CHAPTER 18

ELECTROCHEMISTRY

Review of Oxidation-Reduction Reactions

15. Oxidation: increase in oxidation number; loss of electrons

    Reduction: decrease in oxidation number; gain of electrons

16. See Table 4.2 in Chapter 4 of the text for rules for assigning oxidation numbers.

    a. H (+1), O (−2), N (+5)

    b. Cl (−1), Cu (+2)

    c. O (0)

    d. H (+1), O (−1)

    e. H(+1), O (−2), C (0)

    f. Ag (0)

    g. Pb (+2), O (−2), S (+6)

    h. O (−2), Pb (+4)

    i. Na (+1), O (−2), C (+3)

    j. O (−2), C (+4)

    k. $(NH_4)_2Ce(SO_4)_3$ contains NH_4^+ ions and SO_4^{2-} ions. Thus cerium exists as the Ce^{4+} ion.

    H (+1), N (−3), Ce (+4), S (+6), O (−2)

    l. O (−2), Cr (+3)

17. The species oxidized shows an increase in oxidation numbers and is called the reducing agent. The species reduced shows a decrease in oxidation numbers and is called the oxidizing agent. The pertinent oxidation numbers are listed by the substance oxidized and the substance reduced.

	Redox?	Ox. Agent	Red. Agent	Substance Oxidized	Substance Reduced
a.	Yes	H_2O	CH_4	CH_4 (C, $-4 \rightarrow +2$)	H_2O (H, $+1 \rightarrow 0$)
b.	Yes	$AgNO_3$	Cu	Cu ($0 \rightarrow +2$)	$AgNO_3$ (Ag, $+1 \rightarrow 0$)
c.	Yes	HCl	Zn	Zn ($0 \rightarrow +2$)	HCl (H, $+1 \rightarrow 0$)

d. No; there is no change in any of the oxidation numbers.

18. a. $\underset{-3\ +1}{4\ NH_3(g)} + \underset{0}{5\ O_2(g)} \rightarrow \underset{+2\ -2}{4\ NO(g)} + \underset{+1\ -2}{6\ H_2O(g)}$ oxidation numbers

    $\underset{+2\ -2}{2\ NO(g)} + \underset{0}{O_2(g)} \rightarrow \underset{+4\ -2}{2\ NO_2(g)}$

$$\underset{+4\ -2}{3\ NO_2(g)} + \underset{+1\ -2}{H_2O(l)} \rightarrow \underset{+1\ +5\ -2}{2\ HNO_3(aq)} + \underset{+2\ -2}{NO(g)}$$

All three reactions are oxidation-reduction reactions since there is a change in oxidation numbers of some of the elements in each reaction.

b. $4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$; O_2 is the oxidizing agent and NH_3 is the reducing agent.

$2\ NO + O_2 \rightarrow 2\ NO_2$; O_2 is the oxidizing agent and NO is the reducing agent.

$3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO$; NO_2 is both the oxidizing and reducing agent.

Questions

19. Electrochemistry is the study of the interchange of chemical and electrical energy. A redox (oxidation-reduction) reaction is a reaction in which one or more electrons are transferred. In a galvanic cell, a spontaneous redox reaction occurs that produces an electric current. In an electrolytic cell, electricity is used to force a nonspontaneous redox reaction to occur.

20. Mass balance indicates that we have the same number and type of atoms on both sides of the equation (so that mass is conserved). Similarly, net charge must also be conserved. We cannot have a buildup of charge on one side of the reaction or the other. In redox reactions, electrons are used to balance the net charge between reactants and products.

21. Magnesium is an alkaline earth metal; Mg will oxidize to Mg^{2+}. The oxidation state of hydrogen in HCl is +1. To be reduced, the oxidation state of H must decrease. The obvious choice for the hydrogen product is $H_2(g)$, where hydrogen has a zero oxidation state. The balanced reaction is $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$. Mg goes from the 0 to the +2 oxidation state by losing two electrons. Each H atom goes from the +1 to the 0 oxidation state by gaining one electron. Since there are two H atoms in the balanced equation, then a total of two electrons are gained by the H atoms. Hence two electrons are transferred in the balanced reaction. When the electrons are transferred directly from Mg to H^+, no work is obtained. In order to harness this reaction to do useful work, we must control the flow of electrons through a wire. This is accomplished by making a galvanic cell that separates the reduction reaction from the oxidation reaction in order to control the flow of electrons through a wire to produce a voltage.

22. Galvanic cells use spontaneous redox reactions to produce a voltage. The key is to have an overall positive E^o_{cell} value when manipulating the half-reactions. For any two half-reactions, the half-reaction with the most positive reduction potential will always be the cathode reaction. For negative potentials, this will be the half-reaction with the standard reduction potential closest to zero. The remaining half-reaction (the one with the most negative E^o_{red}) will be reversed and become the anode half-reaction ($E_{ox} = -E^o_{red}$). This combination will always yield a positive overall standard cell potential that can be used to run a galvanic cell.

23. An extensive property is one that depends directly on the amount of substance. The free-energy change for a reaction depends on whether 1 mol of product is produced or 2 mol of product is produced or 1 million mol of product is produced. This is not the case for cell

potentials, which do not depend on the amount of substance. The equation that relates ΔG to E is ΔG = −nFE. It is the n term that converts the intensive property E into the extensive property ΔG. n is the number of moles of electrons transferred in the balanced reaction that ΔG is associated with.

24. $E = E^{\circ}_{\text{cell}} - \dfrac{0.0591}{n}\log Q$

A concentration cell has the same anode and cathode contents; thus $E^{\circ}_{\text{cell}} = 0$ for a concentration cell. No matter which half-reaction you choose, the opposite half-reaction is occurring in the other cell. The driving force to produce a voltage is the −log Q term in the Nernst equation. Q is determined by the concentration of ions in the anode and cathode compartments. The larger the difference in concentrations, the larger is the −log Q term, and the larger is the voltage produced. Therefore, the driving force for concentration cells is the difference in ion concentrations between the cathode and anode compartments. When the ion concentrations are equal, Q = 1 and log Q = 0, and no voltage is produced.

25. A potential hazard when jump starting a car is the possibility for the electrolysis of $H_2O(l)$ to occur. When $H_2O(l)$ is electrolyzed, the products are the explosive gas mixture of $H_2(g)$ and $O_2(g)$. A spark produced during jump-starting a car could ignite any $H_2(g)$ and $O_2(g)$ produced. Grounding the jumper cable far from the battery minimizes the risk of a spark nearby the battery, where $H_2(g)$ and $O_2(g)$ could be collecting.

26. Metals corrode because they oxidize easily. Referencing Table 18.1, most metals are associated with negative standard reduction potentials. This means that the reverse reactions, the oxidation half-reactions, have positive oxidation potentials indicating that they oxidize fairly easily. Another key point is that the reduction of O_2 (which is a reactant in corrosion processes) has a more positive E°_{red} than most of the metals (for O_2, $E^{\circ}_{\text{red}} = 0.40$ V). This means that when O_2 is coupled with most metals, the reaction will be spontaneous since $E^{\circ}_{\text{cell}} > 0$, so corrosion occurs.

The noble metals (Ag, Au, and Pt) all have standard reduction potentials greater than that of O_2. Therefore, O_2 is not capable of oxidizing these metals at standard conditions.

Note: The standard reduction potential for $Pt \rightarrow Pt^{2+} + 2\,e^{-}$ is not in Table 18.1. As expected, its reduction potential is greater than that of O_2 ($E^{\circ}_{\text{Pt}} = 1.19$ V).

27. You need to know the identity of the metal so that you know which molar mass to use. You need to know the oxidation state of the metal ion in the salt so that the moles of electrons transferred can be determined. And finally, you need to know the amount of current and the time the current was passed through the electrolytic cell. If you know these four quantities, then the mass of metal plated out can be calculated.

28. Aluminum is found in nature as an oxide. Aluminum has a great affinity for oxygen, so it is extremely difficult to reduce the Al^{3+} ions in the oxide to pure metal. One potential way is to try to dissolve the aluminum oxide in water in order to free up the ions. Even if aluminum ions would go into solution, water would be preferentially reduced in an electrolytic cell.

Another way to mobilize the ions is to melt the aluminum oxide. This is not practical because of the very high melting point of aluminum oxide.

The key discovery was finding a solvent that would not be more easily reduced than Al^{3+} ions (as water is). The solvent discovered by Hall and Heroult (separately) was Na_3AlF_6. A mixture of Al_2O_3 and Na_3AlF_6 has a melting point much lower than that of pure Al_2O_3. Therefore, Al^{3+} ion mobility is easier to achieve, making it possible to reduce Al^{3+} to Al.

Balancing Oxidation-Reduction Equations

29. Use the method of half-reactions described in Section 18.1 of the text to balance these redox reactions. The first step always is to separate the reaction into the two half-reactions, and then to balance each half-reaction separately.

a. $3\ I^- \rightarrow I_3^- + 2e^-$

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

Adding the two balanced half-reactions so electrons cancel:

$$3\ I^-(aq) + 2\ H^+(aq) + ClO^-(aq) \rightarrow I_3^-(aq) + Cl^-(aq) + H_2O(l)$$

b. $As_2O_3 \rightarrow H_3AsO_4$
$As_2O_3 \rightarrow 2\ H_3AsO_4$
Left 3 − O; right 8 − O

$NO_3^- \rightarrow NO + 2\ H_2O$
$4\ H^+ + NO_3^- \rightarrow NO + 2\ H_2O$
$(3\ e^- + 4\ H^+ + NO_3^- \rightarrow NO + 2\ H_2O) \times 4$

Right hand side has 5 extra O. Balance the oxygen atoms first using H_2O, then balance H using H^+, and finally, balance charge using electrons. This gives:

$$(5\ H_2O + As_2O_3 \rightarrow 2\ H_3AsO_4 + 4\ H^+ + 4\ e^-) \times 3$$

Common factor is a transfer of 12 e^-. Add half-reactions so that electrons cancel.

$$12\ e^- + 16\ H^+ + 4\ NO_3^- \rightarrow 4\ NO + 8\ H_2O$$
$$15\ H_2O + 3\ As_2O_3 \rightarrow 6\ H_3AsO_4 + 12\ H^+ + 12\ e^-$$

$$7\ H_2O(l) + 4\ H^+(aq) + 3\ As_2O_3(s) + 4\ NO_3^-(aq) \rightarrow 4\ NO(g) + 6\ H_3AsO_4(aq)$$

c. $(2\ Br \rightarrow Br_2 + 2\ e^-) \times 5$

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

Common factor is a transfer of 10 e^-.

$$10\ Br^- \rightarrow 5\ Br_2 + 10\ e^-$$
$$10\ e^- + 16\ H^+ + 2\ MnO_4^- \rightarrow 2\ Mn^{2+} + 8\ H_2O$$

$$16\ H^+(aq) + 2\ MnO_4^-(aq) + 10\ Br^-(aq) \rightarrow 5\ Br_2(l) + 2\ Mn^{2+}(aq) + 8\ H_2O(l)$$

d. $CH_3OH \rightarrow CH_2O$
$(CH_3OH \rightarrow CH_2O + 2\ H^+ + 2\ e^-) \times 3$

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

Common factor is a transfer of 6 e^-.

$$3\ CH_3OH \rightarrow 3\ CH_2O + 6\ H^+ + 6\ e^-$$
$$6\ e^- + 14\ H^+ + Cr_2O_7^{2-} \rightarrow 2\ Cr^{3+} + 7\ H_2O$$

$$8\ H^+(aq) + 3\ CH_3OH(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2\ Cr^{3+}(aq) + 3\ CH_2O(aq) + 7\ H_2O(l)$$

30. a. $(Cu \rightarrow Cu^{2+} + 2\ e^-) \times 3$ $NO_3^- \rightarrow NO + 2\ H_2O$

$(3\ e^- + 4\ H^+ + NO_3^- \rightarrow NO + 2\ H_2O) \times 2$

Adding the two balanced half-reactions so that electrons cancel:

$$3\ Cu \rightarrow 3\ Cu^{2+} + 6\ e^-$$
$$6\ e^- + 8\ H^+ + 2\ NO_3^- \rightarrow 2\ NO + 4\ H_2O$$

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

b. $(2\ Cl^- \rightarrow Cl_2 + 2\ e^-) \times 3$ $Cr_2O_7^{2-} \rightarrow 2\ Cr^{3+} + 7\ H_2O$

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

Add the two half-reactions with six electrons transferred:

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

$$14\ H^+(aq) + Cr_2O_7^{2-}(aq) + 6\ Cl^-(aq) \rightarrow 3\ Cl_2(g) + 2\ Cr^{3+}(aq) + 7\ H_2O(l)$$

c. $Pb \rightarrow PbSO_4$ $PbO_2 \rightarrow PbSO_4$

$Pb + H_2SO_4 \rightarrow PbSO_4 + 2\ H^+$ $PbO_2 + H_2SO_4 \rightarrow PbSO_4 + 2\ H_2O$

$Pb + H_2SO_4 \rightarrow PbSO_4 + 2\ H^+ + 2\ e^-$ $2\ e^- + 2\ H^+ + PbO_2 + H_2SO_4 \rightarrow PbSO_4 + 2\ H_2O$

Add the two half-reactions with two electrons transferred:

$$2\ e^- + 2\ H^+ + PbO_2 + H_2SO_4 \rightarrow PbSO_4 + 2\ H_2O$$
$$Pb + H_2SO_4 \rightarrow PbSO_4 + 2\ H^+ + 2\ e^-$$

$$Pb(s) + 2\ H_2SO_4(aq) + PbO_2(s) \rightarrow 2\ PbSO_4(s) + 2\ H_2O(l)$$

This is the reaction that occurs in an automobile lead-storage battery.

