of E° shows that the forward reaction is favored.

19.13 The appropriate half-reactions from Table 19.1 are

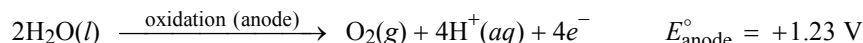


Thus iron(III) should oxidize iodide ion to iodine. This makes the iodide ion/iodine half-reaction the anode. The standard emf can be found using Equation (19.1).

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = 0.77 \text{ V} - 0.53 \text{ V} = 0.24 \text{ V}$$

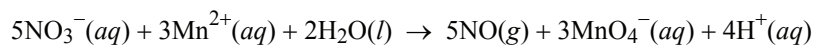
(The emf was not required in this problem, but the fact that it is positive confirms that the reaction should favor products at equilibrium.)

19.14 The half-reaction for oxidation is:



The species that can oxidize water to molecular oxygen must have an E_{red}° more positive than +1.23 V. From Table 19.1 of the text we see that only $\text{Cl}_2(\text{g})$ and $\text{MnO}_4^{-}(\text{aq})$ in acid solution can oxidize water to oxygen.

19.15 The overall reaction is:



$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 0.96 \text{ V} - 1.51 \text{ V} = -0.55 \text{ V}$$

The negative emf indicates that reactants are favored at equilibrium. NO_3^{-} will not oxidize Mn^{2+} to MnO_4^{-} under standard-state conditions.

19.16 Strategy: E_{cell}° is positive for a spontaneous reaction. In each case, we can calculate the standard cell emf from the potentials for the two half-reactions.

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

Solution:

(a) $E^{\circ} = -0.40 \text{ V} - (-2.87 \text{ V}) = 2.47 \text{ V}$. The reaction is spontaneous.

(b) $E^{\circ} = -0.14 \text{ V} - 1.07 \text{ V} = -1.21 \text{ V}$. The reaction is not spontaneous.

(c) $E^{\circ} = -0.25 \text{ V} - 0.80 \text{ V} = -1.05 \text{ V}$. The reaction is not spontaneous.

(d) $E^{\circ} = 0.77 \text{ V} - 0.15 \text{ V} = 0.62 \text{ V}$. The reaction is spontaneous.

19.17 From Table 19.1 of the text, we compare the standard reduction potentials for the half-reactions. The more positive the potential, the better the substance as an oxidizing agent.

(a) Au^{3+} (b) Ag^{+} (c) Cd^{2+} (d) O_2 in acidic solution.

19.18 Strategy: The greater the tendency for the substance to be oxidized, the stronger its tendency to act as a reducing agent. The species that has a stronger tendency to be oxidized will have a smaller reduction potential.

Solution: In each pair, look for the one with the smaller reduction potential. This indicates a greater tendency for the substance to be oxidized.

(a) Li (b) H_2 (c) Fe^{2+} (d) Br^{-}

19.21 We find the standard reduction potentials in Table 19.1 of the text.

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = -0.76 \text{ V} - (-2.37 \text{ V}) = 1.61 \text{ V}$$

$$E_{\text{cell}}^{\circ} = \frac{0.0257 \text{ V}}{n} \ln K$$

$$\ln K = \frac{nE_{\text{cell}}^{\circ}}{0.0257 \text{ V}}$$

$$K = e^{\frac{nE_{\text{cell}}^{\circ}}{0.0257 \text{ V}}}$$

$$K = e^{\frac{(2)(1.61 \text{ V})}{0.0257 \text{ V}}}$$

$$K = 3 \times 10^{54}$$

19.22 Strategy: The relationship between the equilibrium constant, K , and the standard emf is given by Equation (19.5) of the text: $E_{\text{cell}}^{\circ} = (0.0257 \text{ V}/n) \ln K$. Thus, knowing n (the moles of electrons transferred) and the equilibrium constant, we can determine E_{cell}° .

Solution: The equation that relates K and the standard cell emf is:

$$E_{\text{cell}}^{\circ} = \frac{0.0257 \text{ V}}{n} \ln K$$

We see in the reaction that Mg goes to Mg^{2+} and Zn^{2+} goes to Zn. Therefore, two moles of electrons are transferred during the redox reaction. Substitute the equilibrium constant and the moles of e^{-} transferred ($n = 2$) into the above equation to calculate E° .

$$E^{\circ} = \frac{(0.0257 \text{ V}) \ln K}{n} = \frac{(0.0257 \text{ V}) \ln(2.69 \times 10^{12})}{2} = \mathbf{0.368 \text{ V}}$$

19.23 In each case we use standard reduction potentials from Table 19.1 together with Equation (19.5) of the text.

(a) $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 1.07 \text{ V} - 0.53 \text{ V} = 0.54 \text{ V}$

$$\ln K = \frac{nE_{\text{cell}}^{\circ}}{0.0257 \text{ V}}$$

$$K = e^{\frac{nE_{\text{cell}}^{\circ}}{0.0257 \text{ V}}}$$

$$K = e^{\frac{(2)(0.54 \text{ V})}{0.0257 \text{ V}}} = \mathbf{2 \times 10^{18}}$$

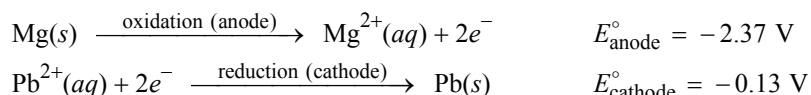
(b) $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 1.61 \text{ V} - 1.36 \text{ V} = 0.25 \text{ V}$

$$K = e^{\frac{(2)(0.25 \text{ V})}{0.0257 \text{ V}}} = \mathbf{3 \times 10^8}$$

(c) $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 1.51 \text{ V} - 0.77 \text{ V} = 0.74 \text{ V}$

$$K = e^{\frac{(5)(0.74 \text{ V})}{0.0257 \text{ V}}} = \mathbf{3 \times 10^{62}}$$

19.24 (a) We break the equation into two half-reactions:



The standard emf is given by

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = -0.13 \text{ V} - (-2.37 \text{ V}) = 2.24 \text{ V}$$

We can calculate ΔG° from the standard emf.

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

$$\Delta G^{\circ} = -(2)(96500 \text{ J/V} \cdot \text{mol})(2.24 \text{ V}) = -432 \text{ kJ/mol}$$

Next, we can calculate K using Equation (19.5) of the text.

$$E_{\text{cell}}^{\circ} = \frac{0.0257 \text{ V}}{n} \ln K$$

or

$$\ln K = \frac{nE_{\text{cell}}^{\circ}}{0.0257 \text{ V}}$$

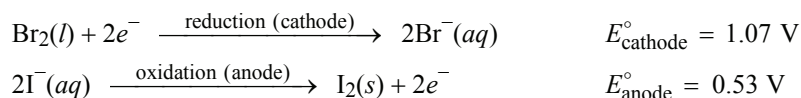
and

$$K = e^{\frac{nE^{\circ}}{0.0257}}$$

$$K = e^{\frac{(2)(2.24)}{0.0257}} = 5 \times 10^{75}$$

Tip: You could also calculate K_c from the standard free energy change, ΔG° , using the equation: $\Delta G^{\circ} = -RT \ln K_c$.

(b) We break the equation into two half-reactions:



The standard emf is

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 1.07 \text{ V} - 0.53 \text{ V} = 0.54 \text{ V}$$

We can calculate ΔG° from the standard emf.

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

$$\Delta G^{\circ} = -(2)(96500 \text{ J/V} \cdot \text{mol})(0.54 \text{ V}) = -104 \text{ kJ/mol}$$

Next, we can calculate K using Equation (19.5) of the text.

$$K = e^{\frac{nE^{\circ}}{0.0257}}$$

$$K = e^{\frac{(2)(0.54)}{0.0257}} = 2 \times 10^{18}$$

(c) This is worked in an analogous manner to parts (a) and (b).

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 1.23 \text{ V} - 0.77 \text{ V} = 0.46 \text{ V}$$

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

$$\Delta G^{\circ} = -(4)(96500 \text{ J/V}\cdot\text{mol})(0.46 \text{ V}) = -178 \text{ kJ/mol}$$

$$K = e^{\frac{nE^{\circ}}{0.0257}}$$

$$K = e^{\frac{(4)(0.46)}{0.0257}} = 1 \times 10^{31}$$

(d) This is worked in an analogous manner to parts (a), (b), and (c).

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 0.53 \text{ V} - (-1.66 \text{ V}) = 2.19 \text{ V}$$

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

$$\Delta G^{\circ} = -(6)(96500 \text{ J/V}\cdot\text{mol})(2.19 \text{ V}) = -1.27 \times 10^3 \text{ kJ/mol}$$

$$K = e^{\frac{nE^{\circ}}{0.0257}}$$

$$K = e^{\frac{(6)(2.19)}{0.0257}} = 8 \times 10^{211}$$

19.25 The half-reactions are: $\text{Fe}^{3+}(\text{aq}) + e^{-} \rightarrow \text{Fe}^{2+}(\text{aq})$ $E_{\text{anode}}^{\circ} = 0.77 \text{ V}$

$\text{Ce}^{4+}(\text{aq}) + e^{-} \rightarrow \text{Ce}^{3+}(\text{aq})$ $E_{\text{cathode}}^{\circ} = 1.61 \text{ V}$

Thus, Ce^{4+} will oxidize Fe^{2+} to Fe^{3+} ; this makes the $\text{Fe}^{2+}/\text{Fe}^{3+}$ half-reaction the anode. The standard cell emf is found using Equation (19.1) of the text.

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 1.61 \text{ V} - 0.77 \text{ V} = 0.84 \text{ V}$$

The values of ΔG° and K_{c} are found using Equations (19.3) and (19.5) of the text.

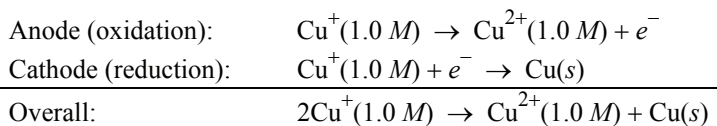
$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ} = -(1)(96500 \text{ J/V}\cdot\text{mol})(0.84 \text{ V}) = -81 \text{ kJ/mol}$$

$$\ln K = \frac{nE_{\text{cell}}^{\circ}}{0.0257 \text{ V}}$$

$$K_{\text{c}} = e^{\frac{nE_{\text{cell}}^{\circ}}{0.0257 \text{ V}}} = e^{\frac{(1)(0.84 \text{ V})}{0.0257 \text{ V}}} = 2 \times 10^{14}$$

19.26 Strategy: The relationship between the standard free energy change and the standard emf of the cell is given by Equation (19.3) of the text: $\Delta G^\circ = -nFE_{\text{cell}}^\circ$. The relationship between the equilibrium constant, K , and the standard emf is given by Equation (19.5) of the text: $E_{\text{cell}}^\circ = (0.0257 \text{ V}/n)\ln K$. Thus, if we can determine E_{cell}° , we can calculate ΔG° and K . We can determine the E_{cell}° of a hypothetical galvanic cell made up of two couples ($\text{Cu}^{2+}/\text{Cu}^+$ and Cu^+/Cu) from the standard reduction potentials in Table 19.1 of the text.

Solution: The half-cell reactions are:



$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = E_{\text{Cu}^+/\text{Cu}}^\circ - E_{\text{Cu}^{2+}/\text{Cu}^+}^\circ$$

$$E_{\text{cell}}^\circ = 0.52 \text{ V} - 0.15 \text{ V} = \mathbf{0.37 \text{ V}}$$

Now, we use Equation (19.3) of the text. The overall reaction shows that $n = 1$.

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

$$\Delta G^\circ = -(1)(96500 \text{ J/V}\cdot\text{mol})(0.37 \text{ V}) = \mathbf{-36 \text{ kJ/mol}}$$

Next, we can calculate K using Equation (19.5) of the text.

$$E_{\text{cell}}^\circ = \frac{0.0257 \text{ V}}{n} \ln K$$

or

$$\ln K = \frac{nE_{\text{cell}}^\circ}{0.0257 \text{ V}}$$

and

$$K = e^{\frac{nE^\circ}{0.0257}}$$

$$K = e^{\frac{(1)(0.37)}{0.0257}} = e^{14.4} = \mathbf{2 \times 10^6}$$

Check: The negative value of ΔG° and the large positive value of K , both indicate that the reaction favors products at equilibrium. The result is consistent with the fact that E° for the galvanic cell is positive.

19.29 If this were a standard cell, the concentrations would all be 1.00 M , and the voltage would just be the standard emf calculated from Table 19.1 of the text. Since cell emf's depend on the concentrations of the reactants and products, we must use the Nernst equation [Equation (19.8) of the text] to find the emf of a nonstandard cell.

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln Q$$

$$E = 1.10 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$E = 1.10 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{0.25}{0.15}$$

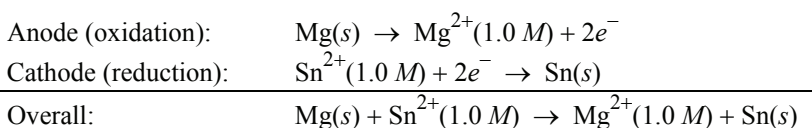
$$E = \mathbf{1.09 \text{ V}}$$

How did we find the value of 1.10 V for E° ?

- 19.30 Strategy:** The standard emf (E°) can be calculated using the standard reduction potentials in Table 19.1 of the text. Because the reactions are not run under standard-state conditions (concentrations are not 1 M), we need Nernst's equation [Equation (19.8) of the text] to calculate the emf (E) of a hypothetical galvanic cell. Remember that solids do not appear in the reaction quotient (Q) term in the Nernst equation. We can calculate ΔG from E using Equation (19.2) of the text: $\Delta G = -nFE_{\text{cell}}$.

Solution:

(a) The half-cell reactions are:



$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = E_{\text{Sn}^{2+}/\text{Sn}}^\circ - E_{\text{Mg}^{2+}/\text{Mg}}^\circ$$

$$E_{\text{cell}}^\circ = -0.14 \text{ V} - (-2.37 \text{ V}) = \mathbf{2.23 \text{ V}}$$

From Equation (19.8) of the text, we write:

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln Q$$

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln \frac{[\text{Mg}^{2+}]}{[\text{Sn}^{2+}]}$$

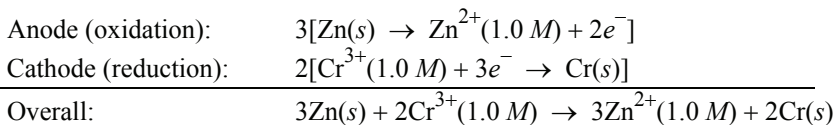
$$E = 2.23 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{0.045}{0.035} = \mathbf{2.23 \text{ V}}$$

We can now find the free energy change at the given concentrations using Equation (19.2) of the text. Note that in this reaction, $n = 2$.

$$\Delta G = -nFE_{\text{cell}}$$

$$\Delta G = -(2)(96500 \text{ J/V}\cdot\text{mol})(2.23 \text{ V}) = \mathbf{-430 \text{ kJ/mol}}$$

(b) The half-cell reactions are:



$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = E_{\text{Cr}^{3+}/\text{Cr}}^\circ - E_{\text{Zn}^{2+}/\text{Zn}}^\circ$$

$$E_{\text{cell}}^\circ = -0.74 \text{ V} - (-0.76 \text{ V}) = \mathbf{0.02 \text{ V}}$$

From Equation (19.8) of the text, we write:

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln Q$$

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln \frac{[\text{Zn}^{2+}]^3}{[\text{Cr}^{3+}]^2}$$

$$E = 0.02 \text{ V} - \frac{0.0257 \text{ V}}{6} \ln \frac{(0.0085)^3}{(0.010)^2} = \mathbf{0.04 \text{ V}}$$

We can now find the free energy change at the given concentrations using Equation (19.2) of the text. Note that in this reaction, $n = 6$.

$$\Delta G = -nFE_{\text{cell}}$$

$$\Delta G = -(6)(96500 \text{ J/V}\cdot\text{mol})(0.04 \text{ V}) = \mathbf{-23 \text{ kJ/mol}}$$

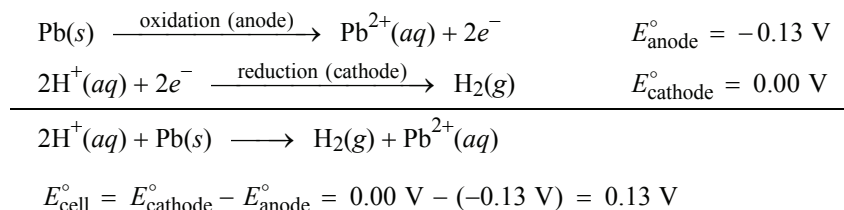
19.31 The overall reaction is: $\text{Zn}(s) + 2\text{H}^+(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{H}_2(g)$

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = 0.00 \text{ V} - (-0.76 \text{ V}) = \mathbf{0.76 \text{ V}}$$

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln \frac{[\text{Zn}^{2+}]P_{\text{H}_2}}{[\text{H}^+]^2}$$

$$E = 0.76 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{(0.45)(2.0)}{(1.8)^2} = \mathbf{0.78 \text{ V}}$$

19.32 Let's write the two half-reactions to calculate the standard cell emf. (Oxidation occurs at the Pb electrode.)



Using the Nernst equation, we can calculate the cell emf, E .

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln \frac{[\text{Pb}^{2+}]P_{\text{H}_2}}{[\text{H}^+]^2}$$

$$E = 0.13 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{(0.10)(1.0)}{(0.050)^2} = \mathbf{0.083 \text{ V}}$$

19.33 As written, the reaction is not spontaneous under standard state conditions; the cell emf is negative.

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = -0.76 \text{ V} - 0.34 \text{ V} = \mathbf{-1.10 \text{ V}}$$

The reaction will become spontaneous when the concentrations of zinc(II) and copper(II) ions are such as to make the emf positive. The turning point is when the emf is zero. We solve the Nernst equation for the $[\text{Cu}^{2+}]/[\text{Zn}^{2+}]$ ratio at this point.

$$E_{\text{cell}} = E^{\circ} - \frac{0.0257 \text{ V}}{n} \ln Q$$

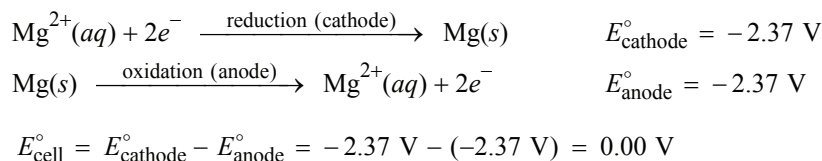
$$0 = -1.10 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]}$$

$$\ln \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]} = -85.6$$

$$\frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]} = e^{-85.6} = 6.7 \times 10^{-38}$$

In other words for the reaction to be spontaneous, the $[\text{Cu}^{2+}]/[\text{Zn}^{2+}]$ ratio must be less than 6.7×10^{-38} . Is the reduction of zinc(II) by copper metal a practical use of copper?

19.34 All concentration cells have the same standard emf: *zero* volts.



We use the Nernst equation to compute the emf. There are two moles of electrons transferred from the reducing agent to the oxidizing agent in this reaction, so $n = 2$.

$$E = E^{\circ} - \frac{0.0257 \text{ V}}{n} \ln Q$$

$$E = E^{\circ} - \frac{0.0257 \text{ V}}{n} \ln \frac{[\text{Mg}^{2+}]_{\text{ox}}}{[\text{Mg}^{2+}]_{\text{red}}}$$

$$E = 0 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{0.24}{0.53} = \mathbf{0.010 \text{ V}}$$

What is the direction of spontaneous change in all concentration cells?

19.37 (a) The total charge passing through the circuit is

$$3.0 \text{ h} \times \frac{8.5 \text{ C}}{1 \text{ s}} \times \frac{3600 \text{ s}}{1 \text{ h}} = 9.2 \times 10^4 \text{ C}$$

From the anode half-reaction we can find the amount of hydrogen.

$$(9.2 \times 10^4 \text{ C}) \times \frac{2 \text{ mol H}_2}{4 \text{ mol e}^{-}} \times \frac{1 \text{ mol e}^{-}}{96500 \text{ C}} = 0.48 \text{ mol H}_2$$

The volume can be computed using the ideal gas equation

$$V = \frac{nRT}{P} = \frac{(0.48 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}{155 \text{ atm}} = \mathbf{0.076 \text{ L}}$$

(b) The charge passing through the circuit in one minute is

$$\frac{8.5 \text{ C}}{1 \text{ s}} \times \frac{60 \text{ s}}{1 \text{ min}} = 510 \text{ C/min}$$

We can find the amount of oxygen from the cathode half-reaction and the ideal gas equation.

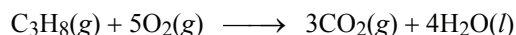
$$\frac{510 \text{ C}}{1 \text{ min}} \times \frac{1 \text{ mol } e^-}{96500 \text{ C}} \times \frac{1 \text{ mol O}_2}{4 \text{ mol } e^-} = 1.3 \times 10^{-3} \text{ mol O}_2/\text{min}$$

$$V = \frac{nRT}{P} = \left(\frac{1.3 \times 10^{-3} \text{ mol O}_2}{1 \text{ min}} \right) \left(\frac{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}{1 \text{ atm}} \right) = 0.032 \text{ L O}_2/\text{min}$$

$$\frac{0.032 \text{ L O}_2}{1 \text{ min}} \times \frac{1.0 \text{ L air}}{0.20 \text{ L O}_2} = \mathbf{0.16 \text{ L of air/min}}$$

19.38 We can calculate the standard free energy change, ΔG° , from the standard free energies of formation, ΔG_f° using Equation (18.12) of the text. Then, we can calculate the standard cell emf, E_{cell}° , from ΔG° .

The overall reaction is:



$$\Delta G_{\text{rxn}}^\circ = 3\Delta G_f^\circ[\text{CO}_2(g)] + 4\Delta G_f^\circ[\text{H}_2\text{O}(l)] - \{\Delta G_f^\circ[\text{C}_3\text{H}_8(g)] + 5\Delta G_f^\circ[\text{O}_2(g)]\}$$

$$\Delta G_{\text{rxn}}^\circ = (3)(-394.4 \text{ kJ/mol}) + (4)(-237.2 \text{ kJ/mol}) - [(1)(-23.5 \text{ kJ/mol}) + (5)(0)] = -2108.5 \text{ kJ/mol}$$

We can now calculate the standard emf using the following equation:

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

or

$$E_{\text{cell}}^\circ = \frac{-\Delta G^\circ}{nF}$$

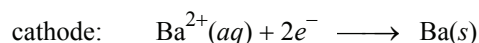
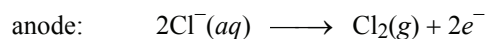
Check the half-reactions on p. 843 of the text to determine that 20 moles of electrons are transferred during this redox reaction.

$$E_{\text{cell}}^\circ = \frac{-(-2108.5 \times 10^3 \text{ J/mol})}{(20)(96500 \text{ J/V} \cdot \text{mol})} = \mathbf{1.09 \text{ V}}$$

Does this suggest that, in theory, it should be possible to construct a galvanic cell (battery) based on any conceivable spontaneous reaction?

19.45 $\text{Mass Mg} = 1.00 F \times \frac{1 \text{ mol Mg}}{2 \text{ mol } e^-} \times \frac{24.31 \text{ g Mg}}{1 \text{ mol Mg}} = \mathbf{12.2 \text{ g Mg}}$

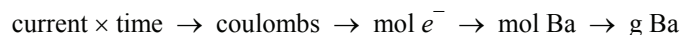
19.46 (a) The only ions present in molten BaCl_2 are Ba^{2+} and Cl^- . The electrode reactions are:



This cathode half-reaction tells us that 2 moles of e^- are required to produce 1 mole of $\text{Ba}(s)$.

(b)

Strategy: According to Figure 19.20 of the text, we can carry out the following conversion steps to calculate the quantity of Ba in grams.



This is a large number of steps, so let's break it down into two parts. First, we calculate the coulombs of electricity that pass through the cell. Then, we will continue on to calculate grams of Ba.

Solution: First, we calculate the coulombs of electricity that pass through the cell.

$$0.50 \text{ A} \times \frac{1 \text{ C}}{1 \text{ A} \cdot \text{s}} \times \frac{60 \text{ s}}{1 \text{ min}} \times 30 \text{ min} = 9.0 \times 10^2 \text{ C}$$

We see that for every mole of Ba formed at the cathode, 2 moles of electrons are needed. The grams of Ba produced at the cathode are:

$$? \text{ g Ba} = (9.0 \times 10^2 \text{ C}) \times \frac{1 \text{ mol } e^-}{96,500 \text{ C}} \times \frac{1 \text{ mol Ba}}{2 \text{ mol } e^-} \times \frac{137.3 \text{ g Ba}}{1 \text{ mol Ba}} = \mathbf{0.64 \text{ g Ba}}$$

19.47 The half-reactions are: $\text{Na}^+ + e^- \rightarrow \text{Na}$
 $\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$

Since 1 g is the same idea as 1 ton as long as we are comparing two quantities, we can write:

$$1 \text{ g Na} \times \frac{1 \text{ mol}}{22.99 \text{ g Na}} \times 1 e^- = 0.043 \text{ mol } e^-$$

$$1 \text{ g Al} \times \frac{1 \text{ mol}}{26.98 \text{ g Al}} \times 3 e^- = 0.11 \text{ mol } e^-$$

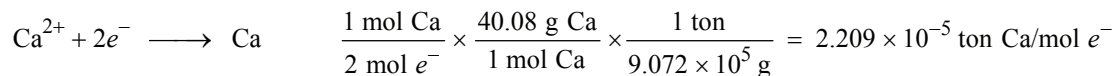
It is cheaper to prepare 1 ton of sodium by electrolysis.

19.48 The cost for producing various metals is determined by the moles of electrons needed to produce a given amount of metal. For each reduction, let's first calculate the number of tons of metal produced per 1 mole of electrons (1 ton = 9.072×10^5 g). The reductions are:

$$\text{Mg}^{2+} + 2e^- \longrightarrow \text{Mg} \quad \frac{1 \text{ mol Mg}}{2 \text{ mol } e^-} \times \frac{24.31 \text{ g Mg}}{1 \text{ mol Mg}} \times \frac{1 \text{ ton}}{9.072 \times 10^5 \text{ g}} = 1.340 \times 10^{-5} \text{ ton Mg/mol } e^-$$

$$\text{Al}^{3+} + 3e^- \longrightarrow \text{Al} \quad \frac{1 \text{ mol Al}}{3 \text{ mol } e^-} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} \times \frac{1 \text{ ton}}{9.072 \times 10^5 \text{ g}} = 9.913 \times 10^{-6} \text{ ton Al/mol } e^-$$

$$\text{Na}^+ + e^- \longrightarrow \text{Na} \quad \frac{1 \text{ mol Na}}{1 \text{ mol } e^-} \times \frac{22.99 \text{ g Na}}{1 \text{ mol Na}} \times \frac{1 \text{ ton}}{9.072 \times 10^5 \text{ g}} = 2.534 \times 10^{-5} \text{ ton Na/mol } e^-$$



Now that we know the tons of each metal produced per mole of electrons, we can convert from \$155/ton Mg to the cost to produce the given amount of each metal.

(a) For aluminum :

$$\frac{\$155}{1 \text{ ton Mg}} \times \frac{1.340 \times 10^{-5} \text{ ton Mg}}{1 \text{ mol } e^{-}} \times \frac{1 \text{ mol } e^{-}}{9.913 \times 10^{-6} \text{ ton Al}} \times 10.0 \text{ tons Al} = \mathbf{\$2.10 \times 10^3}$$

(b) For sodium:

$$\frac{\$155}{1 \text{ ton Mg}} \times \frac{1.340 \times 10^{-5} \text{ ton Mg}}{1 \text{ mol } e^{-}} \times \frac{1 \text{ mol } e^{-}}{2.534 \times 10^{-5} \text{ ton Na}} \times 30.0 \text{ tons Na} = \mathbf{\$2.46 \times 10^3}$$

(c) For calcium:

$$\frac{\$155}{1 \text{ ton Mg}} \times \frac{1.340 \times 10^{-5} \text{ ton Mg}}{1 \text{ mol } e^{-}} \times \frac{1 \text{ mol } e^{-}}{2.209 \times 10^{-5} \text{ ton Ca}} \times 50.0 \text{ tons Ca} = \mathbf{\$4.70 \times 10^3}$$

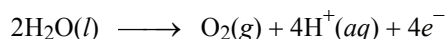
19.49 Find the amount of oxygen using the ideal gas equation

$$n = \frac{PV}{RT} = \frac{\left(755 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right)(0.076 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})} = 3.1 \times 10^{-3} \text{ mol O}_2$$

Since the half-reaction shows that one mole of oxygen requires four faradays of electric charge, we write

$$(3.1 \times 10^{-3} \text{ mol O}_2) \times \frac{4 F}{1 \text{ mol O}_2} = \mathbf{0.012 F}$$

19.50 (a) The half-reaction is:



First, we can calculate the number of moles of oxygen produced using the ideal gas equation.