d. $Mn^{2+} \rightarrow MnO_4^-$

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

$NaBiO_3 \rightarrow Bi^{3+} + Na^+$

$6\ H^+ + NaBiO_3 \rightarrow Bi^{3+} + Na^+ + 3\ H_2O$

$(2\ e^- + 6\ H^+ + NaBiO_3 \rightarrow Bi^{3+} + Na^+ + 3\ H_2O) \times 5$

$$8\ H_2O + 2\ Mn^{2+} \rightarrow 2\ MnO_4^- + 16\ H^+ + 10\ e^-$$
$$10\ e^- + 30\ H^+ + 5\ NaBiO_3 \rightarrow 5\ Bi^{3+} + 5\ Na^+ + 15\ H_2O$$

$$8\ H_2O + 30\ H^+ + 2\ Mn^{2+} + 5\ NaBiO_3 \rightarrow 2\ MnO_4^- + 5\ Bi^{3+} + 5\ Na^+ + 15\ H_2O + 16\ H^+$$

Simplifying:

$$14\ H^+(aq) + 2\ Mn^{2+}(aq) + 5\ NaBiO_3(s) \rightarrow 2\ MnO_4^-(aq) + 5\ Bi^{3+}(aq) + 5\ Na^+(aq) + 7\ H_2O(l)$$

e. $H_3AsO_4 \rightarrow AsH_3$ $(Zn \rightarrow Zn^{2+} + 2\ e^-) \times 4$

$H_3AsO_4 \rightarrow AsH_3 + 4\ H_2O$

$8\ e^- + 8\ H^+ + H_3AsO_4 \rightarrow AsH_3 + 4\ H_2O$

$$\begin{array}{r} 8\ e^- + 8\ H^+ + H_3AsO_4 \rightarrow AsH_3 + 4\ H_2O \\ 4\ Zn \rightarrow 4\ Zn^{2+} + 8\ e^- \\ \hline 8\ H^+(aq) + H_3AsO_4(aq) + 4\ Zn(s) \rightarrow 4\ Zn^{2+}(aq) + AsH_3(g) + 4\ H_2O(l) \end{array}$$

31. Use the same method as with acidic solutions. After the final balanced equation, convert H^+ to OH^- as described in Section 18.1 of the text. The extra step involves converting H^+ into H_2O by adding equal moles of OH^- to each side of the reaction. This converts the reaction to a basic solution while still keeping it balanced.

a. $Al \rightarrow Al(OH)_4^-$ $MnO_4^- \rightarrow MnO_2$

$4\ H_2O + Al \rightarrow Al(OH)_4^- + 4\ H^+$ $3\ e^- + 4\ H^+ + MnO_4^- \rightarrow MnO_2 + 2\ H_2O$

$4\ H_2O + Al \rightarrow Al(OH)_4^- + 4\ H^+ + 3\ e^-$

$$\begin{array}{r} 4\ H_2O + Al \rightarrow Al(OH)_4^- + 4\ H^+ + 3\ e^- \\ 3\ e^- + 4\ H^+ + MnO_4^- \rightarrow MnO_2 + 2\ H_2O \\ \hline 2\ H_2O(l) + Al(s) + MnO_4^-(aq) \rightarrow Al(OH)_4^-(aq) + MnO_2(s) \end{array}$$

H^+ doesn't appear in the final balanced reaction, so we are done.

b. $Cl_2 \rightarrow Cl^-$ $Cl_2 \rightarrow OCl^-$

$2\ e^- + Cl_2 \rightarrow 2\ Cl^-$ $2\ H_2O + Cl_2 \rightarrow 2\ OCl^- + 4\ H^+ + 2\ e^-$

$$\begin{array}{r} 2\ e^- + Cl_2 \rightarrow 2\ Cl^- \\ 2\ H_2O + Cl_2 \rightarrow 2\ OCl^- + 4\ H^+ + 2\ e^- \\ \hline 2\ H_2O + 2\ Cl_2 \rightarrow 2\ Cl^- + 2\ OCl^- + 4\ H^+ \end{array}$$

Now convert to a basic solution. Add 4 OH^- to both sides of the equation. The 4 OH^- will react with the 4 H^+ on the product side to give 4 H_2O. After this step, cancel identical species on both sides (2 H_2O). Applying these steps gives: $4\ OH^- + 2\ Cl_2 \rightarrow 2\ Cl^- + 2\ OCl^- + 2\ H_2O$, which can be further simplified to:

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

c. $NO_2^- \rightarrow NH_3$ $Al \rightarrow AlO_2^-$

$6\ e^- + 7\ H^+ + NO_2^- \rightarrow NH_3 + 2\ H_2O$ $(2\ H_2O + Al \rightarrow AlO_2^- + 4\ H^+ + 3\ e^-) \times 2$

Common factor is a transfer of 6 e^-.

$$\begin{array}{r} 6e^- + 7\ H^+ + NO_2^- \rightarrow NH_3 + 2\ H_2O \\ 4\ H_2O + 2\ Al \rightarrow 2\ AlO_2^- + 8\ H^+ + 6\ e^- \\ \hline OH^- + 2\ H_2O + NO_2^- + 2\ Al \rightarrow NH_3 + 2\ AlO_2^- + H^+ + OH^- \end{array}$$

Reducing gives $OH^-(aq) + H_2O(l) + NO_2^-(aq) + 2\ Al(s) \rightarrow NH_3(g) + 2\ AlO_2^-(aq)$.

32. a. $Cr \rightarrow Cr(OH)_3$

$3\ H_2O + Cr \rightarrow Cr(OH)_3 + 3\ H^+ + 3\ e^-$

$CrO_4^{2-} \rightarrow Cr(OH)_3$

$3\ e^- + 5\ H^+ + CrO_4^{2-} \rightarrow Cr(OH)_3 + H_2O$

$$\begin{array}{r} 3\ H_2O + Cr \rightarrow Cr(OH)_3 + 3\ H^+ + 3\ e^- \\ 3\ e^- + 5\ H^+ + CrO_4^{2-} \rightarrow Cr(OH)_3 + H_2O \\ \hline 2\ OH^- + 2\ H^+ + 2\ H_2O + Cr + CrO_4^{2-} \rightarrow 2\ Cr(OH)_3 + 2\ OH^- \end{array}$$

Two OH^- were added above to each side to convert to a basic solution. The two OH^- react with the 2 H^+ on the reactant side to produce 2 H_2O. The overall balanced equation is:

$$4\ H_2O(l) + Cr(s) + CrO_4^{2-}(aq) \rightarrow 2\ Cr(OH)_3(s) + 2\ OH^-(aq)$$

b. $S^{2-} \rightarrow S$

$(S^{2-} \rightarrow S + 2\ e^-) \times 5$

$MnO_4^- \rightarrow MnS$

$MnO_4^- + S^{2-} \rightarrow MnS$

$(5\ e^- + 8\ H^+ + MnO_4^- + S^{2-} \rightarrow MnS + 4\ H_2O) \times 2$

Common factor is a transfer of 10 e^-.

$$\begin{array}{r} 5\ S^{2-} \rightarrow 5\ S + 10\ e^- \\ 10\ e^- + 16\ H^+ + 2\ MnO_4^- + 2\ S^{2-} \rightarrow 2\ MnS + 8\ H_2O \\ \hline 16\ OH^- + 16\ H^+ + 7\ S^{2-} + 2\ MnO_4^- \rightarrow 5\ S + 2\ MnS + 8\ H_2O + 16\ OH^- \end{array}$$

$16\ H_2O + 7\ S^{2-} + 2\ MnO_4^- \rightarrow 5\ S + 2\ MnS + 8\ H_2O + 16\ OH^-$

Reducing gives $8\ H_2O(l) + 7\ S^{2-}(aq) + 2\ MnO_4^-(aq) \rightarrow 5\ S(s) + 2\ MnS(s) + 16\ OH^-(aq)$.

c. $CN^- \rightarrow CNO^-$

$(H_2O + CN^- \rightarrow CNO^- + 2\ H^+ + 2\ e^-) \times 3$

$MnO_4^- \rightarrow MnO_2$

$(3\ e^- + 4\ H^+ + MnO_4^- \rightarrow MnO_2 + 2\ H_2O) \times 2$

Common factor is a transfer of 6 electrons.

$$\begin{array}{r} 3\ H_2O + 3\ CN^- \rightarrow 3\ CNO^- + 6\ H^+ + 6\ e^- \\ 6\ e^- + 8\ H^+ + 2\ MnO_4^- \rightarrow 2\ MnO_2 + 4\ H_2O \\ \hline 2\ OH^- + 2\ H^+ + 3\ CN^- + 2\ MnO_4^- \rightarrow 3\ CNO^- + 2\ MnO_2 + H_2O + 2\ OH^- \end{array}$$

Reducing gives:

$$H_2O(l) + 3\ CN^-(aq) + 2\ MnO_4^-(aq) \rightarrow 3\ CNO^-(aq) + 2\ MnO_2(s) + 2\ OH^-(aq)$$

33. $NaCl + H_2SO_4 + MnO_2 \rightarrow Na_2SO_4 + MnCl_2 + Cl_2 + H_2O$

We could balance this reaction by the half-reaction method, which is generally the preferred method. However, sometimes a redox reaction is not so complicated and thus balancing by inspection is a possibility. Let's try inspection here. To balance Cl^-, we need 4 NaCl:

$$4\ NaCl + H_2SO_4 + MnO_2 \rightarrow Na_2SO_4 + MnCl_2 + Cl_2 + H_2O$$

Balance the Na^+ and SO_4^{2-} ions next:

$$4\ NaCl + 2\ H_2SO_4 + MnO_2 \rightarrow 2\ Na_2SO_4 + MnCl_2 + Cl_2 + H_2O$$

On the left side: 4 H and 10 O; on the right side: 8 O not counting H_2O

We need 2 H_2O on the right side to balance H and O:

$$4\ NaCl(aq) + 2\ H_2SO_4(aq) + MnO_2(s) \rightarrow 2\ Na_2SO_4(aq) + MnCl_2(aq) + Cl_2(g) + 2\ H_2O(l)$$

34. $Au + HNO_3 + HCl \rightarrow AuCl_4^- + NO$

Only deal with ions that are reacting (omit H^+): $Au + NO_3^- + Cl^- \rightarrow AuCl_4^- + NO$

The balanced half-reactions are:

$Au + 4\ Cl^- \rightarrow AuCl_4^- + 3\ e^-$ $\qquad$ $3\ e^- + 4\ H^+ + NO_3^- \rightarrow NO + 2\ H_2O$

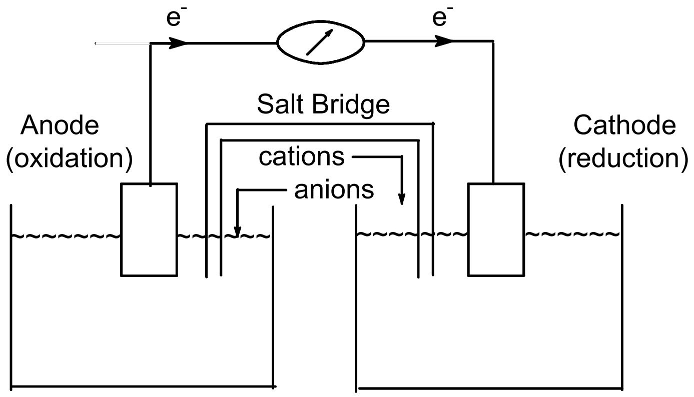
Adding the two balanced half-reactions:

$$Au(s) + 4\ Cl^-(aq) + 4\ H^+(aq) + NO_3^-(aq) \rightarrow AuCl_4^-(aq) + NO(g) + 2\ H_2O(l)$$

Exercises

Galvanic Cells, Cell Potentials, Standard Reduction Potentials, and Free Energy

35. A typical galvanic cell diagram is:



The diagram for all cells will look like this. The contents of each half-cell compartment will be identified for each reaction, with all solute concentrations at 1.0 *M* and all gases at 1.0 atm. For Exercises 35 and 36, the flow of ions through the salt bridge was not asked for in the questions. If asked, however, cations always flow into the cathode compartment, and anions always flow into the anode compartment. This is required to keep each compartment electrically neutral.

a. Table 18.1 of the text lists balanced reduction half-reactions for many substances. For this overall reaction, we need the Cl_2 to Cl^- reduction half-reaction and the Cr^{3+} to $Cr_2O_7^{2-}$ oxidation half-reaction. Manipulating these two half-reactions gives the overall balanced equation.

$$(Cl_2 + 2\,e^- \rightarrow 2\,Cl^-) \times 3$$
$$7\,H_2O + 2\,Cr^{3+} \rightarrow Cr_2O_7^{2-} + 14\,H^+ + 6\,e^-$$
$$\overline{7\,H_2O(l) + 2\,Cr^{3+}(aq) + 3\,Cl_2(g) \rightarrow Cr_2O_7^{2-}(aq) + 6\,Cl^-(aq) + 14\,H^+(aq)}$$

The contents of each compartment are:

Cathode: Pt electrode; Cl_2 bubbled into solution, Cl^- in solution

Anode: Pt electrode; Cr^{3+}, H^+, and $Cr_2O_7^{2-}$ in solution

We need a nonreactive metal to use as the electrode in each case, since all the reactants and products are in solution. Pt is a common choice. Another possibility is graphite.

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

Cathode: Cu electrode; Cu^{2+} in solution; anode: Mg electrode; Mg^{2+} in solution

36. Reference Exercise 35 for a typical galvanic cell diagram. The contents of each half-cell compartment are identified below with all solute concentrations at 1.0 *M* and all gases at 1.0 atm.

a. Reference Table 18.1 for the balanced half-reactions.

$$5\,e^- + 6\,H^+ + IO_3^- \rightarrow 1/2\,I_2 + 3\,H_2O$$
$$(Fe^{2+} \rightarrow Fe^{3+} + e^-) \times 5$$
$$\overline{6\,H^+ + IO_3^- + 5\,Fe^{2+} \rightarrow 5\,Fe^{3+} + 1/2\,I_2 + 3\,H_2O}$$

or $12\,H^+(aq) + 2\,IO_3^-(aq) + 10\,Fe^{2+}(aq) \rightarrow 10\,Fe^{3+}(aq) + I_2(aq) + 6\,H_2O(l)$

Cathode: Pt electrode; IO_3^-, I_2 and H_2SO_4 (H^+ source) in solution.