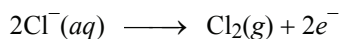
$$n_{\text{O}_2} = \frac{PV}{RT}$$

$$n_{\text{O}_2} = \frac{(1.0 \text{ atm})(0.84 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(298 \text{ K})} = 0.034 \text{ mol O}_2$$

Since 4 moles of electrons are needed for every 1 mole of oxygen, we will need 4 *F* of electrical charge to produce 1 mole of oxygen.

$$? F = 0.034 \text{ mol O}_2 \times \frac{4 F}{1 \text{ mol O}_2} = \mathbf{0.14 F}$$

(b) The half-reaction is:



The number of moles of chlorine produced is:

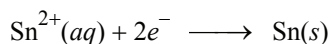
$$n_{\text{Cl}_2} = \frac{PV}{RT}$$

$$n_{\text{Cl}_2} = \frac{\left(750 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right)(1.50 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(298 \text{ K})} = 0.0605 \text{ mol Cl}_2$$

Since 2 moles of electrons are needed for every 1 mole of chlorine gas, we will need 2 F of electrical charge to produce 1 mole of chlorine gas.

$$? F = 0.0605 \text{ mol Cl}_2 \times \frac{2 F}{1 \text{ mol Cl}_2} = \mathbf{0.121 F}$$

(c) The half-reaction is:

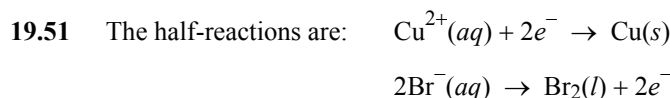


The number of moles of Sn(s) produced is

$$? \text{ mol Sn} = 6.0 \text{ g Sn} \times \frac{1 \text{ mol Sn}}{118.7 \text{ g Sn}} = 0.051 \text{ mol Sn}$$

Since 2 moles of electrons are needed for every 1 mole of Sn, we will need 2 F of electrical charge to reduce 1 mole of Sn^{2+} ions to Sn metal.

$$? F = 0.051 \text{ mol Sn} \times \frac{2 F}{1 \text{ mol Sn}} = \mathbf{0.10 F}$$



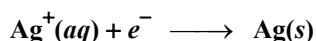
The mass of copper produced is:

$$4.50 \text{ A} \times 1 \text{ h} \times \frac{3600 \text{ s}}{1 \text{ h}} \times \frac{1 \text{ C}}{1 \text{ A} \cdot \text{s}} \times \frac{1 \text{ mol } e^-}{96500 \text{ C}} \times \frac{1 \text{ mol Cu}}{2 \text{ mol } e^-} \times \frac{63.55 \text{ g Cu}}{1 \text{ mol Cu}} = \mathbf{5.33 \text{ g Cu}}$$

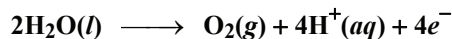
The mass of bromine produced is:

$$4.50 \text{ A} \times 1 \text{ h} \times \frac{3600 \text{ s}}{1 \text{ h}} \times \frac{1 \text{ C}}{1 \text{ A} \cdot \text{s}} \times \frac{1 \text{ mol } e^-}{96500 \text{ C}} \times \frac{1 \text{ mol Br}_2}{2 \text{ mol } e^-} \times \frac{159.8 \text{ g Br}_2}{1 \text{ mol Br}_2} = \mathbf{13.4 \text{ g Br}_2}$$

19.52 (a) The half-reaction is:



- (b) Since this reaction is taking place in an aqueous solution, the probable oxidation is the oxidation of water. (Neither Ag^+ nor NO_3^- can be further oxidized.)



- (c) The half-reaction tells us that 1 mole of electrons is needed to reduce 1 mol of Ag^+ to Ag metal. We can set up the following strategy to calculate the quantity of electricity (in C) needed to deposit 0.67 g of Ag.

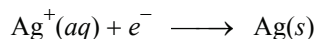
grams Ag \rightarrow mol Ag \rightarrow mol e^- \rightarrow coulombs

$$0.67 \text{ g Ag} \times \frac{1 \text{ mol Ag}}{107.9 \text{ g Ag}} \times \frac{1 \text{ mol } e^-}{1 \text{ mol Ag}} \times \frac{96500 \text{ C}}{1 \text{ mol } e^-} = 6.0 \times 10^2 \text{ C}$$

- 19.53 The half-reaction is: $\text{Co}^{2+} + 2e^- \rightarrow \text{Co}$

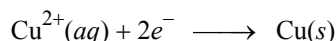
$$2.35 \text{ g Co} \times \frac{1 \text{ mol Co}}{58.93 \text{ g Co}} \times \frac{2 \text{ mol } e^-}{1 \text{ mol Co}} \times \frac{96500 \text{ C}}{1 \text{ mol } e^-} = 7.70 \times 10^3 \text{ C}$$

- 19.54 (a) First find the amount of charge needed to produce 2.00 g of silver according to the half-reaction:



$$2.00 \text{ g Ag} \times \frac{1 \text{ mol Ag}}{107.9 \text{ g Ag}} \times \frac{1 \text{ mol } e^-}{1 \text{ mol Ag}} \times \frac{96500 \text{ C}}{1 \text{ mol } e^-} = 1.79 \times 10^3 \text{ C}$$

The half-reaction for the reduction of copper(II) is:



From the amount of charge calculated above, we can calculate the mass of copper deposited in the second cell.

$$(1.79 \times 10^3 \text{ C}) \times \frac{1 \text{ mol } e^-}{96500 \text{ C}} \times \frac{1 \text{ mol Cu}}{2 \text{ mol } e^-} \times \frac{63.55 \text{ g Cu}}{1 \text{ mol Cu}} = 0.589 \text{ g Cu}$$

- (b) We can calculate the current flowing through the cells using the following strategy.

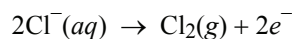
Coulombs \rightarrow Coulombs/hour \rightarrow Coulombs/second

Recall that $1 \text{ C} = 1 \text{ A}\cdot\text{s}$

The current flowing through the cells is:

$$(1.79 \times 10^3 \text{ A}\cdot\text{s}) \times \frac{1 \text{ h}}{3600 \text{ s}} \times \frac{1}{3.75 \text{ h}} = 0.133 \text{ A}$$

19.55 The half-reaction for the oxidation of chloride ion is:



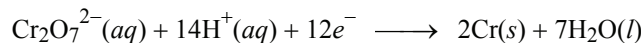
First, let's calculate the moles of e^- flowing through the cell in one hour.

$$1500 \text{ A} \times \frac{1 \text{ C}}{1 \text{ A} \cdot \text{s}} \times \frac{3600 \text{ s}}{1 \text{ h}} \times \frac{1 \text{ mol } e^-}{96500 \text{ C}} = 55.96 \text{ mol } e^-$$

Next, let's calculate the hourly production rate of chlorine gas (in kg). Note that the anode efficiency is 93.0%.

$$55.96 \text{ mol } e^- \times \frac{1 \text{ mol } \text{Cl}_2}{2 \text{ mol } e^-} \times \frac{0.07090 \text{ kg } \text{Cl}_2}{1 \text{ mol } \text{Cl}_2} \times \frac{93.0\%}{100\%} = \mathbf{1.84 \text{ kg } \text{Cl}_2/\text{h}}$$

19.56 *Step 1:* Balance the half-reaction.



Step 2: Calculate the quantity of chromium metal by calculating the volume and converting this to mass using the given density.

$$\text{Volume Cr} = \text{thickness} \times \text{surface area}$$

$$\text{Volume Cr} = (1.0 \times 10^{-2} \text{ mm}) \times \frac{1 \text{ m}}{1000 \text{ mm}} \times 0.25 \text{ m}^2 = 2.5 \times 10^{-6} \text{ m}^3$$

Converting to cm^3 ,

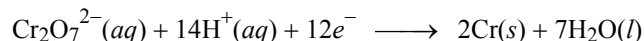
$$(2.5 \times 10^{-6} \text{ m}^3) \times \left(\frac{1 \text{ cm}}{0.01 \text{ m}} \right)^3 = 2.5 \text{ cm}^3$$

Next, calculate the mass of Cr.

$$\text{Mass} = \text{density} \times \text{volume}$$

$$\text{Mass Cr} = 2.5 \text{ cm}^3 \times \frac{7.19 \text{ g}}{1 \text{ cm}^3} = 18 \text{ g Cr}$$

Step 3: Find the number of moles of electrons required to electrodeposit 18 g of Cr from solution. The half-reaction is:



Six moles of electrons are required to reduce 1 mol of Cr metal. But, we are electrodepositing less than 1 mole of Cr(s). We need to complete the following conversions:

$$\text{g Cr} \rightarrow \text{mol Cr} \rightarrow \text{mol } e^-$$

$$? \text{ faradays} = 18 \text{ g Cr} \times \frac{1 \text{ mol Cr}}{52.00 \text{ g Cr}} \times \frac{6 \text{ mol } e^-}{1 \text{ mol Cr}} = 2.1 \text{ mol } e^-$$

Step 4: Determine how long it will take for 2.1 moles of electrons to flow through the cell when the current is 25.0 C/s. We need to complete the following conversions:

$$\text{mol } e^- \rightarrow \text{coulombs} \rightarrow \text{seconds} \rightarrow \text{hours}$$

$$? \text{ h} = 2.1 \text{ mol } e^{-} \times \frac{96,500 \text{ C}}{1 \text{ mol } e^{-}} \times \frac{1 \text{ s}}{25.0 \text{ C}} \times \frac{1 \text{ h}}{3600 \text{ s}} = \mathbf{2.3 \text{ h}}$$

Would any time be saved by connecting several bumpers together in a series?

19.57 The quantity of charge passing through the solution is:

$$0.750 \text{ A} \times \frac{1 \text{ C}}{1 \text{ A} \cdot \text{s}} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{1 \text{ mol } e^{-}}{96500 \text{ C}} \times 25.0 \text{ min} = 1.17 \times 10^{-2} \text{ mol } e^{-}$$

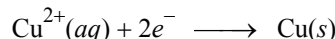
Since the charge of the copper ion is +2, the number of moles of copper formed must be:

$$(1.17 \times 10^{-2} \text{ mol } e^{-}) \times \frac{1 \text{ mol Cu}}{2 \text{ mol } e^{-}} = 5.85 \times 10^{-3} \text{ mol Cu}$$

The units of molar mass are grams per mole. The molar mass of copper is:

$$\frac{0.369 \text{ g}}{5.85 \times 10^{-3} \text{ mol}} = \mathbf{63.1 \text{ g/mol}}$$

19.58 Based on the half-reaction, we know that one faraday will produce half a mole of copper.



First, let's calculate the charge (in C) needed to deposit 0.300 g of Cu.

$$(3.00 \text{ A})(304 \text{ s}) \times \frac{1 \text{ C}}{1 \text{ A} \cdot \text{s}} = 912 \text{ C}$$

We know that one faraday will produce half a mole of copper, but we don't have a half a mole of copper. We have:

$$0.300 \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} = 4.72 \times 10^{-3} \text{ mol}$$

We calculated the number of coulombs (912 C) needed to produce 4.72×10^{-3} mol of Cu. How many coulombs will it take to produce 0.500 moles of Cu? This will be Faraday's constant.

$$\frac{912 \text{ C}}{4.72 \times 10^{-3} \text{ mol Cu}} \times 0.500 \text{ mol Cu} = \mathbf{9.66 \times 10^4 \text{ C} = 1 \text{ F}}$$

19.59 The number of faradays supplied is:

$$1.44 \text{ g Ag} \times \frac{1 \text{ mol Ag}}{107.9 \text{ g Ag}} \times \frac{1 \text{ mol } e^{-}}{1 \text{ mol Ag}} = 0.0133 \text{ mol } e^{-}$$

Since we need three faradays to reduce one mole of X^{3+} , the molar mass of X must be:

$$\frac{0.120 \text{ g X}}{0.0133 \text{ mol } e^{-}} \times \frac{3 \text{ mol } e^{-}}{1 \text{ mol X}} = \mathbf{27.1 \text{ g/mol}}$$

19.60 First we can calculate the number of moles of hydrogen produced using the ideal gas equation.

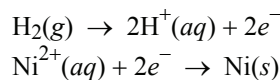
$$n_{\text{H}_2} = \frac{PV}{RT}$$

$$n_{\text{H}_2} = \frac{\left(782 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right)(0.845 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})} = 0.0355 \text{ mol}$$

The number of faradays passed through the solution is:

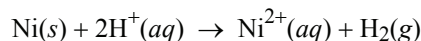
$$0.0355 \text{ mol H}_2 \times \frac{2 F}{1 \text{ mol H}_2} = \mathbf{0.0710 F}$$

19.61 (a) The half-reactions are:

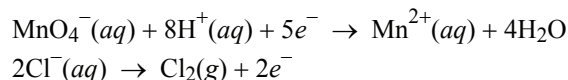


The complete balanced equation is: $\text{Ni}^{2+}(\text{aq}) + \text{H}_2(\text{g}) \rightarrow \text{Ni}(\text{s}) + 2\text{H}^+(\text{aq})$

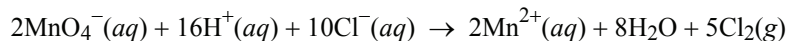
Ni(s) is below and to the right of $\text{H}^+(\text{aq})$ in Table 19.1 of the text (see the half-reactions at -0.25 and 0.00 V). Therefore, the spontaneous reaction is the reverse of the above reaction, that is:



(b) The half-reactions are:

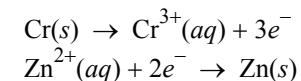


The complete balanced equation is:



In Table 19.1 of the text, $\text{Cl}^-(\text{aq})$ is below and to the right of $\text{MnO}_4^-(\text{aq})$; therefore the spontaneous reaction is as written.

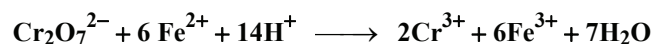
(c) The half-reactions are:



The complete balanced equation is: $2\text{Cr}(\text{s}) + 3\text{Zn}^{2+}(\text{aq}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 3\text{Zn}(\text{s})$

In Table 19.1 of the text, $\text{Zn}(\text{s})$ is below and to the right of $\text{Cr}^{3+}(\text{aq})$; therefore the spontaneous reaction is the reverse of the reaction as written.

19.62 The balanced equation is:



The remainder of this problem is a solution stoichiometry problem.

The number of moles of potassium dichromate in 26.0 mL of the solution is:

$$26.0 \text{ mL} \times \frac{0.0250 \text{ mol}}{1000 \text{ mL soln}} = 6.50 \times 10^{-4} \text{ mol K}_2\text{Cr}_2\text{O}_7$$

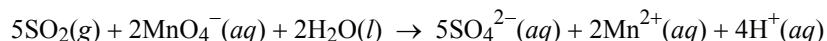
From the balanced equation it can be seen that 1 mole of dichromate is stoichiometrically equivalent to 6 moles of iron(II). The number of moles of iron(II) oxidized is therefore

$$(6.50 \times 10^{-4} \text{ mol Cr}_2\text{O}_7^{2-}) \times \frac{6 \text{ mol Fe}^{2+}}{1 \text{ mol Cr}_2\text{O}_7^{2-}} = 3.90 \times 10^{-3} \text{ mol Fe}^{2+}$$

Finally, the molar concentration of Fe^{2+} is:

$$\frac{3.90 \times 10^{-3} \text{ mol}}{25.0 \times 10^{-3} \text{ L}} = 0.156 \text{ mol/L} = \mathbf{0.156 \text{ M Fe}^{2+}}$$

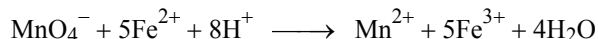
19.63 The balanced equation is:



The mass of SO_2 in the water sample is given by

$$7.37 \text{ mL} \times \frac{0.00800 \text{ mol KMnO}_4}{1000 \text{ mL soln}} \times \frac{5 \text{ mol SO}_2}{2 \text{ mol KMnO}_4} \times \frac{64.07 \text{ g SO}_2}{1 \text{ mol SO}_2} = \mathbf{9.44 \times 10^{-3} \text{ g SO}_2}$$

19.64 The balanced equation is:



First, let's calculate the number of moles of potassium permanganate in 23.30 mL of solution.

$$23.30 \text{ mL} \times \frac{0.0194 \text{ mol}}{1000 \text{ mL soln}} = 4.52 \times 10^{-4} \text{ mol KMnO}_4$$

From the balanced equation it can be seen that 1 mole of permanganate is stoichiometrically equivalent to 5 moles of iron(II). The number of moles of iron(II) oxidized is therefore

$$(4.52 \times 10^{-4} \text{ mol MnO}_4^-) \times \frac{5 \text{ mol Fe}^{2+}}{1 \text{ mol MnO}_4^-} = 2.26 \times 10^{-3} \text{ mol Fe}^{2+}$$

The mass of Fe^{2+} oxidized is:

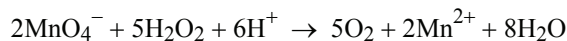
$$\text{mass Fe}^{2+} = (2.26 \times 10^{-3} \text{ mol Fe}^{2+}) \times \frac{55.85 \text{ g Fe}^{2+}}{1 \text{ mol Fe}^{2+}} = 0.126 \text{ g Fe}^{2+}$$

Finally, the mass percent of iron in the ore can be calculated.

$$\text{mass \% Fe} = \frac{\text{mass of iron}}{\text{total mass of sample}} \times 100\%$$

$$\mathbf{\%Fe} = \frac{0.126 \text{ g}}{0.2792 \text{ g}} \times 100\% = \mathbf{45.1\%}$$

19.65 (a) The balanced equation is:



- (b) The number of moles of potassium permanganate in 36.44 mL of the solution is

$$36.44 \text{ mL} \times \frac{0.01652 \text{ mol}}{1000 \text{ mL soln}} = 6.020 \times 10^{-4} \text{ mol of KMnO}_4$$

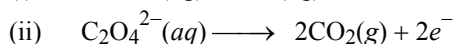
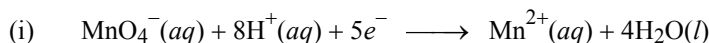
From the balanced equation it can be seen that in this particular reaction 2 moles of permanganate is stoichiometrically equivalent to 5 moles of hydrogen peroxide. The number of moles of H_2O_2 oxidized is therefore

$$(6.020 \times 10^{-4} \text{ mol MnO}_4^-) \times \frac{5 \text{ mol H}_2\text{O}_2}{2 \text{ mol MnO}_4^-} = 1.505 \times 10^{-3} \text{ mol H}_2\text{O}_2$$

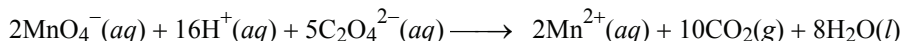
The molar concentration of H_2O_2 is:

$$[\text{H}_2\text{O}_2] = \frac{1.505 \times 10^{-3} \text{ mol}}{25.0 \times 10^{-3} \text{ L}} = 0.0602 \text{ mol/L} = \mathbf{0.0602 \text{ M}}$$

- 19.66 (a) The half-reactions are:



We combine the half-reactions to cancel electrons, that is, $[2 \times \text{equation (i)}] + [5 \times \text{equation (ii)}]$



- (b) We can calculate the moles of KMnO_4 from the molarity and volume of solution.

$$24.0 \text{ mL KMnO}_4 \times \frac{0.0100 \text{ mol KMnO}_4}{1000 \text{ mL soln}} = 2.40 \times 10^{-4} \text{ mol KMnO}_4$$

We can calculate the mass of oxalic acid from the stoichiometry of the balanced equation. The mole ratio between oxalate ion and permanganate ion is 5:2.

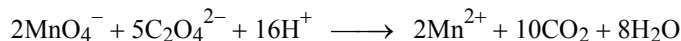
$$(2.40 \times 10^{-4} \text{ mol KMnO}_4) \times \frac{5 \text{ mol H}_2\text{C}_2\text{O}_4}{2 \text{ mol KMnO}_4} \times \frac{90.04 \text{ g H}_2\text{C}_2\text{O}_4}{1 \text{ mol H}_2\text{C}_2\text{O}_4} = 0.0540 \text{ g H}_2\text{C}_2\text{O}_4$$

Finally, the percent by mass of oxalic acid in the sample is:

$$\% \text{ oxalic acid} = \frac{0.0540 \text{ g}}{1.00 \text{ g}} \times 100\% = \mathbf{5.40\%}$$

19.67	E	ΔG	Cell Reaction
	> 0	< 0	spontaneous
	< 0	> 0	nonspontaneous
	$= 0$	$= 0$	at equilibrium

- 19.68 The balanced equation is:



Therefore, 2 mol MnO_4^- reacts with 5 mol $\text{C}_2\text{O}_4^{2-}$

$$\text{Moles of MnO}_4^- \text{ reacted} = 24.2 \text{ mL} \times \frac{9.56 \times 10^{-4} \text{ mol MnO}_4^-}{1000 \text{ mL soln}} = 2.31 \times 10^{-5} \text{ mol MnO}_4^-$$

Recognize that the mole ratio of Ca^{2+} to $\text{C}_2\text{O}_4^{2-}$ is 1:1 in CaC_2O_4 . The mass of Ca^{2+} in 10.0 mL is:

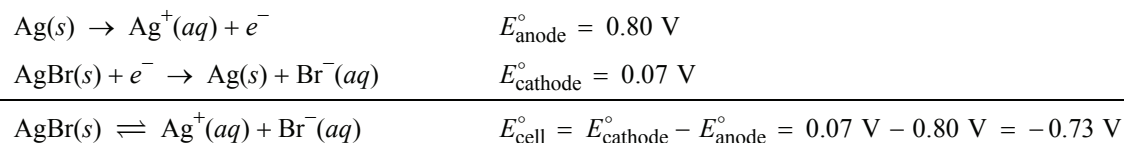
$$(2.31 \times 10^{-5} \text{ mol MnO}_4^-) \times \frac{5 \text{ mol Ca}^{2+}}{2 \text{ mol MnO}_4^-} \times \frac{40.08 \text{ g Ca}^{2+}}{1 \text{ mol Ca}^{2+}} = 2.31 \times 10^{-3} \text{ g Ca}^{2+}$$

Finally, converting to mg/mL, we have:

$$\frac{2.31 \times 10^{-3} \text{ g Ca}^{2+}}{10.0 \text{ mL}} \times \frac{1000 \text{ mg}}{1 \text{ g}} = \mathbf{0.231 \text{ mg Ca}^{2+}/\text{mL blood}}$$

19.69 The solubility equilibrium of AgBr is: $\text{AgBr}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Br}^-(aq)$

By reversing the second given half-reaction and adding it to the first, we obtain:



At equilibrium, we have:

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln[\text{Ag}^+][\text{Br}^-]$$

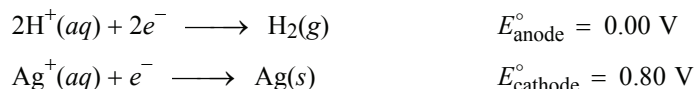
$$0 = -0.73 \text{ V} - \frac{0.0257 \text{ V}}{1} \ln K_{\text{sp}}$$

$$\ln K_{\text{sp}} = -28.4$$

$$K_{\text{sp}} = \mathbf{5 \times 10^{-13}}$$

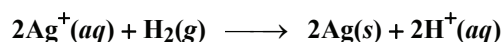
(Note that this value differs from that given in Table 16.2 of the text, since the data quoted here were obtained from a student's lab report.)

19.70 (a) The half-reactions are:



$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = 0.80 \text{ V} - 0.00 \text{ V} = \mathbf{0.80 \text{ V}}$$

(b) The spontaneous cell reaction under standard-state conditions is:



- (c) Using the Nernst equation we can calculate the cell potential under nonstandard-state conditions.

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln \frac{[\text{H}^+]^2}{[\text{Ag}^+]^2 P_{\text{H}_2}}$$

- (i) The potential is:

$$E = 0.80 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{(1.0 \times 10^{-2})^2}{(1.0)^2 (1.0)} = \mathbf{0.92 \text{ V}}$$

- (ii) The potential is:

$$E = 0.80 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{(1.0 \times 10^{-5})^2}{(1.0)^2 (1.0)} = \mathbf{1.10 \text{ V}}$$

- (d) From the results in part (c), we deduce that this cell is a pH meter; its potential is a sensitive function of the hydrogen ion concentration. Each 1 unit increase in pH causes a voltage increase of 0.060 V.

- 19.71 (a) If this were a standard cell, the concentrations would all be 1.00 M, and the voltage would just be the standard emf calculated from Table 19.1 of the text. Since cell emf's depend on the concentrations of the reactants and products, we must use the Nernst equation [Equation (19.8) of the text] to find the emf of a nonstandard cell.

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln Q$$

$$E = 3.17 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2}$$

$$E = 3.17 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{0.10}{[0.10]^2}$$

$$E = \mathbf{3.14 \text{ V}}$$

- (b) First we calculate the concentration of silver ion remaining in solution after the deposition of 1.20 g of silver metal

$$\text{Ag originally in solution: } \frac{0.100 \text{ mol Ag}^+}{1 \text{ L}} \times 0.346 \text{ L} = 3.46 \times 10^{-2} \text{ mol Ag}^+$$

$$\text{Ag deposited: } 1.20 \text{ g Ag} \times \frac{1 \text{ mol}}{107.9 \text{ g}} = 1.11 \times 10^{-2} \text{ mol Ag}$$

$$\text{Ag remaining in solution: } (3.46 \times 10^{-2} \text{ mol Ag}) - (1.11 \times 10^{-2} \text{ mol Ag}) = 2.35 \times 10^{-2} \text{ mol Ag}$$

$$[\text{Ag}^+] = \frac{2.35 \times 10^{-2} \text{ mol}}{0.346 \text{ L}} = 6.79 \times 10^{-2} \text{ M}$$

The overall reaction is: $\text{Mg}(s) + 2\text{Ag}^+(aq) \rightarrow \text{Mg}^{2+}(aq) + 2\text{Ag}(s)$

We use the balanced equation to find the amount of magnesium metal suffering oxidation and dissolving.

$$(1.11 \times 10^{-2} \text{ mol Ag}) \times \frac{1 \text{ mol Mg}}{2 \text{ mol Ag}} = 5.55 \times 10^{-3} \text{ mol Mg}$$

The amount of magnesium originally in solution was

$$0.288 \text{ L} \times \frac{0.100 \text{ mol}}{1 \text{ L}} = 2.88 \times 10^{-2} \text{ mol}$$

The new magnesium ion concentration is:

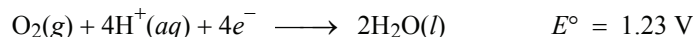
$$\frac{[(5.55 \times 10^{-3}) + (2.88 \times 10^{-2})] \text{ mol}}{0.288 \text{ L}} = 0.119 \text{ M}$$

The new cell emf is:

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln Q$$

$$E = 3.17 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{0.119}{(6.79 \times 10^{-2})^2} = \mathbf{3.13 \text{ V}}$$

- 19.72** The overvoltage of oxygen is not large enough to prevent its formation at the anode. Applying the diagonal rule, we see that water is oxidized before fluoride ion.



The very positive standard reduction potential indicates that F^- has essentially no tendency to undergo oxidation. The oxidation potential of chloride ion is much smaller (-1.36 V), and hence $\text{Cl}_2(\text{g})$ can be prepared by electrolyzing a solution of NaCl .

This fact was one of the major obstacles preventing the discovery of fluorine for many years. HF was usually chosen as the substance for electrolysis, but two problems interfered with the experiment. First, any water in the HF was oxidized before the fluoride ion. Second, pure HF without any water in it is a nonconductor of electricity (HF is a weak acid!). The problem was finally solved by dissolving KF in liquid HF to give a conducting solution.

- 19.73** The cell voltage is given by:

$$E = E^\circ - \frac{0.0257 \text{ V}}{2} \ln \frac{[\text{Cu}^{2+}]_{\text{dilute}}}{[\text{Cu}^{2+}]_{\text{concentrated}}}$$

$$E = 0 - \frac{0.0257 \text{ V}}{2} \ln \frac{0.080}{1.2} = \mathbf{0.035 \text{ V}}$$

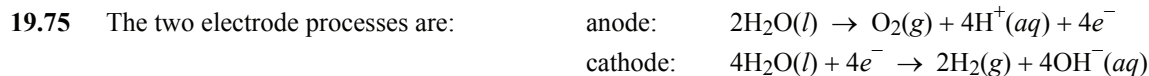
- 19.74** We can calculate the amount of charge that 4.0 g of MnO_2 can produce.

$$4.0 \text{ g MnO}_2 \times \frac{1 \text{ mol}}{86.94 \text{ g}} \times \frac{2 \text{ mol e}^-}{2 \text{ mol MnO}_2} \times \frac{96500 \text{ C}}{1 \text{ mol e}^-} = 4.44 \times 10^3 \text{ C}$$

Since a current of one ampere represents a flow of one coulomb per second, we can find the time it takes for this amount of charge to pass.

$$0.0050 \text{ A} = 0.0050 \text{ C/s}$$

$$(4.44 \times 10^3 \text{ C}) \times \frac{1 \text{ s}}{0.0050 \text{ C}} \times \frac{1 \text{ h}}{3600 \text{ s}} = 2.5 \times 10^2 \text{ h}$$



The amount of hydrogen formed is twice the amount of oxygen. Notice that the solution at the anode will become acidic and that the solution at the cathode will become basic (test with litmus paper). What are the relative amounts of H^+ and OH^- formed in this process? Would the solutions surrounding the two electrodes neutralize each other exactly? If not, would the resulting solution be acidic or basic?