Note: $I_2(s)$ would make a poor electrode since it sublimes.

Anode: Pt electrode; Fe^{2+} and Fe^{3+} in solution b.

$$
\begin{array}{l}
(\mathrm{Ag^+ + e^- \rightarrow Ag}) \times 2 \\
\qquad\quad \mathrm{Zn \rightarrow Zn^{2+} + 2\ e^{-}} \\
\hline
\mathrm{Zn(s) + 2\ Ag^+(aq) \rightarrow 2\ Ag(s) + Zn^{2+}(aq)}
\end{array}
$$

Cathode: Ag electrode; Ag^+ in solution; anode: Zn electrode; Zn^{2+} in solution

37. To determine E° for the overall cell reaction, we must add the standard reduction potential to the standard oxidation potential $(E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox})$. Reference Table 18.1 for values of standard reduction potentials. Remember that $E^\circ_{ox} = -E^\circ_{red}$ and that standard potentials are <u>not</u> multiplied by the integer used to obtain the overall balanced equation.

35a. $E^\circ_{cell} = E^\circ_{Cl_2 \rightarrow Cl^-} + E^\circ_{Cr^{3+} \rightarrow Cr_2O_7^{2-}} = 1.36\ V + (-1.33\ V) = 0.03\ V$

35b. $E^\circ_{cell} = E^\circ_{Cu^{2+} \rightarrow Cu} + E^\circ_{Mg \rightarrow Mg^{2+}} = 0.34\ V + 2.37\ V = 2.71\ V$

38. 36a. $E^\circ_{cell} = E^\circ_{IO_3^- \rightarrow I_2} + E^\circ_{Fe^{2+} \rightarrow Fe^{3+}} = 1.20\ V + (-0.77\ V) = 0.43\ V$

36b. $E^\circ_{cell} = E^\circ_{Ag^+ \rightarrow Ag} + E^\circ_{Zn \rightarrow Zn^{2+}} = 0.80\ V + 0.76\ V = 1.56\ V$

39. Reference Exercise 35 for a typical galvanic cell design. The contents of each half-cell compartment are identified below with all solute concentrations at 1.0 *M* and all gases at 1.0 atm. For each pair of half-reactions, the half-reaction with the largest (most positive) standard reduction potential will be the cathode reaction, and the half-reaction with the smallest (most negative) reduction potential will be reversed to become the anode reaction. Only this combination gives a spontaneous overall reaction, i.e., a reaction with a positive overall standard cell potential. Note that in a galvanic cell as illustrated in Exercise 35, the cations in the salt bridge migrate to the cathode, and the anions migrate to the anode.

a.

$$
\begin{array}{ll}
\mathrm{Cl_2 + 2\ e^- \rightarrow 2\ Cl^-} & E^\circ = 1.36\ \mathrm{V} \\
\qquad \mathrm{2\ Br^- \rightarrow Br_2 + 2\ e^-} & -E^\circ = -1.09\ \mathrm{V} \\
\hline
\mathrm{Cl_2(g) + 2\ Br^-(aq) \rightarrow Br_2(aq) + 2\ Cl^-(aq)} & E^\circ_{cell} = 0.27\ \mathrm{V}
\end{array}
$$

The contents of each compartment are:

Cathode: Pt electrode; $Cl_2(g)$ bubbled in, Cl^- in solution

Anode: Pt electrode; Br_2 and Br^- in solution

b.

$$
\begin{array}{ll}
(\mathrm{2\ e^- + 2\ H^+ + IO_4^- \rightarrow IO_3^- + H_2O}) \times 5 & E^\circ = 1.60\ \mathrm{V} \\
\quad (\mathrm{4\ H_2O + Mn^{2+} \rightarrow MnO_4^- + 8\ H^+ + 5\ e^-}) \times 2 & -E^\circ = -1.51\ \mathrm{V} \\
\hline
\mathrm{10\ H^+ + 5\ IO_4^- + 8\ H_2O + 2\ Mn^{2+} \rightarrow 5\ IO_3^- + 5\ H_2O + 2\ MnO_4^- + 16\ H^+} & E^\circ_{cell} = 0.09\ \mathrm{V}
\end{array}
$$

This simplifies to:

$$3\ H_2O(l) + 5\ IO_4^-(aq) + 2\ Mn^{2+}(aq) \rightarrow 5\ IO_3^-\ (aq) + 2\ MnO_4^-\ (aq) + 6\ H^+(aq) \qquad E^o_{cell} = 0.09\ V$$

Cathode: Pt electrode; IO_4^-, IO_3^-, and H_2SO_4 (as a source of H^+) in solution

Anode: Pt electrode; Mn^{2+}, MnO_4^- and H_2SO_4 in solution

40. Reference Exercise 35 for a typical galvanic cell design. The contents of each half-cell compartment are identified below, with all solute concentrations at 1.0 *M* and all gases at 1.0 atm.

a. $$\begin{array}{lr} H_2O_2 + 2\ H^+ + 2\ e^- \rightarrow 2\ H_2O & E° = 1.78\ V \\ H_2O_2 \rightarrow O_2 + 2\ H^+ + 2\ e^- & -E° = -0.68\ V \\ \hline 2\ H_2O_2(aq) \rightarrow 2\ H_2O(l) + O_2(g) & E^o_{cell} = 1.10\ V \end{array}$$

Cathode: Pt electrode; H_2O_2 and H^+ in solution

Anode: Pt electrode; $O_2(g)$ bubbled in, H_2O_2 and H^+ in solution

b. $$\begin{array}{lr} (Fe^{3+} + 3\ e^- \rightarrow Fe) \times 2 & E° = -0.036\ V \\ (Mn \rightarrow Mn^{2+} + 2\ e^-) \times 3 & -E° = 1.18\ V \\ \hline 2\ Fe^{3+}(aq) + 3\ Mn(s) \rightarrow 2\ Fe(s) + 3\ Mn^{2+}(aq) & E^o_{cell} = 1.14\ V \end{array}$$

Cathode: Fe electrode; Fe^{3+} in solution; anode: Mn electrode; Mn^{2+} in solution

41. In standard line notation, the anode is listed first, and the cathode is listed last. A double line separates the two compartments. By convention, the electrodes are on the ends with all solutes and gases toward the middle. A single line is used to indicate a phase change. We also included all concentrations.

35a. Pt | Cr^{3+} (1.0 *M*), $Cr_2O_7^{2-}$ (1.0 *M*), H^+ (1.0 *M*) || Cl_2 (1.0 atm) | Cl^- (1.0 *M*) | Pt

35b. Mg | Mg^{2+} (1.0 *M*) || Cu^{2+} (1.0 *M*) | Cu

39a. Pt | Br^- (1.0 *M*), Br_2 (1.0 *M*) || Cl_2 (1.0 atm) | Cl^- (1.0 *M*) | Pt

39b. Pt | Mn^{2+} (1.0 *M*), MnO_4^- (1.0 *M*), H^+ (1.0 *M*) || IO_4^- (1.0 *M*), H^+ (1.0 *M*), IO_3^- (1.0 *M*) | Pt

42. 36a. Pt | Fe^{2+} (1.0 *M*), Fe^{3+} (1.0 *M*) || IO_3^- (1.0 *M*), H^+ (1.0 *M*), I_2 (1.0 *M*) | Pt

36b. Zn | Zn^{2+} (1.0 *M*) || Ag^+ (1.0 *M*) | Ag

40a. Pt | H_2O_2 (1.0 *M*), H^+ (1.0 *M*) | O_2 (1.0 atm)|| H_2O_2 (1.0 *M*), H^+ (1.0 *M*) | Pt

40b. Mn | Mn^{2+} (1.0 *M*) || Fe^{3+} (1.0 *M*) | Fe

43. Locate the pertinent half-reactions in Table 18.1, and then figure which combination will give a positive standard cell potential. In all cases, the anode compartment contains the species with the smallest standard reduction potential. For part a, the copper compartment is the anode, and in part b, the cadmium compartment is the anode.

a.
$Au^{3+} + 3\ e^- \rightarrow Au$ $\quad E° = 1.50\ V$
$(Cu^+ \rightarrow Cu^{2+} + e^-) \times 3$ $\quad -E° = -0.16\ V$

$Au^{3+}(aq) + 3\ Cu^+(aq) \rightarrow Au(s) + 3\ Cu^{2+}(aq)$ $\quad E^o_{cell} = 1.34\ V$

b.
$(VO_2^+ + 2\ H^+ + e^- \rightarrow VO^{2+} + H_2O) \times 2$ $\quad E° = 1.00\ V$
$Cd \rightarrow Cd^{2+} + 2e^-$ $\quad -E° = 0.40\ V$

$2\ VO_2^+(aq) + 4\ H^+(aq) + Cd(s) \rightarrow 2\ VO^{2+}(aq) + 2\ H_2O(l) + Cd^{2+}(aq)$ $\quad E^o_{cell} = 1.40\ V$

44. a.
$(H_2O_2 + 2\ H^+ + 2\ e^- \rightarrow 2\ H_2O) \times 3$ $\quad E° = 1.78\ V$
$2\ Cr^{3+} + 7\ H_2O \rightarrow Cr_2O_7^{2-} + 14\ H^+ + 6\ e^-$ $\quad -E° = -1.33\ V$

$3\ H_2O_2(aq) + 2\ Cr^{3+}(aq) + H_2O(l) \rightarrow Cr_2O_7^{2-}(aq) + 8\ H^+(aq)$ $\quad E^o_{cell} = 0.45\ V$

b.
$(2\ H^+ + 2\ e^- \rightarrow H_2) \times 3$ $\quad E° = 0.00\ V$
$(Al \rightarrow Al^{3+} + 3\ e^-) \times 2$ $\quad -E° = 1.66\ V$

$6\ H^+(aq) + 2\ Al(s) \rightarrow 3\ H_2(g) + 2\ Al^{3+}(aq)$ $\quad E^o_{cell} = 1.66\ V$

45. a.
$(5\ e^- + 8\ H^+ + MnO_4^- \rightarrow Mn^{2+} + 4\ H_2O) \times 2$ $\quad E° = 1.51\ V$
$(2\ I^- \rightarrow I_2 + 2\ e^-) \times 5$ $\quad -E° = -0.54\ V$

$16\ H^+(aq) + 2\ MnO_4^-(aq) + 10\ I^-(aq) \rightarrow 5\ I_2(aq) + 2\ Mn^{2+}(aq) + 8\ H_2O(l)$ $\quad E^o_{cell} = 0.97\ V$

This reaction is spontaneous at standard conditions because $E^o_{cell} > 0$.

b.
$(5\ e^- + 8\ H^+ + MnO_4^- \rightarrow Mn^{2+} + 4\ H_2O) \times 2$ $\quad E° = 1.51\ V$
$(2\ F^- \rightarrow F_2 + 2\ e^-) \times 5$ $\quad -E° = -2.87\ V$

$16\ H^+(aq) + 2\ MnO_4^-(aq) + 10\ F^-(aq) \rightarrow 5\ F_2(aq) + 2\ Mn^{2+}(aq) + 8\ H_2O(l)$ $\quad E^o_{cell} = -1.36\ V$

This reaction is not spontaneous at standard conditions because $E^o_{cell} < 0$.

46. a.
$H_2 \rightarrow 2H^+ + 2\ e^-$ $\quad E° = 0.00\ V$
$H_2 + 2\ e^- \rightarrow 2H^-$ $\quad -E° = -2.23\ V$

$2H_2(g) \rightarrow 2H^+(aq) + 2\ H^-(aq)$ $\quad E^o_{cell} = -2.23\ V$ Not spontaneous

b. $Au^{3+} + 3\ e^- \rightarrow Au$ $E° = 1.50\ V$

$(Ag \rightarrow Ag^+ + e^-) \times 3$ $-E° = -0.80\ V$

$Au^{3+}(aq) + 3\ Ag(s) \rightarrow Au(s) + 3\ Ag^+(aq)$ $E^o_{cell} = 0.70\ V$

Spontaneous

47. $Cl_2 + 2\ e^- \rightarrow 2\ Cl^-$ $E° = 1.36\ V$

$(ClO_2^- \rightarrow ClO_2 + e^-) \times 2$ $-E° = -0.954\ V$

$2\ ClO_2^-(aq) + Cl_2(g) \rightarrow 2\ ClO_2(aq) + 2\ Cl^-(aq)$ $E^o_{cell} = 0.41\ V = 0.41\ J/C$

$\Delta G° = -nFE^o_{cell} = -(2\ mol\ e^-)(96{,}485\ C/mol\ e^-)(0.41\ J/C) = -7.9 \times 10^4\ J = -79\ kJ$

48. a. $(4\ H^+ + NO_3^- + 3\ e^- \rightarrow NO + 2\ H_2O) \times 2$ $E° = 0.96\ V$

$(Mn \rightarrow Mn^{2+} + 2\ e^-) \times 3$ $-E° = 1.18\ V$

$3\ Mn(s) + 8\ H^+(aq) + 2\ NO_3^-(aq) \rightarrow 2\ NO(g) + 4\ H_2O(l) + 3\ Mn^{2+}(aq)$ $E^o_{cell} = 2.14\ V$

$(2\ e^- + 2\ H^+ + IO_4^- \rightarrow IO_3^- + H_2O) \times 5$ $E° = 1.60\ V$

$(Mn^{2+} + 4\ H_2O \rightarrow MnO_4^- + 8\ H^+ + 5\ e^-) \times 2$ $-E° = -1.51\ V$

$5\ IO_4^-(aq) + 2\ Mn^{2+}(aq) + 3\ H_2O(l) \rightarrow 5\ IO_3^-(aq) + 2\ MnO_4^-(aq) + 6\ H^+(aq)$ $E^o_{cell} = 0.09\ V$

b. Nitric acid oxidation (see above for E^o_{cell}):

$\Delta G° = -nFE^o_{cell} - (6\ mol\ e^-)(96{,}485\ C/mol\ e^-)(2.14\ J/C) = -1.24 \times 10^6\ J = -1240\ kJ$

Periodate oxidation (see above for E^o_{cell}):

$\Delta G° = -(10\ mol\ e^-)(96{,}485\ C/mol\ e^-)(0.09\ J/C)(1\ kJ/1000\ J) = -90\ kJ$

49. Because the cells are at standard conditions, $w_{max} = \Delta G = \Delta G° = -nFE^o_{cell}$. See Exercise 43 for the balanced overall equations and for E^o_{cell}.