19.76 Since this is a concentration cell, the standard emf is zero. (Why?) Using the Nernst equation, we can write equations to calculate the cell voltage for the two cells.

$$(1) \quad E_{\text{cell}} = -\frac{RT}{nF} \ln Q = -\frac{RT}{2F} \ln \frac{[\text{Hg}_2^{2+}]_{\text{soln A}}}{[\text{Hg}_2^{2+}]_{\text{soln B}}}$$

$$(2) \quad E_{\text{cell}} = -\frac{RT}{nF} \ln Q = -\frac{RT}{1F} \ln \frac{[\text{Hg}^+]_{\text{soln A}}}{[\text{Hg}^+]_{\text{soln B}}}$$

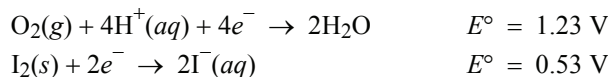
In the first case, two electrons are transferred per mercury ion ($n = 2$), while in the second only one is transferred ($n = 1$). Note that the concentration ratio will be 1:10 in both cases. The voltages calculated at 18°C are:

$$(1) \quad E_{\text{cell}} = \frac{-(8.314 \text{ J/K} \cdot \text{mol})(291 \text{ K})}{2(96500 \text{ J} \cdot \text{V}^{-1}\text{mol}^{-1})} \ln 10^{-1} = 0.0289 \text{ V}$$

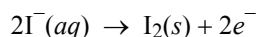
$$(2) \quad E_{\text{cell}} = \frac{-(8.314 \text{ J/K} \cdot \text{mol})(291 \text{ K})}{1(96500 \text{ J} \cdot \text{V}^{-1}\text{mol}^{-1})} \ln 10^{-1} = 0.0577 \text{ V}$$

Since the calculated cell potential for cell (1) agrees with the measured cell emf, we conclude that the mercury(I) ion exists as Hg_2^{2+} in solution.

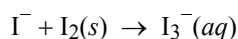
19.77 According to the following standard reduction potentials:



we see that it is easier to oxidize the iodide ion than water (because O_2 is a stronger oxidizing agent than I_2). Therefore, the anode reaction is:



The solution surrounding the anode will become brown because of the formation of the triiodide ion:



The cathode reaction will be the same as in the NaCl electrolysis. (Why?) Since OH^- is a product, the solution around the cathode will become basic which will cause the phenolphthalein indicator to turn red.

19.78 We begin by treating this like an ordinary stoichiometry problem (see Chapter 3).

Step 1: Calculate the number of moles of Mg and Ag^+ .

The number of moles of magnesium is:

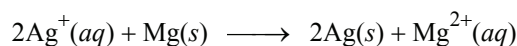
$$1.56 \text{ g Mg} \times \frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}} = 0.0642 \text{ mol Mg}$$

The number of moles of silver ion in the solution is:

$$\frac{0.100 \text{ mol Ag}^+}{1 \text{ L}} \times 0.1000 \text{ L} = 0.0100 \text{ mol Ag}^+$$

Step 2: Calculate the mass of Mg remaining by determining how much Mg reacts with Ag^+ .

The balanced equation for the reaction is:



Since you need twice as much Ag^+ compared to Mg for complete reaction, Ag^+ is the limiting reagent. The amount of Mg consumed is:

$$0.0100 \text{ mol Ag}^+ \times \frac{1 \text{ mol Mg}}{2 \text{ mol Ag}^+} = 0.00500 \text{ mol Mg}$$

The amount of magnesium remaining is:

$$(0.0642 - 0.00500) \text{ mol Mg} \times \frac{24.31 \text{ g Mg}}{1 \text{ mol Mg}} = \mathbf{1.44 \text{ g Mg}}$$

Step 3: Assuming complete reaction, calculate the concentration of Mg^{2+} ions produced.

Since the mole ratio between Mg and Mg^{2+} is 1:1, the mol of Mg^{2+} formed will equal the mol of Mg reacted. The concentration of Mg^{2+} is:

$$[\text{Mg}^{2+}]_0 = \frac{0.00500 \text{ mol}}{0.100 \text{ L}} = 0.0500 \text{ M}$$

Step 4: We can calculate the equilibrium constant for the reaction from the standard cell emf.

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 0.80 \text{ V} - (-2.37 \text{ V}) = 3.17 \text{ V}$$

We can then compute the equilibrium constant.

$$K = e^{\frac{nE_{\text{cell}}^{\circ}}{0.0257}}$$

$$K = e^{\frac{(2)(3.17)}{0.0257}} = 1 \times 10^{107}$$

Step 5: To find equilibrium concentrations of Mg^{2+} and Ag^+ , we have to solve an equilibrium problem.

Let x be the small amount of Mg^{2+} that reacts to achieve equilibrium. The concentration of Ag^+ will be $2x$ at equilibrium. Assume that essentially all Ag^+ has been reduced so that the initial concentration of Ag^+ is zero.

	$2\text{Ag}^+(aq) + \text{Mg}(s) \rightleftharpoons 2\text{Ag}(s) + \text{Mg}^{2+}(aq)$	
Initial (M):	0.0000	0.0500
Change (M):	$+2x$	$-x$
Equilibrium (M):	$2x$	$(0.0500 - x)$

$$K = \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2}$$

$$1 \times 10^{107} = \frac{(0.0500 - x)}{(2x)^2}$$

We can assume $0.0500 - x \approx 0.0500$.

$$1 \times 10^{107} \approx \frac{0.0500}{(2x)^2}$$

$$(2x)^2 = \frac{0.0500}{1 \times 10^{107}} = 0.0500 \times 10^{-107}$$

$$(2x)^2 = 5.00 \times 10^{-109} = 50.0 \times 10^{-110}$$

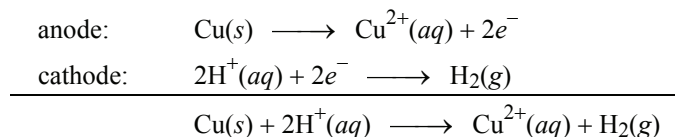
$$2x = 7 \times 10^{-55} M$$

$$[\text{Ag}^+] = 2x = 7 \times 10^{-55} M$$

$$[\text{Mg}^{2+}] = 0.0500 - x = 0.0500 M$$

19.79 Weigh the zinc and copper electrodes before operating the cell and re-weigh afterwards. The anode (Zn) should lose mass and the cathode (Cu) should gain mass.

19.80 (a) Since this is an acidic solution, the gas must be hydrogen gas from the reduction of hydrogen ion. The two electrode reactions and the overall cell reaction are:



Since 0.584 g of copper was consumed, the amount of hydrogen gas produced is:

$$0.584 \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \times \frac{1 \text{ mol H}_2}{1 \text{ mol Cu}} = 9.20 \times 10^{-3} \text{ mol H}_2$$

At STP, 1 mole of an ideal gas occupies a volume of 22.41 L. Thus, the volume of H_2 at STP is:

$$V_{\text{H}_2} = (9.20 \times 10^{-3} \text{ mol H}_2) \times \frac{22.41 \text{ L}}{1 \text{ mol}} = \mathbf{0.206 \text{ L}}$$

(b) From the current and the time, we can calculate the amount of charge:

$$1.18 \text{ A} \times \frac{1 \text{ C}}{1 \text{ A} \cdot \text{s}} \times (1.52 \times 10^3 \text{ s}) = 1.79 \times 10^3 \text{ C}$$

Since we know the charge of an electron, we can compute the number of electrons.

$$(1.79 \times 10^3 \text{ C}) \times \frac{1 e^-}{1.6022 \times 10^{-19} \text{ C}} = 1.12 \times 10^{22} e^-$$

Using the amount of copper consumed in the reaction and the fact that 2 mol of e^- are produced for every 1 mole of copper consumed, we can calculate Avogadro's number.

$$\frac{1.12 \times 10^{22} e^-}{9.20 \times 10^{-3} \text{ mol Cu}} \times \frac{1 \text{ mol Cu}}{2 \text{ mol } e^-} = \mathbf{6.09 \times 10^{23} / \text{mol } e^-}$$

In practice, Avogadro's number can be determined by electrochemical experiments like this. The charge of the electron can be found independently by Millikan's experiment.

19.81 The reaction is: $\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$

First, let's calculate the number of coulombs of electricity that must pass through the cell to deposit 60.2 g of Al.

$$60.2 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \times \frac{3 \text{ mol } e^-}{1 \text{ mol Al}} \times \frac{96500 \text{ C}}{1 \text{ mol } e^-} = 6.46 \times 10^5 \text{ C}$$

The time (in min) needed to pass this much charge is:

$$t_{\text{min}} = (6.46 \times 10^5 \text{ C}) \times \frac{1 \text{ A} \cdot \text{s}}{1 \text{ C}} \times \frac{1}{0.352 \text{ A}} \times \frac{1 \text{ min}}{60 \text{ s}} = \mathbf{3.06 \times 10^4 \text{ min}}$$

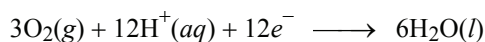
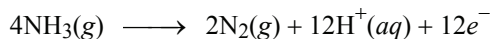
19.82 (a) We can calculate ΔG° from standard free energies of formation.

$$\Delta G^\circ = 2\Delta G_f^\circ(\text{N}_2) + 6\Delta G_f^\circ(\text{H}_2\text{O}) - [4\Delta G_f^\circ(\text{NH}_3) + 3\Delta G_f^\circ(\text{O}_2)]$$

$$\Delta G = 0 + (6)(-237.2 \text{ kJ/mol}) - [(4)(-16.6 \text{ kJ/mol}) + 0]$$

$$\Delta G = \mathbf{-1356.8 \text{ kJ/mol}}$$

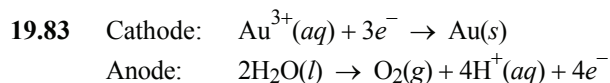
(b) The half-reactions are:



The overall reaction is a 12-electron process. We can calculate the standard cell emf from the standard free energy change, ΔG° .

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

$$E_{\text{cell}}^\circ = \frac{-\Delta G^\circ}{nF} = \frac{-\left(\frac{-1356.8 \text{ kJ}}{1 \text{ mol}} \times \frac{1000 \text{ J}}{1 \text{ kJ}}\right)}{(12)(96500 \text{ J/V} \cdot \text{mol})} = \mathbf{1.17 \text{ V}}$$



- (a) First, from the amount of gold deposited, we can calculate the moles of O_2 produced. Then, using the ideal gas equation, we can calculate the volume of O_2 .

$$9.26 \text{ g Au} \times \frac{1 \text{ mol Au}}{197.0 \text{ g Au}} \times \frac{3 \text{ mol } e^{-}}{1 \text{ mol Au}} \times \frac{1 \text{ mol O}_2}{4 \text{ mol } e^{-}} = 0.03525 \text{ mol O}_2$$

$$V_{\text{O}_2} = \frac{n_{\text{O}_2}RT}{P} = \frac{(0.03525 \text{ mol}) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (296 \text{ K})}{\left(747 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \right)} = \mathbf{0.872 \text{ L}}$$

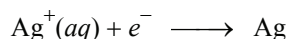
- (b) Current (I) = $\frac{\text{charge } (Q)}{t \text{ (s)}}$

$$t = 2.00 \text{ h} \times \frac{60 \text{ min}}{1 \text{ h}} \times \frac{60 \text{ s}}{1 \text{ min}} = 7.20 \times 10^3 \text{ s}$$

$$Q = 9.26 \text{ g Au} \times \frac{1 \text{ mol Au}}{197.0 \text{ g Au}} \times \frac{3 \text{ mol } e^{-}}{1 \text{ mol Au}} \times \frac{96500 \text{ C}}{1 \text{ mol } e^{-}} \times \frac{1 \text{ A} \cdot \text{s}}{1 \text{ C}} = 1.36 \times 10^4 \text{ A} \cdot \text{s}$$

$$\text{Current } (I) = \frac{\text{charge } (Q)}{t \text{ (s)}} = \frac{1.36 \times 10^4 \text{ A} \cdot \text{s}}{7.20 \times 10^3 \text{ s}} = \mathbf{1.89 \text{ A}}$$

- 19.84** The reduction of Ag^{+} to Ag metal is:



We can calculate both the moles of Ag deposited and the moles of Au deposited.

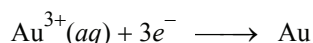
$$? \text{ mol Ag} = 2.64 \text{ g Ag} \times \frac{1 \text{ mol Ag}}{107.9 \text{ g Ag}} = 2.45 \times 10^{-2} \text{ mol Ag}$$

$$? \text{ mol Au} = 1.61 \text{ g Au} \times \frac{1 \text{ mol Au}}{197.0 \text{ g Au}} = 8.17 \times 10^{-3} \text{ mol Au}$$

We do not know the oxidation state of Au ions, so we will represent the ions as Au^{n+} . If we divide the mol of Ag by the mol of Au, we can determine the ratio of Ag^{+} reduced compared to Au^{n+} reduced.

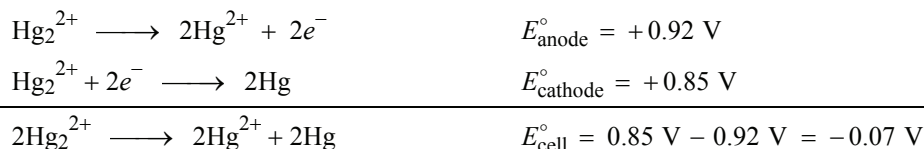
$$\frac{2.45 \times 10^{-2} \text{ mol Ag}}{8.17 \times 10^{-3} \text{ mol Au}} = 3$$

That is, the same number of electrons that reduced the Ag^{+} ions to Ag reduced only one-third the number of moles of the Au^{n+} ions to Au. Thus, each Au^{n+} required three electrons per ion for every one electron for Ag^{+} . The oxidation state for the gold ion is **+3**; the ion is Au^{3+} .

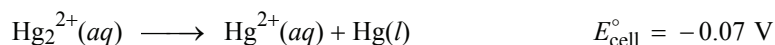


19.85 Heating the garage will melt the snow on the car which is contaminated with salt. The aqueous salt will hasten corrosion.

19.86 We reverse the first half-reaction and add it to the second to come up with the overall balanced equation



Since the standard cell potential is an intensive property,



We calculate ΔG° from E° .