43a. $w_{max} = -(3\ mol\ e^-)(96{,}485\ C/mol\ e^-)(1.34\ J/C) = -3.88 \times 10^5\ J = -388\ kJ$

43b. $w_{max} = -(2\ mol\ e^-)(96{,}485\ C/mol\ e^-)(1.40\ J/C) = -2.70 \times 10^5\ J = -270.\ kJ$

50. Because the cells are at standard conditions, $w_{max} = \Delta G = \Delta G° = -nFE^o_{cell}$. See Exercise 44 for the balanced overall equations and for E^o_{cell}.

44a. $w_{max} = -(6\ mol\ e^-)(96{,}485\ C/mol\ e^-)(0.45\ J/C) = -2.6 \times 10^5\ J = -260\ kJ$

44b. $w_{max} = -(6\ mol\ e^-)(96{,}485\ C/mol\ e^-)(1.66\ J/C) = -9.61 \times 10^5\ J = -961\ kJ$

51. $2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$ $\Delta G° = \Sigma n_p \Delta G^o_{f,\ products} - \Sigma n_r \Delta G^o_{f,\ reactants}$

$= 2(-157) - [2(-237)] = 160.\ kJ$

$$\Delta G° = -nFE°,\ \ E° = \frac{-\Delta G°}{nF} = \frac{-1.60 \times 10^5\ \text{J}}{(2\ \text{mol e}^-)(96{,}485\ \text{C/mol e}^-)} = -0.829\ \text{J/C} = -0.829\ \text{V}$$

The two values agree to two significant figures (–0.83 V in Table 18.1).

52. $Fe^{2+} + 2\ e^- \rightarrow Fe \quad E° = -0.44\ V = -0.44\ J/C$

$\Delta G° = -nFE° = -(2\ \text{mol e}^-)(96{,}485\ \text{C/mol e}^-)(-0.44\ \text{J/C})(1\ \text{kJ}/1000\ \text{J}) = 85\ \text{kJ}$

$85\ \text{kJ} = 0 - [\Delta G^{o}_{f,Fe^{2+}} + 0],\ \Delta G^{o}_{f,Fe^{2+}} = -85\ \text{kJ}$

We can get $\Delta G^{o}_{f,Fe^{3+}}$ two ways. Consider: $Fe^{3+} + e^- \rightarrow Fe^{2+} \quad E° = 0.77\ V$

$\Delta G° = -(1\ \text{mol e})(96{,}485\ \text{C/mol e}^-)(0.77\ \text{J/C}) = -74{,}300\ \text{J} = -74\ \text{kJ}$

$Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad \Delta G° = 74\ \text{kJ}$
$Fe \rightarrow Fe^{2+} + 2\ e^- \qquad \Delta G° = -85\ \text{kJ}$

$Fe \rightarrow Fe^{3+} + 3\ e^- \qquad \Delta G° = -11\ \text{kJ},\quad \Delta G^{o}_{f,Fe^{3+}} = -11\ \text{kJ/mol}$

or consider: $Fe^{3+} + 3\ e^- \rightarrow Fe \qquad E° = -0.036\ V$

$\Delta G° = -(3\ \text{mol e}^-)(96{,}485\ \text{C/mol e}^-)(-0.036\ \text{J/C}) = 10{,}400\ \text{J} \approx 10.\ \text{kJ}$

$10.\ \text{kJ} = 0 - [\Delta G^{o}_{f,Fe^{3+}} + 0],\ \Delta G^{o}_{f,Fe^{3+}} = -10.\ \text{kJ/mol}$; round-off error explains the 1-kJ discrepancy.

53. Good oxidizing agents are easily reduced. Oxidizing agents are on the left side of the reduction half-reactions listed in Table 18.1. We look for the largest, most positive standard reduction potentials to correspond to the best oxidizing agents. The ordering from worst to best oxidizing agents is:

	K^+	<	H_2O	<	Cd^{2+}	<	I_2	<	$AuCl_4^-$	<	IO_3^-
E° (V)	−2.87		−0.83		−0.40		0.54		0.99		1.20

54. Good reducing agents are easily oxidized. The reducing agents are on the right side of the reduction half-reactions listed in Table 18.1. The best reducing agents have the most negative standard reduction potentials (E°) or the most positive standard oxidation potentials E^{o}_{ox} (= −E°). The ordering from worst to best reducing agents is:

	F^-	<	H_2O	<	I_2	<	Cu^+	<	H^-	<	K
−E° (V)	−2.92		−1.23		−1.20		−0.16		2.23		2.92

55. a. $2\ H^+ + 2\ e^- \rightarrow H_2 \quad E° = 0.00\ V;\ \ Cu \rightarrow Cu^{2+} + 2\ e^- \quad -E° = -0.34\ V$

$E^{o}_{cell} = -0.34\ V$; no, H^+ cannot oxidize Cu to Cu^{2+} at standard conditions ($E^{o}_{cell} < 0$).

b. $Fe^{3+} + e^- \rightarrow Fe^{2+} \quad E° = 0.77\ V;\ \ 2\ I^- \rightarrow I_2 + 2\ e^- \quad -E° = -0.54\ V$

$E^{o}_{cell} = 0.77 - 0.54 = 0.23\ V$; yes, Fe^{3+} can oxidize I^- to I_2.

c. $H_2 \rightarrow 2\ H^+ + 2\ e^-$ $-E° = 0.00$ V; $Ag^+ + e^- \rightarrow Ag$ $E° = 0.80$ V

$E^o_{cell} = 0.80$ V; yes, H_2 can reduce Ag^+ to Ag at standard conditions ($E^o_{cell} > 0$).

56. a. $H_2 \rightarrow 2\ H^+ + 2\ e^-$ $-E° = 0.00$ V; $Ni^{2+} + 2\ e^- \rightarrow Ni$ $E° = -0.23$ V

$E^\circ_{cell} = -0.23$ V; no, H_2 cannot reduce Ni^{2+} to Ni at standard conditions ($E^\circ_{cell} < 0$).

b. $Fe^{2+} \rightarrow Fe^{3+} + e^-$ $-E° = -0.77$ V; $VO_2^+ + 2\ H^+ + e^- \rightarrow VO^{2+} + H_2O$ $E° = 1.00$ V

$E^\circ_{cell} = 1.00 - 0.77 = 0.23$ V; yes, Fe^{2+} can reduce VO_2^+ at standard conditions.

c. $Fe^{2+} \rightarrow Fe^{3+} + e^-$ $-E° = -0.77$ V; $Cr^{3+} + e^- \rightarrow Cr^{2+}$ $E° = -0.50$ V

$E^\circ_{cell} = 0.50 - 0.77 = -1.27$ V; no, Fe^{2+} cannot reduce Cr^{3+} to Cr^{2+} at standard conditions.

57. $Cl_2 + 2\ e^- \rightarrow 2\ Cl^-$ $E° = 1.36$ V $Ag^+ + e^- \rightarrow Ag$ $E° = 0.80$ V
$Pb^{2+} + 2\ e^- \rightarrow Pb$ $E° = -0.13$ V $Zn^{2+} + 2\ e^- \rightarrow Zn$ $E° = -0.76$ V
$Na^+ + e^- \rightarrow Na$ $E° = -2.71$ V

a. Oxidizing agents (species reduced) are on the left side of the preceding reduction half-reactions. Of the species available, Ag^+ would be the best oxidizing agent since it has the largest E° value. Note that Cl_2 is a better oxidizing agent than Ag^+, but it is not one of the choices listed.

b. Reducing agents (species oxidized) are on the right side of the reduction half-reactions. Of the species available, Zn would be the best reducing agent since it has the largest −E° value.

c. $SO_4^{2-} + 4\ H^+ + 2\ e^- \rightarrow H_2SO_3 + H_2O$ $E° = 0.20$ V; SO_4^{2-} can oxidize Pb and Zn at standard conditions. When SO_4^{2-} is coupled with these reagents, E^o_{cell} is positive.

d. $Al \rightarrow Al^{3+} + 3\ e^-$ $-E° = 1.66$ V; Al can reduce Ag^+ and Zn^{2+} at standard conditions because $E^o_{cell} > 0$.

58. $Br_2 + 2\ e^- \rightarrow 2\ Br^-$ $E° = 1.09$ V $La^{3+} + 3\ e^- \rightarrow La$ $E° = -2.37$ V
$2\ H^+ + 2\ e^- \rightarrow H_2$ $E° = 0.00$ V $Ca^{2+} + 2\ e^- \rightarrow Ca$ $E° = -2.76$ V
$Cd^{2+} + 2\ e^- \rightarrow Cd$ $E° = -0.40$ V

a. Oxidizing agents are on the left side of the preceding reduction half-reactions. Br_2 is the best oxidizing agent (largest E°).

b. Reducing agents are on the right side of the reduction half-reactions. Ca is the best reducing agent (largest –E°).

c. $MnO_4^- + 8\,H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O$ E° = 1.51 V; permanganate can oxidize Br^-, H_2, Cd, and Ca at standard conditions. When MnO_4^- is coupled with these reagents, E°_{cell} is positive. *Note*: La is not one of the choices given in the question or it would have been included.

d. $Zn \rightarrow Zn^{2+} + 2\,e^-$ $-E° = 0.76$ V; zinc can reduce Br_2 and H^+ beause $E^{\circ}_{cell} > 0$.

59. a. $2\,Br^- \rightarrow Br_2 + 2\,e^-$ $-E° = -1.09$ V; $2\,Cl^- \rightarrow Cl_2 + 2\,e^-$ $-E° = -1.36$ V; $E° > 1.09$ V to oxidize Br^-; $E° < 1.36$ V to not oxidize Cl^-; $Cr_2O_7^{2-}$, O_2, MnO_2, and IO_3^- are all possible since when all of these oxidizing agents are coupled with Br^-, $E^{o}_{cell} > 0$, and when coupled with Cl^-, $E^{o}_{cell} < 0$ (assuming standard conditions).

b. $Mn \rightarrow Mn^{2+} + 2\,e^-$ $-E° = 1.18$; $Ni \rightarrow Ni^{2+} + 2\,e^-$ $-E° = 0.23$ V; any oxidizing agent with $-0.23\text{ V} > E° > -1.18$ V will work. $PbSO_4$, Cd^{2+}, Fe^{2+}, Cr^{3+}, Zn^{2+}, and H_2O will be able to oxidize Mn but not Ni (assuming standard conditions).

60. a. $Cu^{2+} + 2\,e^- \rightarrow Cu$ E° = 0.34 V; $Cu^{2+} + e^- \rightarrow Cu^+$ E° = 0.16 V; to reduce Cu^{2+} to Cu but not reduce Cu^{2+} to Cu^+, the reducing agent must have a standard oxidation potential $E^{o}_{ox} = -E°$) between -0.34 and -0.16 V (so E^{o}_{cell} is positive only for the Cu^{2+} to Cu reduction). The reducing agents (species oxidized) are on the right side of the half-reactions in Table 18.1. The reagents at standard conditions that have E^{o}_{ox} $(=-E°)$ between -0.34 and -0.16 V are Ag (in 1.0 *M* Cl^-) and H_2SO_3.

b. $Br_2 + 2\,e^- \rightarrow 2\,Br^-$ E° = 1.09 V; $I_2 + 2\,e^- \rightarrow 2\,I^-$ E° = 0.54 V; from Table 18.1, VO^{2+}, Au (in 1.0 *M* Cl^-), NO, ClO_2^-, Hg_2^{2+}, Ag, Hg, Fe^{2+}, H_2O_2, and MnO_4^- are all capable at standard conditions of reducing Br_2 to Br^- but not reducing I_2 to I^-. When these reagents are coupled with Br_2, $E^{o}_{cell} > 0$, and when coupled with I_2, $E^{o}_{cell} < 0$.

61.
$$ClO^- + H_2O + 2\,e^- \rightarrow 2\,OH^- + Cl^- \qquad E° = 0.90\text{ V}$$
$$2\,NH_3 + 2\,OH^- \rightarrow N_2H_4 + 2\,H_2O + 2\,e^- \qquad -E° = 0.10\text{ V}$$

$$ClO^-(aq) + 2\,NH_3(aq) \rightarrow Cl^-(aq) + N_2H_4(aq) + H_2O(l) \qquad E^{o}_{cell} = 1.00\text{ V}$$

Because E^{o}_{cell} is positive for this reaction, at standard conditions, ClO^- can spontaneously oxidize NH_3 to the somewhat toxic N_2H_4.

62.
$$Tl^{3+} + 2\,e^- \rightarrow Tl^+ \qquad E° = 1.25\text{ V}$$
$$3\,I^- \rightarrow I_3^- + 2\,e^- \qquad -E° = -0.55\text{ V}$$

$$Tl^{3+} + 3\,I^- \rightarrow Tl^+ + I_3^- \qquad E^{o}_{cell} = 0.70\text{ V}$$

In solution, Tl^{3+}can oxidize I^- to I_3^-. Thus we expect TlI_3 to be thallium(I) triiodide.