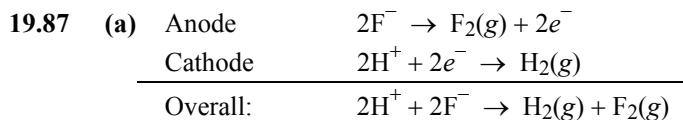
$$\Delta G^\circ = -nFE^\circ = -(1)(96500 \text{ J/V}\cdot\text{mol})(-0.07 \text{ V}) = \mathbf{6.8 \text{ kJ/mol}}$$

The corresponding equilibrium constant is:

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

We calculate K from ΔG° .

$$\begin{aligned}
 \Delta G^\circ &= -RT \ln K \\
 \ln K &= \frac{-6.8 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K})} \\
 \mathbf{K} &= \mathbf{0.064}
 \end{aligned}$$



(b) KF increases the electrical conductivity (what type of electrolyte is HF(l))? The K^+ is not reduced.

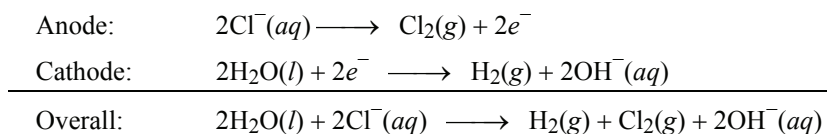
(c) Calculating the moles of F_2

$$502 \text{ A} \times 15 \text{ h} \times \frac{3600 \text{ s}}{1 \text{ h}} \times \frac{1 \text{ C}}{1 \text{ A}\cdot\text{s}} \times \frac{1 \text{ mol } e^-}{96500 \text{ C}} \times \frac{1 \text{ mol } \text{F}_2}{2 \text{ mol } e^-} = 140 \text{ mol } \text{F}_2$$

Using the ideal gas law:

$$V = \frac{nRT}{P} = \frac{(140 \text{ mol})(0.0821 \text{ L}\cdot\text{atm/K}\cdot\text{mol})(297 \text{ K})}{1.2 \text{ atm}} = \mathbf{2.8 \times 10^3 \text{ L}}$$

19.88 The reactions for the electrolysis of $\text{NaCl}(aq)$ are:



From the pH of the solution, we can calculate the OH^- concentration. From the $[\text{OH}^-]$, we can calculate the moles of OH^- produced. Then, from the moles of OH^- we can calculate the average current used.

$$\begin{aligned}\text{pH} &= 12.24 \\ \text{pOH} &= 14.00 - 12.24 = 1.76 \\ [\text{OH}^-] &= 1.74 \times 10^{-2} \text{ M}\end{aligned}$$

The moles of OH^- produced are:

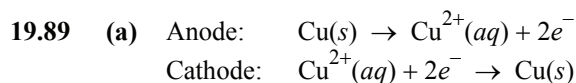
$$\frac{1.74 \times 10^{-2} \text{ mol}}{1 \text{ L}} \times 0.300 \text{ L} = 5.22 \times 10^{-3} \text{ mol OH}^-$$

From the balanced equation, it takes 1 mole of e^- to produce 1 mole of OH^- ions.

$$(5.22 \times 10^{-3} \text{ mol OH}^-) \times \frac{1 \text{ mol } e^-}{1 \text{ mol OH}^-} \times \frac{96500 \text{ C}}{1 \text{ mol } e^-} = 504 \text{ C}$$

Recall that $1 \text{ C} = 1 \text{ A}\cdot\text{s}$

$$504 \text{ C} \times \frac{1 \text{ A}\cdot\text{s}}{1 \text{ C}} \times \frac{1 \text{ min}}{60 \text{ s}} \times \frac{1}{6.00 \text{ min}} = \mathbf{1.4 \text{ A}}$$



The overall reaction is: $\text{Cu}(s) \rightarrow \text{Cu}(s)$ Cu is transferred from the anode to cathode.

(b) Consulting Table 19.1 of the text, the Zn will be oxidized, but Zn^{2+} will not be reduced at the cathode. Ag will not be oxidized at the anode.

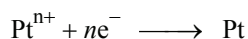
(c) The moles of Cu: $1000 \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} = 15.7 \text{ mol Cu}$

The coulombs required: $15.7 \text{ mol Cu} \times \frac{2 \text{ mol } e^-}{1 \text{ mol Cu}} \times \frac{96500 \text{ C}}{1 \text{ mol } e^-} = 3.03 \times 10^6 \text{ C}$

The time required: $? \text{ s} = \frac{3.03 \times 10^6 \text{ C}}{18.9 \text{ A}} = 1.60 \times 10^5 \text{ s}$

$$(1.60 \times 10^5 \text{ s}) \times \frac{1 \text{ hr}}{3600 \text{ s}} = \mathbf{44.4 \text{ hr}}$$

19.90 The reaction is:



Thus, we can calculate the charge of the platinum ions by realizing that n mol of e^- are required per mol of Pt formed.

The moles of Pt formed are:

$$9.09 \text{ g Pt} \times \frac{1 \text{ mol Pt}}{195.1 \text{ g Pt}} = 0.0466 \text{ mol Pt}$$

Next, calculate the charge passed in C.

$$C = 2.00 \text{ h} \times \frac{3600 \text{ s}}{1 \text{ h}} \times \frac{2.50 \text{ C}}{1 \text{ s}} = 1.80 \times 10^4 \text{ C}$$

Convert to moles of electrons.

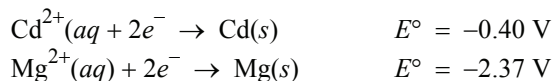
$$? \text{ mol } e^- = (1.80 \times 10^4 \text{ C}) \times \frac{1 \text{ mol } e^-}{96500 \text{ C}} = 0.187 \text{ mol } e^-$$

We now know the number of moles of electrons ($0.187 \text{ mol } e^-$) needed to produce 0.0466 mol of Pt metal. We can calculate the number of moles of electrons needed to produce 1 mole of Pt metal.

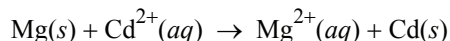
$$\frac{0.187 \text{ mol } e^-}{0.0466 \text{ mol Pt}} = 4.01 \text{ mol } e^-/\text{mol Pt}$$

Since we need 4 moles of electrons to reduce 1 mole of Pt ions, the charge on the Pt ions must be **+4**.

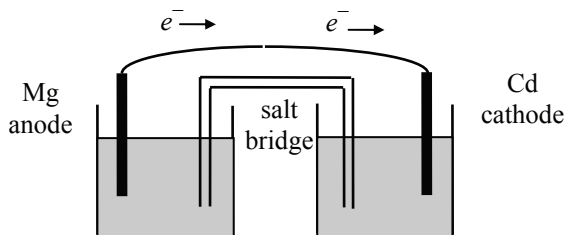
19.91 Using the standard reduction potentials found in Table 19.1



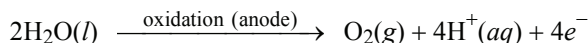
Thus Cd^{2+} will oxidize Mg so that the magnesium half-reaction occurs at the anode.



$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = -0.40 \text{ V} - (-2.37 \text{ V}) = \mathbf{1.97 \text{ V}}$$



19.92 The half-reaction for the oxidation of water to oxygen is:



Knowing that one mole of any gas at STP occupies a volume of 22.41 L , we find the number of moles of oxygen.

$$4.26 \text{ L O}_2 \times \frac{1 \text{ mol}}{22.41 \text{ L}} = 0.190 \text{ mol O}_2$$

Since four electrons are required to form one oxygen molecule, the number of electrons must be:

$$0.190 \text{ mol O}_2 \times \frac{4 \text{ mol e}^-}{1 \text{ mol O}_2} \times \frac{6.022 \times 10^{23} \text{ e}^-}{1 \text{ mol}} = 4.58 \times 10^{23} \text{ e}^-$$

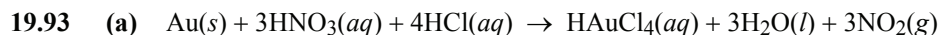
The amount of charge passing through the solution is:

$$6.00 \text{ A} \times \frac{1 \text{ C}}{1 \text{ A} \cdot \text{s}} \times \frac{3600 \text{ s}}{1 \text{ h}} \times 3.40 \text{ h} = 7.34 \times 10^4 \text{ C}$$

We find the electron charge by dividing the amount of charge by the number of electrons.

$$\frac{7.34 \times 10^4 \text{ C}}{4.58 \times 10^{23} \text{ e}^-} = \mathbf{1.60 \times 10^{-19} \text{ C/e}^-}$$

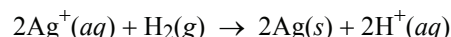
In actual fact, this sort of calculation can be used to find Avogadro's number, not the electron charge. The latter can be measured independently, and one can use this charge together with electrolytic data like the above to calculate the number of objects in one mole. See also Problem 19.80.



(b) To increase the acidity and to form the stable complex ion, AuCl_4^- .

19.94 Cells of higher voltage require very reactive oxidizing and reducing agents, which are difficult to handle. (From Table 19.1 of the text, we see that 5.92 V is the theoretical limit of a cell made up of Li^+/Li and F_2/F^- electrodes under standard-state conditions.) Batteries made up of several cells in series are easier to use.

19.95 The overall cell reaction is:



We write the Nernst equation for this system.

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln Q$$

$$E = 0.080 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{[\text{H}^+]^2}{[\text{Ag}^+]^2 P_{\text{H}_2}}$$

The measured voltage is 0.589 V, and we can find the silver ion concentration as follows:

$$0.589 \text{ V} = 0.080 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{1}{[\text{Ag}^+]^2}$$

$$\ln \frac{1}{[\text{Ag}^+]^2} = 16.42$$

$$\frac{1}{[\text{Ag}^+]^2} = 1.4 \times 10^7$$

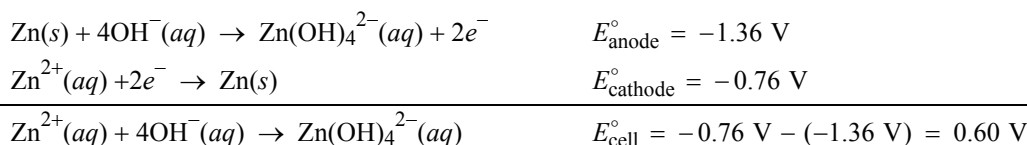
$$[\text{Ag}^+] = 2.7 \times 10^{-4} \text{ M}$$

Knowing the silver ion concentration, we can calculate the oxalate ion concentration and the solubility product constant.

$$[\text{C}_2\text{O}_4^{2-}] = \frac{1}{2}[\text{Ag}^+] = 1.35 \times 10^{-4} \text{ M}$$

$$K_{\text{sp}} = [\text{Ag}^+]^2[\text{C}_2\text{O}_4^{2-}] = (2.7 \times 10^{-4})^2(1.35 \times 10^{-4}) = \mathbf{9.8 \times 10^{-12}}$$

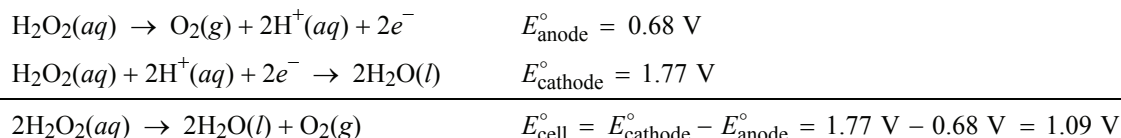
19.96 The half-reactions are:



$$E_{\text{cell}}^\circ = \frac{0.0257 \text{ V}}{n} \ln K_{\text{f}}$$

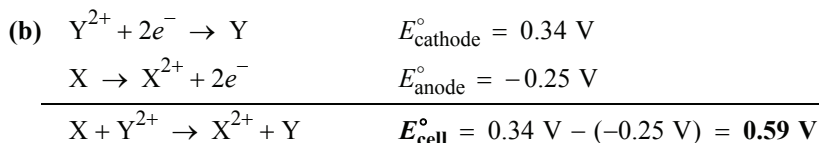
$$K_{\text{f}} = e^{\frac{nE^\circ}{0.0257}} = e^{\frac{(2)(0.60)}{0.0257}} = \mathbf{2 \times 10^{20}}$$

19.97 The half reactions are:

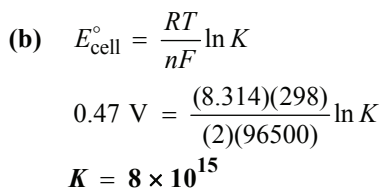
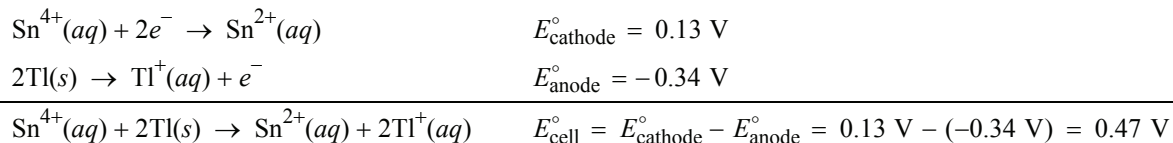


Thus, products are favored at equilibrium. H_2O_2 is not stable (it disproportionates).

19.98 (a) Since electrons flow from X to SHE, E° for X must be negative. Thus E° for Y must be positive.



19.99 (a) The half reactions are:



$$(c) \quad E = E^\circ - \frac{0.0257}{2} \ln \frac{(1.0)(10.0)^2}{(1.0)} = (0.47 - 0.0592) \text{ V} = \mathbf{0.41 \text{ V}}$$

- 19.100 (a)** Gold does not tarnish in air because the reduction potential for oxygen is insufficient to result in the oxidation of gold.

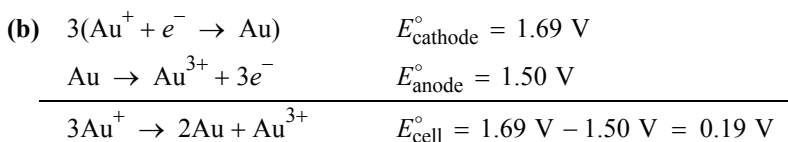


That is, $E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ < 0$, for either oxidation by O_2 to Au^+ or Au^{3+} .

$$E_{\text{cell}}^\circ = 1.23 \text{ V} - 1.50 \text{ V} < 0$$

or

$$E_{\text{cell}}^\circ = 1.23 \text{ V} - 1.69 \text{ V} < 0$$

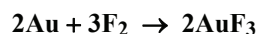


Calculating ΔG ,

$$\Delta G^\circ = -nFE^\circ = -(3)(96,500 \text{ J/V}\cdot\text{mol})(0.19 \text{ V}) = -55.0 \text{ kJ/mol}$$

For spontaneous electrochemical equations, ΔG° must be negative. Thus, **the disproportionation occurs spontaneously.**

- (c) Since the most stable oxidation state for gold is Au^{3+} , the predicted reaction is:



- 19.101** It is mercury ion in solution that is extremely hazardous. Since mercury metal does not react with hydrochloric acid (the acid in gastric juice), it does not dissolve and passes through the human body unchanged. Nitric acid (not part of human gastric juices) dissolves mercury metal (see Problem 19.113); if nitric acid were secreted by the stomach, ingestion of mercury metal would be fatal.