The Nernst Equation

63.

$$\begin{array}{lr} H_2O_2 + 2\,H^+ + 2\,e^- \rightarrow 2\,H_2O & E° = 1.78\text{ V} \\ (Ag \rightarrow Ag^+ + e^-) \times 2 & -E° = -0.80\text{ V} \\ \hline H_2O_2(aq) + 2\,H^+(aq) + 2\,Ag(s) \rightarrow 2\,H_2O(l) + 2\,Ag^+(aq) & E^o_{cell} = 0.98\text{ V} \end{array}$$

a. A galvanic cell is based on spontaneous redox reactions. At standard conditions, this reaction produces a voltage of 0.98 V. Any change in concentration that increases the tendency of the forward reaction to occur will increase the cell potential. Conversely, any change in concentration that decreases the tendency of the forward reaction to occur (increases the tendency of the reverse reaction to occur) will decrease the cell potential. Using Le Chatelier's principle, increasing the reactant concentrations of H_2O_2 and H^+ from 1.0 to 2.0 *M* will drive the forward reaction further to right (will further increase the tendency of the forward reaction to occur). Therefore, E_{cell} will be greater than E^o_{cell}.

b. Here, we decreased the reactant concentration of H^+ and increased the product concentration of Ag^+ from the standard conditions. This decreases the tendency of the forward reaction to occur, which will decrease E_{cell} as compared to E^o_{cell} ($E_{cell} < E^o_{cell}$).

64. The concentrations of Fe^{2+} in the two compartments are now 0.01 and 1×10^{-7} *M*. The driving force for this reaction is to equalize the Fe^{2+} concentrations in the two compartments. This occurs if the compartment with 1×10^{-7} *M* Fe^{2+} becomes the anode (Fe will be oxidized to Fe^{2+}) and the compartment with the 0.01 *M* Fe^{2+} becomes the cathode (Fe^{2+} will be reduced to Fe). Electron flow, as always for galvanic cells, goes from the anode to the cathode, so electron flow will go from the right compartment ($[Fe^{2+}] = 1 \times 10^{-7}$ *M*) to the left compartment ($[Fe^{2+}] = 0.01$ *M*).

65. For concentration cells, the driving force for the reaction is the difference in ion concentrations between the anode and cathode. In order to equalize the ion concentrations, the anode always has the smaller ion concentration. The general setup for this concentration cell is:

$$\begin{array}{llr} \text{Cathode:} & Ag^+(x\,M) + e^- \rightarrow Ag & E° = 0.80\text{ V} \\ \text{Anode:} & Ag \rightarrow Ag^+\,(y\,M) + e^- & -E° = -0.80\text{ V} \\ \hline & Ag^+(\text{cathode}, x\,M) \rightarrow Ag^+\,(\text{anode}, y\,M) & E^o_{cell} = 0.00\text{ V} \end{array}$$

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log Q = \frac{-0.0591}{1}\log\frac{[Ag^+]_{anode}}{[Ag^+]_{cathode}}$$

For each concentration cell, we will calculate the cell potential using the preceding equation. Remember that the anode always has the smaller ion concentration.

a. Both compartments are at standard conditions ($[Ag^+] = 1.0$ *M*), so $E_{cell} = E^o_{cell} = 0$ V. No voltage is produced since no reaction occurs. Concentration cells only produce a voltage when the ion concentrations are <u>not</u> equal.

b. Cathode = 2.0 *M* Ag^+; anode = 1.0 *M* Ag^+; electron flow is always from the anode to the cathode, so electrons flow to the right in the diagram.

$$E_{cell} = \frac{-0.0591}{n}\log\frac{[Ag^+]_{anode}}{[Ag^+]_{cathode}} = \frac{-0.0591}{1}\log\frac{1.0}{2.0} = 0.018\ V$$

c. Cathode = 1.0 *M* Ag^+; anode = 0.10 *M* Ag^+; electrons flow to the left in the diagram.

$$E_{cell} = \frac{-0.0591}{n}\log\frac{[Ag^+]_{anode}}{[Ag^+]_{cathode}} = \frac{-0.0591}{1}\log\frac{0.10}{1.0} = 0.059\ V$$

d. Cathode = 1.0 *M* Ag^+; anode = 4.0×10^{-5} *M* Ag^+; electrons flow to the left in the diagram.

$$E_{cell} = \frac{-0.0591}{n}\log\frac{4.0\times10^{-5}}{1.0} = 0.26\ V$$

e. The ion concentrations are the same; thus $\log([Ag^+]_{anode}/[Ag^+]_{cathode}) = \log(1.0) = 0$ and $E_{cell} = 0$. No electron flow occurs.

66. As is the case for all concentration cells, $E^o_{cell} = 0$, and the smaller ion concentration is always in the anode compartment. The general Nernst equation for the Ni | Ni^{2+}(*x M*) || Ni^{2+}(*y M*) | Ni concentration cell is:

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log Q = \frac{-0.0591}{2}\log\frac{[Ni^{2+}]_{anode}}{[Ni^{2+}]_{cathode}}$$

a. Both compartments are at standard conditions ($[Ni^{2+}] = 1.0$ *M*), and $E_{cell} = E^o_{cell} = 0$ V. No electron flow occurs.

b. Cathode = 2.0 *M* Ni^{2+}; anode = 1.0 *M* Ni^{2+}; electron flow is always from the anode to the cathode, so electrons flow to the right in the diagram.

$$E_{cell} = \frac{-0.0591}{2}\log\frac{[Ni^{2+}]_{anode}}{[Ni^{2+}]_{cathode}} = \frac{-0.0591}{2}\log\frac{1.0}{2.0} = 8.9 \times 10^{-3}\ V$$

c. Cathode = 1.0 *M* Ni^{2+}; anode = 0.10 *M* Ni^{2+}; electrons flow to the left in the diagram.

$$E_{cell} = \frac{-0.0591}{2}\log\frac{0.10}{1.0} = 0.030\ V$$

d. Cathode = 1.0 *M* Ni^{2+}; anode = 4.0×10^{-5} *M* Ni^{2+}; electrons flow to the left in the diagram.

$$E_{cell} = \frac{-0.0591}{2}\log\frac{4.0\times10^{-5}}{1.0} = 0.13\ V$$

e. Because both concentrations are equal, $\log(2.5/2.5) = \log 1.0 = 0$, and $E_{cell} = 0$. No electron flow occurs.

67. n = 2 for this reaction (lead goes from $Pb \rightarrow Pb^{2+}$ in $PbSO_4$).

$$E = E° - \frac{-0.0591}{2}\log\frac{1}{[H^+]^2[HSO_4{}^-]^2} = 2.04\text{ V} - \frac{-0.0591}{2}\log\frac{1}{(4.5)^2(4.5)^2}$$

$$E = 2.04\text{ V} + 0.077\text{ V} = 2.12\text{ V}$$

68.

$$\begin{array}{ll} Cr_2O_7{}^{2-} + 14\,H^+ + 6\,e^- \rightarrow 2\,Cr^{3+} + 7\,H_2O & E° = 1.33\text{ V} \\ (Al \rightarrow Al^{3+} + 3\,e^-) \times 2 & -E° = 1.66 \\ \hline Cr_2O_7{}^{2-} + 14\,H^+ + 2\,Al \rightarrow 2\,Al^{3+} + 2\,Cr^{3+} + 7\,H_2O & E^o_{cell} = 2.99\text{ V} \end{array}$$

$$E = E° - \frac{0.0591}{n}\log Q,\quad E = 2.99\text{ V} - \frac{0.0591}{6}\log\frac{[Al^{3+}]^2[Cr^{3+}]^2}{[Cr_2O_7{}^{2-}][H^+]^{14}}$$

$$3.01 = 2.99 - \frac{0.0591}{n}\log Q\,\frac{(0.30)^2(0.15)^2}{(0.55)[H^+]^{14}},\quad \frac{-6(0.02)}{0.0591} = \log\left(\frac{3.7\times10^{-3}}{[H^+]^{14}}\right)$$

$$\frac{3.7\times10^{-3}}{[H^+]^{14}} = 10^{-2.0} = 0.01,\ [H^+]^{14} = 0.37,\ [H^+] = 0.93 = 0.9\ M,\ \text{pH} = -\log(0.9) = 0.05$$

69.

$$\begin{array}{ll} Cu^{2+} + 2\,e^- \rightarrow Cu & E° = 0.34\text{ V} \\ Zn \rightarrow Zn^{2+} + 2\,e^- & -E° = 0.76\text{ V} \\ \hline Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s) & E^o_{cell} = 1.10\text{ V} \end{array}$$

Because Zn^{2+} is a product in the reaction, the Zn^{2+} concentration increases from 1.00 to 1.20 *M*. This means that the reactant concentration of Cu^{2+} must decrease from 1.00 to 0.80 *M* (from the 1 : 1 mole ratio in the balanced reaction).

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log Q = 1.10\text{ V} - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E_{cell} = 1.10\text{ V} - \frac{0.0591}{2}\log\frac{1.20}{0.80} = 1.10\text{ V} - 0.0052\text{ V} = 1.09\text{ V}$$

70.

$$\begin{array}{ll} (Pb^{2+} + 2\,e^- \rightarrow Pb) \times 3 & E° = -0.13\text{ V} \\ (Al \rightarrow Al^{3+} + 3\,e^-) \times 2 & -E° = 1.66\text{ V} \\ \hline 3\,Pb^{2+}(aq) + 2\,Al(s) \rightarrow 3\,Pb(s) + 2\,Al^{3+}(aq) & E^o_{cell} = 1.53\text{ V} \end{array}$$

From the balanced reaction, when the Al^{3+} has increased by 0.60 mol/L (Al^{3+} is a product in the spontaneous reaction), then the Pb^{2+} concentration has decreased by 3/2 (0.60 mol/L) = 0.90 *M*.

$$E_{cell} = 1.53\text{ V} - \frac{0.0591}{6}\log\frac{[Al^{3+}]^2}{[Pb^{2+}]^3} = 1.53 - \frac{0.0591}{6}\log\frac{(1.60)^2}{(0.10)^3}$$

$$E_{cell} = 1.53\text{ V} - 0.034\text{ V} = 1.50\text{ V}$$

71. See Exercises 35, 37, and 39 for balanced reactions and standard cell potentials. Balanced reactions are necessary to determine n, the moles of electrons transferred.

35a. $7\ H_2O + 2\ Cr^{3+} + 3\ Cl_2 \rightarrow Cr_2O_7^{2-} + 6\ Cl^- + 14\ H^+ \quad E^\circ_{cell} = 0.03\ V = 0.03\ J/C$

$$\Delta G^\circ = -nFE^\circ_{cell} = -(6\ mol\ e^-)(96{,}485\ C/mol\ e^-)(0.03\ J/C) = -1.7 \times 10^4\ J = -20\ kJ$$

$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log Q$; at equilibrium, $E_{cell} = 0$ and $Q = K$, so:

$$E^\circ_{cell} = \frac{0.0591}{n}\log K,\ \log K = \frac{nE^\circ}{0.0591} = \frac{6(0.03)}{0.0591} = 3.05,\ K = 10^{3.05} = 1 \times 10^3$$

Note: When determining exponents, we will round off to the correct number of significant figures after the calculation is complete in order to help eliminate excessive round-off error.

35b. $\Delta G^\circ = -(2\ mol\ e^-)(96{,}485\ C/mol\ e^-)(2.71\ J/C) = -5.23 \times 10^5\ J = -523\ kJ$

$$\log K = \frac{2(2.71)}{0.0591} = 91.709,\ K = 5.12 \times 10^{91}$$

39a. $\Delta G^\circ = -(2\ mol\ e^-)(96{,}485\ C/mol\ ^-)(0.27\ J/C) = -5.21 \times 10^4\ J = -52\ kJ$

$$\log K = \frac{2(0.27)}{0.0591} = 9.14,\ K = 1.4 \times 10^9$$

39b. $\Delta G^\circ = -\ (10\ mol\ e^-)(96{,}485\ C/mol\ e^-)(0.09\ J/C) = -8.7 \times 10^4\ J = -90\ kJ$

$$\log K = \frac{10(0.09)}{0.0591} = 15.23,\ K = 2 \times 10^{15}$$

72. $\Delta G^\circ = -nFE^\circ_{cell};\ E^\circ_{cell} = \frac{0.0591}{n}\log K,\ \log K = \frac{nE^\circ}{0.0591}$

36a. $\Delta G^\circ = -\ (10\ mol\ e^-)(96{,}485\ C/mol\ e^-)(0.43\ J/C) = -4.1 \times 10^5\ J = -410\ kJ$

$$\log K = \frac{10(0.43)}{0.0591} = 72.76,\ K = 10^{72.76} = 5.8 \times 10^{72}$$

36b. $\Delta G^\circ = -\ (2\ mol\ e^-)(96{,}485\ C/mol\ e^-)(1.56\ J/C) = -3.01 \times 10^5\ J = -301\ kJ$

$$\log K = \frac{2(1.56)}{0.0591} = 52.792,\ K = 6.19 \times 10^{52}$$

40a. $\Delta G° = -(2\text{ mol }^-)(96{,}485\text{ C/mol e}^-)(1.10\text{ J/C}) = -2.12 \times 10^5\text{ J} = -212\text{ kJ}$

$$\log K = \frac{2(1.10)}{0.0591} = 37.225,\ \ K = 1.68 \times 10^{37}$$

40b. $\Delta G° = -\ (6\text{ mol e}^-)(96{,}485\text{ C/mol e}^-)(1.14\text{ J/C}) = -6.60 \times 10^5\text{ J} = -660.\text{ kJ}$

$$\log K = \frac{6(1.14)}{0.0591} = 115.736,\ \ \ K = 5.45 \times 10^{115}$$

73. a.

$$\begin{array}{ll} \mathrm{Fe^{2+} + 2\,e^- \rightarrow Fe} & E° = -0.44\text{ V} \\ \mathrm{Zn \rightarrow Zn^{2+} + 2\,e^-} & -E° = 0.76\text{ V} \\ \hline \mathrm{Fe^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Fe(s)} & E^{o}_{cell} = 0.32\text{ V} = 0.32\text{ J/C} \end{array}$$

b. $\Delta G^{o} = -\,nFE^{o}_{cell} = -(2\text{ mol e}^-)(96{,}485\text{ C/mol e}^-)(0.32\text{ J/C}) = -6.2 \times 10^4\text{ J} = -62\text{ kJ}$

$$E^{o}_{cell} = \frac{0.0591}{n}\log K,\ \ \log K = \frac{nE^{o}}{0.0591} = \frac{2(0.32)}{0.0591} = 10.83,\ \ K = 10^{10.83} = 6.8 \times 10^{10}$$

c. $E_{cell} = E^{o}_{cell} - \dfrac{0.0591}{n}\log Q = 0.32\text{ V} - \dfrac{0.0591}{n}\log\dfrac{[\mathrm{Zn^{2+}}]}{[\mathrm{Fe^{2+}}]}$

$$E_{cell} = 0.32 - \frac{0.0591}{2}\log\frac{0.10}{1.0 \times 10^{-5}} = 0.32 - 0.12 = 0.20\text{ V}$$

74. a.

$$\begin{array}{ll} \mathrm{Au^{3+} + 3\,e^- \rightarrow Au} & E° = 1.50\text{ V} \\ \mathrm{(Tl \rightarrow Tl^{+} + e^-) \times 3} & -E° = 0.34\text{ V} \\ \hline \mathrm{Au^{3+}(aq) + 3\,Tl(s) \rightarrow Au(s) + 3\,Tl^{+}(aq)} & E^{o}_{cell} = 1.84\text{ V} \end{array}$$

b. $\Delta G° = -\,nFE^{o}_{cell} = -(3\text{ mol e}^-)(96{,}485\text{ C/mol e}^-)(1.84\text{ J/C}) = -5.33 \times 10^5\text{ J} = -533\text{ kJ}$

$$\log K = \frac{nE^{o}}{0.0591} = \frac{3(1.84)}{0.0591} = 93.401,\ \ K = 10^{93.401} = 2.52 \times 10^{93}$$

c. At 25°C, $E_{cell} = E^{o}_{cell} - \dfrac{0.0591}{n}\log Q$, where $Q = \dfrac{[\mathrm{Tl^{+}}]^3}{[\mathrm{Au^{3+}}]}$.

$$E_{cell} = 1.84\text{ V} - \frac{0.0591}{3}\log\frac{[\mathrm{Tl^{+}}]^3}{[\mathrm{Au^{3+}}]} = 1.84 - \frac{0.0591}{3}\log\frac{(1.0 \times 10^{-4})^3}{1.0 \times 10^{-2}}$$

$$E_{cell} = 1.84 - (-0.20) = 2.04\text{ V}$$

75. $Cu^{2+}(aq) + H_2(g) \rightarrow 2\ H^+(aq) + Cu(s)$ $E^{o}_{cell} = 0.34\ V - 0.00\ V = 0.34\ V$; n = 2 mol electrons

$P_{H_2} = 1.0$ atm and $[H^+] = 1.0\ M$: $E_{cell} = E^{o}_{cell} - \dfrac{0.0591}{n}\log\dfrac{1}{[Cu^{2+}]}$

a. $E_{cell} = 0.34\ V - \dfrac{0.0591}{2}\log\dfrac{1}{2.5\times10^{-4}} = 0.34\ V - 0.11V = 0.23\ V$

b. $0.195\ V = 0.34\ V - \dfrac{0.0591}{2}\log\dfrac{1}{[Cu^{2+}]}$, $\log\dfrac{1}{[Cu^{2+}]} = 4.91$, $[Cu^{2+}] = 10^{-4.91}$

$= 1.2 \times 10^{-5}\ M$

Note: When determining exponents, we will carry extra significant figures.

76. $3\ Ni^{2+}(aq) + 2\ Al(s) \rightarrow 2\ Al^{3+}(aq) + 3\ Ni(s)$ $E^{o}_{cell} = -0.23 + 1.66 = 1.43\ V$;
n = 6 mol electrons for this reaction.

a. $E_{cell} = 1.43\ V - \dfrac{0.0591}{6}\log\dfrac{[Al^{3+}]^2}{[Ni^{2+}]^3} = 1.43 - \dfrac{0.0591}{6}\log\dfrac{(7.2\times10^{-3})^2}{(1.0)^3}$

$E_{cell} = 1.43\ V - (-0.042\ V) = 1.47\ V$

b. $1.62\ V = 1.43\ V - \dfrac{0.0591}{6}\log\dfrac{[Al^{3+}]^2}{(1.0)^3}$, $\log [Al^{3+}]^2 = -19.29$

$[Al^{3+}]^2 = 10^{-19.29}$, $[Al^{3+}] = 2.3 \times 10^{-10}\ M$

77. $Cu^{2+}(aq) + H_2(g) \rightarrow 2\ H^+(aq) + Cu(s)$ $E^{o}_{cell} = 0.34\ V - 0.00\ V = 0.34\ V$; n = 2

$P_{H_2} = 1.0$ atm and $[H^+] = 1.0\ M$: $E_{cell} = E^{o}_{cell} - \dfrac{0.0591}{2}\log\dfrac{1}{[Cu^{2+}]}$

Use the K_{sp} expression to calculate the Cu^{2+} concentration in the cell.

$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2\ OH^-(aq)$ $K_{sp} = 1.6 \times 10^{-19} = [Cu^{2+}][OH^-]^2$

From problem, $[OH^-] = 0.10\ M$, so: $[Cu^{2+}] = \dfrac{1.6\times10^{-19}}{(0.10)^2} = 1.6 \times 10^{-17}\ M$

$E_{cell} = E^{o}_{cell} - \dfrac{0.0591}{2}\log\dfrac{1}{[Cu^{2+}]} = 0.34\ V - \dfrac{0.0591}{2}\log\dfrac{1}{1.6\times10^{-17}}$

$E_{cell} = 0.34 - 0.50 = -0.16\ V$

Because $E_{cell} < 0$, the forward reaction is not spontaneous, but the reverse reaction is spontaneous. The Cu electrode becomes the anode and $E_{cell} = 0.16$ V for the reverse reaction. The cell reaction is $2\ H^+(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + H_2(g)$.

78. $3\ \mathrm{Ni^{2+}(aq)} + 2\ \mathrm{Al(s)} \rightarrow 2\ \mathrm{Al^{3+}(aq)} + 3\ \mathrm{Ni(s)}$ $E^{\circ}_{\mathrm{cell}} = -0.23\ \mathrm{V} + 1.66\ \mathrm{V} = 1.43\ \mathrm{V}$; n = 6

$$E_{\mathrm{cell}} = E^{\circ}_{\mathrm{cell}} - \frac{0.0591}{n}\log\frac{[\mathrm{Al^{3+}}]^2}{[\mathrm{Ni^{2+}}]^3},\quad 1.82\ \mathrm{V} = 1.43\ \mathrm{V} - \frac{0.0591}{6}\log\frac{[\mathrm{Al^{3+}}]^2}{(1.0)^3}$$

$\log\,[\mathrm{Al^{3+}}]^2 = -39.59$, $[\mathrm{Al^{3+}}]^2 = 10^{-39.59}$, $[\mathrm{Al^{3+}}] = 1.6 \times 10^{-20}\ M$

$\mathrm{Al(OH)_3(s)} \rightleftharpoons \mathrm{Al^{3+}(aq)} + 3\ \mathrm{OH^-(aq)}$ $K_{sp} = [\mathrm{Al^{3+}}][\mathrm{OH^-}]^3$; from the problem, $[\mathrm{OH^-}] = 1.0 \times 10^{-4}\ M$.

$K_{sp} = (1.6 \times 10^{-20})(1.0 \times 10^{-4})^3 = 1.6 \times 10^{-32}$

79.

Cathode:	$\mathrm{M^{2+}} + 2e^- \rightarrow \mathrm{M(s)}$	$E° = -0.31\ \mathrm{V}$
Anode:	$\mathrm{M(s)} \rightarrow \mathrm{M^{2+}} + 2e^-$	$-E° = 0.31\ \mathrm{V}$
	$\mathrm{M^{2+}}\ (\text{cathode}) \rightarrow \mathrm{M^{2+}}\ (\text{anode})$	$E^{\circ}_{\mathrm{cell}} = 0.00\ \mathrm{V}$

$$E_{\mathrm{cell}} = 0.44\ \mathrm{V} = 0.00\ \mathrm{V} - \frac{0.0591}{2}\log\frac{[\mathrm{M^{2+}}]_{\mathrm{anode}}}{[\mathrm{M^{2+}}]_{\mathrm{cathode}}},\quad 0.44 = -\frac{0.0591}{2}\log\frac{[\mathrm{M^{2+}}]_{\mathrm{anode}}}{1.0}$$

$$\log\,[\mathrm{M^{2+}}]_{\mathrm{anode}} = -\frac{2(0.44)}{0.0591} = -14.89,\quad [\mathrm{M^{2+}}]_{\mathrm{anode}} = 1.3 \times 10^{-15}\ M$$

Because we started with equal numbers of moles of $\mathrm{SO_4^{2-}}$ and $\mathrm{M^{2+}}$, $[\mathrm{M^{2+}}] = [\mathrm{SO_4^{2-}}]$ at equilibrium.

$K_{sp} = [\mathrm{M^{2+}}][\mathrm{SO_4^{2-}}] = (1.3 \times 10^{-15})^2 = 1.7 \times 10^{-30}$

80. a. $\mathrm{Ag^+}$ (x M, anode) → $\mathrm{Ag^+}$ (0.10 M, cathode); for the silver concentration cell, $E° = 0.00$ (as is always the case for concentration cells) and n = 1.

$$E = 0.76\ \mathrm{V} = 0.00 - \frac{0.0591}{1}\log\frac{[\mathrm{Ag^+}]_{\mathrm{anode}}}{[\mathrm{Ag^+}]_{\mathrm{cathode}}}$$

$$0.76 = -(0.0591)\log\frac{[\mathrm{Ag^+}]_{\mathrm{anode}}}{0.10},\quad \frac{[\mathrm{Ag^+}]_{\mathrm{anode}}}{0.10} = 10^{-12.86},\quad [\mathrm{Ag^+}]_{\mathrm{anode}} = 1.4 \times 10^{-14}\ M$$

b. $\mathrm{Ag^+(aq)} + 2\ \mathrm{S_2O_3^{2-}(aq)} \rightleftharpoons \mathrm{Ag(S_2O_3)_2^{3-}(aq)}$

$$K = \frac{[\mathrm{Ag(S_2O_3)_2}^{3-}]}{[\mathrm{Ag^+}][\mathrm{S_2O_3}^{2-}]^2} = \frac{1.0 \times 10^{-3}}{1.4 \times 10^{-14}(0.050)^2} = 2.9 \times 10^{13}$$

81. a. Possible reaction: $\mathrm{I_2(s)} + 2\ \mathrm{Cl^-(aq)} \rightarrow 2\ \mathrm{I^-(aq)} + \mathrm{Cl_2(g)}$ $E^{\circ}_{\mathrm{cell}} = 0.54\ \mathrm{V} - 1.36\ \mathrm{V} = -0.82\ \mathrm{V}$

This reaction is not spontaneous at standard conditions because $E^{\circ}_{\mathrm{cell}} < 0$; no reaction occurs.

b. Possible reaction: $Cl_2(g) + 2\ I^-(aq) \rightarrow I_2(s) + 2\ Cl^-(aq)$ $E^o_{cell} = 0.82$ V; this reaction is spontaneous at standard conditions because $E^o_{cell} > 0$. The reaction will occur.

$Cl_2(g) + 2\ I^-(aq) \rightarrow I_2(s) + 2\ Cl^-(aq)$ $E^o_{cell} = 0.82\ V = 0.82\ J/C$

$$\Delta G° = -nFE^o_{cell} = -(2\ mol\ e^-)(96{,}485\ C/mol\ e^-)(0.82\ J/C) = -1.6 \times 10^5\ J = -160\ kJ$$

$$E° = \frac{0.0591}{n}\log K,\ \log K = \frac{nE°}{0.0591} = \frac{2(0.82)}{0.0591} = 27.75,\ K = 10^{27.75} = 5.6 \times 10^{27}$$

c. Possible reaction: $2\ Ag(s) + Cu^{2+}(aq) \rightarrow Cu(s) + 2\ Ag^+(aq)$ $E^o_{cell} = -0.46$ V; no reaction occurs.

d. Fe^{2+} can be oxidized or reduced. The other species present are H^+, SO_4^{2-}, H_2O, and O_2 from air. Only O_2 in the presence of H^+ has a large enough standard reduction potential to oxidize Fe^{2+} to Fe^{3+} (resulting in $E^o_{cell} > 0$). All other combinations, including the possible reduction of Fe^{2+}, give negative cell potentials. The spontaneous reaction is:

$$4\ Fe^{2+}(aq) + 4\ H^+(aq) + O_2(g) \rightarrow 4\ Fe^{3+}(aq) + 2\ H_2O(l) \quad E^o_{cell} = 1.23 - 0.77 = 0.46\ V$$

$$\Delta G° = -nFE^o_{cell} = -(4\ mol\ e^-)(96{,}485\ C/mol\ e^-)(0.46\ J/C)(1\ kJ/1000\ J) = -180\ kJ$$

$$\log K = \frac{4(0.46)}{0.0591} = 31.13,\ K = 1.3 \times 10^{31}$$

82. a.