- 19.102** The balanced equation is: $5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \longrightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$

Calculate the amount of iron(II) in the original solution using the mole ratio from the balanced equation.

$$23.0 \text{ mL} \times \frac{0.0200 \text{ mol KMnO}_4}{1000 \text{ mL soln}} \times \frac{5 \text{ mol Fe}^{2+}}{1 \text{ mol KMnO}_4} = 0.00230 \text{ mol Fe}^{2+}$$

The concentration of iron(II) must be:

$$[\text{Fe}^{2+}] = \frac{0.00230 \text{ mol}}{0.0250 \text{ L}} = \mathbf{0.0920 \text{ M}}$$

The total iron concentration can be found by simple proportion because the same sample volume (25.0 mL) and the same KMnO_4 solution were used.

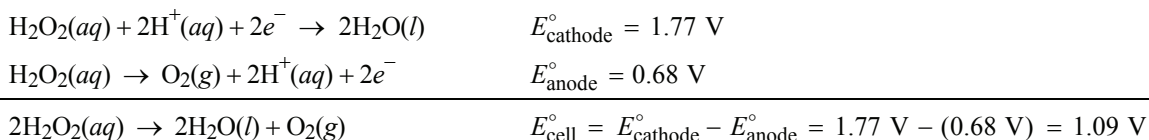
$$[\text{Fe}]_{\text{total}} = \frac{40.0 \text{ mL KMnO}_4}{23.0 \text{ mL KMnO}_4} \times 0.0920 \text{ M} = 0.160 \text{ M}$$

$$[\text{Fe}^{3+}] = [\text{Fe}]_{\text{total}} - [\text{Fe}^{2+}] = 0.0680 \text{ M}$$

Why are the two titrations with permanganate necessary in this problem?

19.103 Viewed externally, the anode looks negative because of the flow of the electrons (from $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$) toward the cathode. In solution, anions move toward the anode because they are attracted by the Zn^{2+} ions surrounding the anode.

19.104 From Table 19.1 of the text.



Because E° is positive, the decomposition is **spontaneous**.

19.105 (a) The overall reaction is: $\text{Pb} + \text{PbO}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$

$$\text{Initial mass of H}_2\text{SO}_4: 724 \text{ mL} \times \frac{1.29 \text{ g}}{1 \text{ mL}} \times 0.380 = 355 \text{ g}$$

$$\text{Final mass of H}_2\text{SO}_4: 724 \text{ mL} \times \frac{1.19 \text{ g}}{1 \text{ mL}} \times 0.260 = 224 \text{ g}$$

$$\text{Mass of H}_2\text{SO}_4 \text{ reacted} = 355 \text{ g} - 224 \text{ g} = 131 \text{ g}$$

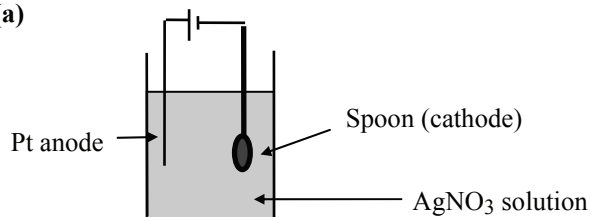
$$\text{Moles of H}_2\text{SO}_4 \text{ reacted} = 131 \text{ g} \times \frac{1 \text{ mol}}{98.09 \text{ g}} = 1.34 \text{ mol}$$

$$Q = 1.34 \text{ mol H}_2\text{SO}_4 \times \frac{2 \text{ mol } e^-}{2 \text{ mol H}_2\text{SO}_4} \times \frac{96500 \text{ C}}{1 \text{ mol } e^-} = 1.29 \times 10^5 \text{ C}$$

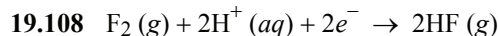
$$\text{(b) } t = \frac{Q}{I} = \frac{1.29 \times 10^5 \text{ C}}{22.4 \text{ A}} = 5.76 \times 10^3 \text{ s} = 1.60 \text{ hr}$$

19.106 (a) unchanged **(b)** unchanged **(c)** squared **(d)** doubled **(e)** doubled

19.107 (a)



$$(b) \quad t = \frac{Q}{I} = \frac{\left(0.884 \text{ g} \times \frac{1 \text{ mol}}{107.9 \text{ g}}\right) \left(\frac{96500 \text{ C}}{1 \text{ mol}}\right)}{18.5 \times 10^{-3} \text{ A}} = 4.27 \times 10^4 \text{ s} = \mathbf{11.9 \text{ hr}}$$



$$E = E^\circ - \frac{RT}{2F} \ln \frac{P_{\text{HF}}^2}{P_{\text{F}_2} [\text{H}^+]^2}$$

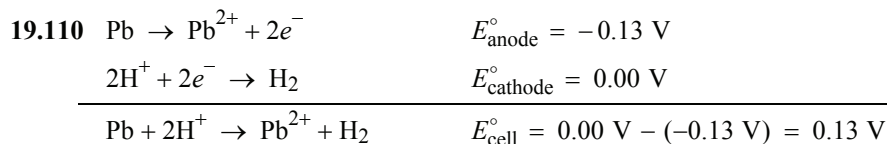
With increasing $[\text{H}^+]$, E will be larger. F_2 will become a **stronger oxidizing agent**.

19.109 Advantages:

- (a) No start-up problems, (b) much quieter, (c) no pollution (smog),
 (d) more energy efficient in the sense that when the car is not moving (for example at a traffic light), no electricity is consumed.

Disadvantages:

- (a) Driving range is more limited than automobiles,
 (b) total mass of batteries is appreciable,
 (c) production of electricity needed to charge the batteries leads to pollution.



$$\text{pH} = 1.60$$

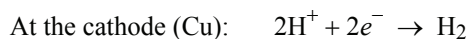
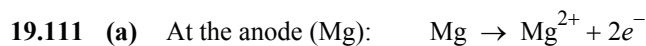
$$[\text{H}^+] = 10^{-1.60} = 0.025 \text{ M}$$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Pb}^{2+}] P_{\text{H}_2}}{[\text{H}^+]^2}$$

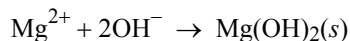
$$0 = 0.13 - \frac{0.0257 \text{ V}}{2} \ln \frac{(0.035) P_{\text{H}_2}}{0.025^2}$$

$$\frac{0.26}{0.0257} = \ln \frac{(0.035) P_{\text{H}_2}}{0.025^2}$$

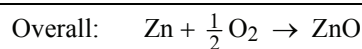
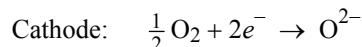
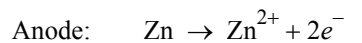
$$P_{\text{H}_2} = \mathbf{4.4 \times 10^2 \text{ atm}}$$



- (b) The solution does not turn blue.
- (c) After all the HCl has been neutralized, the white precipitate is:



- 19.112 (a) The half-reactions are:



To calculate the standard emf, we first need to calculate ΔG° for the reaction. From Appendix 3 of the text we write:

$$\Delta G^{\circ} = \Delta G_{\text{f}}^{\circ}(\text{ZnO}) - [\Delta G_{\text{f}}^{\circ}(\text{Zn}) + \frac{1}{2}\Delta G_{\text{f}}^{\circ}(\text{O}_2)]$$

$$\Delta G^{\circ} = -318.2 \text{ kJ/mol} - [0 + 0]$$

$$\Delta G^{\circ} = -318.2 \text{ kJ/mol}$$

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

$$-318.2 \times 10^3 \text{ J/mol} = -(2)(96,500 \text{ J/V}\cdot\text{mol})E^{\circ}$$

$$E^{\circ} = \mathbf{1.65 \text{ V}}$$

- (b) We use the following equation:

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

$$E = 1.65 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{1}{P_{\text{O}_2}}$$

$$E = 1.65 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{1}{0.21}$$

$$E = 1.65 \text{ V} - 0.020 \text{ V}$$

$$E = \mathbf{1.63 \text{ V}}$$

- (c) Since the free energy change represents the maximum work that can be extracted from the overall reaction, the maximum amount of energy that can be obtained from this reaction is the free energy change. To calculate the energy density, we multiply the free energy change by the number of moles of Zn present in 1 kg of Zn.

$$\text{energy density} = \frac{318.2 \text{ kJ}}{1 \text{ mol Zn}} \times \frac{1 \text{ mol Zn}}{65.39 \text{ g Zn}} \times \frac{1000 \text{ g Zn}}{1 \text{ kg Zn}} = \mathbf{4.87 \times 10^3 \text{ kJ/kg Zn}}$$

- (d) One ampere is 1 C/s. The charge drawn every second is given by nF .

$$\text{charge} = nF$$

$$2.1 \times 10^5 \text{ C} = n(96,500 \text{ C/mol } e^{-})$$

$$n = 2.2 \text{ mol } e^{-}$$

From the overall balanced reaction, we see that 4 moles of electrons will reduce 1 mole of O_2 ; therefore, the number of moles of O_2 reduced by 2.2 moles of electrons is:

$$\text{mol } O_2 = 2.2 \text{ mol } e^- \times \frac{1 \text{ mol } O_2}{4 \text{ mol } e^-} = 0.55 \text{ mol } O_2$$

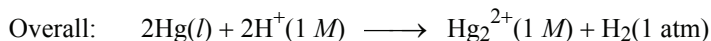
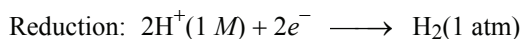
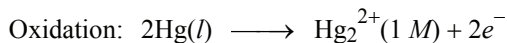
The volume of oxygen at 1.0 atm partial pressure can be obtained by using the ideal gas equation.

$$V_{O_2} = \frac{nRT}{P} = \frac{(0.55 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(298 \text{ K})}{(1.0 \text{ atm})} = 13 \text{ L}$$

Since air is 21 percent oxygen by volume, the volume of air required every second is:

$$V_{\text{air}} = 13 \text{ L } O_2 \times \frac{100\% \text{ air}}{21\% O_2} = \mathbf{62 \text{ L of air}}$$

19.113 (a) HCl: First, we write the half-reactions.



The standard emf, E° , is given by

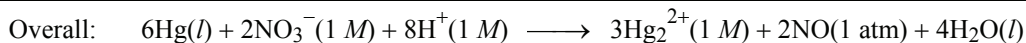
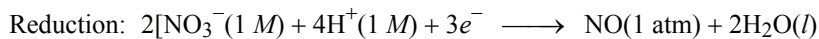
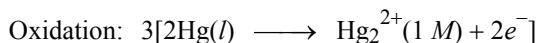
$$E^\circ = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$E^\circ = 0 - 0.85 \text{ V}$$

$$\mathbf{E^\circ = -0.85V}$$

(We omit the subscript “cell” because this reaction is not carried out in an electrochemical cell.) Since E° is negative, we conclude that mercury is not oxidized by hydrochloric acid under standard-state conditions.

(b) HNO_3 : The reactions are:



Thus,

$$E^\circ = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$E^\circ = 0.96\text{V} - 0.85\text{V}$$

$$\mathbf{E^\circ = 0.11V}$$

Since E° is positive, products are favored at equilibrium under standard-state conditions.

The test tube on the left contains HNO_3 and Hg. HNO_3 can oxidize Hg and the product NO reacts with oxygen to form the brown gas NO_2 .

19.114 We can calculate $\Delta G_{\text{rxn}}^{\circ}$ using the following equation.

$$\Delta G_{\text{rxn}}^{\circ} = \Sigma n \Delta G_f^{\circ}(\text{products}) - \Sigma m \Delta G_f^{\circ}(\text{reactants})$$

$$\Delta G_{\text{rxn}}^{\circ} = 0 + 0 - [(1)(-293.8 \text{ kJ/mol}) + 0] = 293.8 \text{ kJ/mol}$$

Next, we can calculate E° using the equation

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

We use a more accurate value for Faraday's constant.

$$293.8 \times 10^3 \text{ J/mol} = -(1)(96485.3 \text{ J/V}\cdot\text{mol})E^{\circ}$$

$$E^{\circ} = -3.05 \text{ V}$$

19.115 (a) First, we calculate the coulombs of electricity that pass through the cell.

$$0.22 \text{ A} \times \frac{1 \text{ C}}{1 \text{ A}\cdot\text{s}} \times \frac{3600 \text{ s}}{1 \text{ h}} \times 31.6 \text{ h} = 2.5 \times 10^4 \text{ C}$$

We see that for every mole of Cu formed at the cathode, 2 moles of electrons are needed. The grams of Cu produced at the cathode are:

$$? \text{ g Cu} = (2.5 \times 10^4 \text{ C}) \times \frac{1 \text{ mol } e^{-}}{96,500 \text{ C}} \times \frac{1 \text{ mol Cu}}{2 \text{ mol } e^{-}} \times \frac{63.55 \text{ g Cu}}{1 \text{ mol Cu}} = \mathbf{8.2 \text{ g Cu}}$$

(b) 8.2 g of Cu is 0.13 mole of Cu. The moles of Cu^{2+} in the original solution are:

$$0.218 \text{ L} \times \frac{1 \text{ mol Cu}^{2+}}{1 \text{ L soln}} = 0.218 \text{ mol Cu}^{2+}$$

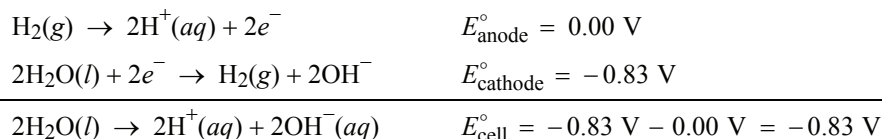
The mole ratio between Cu^{2+} and Cu is 1:1, so the moles of Cu^{2+} remaining in solution are:

$$\text{moles Cu}^{2+} \text{ remaining} = 0.218 \text{ mol} - 0.13 \text{ mol} = 0.088 \text{ mol Cu}^{2+}$$

The concentration of Cu^{2+} remaining is:

$$[\text{Cu}^{2+}] = \frac{0.088 \text{ mol Cu}^{2+}}{0.218 \text{ L soln}} = \mathbf{0.40 \text{ M}}$$

19.116 First, we need to calculate E_{cell}° , then we can calculate K from the cell potential.



We want to calculate K for the reaction: $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}^+(\text{aq}) + \text{OH}^{-}(\text{aq})$. The cell potential for this reaction will be the same as the above reaction, but the moles of electrons transferred, n , will equal one.

$$E_{\text{cell}}^{\circ} = \frac{0.0257 \text{ V}}{n} \ln K_{\text{w}}$$

$$\ln K_{\text{w}} = \frac{nE_{\text{cell}}^{\circ}}{0.0257 \text{ V}}$$

$$K_{\text{w}} = e^{\frac{nE^{\circ}}{0.0257}}$$

$$K_{\text{w}} = e^{\frac{(1)(-0.83)}{0.0257}} = e^{-32} = \mathbf{1 \times 10^{-14}}$$

19.117 H₂/O₂ Fuel Cell

- Pros:
- (1) Almost inexhaustible supplies of H₂ (from H₂O) and O₂ (from air).
 - (2) There is no pollution because the product generated is H₂O.
 - (3) The generation of electricity is not restricted by second law efficiency as in combustion reactions.
 - (4) There is no thermal pollution.