$$\begin{array}{ll} Cu^+ + e^- \rightarrow Cu & E° = 0.52\ V \\ Cu^+ \rightarrow Cu^{2+} + e^- & -E° = -0.16\ V \\ \hline 2\ Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s) & E^o_{cell} = 0.36\ V;\ \text{spontaneous} \end{array}$$

$$\Delta G° = -nFE^o_{cell} = -(1\ mol\ e^-)(96{,}485\ C/mol\ e^-)(0.36\ J/C) = -34{,}700\ J = -35\ kJ$$

$$E^o_{cell} = \frac{0.0591}{n}\log K,\ \log K = \frac{nE°}{0.0591} = \frac{1(0.36)}{0.0591} = 6.09,\ K = 10^{6.09} = 1.2 \times 10^6$$

b.

$$\begin{array}{ll} Fe^{2+} + 2\ e^- \rightarrow Fe & E° = -0.44\ V \\ (Fe^{2+} \rightarrow Fe^{3+} + e^-) \times 2 & -E° = -0.77\ V \\ \hline 3\ Fe^{2+}(aq) \rightarrow 2\ Fe^{3+}(aq) + Fe(s) & E^o_{cell} = -1.21\ V;\ \text{not spontaneous} \end{array}$$

c.

$$\begin{array}{ll} HClO_2 + 2\ H^+ + 2\ e^- \rightarrow HClO + H_2O & E° = 1.65\ V \\ HClO_2 + H_2O \rightarrow ClO_3^- + 3\ H^+ + 2\ e^- & -E° = -1.21\ V \\ \hline 2\ HClO_2(aq) \rightarrow ClO_3^-(aq) + H^+(aq) + HClO(aq) & E^o_{cell} = 0.44\ V;\ \text{spontaneous} \end{array}$$

$$\Delta G° = -nFE^o_{cell} = -(2 \text{ mol } e^-)(96{,}485 \text{ C/mol } e^-)(0.44 \text{ J/C}) = -84{,}900 \text{ J} = -85 \text{ kJ}$$

$$\log K = \frac{nE^o}{0.0591} = \frac{2(0.44)}{0.0591} = 14.89,\ K = 7.8 \times 10^{14}$$

83. $(Cr^{2+} \rightarrow Cr^{3+} + e^-) \times 2$

$Co^{2+} + 2\,e^- \rightarrow Co$

$2\,Cr^{2+} + Co^{2+} \rightarrow 2\,Cr^{3+} + Co$

$$E^o_{cell} = \frac{0.0591}{n}\log K = \frac{0.0591}{2}\log(2.79 \times 10^7) = 0.220 \text{ V}$$

$$E = E° - \frac{0.0591}{n}\log\frac{[Cr^{3+}]^2}{[Cr^{2+}]^2[Co^{2+}]} = 0.220 \text{ V} - \frac{0.0591}{2}\log\frac{(2.0)^2}{(0.30)^2(0.20)} = 0.151 \text{ V}$$

$$\Delta G = -nFE = -(2 \text{ mol } e^-)(96{,}485 \text{ C/mol } e^-)(0.151 \text{ J/C}) = -2.91 \times 10^4 \text{ J} = -29.1 \text{ kJ}$$

84. $2\,Ag^+(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + 2\,Ag(s)$ $E^o_{cell} = 0.80 - 0.34 = 0.46$ V and n = 2

Because $[Ag^+] = 1.0\ M$, $E_{cell} = 0.46 \text{ V} - \frac{0.0591}{2}\log[Cu^{2+}]$.

Use the equilibrium reaction to calculate the Cu^{2+} concentration in the cell.

$$Cu^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq) \quad K = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4} = 1.0 \times 10^{13}$$

From the problem, $[NH_3] = 5.0\ M$ and $[Cu(NH_3)_4^{2+}] = 0.010\ M$:

$$1.0 \times 10^{13} = \frac{0.010}{[Cu^{2+}](5.0)^4},\ [Cu^{2+}] = 1.6 \times 10^{-18}\ M$$

$$E_{cell} = 0.46 - \frac{0.0591}{2}\log(1.6 \times 10^{-18}) = 0.46 - (-0.53) = 0.99 \text{ V}$$

85. The K_{sp} reaction is $FeS(s) \rightleftharpoons Fe^{2+}(aq) + S^{2-}(aq)$ $K = K_{sp}$. Manipulate the given equations so that when added together we get the K_{sp} reaction. Then we can use the value of E^o_{cell} for the reaction to determine K_{sp}.

$FeS + 2\,e^- \rightarrow Fe + S^{2-}$ $E° = -1.01$ V

$Fe \rightarrow Fe^{2+} + 2\,e^-$ $-E° = 0.44$ V

$Fe(s) \rightarrow Fe^{2+}(aq) + S^{2-}(aq)$ $E^o_{cell} = -0.57$ V

$$\log K_{sp} = \frac{nE°}{0.0591} = \frac{2(-0.57)}{0.0591} = -19.29,\ K_{sp} = 10^{-19.29} = 5.1 \times 10^{-20}$$

86. $Al^{3+} + 3\,e^- \rightarrow Al \qquad E° = -1.66\text{ V}$

$Al + 6\,F^- \rightarrow AlF_6^{3-} + 3\,e^- \qquad -E° = 2.07\text{ V}$

$Al^{3+}(aq) + 6\,F^-(aq) \rightarrow AlF_6^{3-}(aq) \qquad E^o_{cell} = 0.41\text{ V} \qquad K = ?$

$$\log K = \frac{nE^o}{0.0591} = \frac{3(0.41)}{0.0591} = 20.81,\ K = 10^{20.81} = 6.5 \times 10^{20}$$

87. $e^- + AgI \rightarrow Ag + I^- \qquad E^o_{AgI} = ?$

$Ag \rightarrow Ag^+ + e^- \qquad -E° = -0.80\text{ V}$

$AgI(s) \rightarrow Ag^+(aq) + I^-(aq) \qquad E^o_{cell} = E^o_{AgI} - 0.80 \quad K = K_{sp} = 1.5 \times 10^{-16}$

For this overall reaction:

$$E^o_{cell} = \frac{0.0591}{n}\log K_{sp} = \frac{0.0591}{1}\log(1.5 \times 10^{-16}) = -0.94\text{ V}$$

$$E^\circ_{cell} = -0.94\text{ V} = E^\circ_{AgI} - 0.80\text{ V},\ E^\circ_{AgI} = -0.94 + 0.80 = -0.14\text{ V}$$

88. $CuI + e^- \rightarrow Cu + I^- \qquad E^o_{CuI} = ?$

$Cu \rightarrow Cu^+ + e^- \qquad -E° = -0.52\text{ V}$

$CuI(s) \rightarrow Cu^+(aq) + I^-(aq) \qquad E^o_{cell} = E^o_{CuI} - 0.52\text{ V}$

For this overall reaction, $K = K_{sp} = 1.1 \times 10^{-12}$:

$$E^o_{cell} = \frac{0.0591}{n}\log K_{sp} = \frac{0.0591}{1}\log(1.1\times10^{-12}) = -0.71\text{ V}$$

$$E^o_{cell} = -0.71\text{ V} = E^o_{CuI} - 0.52,\ E^o_{CuI} = -0.19\text{ V}$$

Electrolysis

89. a. $Al^{3+} + 3\,e^- \rightarrow Al$; 3 mol e^- are needed to produce 1 mol Al from Al^{3+}.

$$1.0 \times 10^3\text{ g Al} \times \frac{1\text{ mol Al}}{26.98\text{ g Al}} \times \frac{3\text{ mol }e^-}{\text{mol Al}} \times \frac{96{,}485\text{ C}}{\text{mol }e^-} \times \frac{1\text{ s}}{100.0\text{ C}} = 1.07 \times 10^5\text{ s} = 30.\text{ hours}$$

b. $$1.0\text{ g Ni} \times \frac{1\text{ mol Ni}}{58.69\text{ g Ni}} \times \frac{2\text{ mol }e^-}{\text{mol Ni}} \times \frac{96{,}485\text{ C}}{\text{mol }e^-} \times \frac{1\text{ s}}{100.0\text{ C}} = 33\text{ s}$$

c. $$5.0\text{ mol Ag} \times \frac{1\text{ mol }e^-}{\text{mol Ag}} \times \frac{96{,}485\text{ C}}{\text{mol }e^-} \times \frac{1\text{ s}}{100.0\text{ C}} = 4.8 \times 10^3\text{ s} = 1.3\text{ hours}$$

90. The oxidation state of bismuth in BiO^+ is +3 because oxygen has a −2 oxidation state in this ion. Therefore, 3 moles of electrons are required to reduce the bismuth in BiO^+ to Bi(s).

$$10.0\text{ g Bi} \times \frac{1\text{ mol Bi}}{209.0\text{ g Bi}} \times \frac{3\text{ mol e}^-}{\text{mol Bi}} \times \frac{96{,}485\text{ C}}{\text{mol e}^-} \times \frac{1\text{ s}}{25.0\text{ C}} = 554\text{ s} = 9.23\text{ min}$$

91. $$15\text{ A} = \frac{15\text{ C}}{\text{s}} \times \frac{60\text{ s}}{\text{min}} \times \frac{60\text{ min}}{\text{h}} = 5.4 \times 10^4\text{ C of charge passed in 1 hour}$$

a. $$5.4 \times 10^4\text{ C} \times \frac{1\text{ mol e}^-}{96{,}485\text{ C}} \times \frac{1\text{ mol Co}}{2\text{ mol e}^-} \times \frac{58.93\text{ g Co}}{\text{mol Co}} = 16\text{ g Co}$$

b. $$5.4 \times 10^4\text{ C} \times \frac{1\text{ mol e}^-}{96{,}485\text{ C}} \times \frac{1\text{ mol Hf}}{4\text{ mol e}^-} \times \frac{178.5\text{ g Hf}}{\text{mol Hf}} = 25\text{ g Hf}$$

c. $$2\text{ I}^- \rightarrow I_2 + 2\text{ e}^-;\ 5.4 \times 10^4\text{ C} \times \frac{1\text{ mol e}^-}{96{,}485\text{ C}} \times \frac{1\text{ mol I}_2}{2\text{ mol e}^-} \times \frac{253.8\text{ g I}_2}{\text{mol I}_2} = 71\text{ g I}_2$$

d. $CrO_3(l) \rightarrow Cr^{6+} + 3\ O^{2-}$; 6 mol e^- are needed to produce 1 mol Cr from molten CrO_3.

$$5.4 \times 10^4\text{ C} \times \frac{1\text{ mol e}^-}{96{,}485\text{ C}} \times \frac{1\text{ mol Cr}}{6\text{ mol e}^-} \times \frac{52.00\text{ g Cr}}{\text{mol Cr}} = 4.9\text{ g Cr}$$

92. Al is in the +3 oxidation in Al_2O_3, so 3 mol e^- are needed to convert Al^{3+} into Al(s).

$$2.00\text{ h} \times \frac{60\text{ min}}{\text{h}} \times \frac{60\text{ s}}{\text{min}} \times \frac{1.00 \times 10^6\text{ C}}{\text{s}} \times \frac{1\text{ mol e}^-}{96{,}485\text{ C}} \times \frac{1\text{ mol Al}}{3\text{ mol e}^-} \times \frac{26.98\text{ g Al}}{\text{mol Al}} = 6.71 \times 10^5\text{ g}$$

93. $$74.1\text{ s} \times \frac{2.00\text{ C}}{\text{s}} \times \frac{1\text{ mol e}^-}{96{,}485\text{ C}} \times \frac{1\text{ mol M}}{3\text{ mol e}^-} = 5.12 \times 10^{-4}\text{ mol M, where M = unknown metal}$$

$$\text{Molar mass} = \frac{0.107\text{ g M}}{5.12 \times 10^{-4}\text{ mol M}} = \frac{209\text{ g}}{\text{mol}};\ \text{the element is bismuth.}$$

94. Alkaline earth metals form +2 ions, so 2 mol of e^- are transferred to form the metal M.

$$\text{Mol M} = 748\text{ s} \times \frac{5.00\text{ C}}{\text{s}} \times \frac{1\text{ mol e}^-}{96{,}485\text{ C}} \times \frac{1\text{ mol M}}{2\text{ mol e}^-} \times \frac{1\text{ mol e}^-}{96{,}485\text{ C}} = 1.94 \times 10^{-2}\text{ mol M}$$

$$\text{Molar mass of M} = \frac{0.471\text{ g M}}{1.94 \times 10^{-2}\text{ mol M}} = 24.3\text{ g/mol};\ \text{MgCl}_2\text{ was electrolyzed.}$$

95. F_2 is produced at the anode: $2\ F^- \rightarrow F_2 + 2\ e^-$

$$2.00\text{ h} \times \frac{60\text{ min}}{\text{h}} \times \frac{60\text{ s}}{\text{min}} \times \frac{10.0\text{ C}}{\text{s}} \times \frac{1\text{ mol e}^-}{96{,}485\text{ C}} = 0.746\text{ mol e}^-$$

$$0.746\text{ mol e}^- \times \frac{1\text{ mol F}_2}{2\text{ mol e}^-} = 0.373\text{ mol F}_2;\ \ PV = nRT,\ \ V = \frac{nRT}{P}$$

$$\frac{(0.373\text{ mol})(0.08206\text{ L atm/K} \bullet \text{mol})(298\text{ K})}{1.00\text{ atm}} = 9.12\text{ L F}_2$$

K is produced at the cathode: $K^+ + e^- \rightarrow K$

$$0.746\text{ mol e}^- \times \frac{1\text{ mol K}}{\text{mol e}^-} \times \frac{39.10\text{ g K}}{\text{mol K}} = 29.2\text{ g K}$$

96. The half-reactions for the electrolysis of water are:

$$\begin{array}{r} (2\,e^- + 2\,H_2O \rightarrow H_2 + 2\,OH^-) \times 2 \\ 2\,H_2O \rightarrow 4\,H^+ + O_2 + 4\,e^- \\ \hline 2\,H_2O(l) \rightarrow 2\,H_2(g) + O_2(g) \end{array}$$

Note: $4\,H^+ + 4\,OH^- \rightarrow 4\,H_2O$ and n = 4 for this reaction as it is written.