- Cons:
- (1) A large input of energy is required to generate H₂.
 - (2) Storage of hydrogen gas is problematic.
 - (3) Electrocatalysts are expensive.
 - (4) The impact of appreciable leakage of H₂ into the atmosphere is uncertain. How will H₂ affect climate and O₃ in the stratosphere?

Coal-fired Power Station

- Pros:
- (1) Large deposits of coal.
 - (2) Technology available at acceptable cost. Use of coal and oil are interchangeable.

- Cons:
- (1) The emission pollution to the environment (CO₂, NO_x, SO₂, Hg, etc.) leads to global warming, acid rain, and smog.
 - (2) Combustion reactions cause thermal pollution.
 - (3) The generation of electricity by combustion reactions is restricted by second law efficiency.
 - (4) Mining coal is unsafe and damaging to the environment.

19.118 (a) $1\text{A}\cdot\text{h} = 1\text{A} \times 3600\text{s} = 3600 \text{ C}$



Two moles of electrons are produced by 1 mole of Pb. Recall that the charge of 1 mol e^{-} is 96,500 C. We can set up the following conversions to calculate the capacity of the battery.

mol Pb \rightarrow mol e^{-} \rightarrow coulombs \rightarrow ampere hour

$$406 \text{ g Pb} \times \frac{1 \text{ mol Pb}}{207.2 \text{ g Pb}} \times \frac{2 \text{ mol } e^{-}}{1 \text{ mol Pb}} \times \frac{96500 \text{ C}}{1 \text{ mol } e^{-}} = (3.74 \times 10^5 \text{ C}) \times \frac{1 \text{ h}}{3600 \text{ s}} = \mathbf{104 \text{ A}\cdot\text{h}}$$

This ampere-hour cannot be fully realized because the concentration of H₂SO₄ keeps decreasing.

(c) $E_{\text{cell}}^{\circ} = 1.70 \text{ V} - (-0.31 \text{ V}) = \mathbf{2.01 \text{ V}}$ (From Table 19.1 of the text)

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

$$\Delta G^\circ = -(2)(96500 \text{ J/V}\cdot\text{mol})(2.01 \text{ V}) = -3.88 \times 10^5 \text{ J/mol}$$

Spontaneous as expected.

19.119 First, we start with Equation (19.3) of the text.

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

Then, we substitute into Equation (18.10) of the text.

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

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

$$E^\circ = \frac{-\Delta H^\circ + T\Delta S^\circ}{nF}$$

The reaction is: $\text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s)$

We use data in Appendix 3 of the text to calculate ΔH° and ΔS° .

$$\Delta H^\circ = \Delta H_f^\circ[\text{Cu}(s)] + \Delta H_f^\circ[\text{Zn}^{2+}(aq)] - \{\Delta H_f^\circ[\text{Zn}(s)] + \Delta H_f^\circ[\text{Cu}^{2+}(aq)]\}$$

$$\Delta H^\circ = 0 + (-152.4 \text{ kJ/mol}) - (0 + 64.39 \text{ kJ/mol}) = -216.8 \text{ kJ/mol}$$

$$\Delta S^\circ = S^\circ[\text{Cu}(s)] + S^\circ[\text{Zn}^{2+}(aq)] - \{S^\circ[\text{Zn}(s)] + S^\circ[\text{Cu}^{2+}(aq)]\}$$

$$\Delta S^\circ = 33.3 \text{ J/K}\cdot\text{mol} + (-106.48 \text{ J/K}\cdot\text{mol}) - (41.6 \text{ J/K}\cdot\text{mol} - 99.6 \text{ J/K}\cdot\text{mol}) = -15.2 \text{ J/K}\cdot\text{mol}$$

At 298 K (25°C),

$$E^\circ = \frac{-\left(\frac{-216.8 \text{ kJ}}{1 \text{ mol}} \times \frac{1000 \text{ J}}{1 \text{ kJ}}\right) + (298 \text{ K})\left(-15.2 \frac{\text{J}}{\text{K}\cdot\text{mol}}\right)}{(2)(96500 \text{ J/V}\cdot\text{mol})} = 1.100 \text{ V (carried to 3 decimal places)}$$

At 353 K (80°C),

$$E^\circ = \frac{-\left(\frac{-216.8 \text{ kJ}}{1 \text{ mol}} \times \frac{1000 \text{ J}}{1 \text{ kJ}}\right) + (353 \text{ K})\left(-15.2 \frac{\text{J}}{\text{K}\cdot\text{mol}}\right)}{(2)(96500 \text{ J/V}\cdot\text{mol})} = 1.095 \text{ V}$$

This calculation shows that E° is practically independent of temperature. In practice, E° does decrease more noticeably with temperature. The reason is that we have assumed ΔH° and ΔS° to be independent of temperature, which is technically not correct.

19.120 The surface area of an open cylinder is $2\pi rh$. The surface area of the culvert is

$$2\pi(0.900 \text{ m})(40.0 \text{ m}) \times 2 \text{ (for both sides of the iron sheet)} = 452 \text{ m}^2$$

Converting to units of cm^2 ,

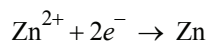
$$452 \text{ m}^2 \times \left(\frac{100 \text{ cm}}{1 \text{ m}}\right)^2 = 4.52 \times 10^6 \text{ cm}^2$$

The volume of the Zn layer is

$$0.200 \text{ mm} \times \frac{1 \text{ cm}}{10 \text{ mm}} \times (4.52 \times 10^6 \text{ cm}^2) = 9.04 \times 10^4 \text{ cm}^3$$

The mass of Zn needed is

$$(9.04 \times 10^4 \text{ cm}^3) \times \frac{7.14 \text{ g}}{1 \text{ cm}^3} = 6.45 \times 10^5 \text{ g Zn}$$



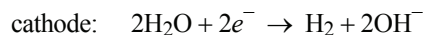
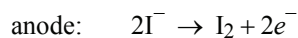
$$Q = (6.45 \times 10^5 \text{ g Zn}) \times \frac{1 \text{ mol Zn}}{65.39 \text{ g Zn}} \times \frac{2 \text{ mol } e^-}{1 \text{ mol Zn}} \times \frac{96500 \text{ C}}{1 \text{ mol } e^-} = 1.90 \times 10^9 \text{ C}$$

$$1 \text{ J} = 1 \text{ C} \times 1 \text{ V}$$

$$\text{Total energy} = \frac{(1.90 \times 10^9 \text{ C})(3.26 \text{ V})}{0.95 \leftarrow (\text{efficiency})} = 6.52 \times 10^9 \text{ J}$$

$$\text{Cost} = (6.52 \times 10^9 \text{ J}) \times \frac{1 \text{ kw}}{1000 \frac{\text{J}}{\text{s}}} \times \frac{1 \text{ h}}{3600 \text{ s}} \times \frac{\$0.12}{1 \text{ kwh}} = \mathbf{\$217}$$

19.121 (a) The half-cell reactions are:



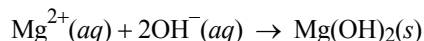
$$n_{\text{H}_2} = \frac{PV}{RT} = \frac{\left(779 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right)(1.22 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(299 \text{ K})} = 0.05094 \text{ mol}$$

$$Q = 0.05094 \text{ mol} \times \frac{2 \text{ mol } e^-}{1 \text{ mol H}_2} \times \frac{96500 \text{ C}}{1 \text{ mol } e^-} = \mathbf{9.83 \times 10^3 \text{ C}}$$

(b) $Q = It$

$$t = \frac{Q}{I} = \frac{9.83 \times 10^3 \text{ C}}{7.55 \text{ A}} \times \frac{1 \text{ A} \cdot \text{s}}{1 \text{ C}} = 1302 \text{ s} = \mathbf{21.7 \text{ min}}$$

(c) The white precipitate is **Mg(OH)₂**.



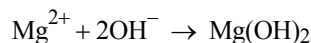
From Table 16.2 of the text, we see that Mg(OH)₂ is insoluble ($K_{\text{sp}} = 1.2 \times 10^{-11}$) From the cathode half-cell reaction,

$$n_{\text{OH}^-} = 2n_{\text{H}_2}$$

$$[\text{OH}^-] = \frac{(2)(0.05094 \text{ mol})}{0.900 \text{ L}} = 0.113 \text{ M}$$

$$[\text{Mg}^{2+}] = 0.200 \text{ M}$$

We assume that all of the OH^- ions are converted to $\text{Mg}(\text{OH})_2$ (hydroxide ion is the limiting reagent).



Because the mole ratio between OH^- and $\text{Mg}(\text{OH})_2$ is 2:1, the moles of $\text{Mg}(\text{OH})_2$ produced is 0.05094 mole.

The mass of $\text{Mg}(\text{OH})_2$ produced is:

$$0.05094 \text{ mol Mg}(\text{OH})_2 \times \frac{58.33 \text{ g Mg}(\text{OH})_2}{1 \text{ mol Mg}(\text{OH})_2} = \mathbf{2.97 \text{ g Mg}(\text{OH})_2}$$

- 19.122** It might appear that because the sum of the first two half-reactions gives Equation (3), E_3° is given by $E_1^\circ + E_2^\circ = 0.33 \text{ V}$. This is not the case, however, because emf is not an extensive property. We cannot set $E_3^\circ = E_1^\circ + E_2^\circ$. On the other hand, the Gibbs energy is an extensive property, so we can add the separate Gibbs energy changes to obtain the overall Gibbs energy change.

$$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$

Substituting the relationship $\Delta G^\circ = -nFE^\circ$, we obtain

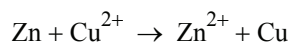
$$n_3FE_3^\circ = n_1FE_1^\circ + n_2FE_2^\circ$$

$$E_3^\circ = \frac{n_1E_1^\circ + n_2E_2^\circ}{n_3}$$

$n_1 = 2$, $n_2 = 1$, and $n_3 = 3$.

$$E_3^\circ = \frac{(2)(-0.44 \text{ V}) + (1)(0.77 \text{ V})}{3} = \mathbf{-0.037 \text{ V}}$$

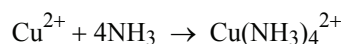
- 19.123 (a)** The reaction is:



Using the Nernst equation:

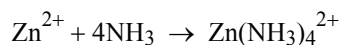
$$E = E^\circ - \frac{0.0257}{2} \ln \frac{0.20}{0.20} = \mathbf{1.10 \text{ V}}$$

- (i) If NH_3 is added to the CuSO_4 solution:



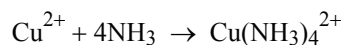
The concentration of copper ions $[\text{Cu}^{2+}]$ decreases, so the \ln term becomes greater than 1 and E decreases.

(ii) If NH_3 is added to the ZnSO_4 solution:



The concentration of zinc ions $[\text{Zn}^{2+}]$ decreases, so the \ln term becomes less than 1 and E increases.

(b) After addition of 25.0 mL of 3.0 M NH_3 ,



Assume that all Cu^{2+} becomes $\text{Cu}(\text{NH}_3)_4^{2+}$:

$$[\text{Cu}(\text{NH}_3)_4^{2+}] = 0.10 \text{ M}$$

$$[\text{NH}_3] = \frac{3.0 \text{ M}}{2} - 0.40 \text{ M} = 1.10 \text{ M}$$

$$E = E^\circ - \frac{0.0257}{2} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$0.68 \text{ V} = 1.10 \text{ V} - \frac{0.0257}{2} \ln \frac{0.20}{[\text{Cu}^{2+}]}$$

$$[\text{Cu}^{2+}] = 1.3 \times 10^{-15} \text{ M}$$

$$K_f = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = \frac{0.10}{(1.3 \times 10^{-15})(1.1)^4} = 5.3 \times 10^{13}$$

Note: this value differs somewhat from that listed in Table 16.4 of the text.

19.124 First, calculate the standard emf of the cell from the standard reduction potentials in Table 19.1 of the text. Then, calculate the equilibrium constant from the standard emf using Equation (19.5) of the text.

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = 0.34 \text{ V} - (-0.76 \text{ V}) = 1.10 \text{ V}$$

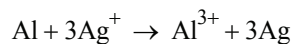
$$\ln K = \frac{nE_{\text{cell}}^\circ}{0.0257 \text{ V}}$$

$$K = e^{\frac{nE_{\text{cell}}^\circ}{0.0257 \text{ V}}} = e^{\frac{(2)(1.10 \text{ V})}{0.0257 \text{ V}}}$$

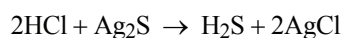
$$K = 2 \times 10^{37}$$

The very large equilibrium constant means that the oxidation of Zn by Cu^{2+} is virtually complete.

19.125 (a) From Table 19.1 of the text, we see that Al can reduce Ag^+ (applying the diagonal rule); $\text{Al} \rightarrow \text{Al}^{3+} + 3e^-$; $\text{Ag}^+ + e^- \rightarrow \text{Ag}$



- (b) A NaHCO_3 solution is basic. The surplus OH^- ions will convert Al^{3+} ions to $\text{Al}(\text{OH})_3$, which precipitates out of solution. Otherwise, the Al^{3+} ions formed can form Al_2O_3 , which increases the tenacious oxide layer over the aluminum foil, thus preventing further electrochemical reaction. (The Al_2O_3 layer is responsible for preventing aluminum beverage cans from corroding.)
- (c) Heating the solution speeds up the process and drives air (oxygen) out of solution which minimizes Al_2O_3 formation.
- (d) HCl reacts with Ag_2S .



The H_2S gas has an unpleasant odor (and in fact is poisonous). Also, this method removes Ag from the spoon as AgCl . The method described in part (a) does not.