$$15.0\text{ min} \times \frac{60\text{ s}}{\text{min}} \times \frac{2.50\text{ C}}{\text{s}} \times \frac{1\text{ mol e}^-}{96{,}485\text{ C}} \times \frac{2\text{ mol H}_2}{4\text{ mol e}^-} = 1.17 \times 10^{-2}\text{ mol H}_2$$

At STP, 1 mol of an ideal gas occupies a volume of 22.42 L (see Chapter 5 of the text).

$$1.17 \times 10^{-2}\text{ mol H}_2 \times \frac{22.42\text{ L}}{\text{mol H}_2} = 0.262\text{ L} = 262\text{ mL H}_2$$

$$1.17 \times 10^{-2}\text{ mol H}_2 \times \frac{1\text{ mol O}_2}{2\text{ mol H}_2} \times \frac{22.42\text{ L}}{\text{mol O}_2} = 0.131\text{ L} = 131\text{ mL O}_2$$

97. $Al^{3+} + 3\,e^- \rightarrow Al$; 3 mol e^- are needed to produce Al from Al^{3+}

$$2000\text{ lb Al} \times \frac{453.6\text{ g}}{\text{lb}} \times \frac{1\text{ mol Al}}{26.98\text{ g}} \times \frac{3\text{ mol e}^-}{\text{mol Al}} \times \frac{96{,}485\text{ C}}{\text{mol e}^-} = 1 \times 10^{10}\text{ C of electricity needed}$$

$$\frac{1 \times 10^{10}\text{ C}}{24\text{ h}} \times \frac{1\text{ h}}{60\text{ min}} \times \frac{1\text{ min}}{60\text{ s}} = 1 \times 10^5\text{ C/s} = 1 \times 10^5\text{ A}$$

98. Barium is in the +2 oxidation state in $BaCl_2$. $Ba^{2+} + 2e^- \rightarrow Ba$

$$1.00 \times 10^6\text{ g Ba} \times \frac{1\text{ mol Ba}}{137.3\text{ g}} \times \frac{2\text{ mol e}^-}{\text{mol Ba}} \times \frac{96{,}485\text{ C}}{\text{mol e}^-} = 1.41 \times 10^9\text{ C of electricity needed}$$

$$\frac{1.41 \times 10^9\ \text{C}}{4.00\ \text{h}} \times \frac{1\ \text{h}}{3600\ \text{s}} = 9.79 \times 10^4\ \text{A}$$

99. $2.30\ \text{min} \times \dfrac{60\ \text{s}}{\text{min}} = 138\ \text{s};\ \ 138\ \text{s} \times \dfrac{2.00\ \text{C}}{\text{s}} \times \dfrac{1\ \text{mol e}^-}{96{,}485\ \text{C}} \times \dfrac{1\ \text{mol Ag}}{\text{mol e}^-} = 2.86 \times 10^{-3}\ \text{mol Ag}$

$[\text{Ag}^+] = 2.86 \times 10^{-3}\ \text{mol Ag}^+/0.250\ \text{L} = 1.14 \times 10^{-2}\ M$

100. $0.50\ \text{L} \times 0.010\ \text{mol Pt}^{4+}/\text{L} = 5.0 \times 10^{-3}\ \text{mol Pt}^{4+}$

To plate out 99% of the Pt^{4+}, we will produce $0.99 \times 5.0 \times 10^{-3}$ mol Pt.

$$0.99 \times 5.0 \times 10^{-3}\ \text{mol Pt} \times \frac{4\ \text{mol e}^-}{\text{mol Pt}} \times \frac{96{,}485\ \text{C}}{\text{mol e}^-} \times \frac{1\ \text{s}}{4.00\ \text{C}} \times \frac{1\ \text{mol Ag}}{\text{mol e}^-} = 480\ \text{s}$$

101. $\text{Au}^{3+} + 3\ \text{e}^- \rightarrow \text{Au}$ $\quad E° = 1.50\ \text{V}$ $\qquad \text{Ni}^{2+} + 2\ \text{e}^- \rightarrow \text{Ni}$ $\quad E° = -0.23\ \text{V}$
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$ $\quad E° = 0.80\ \text{V}$ $\qquad \text{Cd}^{2+} + 2\ \text{e}^- \rightarrow \text{Cd}$ $\quad E° = -0.40\ \text{V}$

$2\ \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\ \text{OH}^-$ $\quad E° = -0.83\ \text{V}$

Au(s) will plate out first since it has the most positive reduction potential, followed by Ag(s), which is followed by Ni(s), and finally Cd(s) will plate out last since it has the most negative reduction potential of the metals listed. Water will not interfere with the plating process.

102. To begin plating out Pd:

$$E = 0.62 - \frac{0.0591}{2} \log \frac{[\text{Cl}^-]^4}{[\text{PdCl}_4{}^{2-}]} = 0.62 - \frac{0.0591}{2} \log \frac{(1.0)^4}{0.020}$$

$E = 0.62\ \text{V} - 0.050\ \text{V} = 0.57\ \text{V}$

When 99% of Pd has plated out, $[\text{PdCl}_4{}^-] = \dfrac{0.020}{100} = 0.00020\ M$.

$$E = 0.62 - \frac{0.0591}{2} \log \frac{(1.0)^4}{2.0 \times 10^{-4}} = 0.62\ \text{V} - 0.11\text{V} = 0.51\ \text{V}$$

To begin Pt plating: $E = 0.73\ \text{V} - \dfrac{0.0591}{2} \log \dfrac{(1.0)^4}{0.020} = 0.73 - 0.050 = 0.68\ \text{V}$

When 99% of Pt plated: $E = 0.73 - \dfrac{0.0591}{2} \log \dfrac{(1.0)^4}{2.0 \times 10^{-4}} = 0.73 - 0.11 = 0.62\ \text{V}$

To begin Ir plating: $E = 0.77\ \text{V} - \dfrac{0.0591}{3} \log \dfrac{(1.0)^4}{0.020} = 0.77 - 0.033 = 0.74\ \text{V}$

When 99% of Ir plated: $E = 0.77 - \frac{0.0591}{3}\log\frac{(1.0)^4}{2.0 \times 10^{-4}} = 0.77 - 0.073 = 0.70$ V

Yes, because the range of potentials for plating out each metal do not overlap, we should be able to separate the three metals. The exact potential to apply depends on the oxidation reaction. The order of plating will be Ir(s) first, followed by Pt(s), and finally, Pd(s) as the potential is gradually increased.

103. Reduction occurs at the cathode, and oxidation occurs at the anode. First, determine all the species present; then look up pertinent reduction and/or oxidation potentials in Table 18.1 for all these species. The cathode reaction will be the reaction with the most positive reduction potential, and the anode reaction will be the reaction with the most positive oxidation potential.

a. Species present: Ni^{2+} and Br^-; Ni^{2+} can be reduced to Ni, and Br^- can be oxidized to Br_2 (from Table 18.1). The reactions are:

Cathode: $Ni^{2+} + 2e^- \rightarrow Ni$ E° = −0.23 V
Anode: $2\ Br^- \rightarrow Br_2 + 2\ e^-$ −E° = −1.09 V

b. Species present: Al^{3+} and F^-; Al^{3+} can be reduced, and F^- can be oxidized. The reactions are:

Cathode: $Al^{3+} + 3\ e^- \rightarrow Al$ E° = −1.66 V
Anode: $2\ F^- \rightarrow F_2 + 2\ e^-$ −E° = −2.87 V

c. Species present: Mn^{2+} and I^-; Mn^{2+} can be reduced, and I^- can be oxidized. The reactions are:

Cathode: $Mn^{2+} + 2\ e^- \rightarrow Mn$ E° = −1.18 V
Anode: $2\ I^- \rightarrow I_2 + 2\ e^-$ −E° = −0.54 V

104. Reduction occurs at the cathode, and oxidation occurs at the anode. First, determine all the species present; then look up pertinent reduction and/or oxidation potentials in Table 18.1 for all these species. The cathode reaction will be the reaction with the most positive reduction potential, and the anode reaction will be the reaction with the most positive oxidation potential.

a. Species present: K^+ and F^-; K^+ can be reduced to K, and F^- can be oxidized to F_2 (from Table 18.1). The reactions are:

Cathode: $K^+ + e^- \rightarrow K$ E° = −2.92 V
Anode: $2\ F^- \rightarrow F_2 + 2\ e^-$ −E° = −2.87 V

b. Species present: Cu^{2+} and Cl^-; Cu^{2+} can be reduced, and Cl^- can be oxidized. The reactions are:

Cathode: $Cu^{2+} + 2\ e^- \rightarrow Cu$ E° = 0.34 V
Anode: $2\ Cl^- \rightarrow Cl_2 + 2\ e^-$ −E° = −1.36 V

c. Species present: Mg^{2+} and I^-; Mg^{2+} can be reduced, and I^- can be oxidized. The reactions are:

Cathode: $Mg^{2+} + 2\ e^- \rightarrow Mg$ $E° = -2.37\ V$
Anode: $2\ I^- \rightarrow I_2 + 2\ e^-$ $-E° = -0.54\ V$

105. These are all in aqueous solutions, so we must also consider the reduction and oxidation of H_2O in addition to the potential redox reactions of the ions present. For the cathode reaction, the species with the most positive reduction potential will be reduced, and for the anode reaction, the species with the most positive oxidation potential will be oxidized.

a. Species present: Ni^{2+}, Br^-, and H_2O. Possible cathode reactions are:

$Ni^{2+} + 2e^- \rightarrow Ni$ $E° = -0.23\ V$
$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$ $E° = -0.83\ V$

Because it is easier to reduce Ni^{2+} than H_2O (assuming standard conditions), Ni^{2+} will be reduced by the preceding cathode reaction.

Possible anode reactions are:

$2\ Br^- \rightarrow Br_2 + 2\ e^-$ $-E° = -1.09\ V$
$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$ $-E° = -1.23\ V$

Because Br^- is easier to oxidize than H_2O (assuming standard conditions), Br^- will be oxidized by the preceding anode reaction.

b. Species present: Al^{3+}, F^-, and H_2O; Al^{3+} and H_2O can be reduced. The reduction potentials are $E° = -1.66\ V$ for Al^{3+} and $E° = -0.83\ V$ for H_2O (assuming standard conditions). H_2O will be reduced at the cathode ($2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$).

F^- and H_2O can be oxidized. The oxidation potentials are $-E° = -2.87\ V$ for F^- and $-E° = -1.23\ V$ for H_2O (assuming standard conditions). From the potentials, we would predict H_2O to be oxidized at the anode ($2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$).

c. Species present: Mn^{2+}, I^-, and H_2O; Mn^{2+} and H_2O can be reduced. The possible cathode reactions are:

$Mn^{2+} + 2\ e^- \rightarrow Mn$ $E° = -1.18\ V$
$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$ $E° = -0.83\ V$

Reduction of H_2O will occur at the cathode since $E^{o}_{H_2O}$ is most positive.

I^- and H_2O can be oxidized. The possible anode reactions are:

$2\ I^- \rightarrow I_2 + 2\ e^-$ $-E° = -0.54\ V$
$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$ $-E° = -1.23\ V$

Oxidation of I^- will occur at the anode since $-E^{o}_{I^-}$ is most positive.

106. These are all in aqueous solutions, so we must also consider the reduction and oxidation of H_2O in addition to the potential redox reactions of the ions present. For the cathode reaction, the species with the most positive reduction potential will be reduced, and for the anode reaction, the species with the most positive oxidation potential will be oxidized.

a. Species present: K^+, F^-, and H_2O. Possible cathode reactions are:

$K^+ + e^- \rightarrow K$ $E° = -2.92$ V
$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$ $E° = -0.83$ V

Because it is easier to reduce H_2O than K^+ (assuming standard conditions), H_2O will be reduced by the preceding cathode reaction.

Possible anode reactions are:

$2\ F^- \rightarrow F_2 + 2\ e^-$ $-E° = -2.87$ V
$2\ H_2O \rightarrow 4\ H^+ + O_2 + 4\ e^-$ $-E° = -1.23$ V

Because H_2O is easier to oxidize than F^- (assuming standard conditions), H_2O will be oxidized by the preceding anode reaction.

b. Species present: Cu^{2+}, Cl^-, and H_2O; Cu^{2+} and H_2O can be reduced. The reduction potentials are $E° = 0.34$ V for Cu^{2+} and $E° = -0.83$ V for H_2O (assuming standard conditions). Cu^{2+} will be reduced to Cu at the cathode ($Cu^{2+} + 2\ e^- \rightarrow Cu$).

Cl^- and H_2O can be oxidized. The oxidation potentials are $-E° = -1.36$ V for Cl^- and $-E° = -1.23$ V for H_2O (assuming standard conditions). From the potentials, we would predict H_2O to be oxidized at the anode ($2\ H_2O \rightarrow 4\ H^+ + O_2 + 4\ e^-$). *Note*: In real life, Cl^- is oxidized to Cl_2 when water is present due to a phenomenon called overvoltage (see Section 18.8 of the text). Because overvoltage is difficult to predict, we will generally ignore it.

c. Species present: Mg^{2+}, I^-, and H_2O: The only possible cathode reactions are:

$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$ $E° = -0.83$ V
$Mg^{2+} + 2\ e^- \rightarrow Mg$ $E° = -2.37$ V

Reduction of H_2O will occur at the cathode since $E^o_{H_2O}$ is more positive. The only possible anode reactions are:

$2\ I^- \rightarrow I_2 + 2\ e^-$ $-E° = -0.54$ V
$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$ $-E° = -1.23$ V

Oxidation of I^- will occur at the anode because $-E^o_{H_2O}$ is more positive.

Connecting to Biochemistry

107.

$$\begin{array}{r} 2(6\,e^- + 14\,H^+ + Cr_2O_7^{2-} \rightarrow 2\,Cr^{3+} + 7\,H_2O) \\ 3\,H_2O + C_2H_5OH \rightarrow 2\,CO_2 + 12\,H^+ + 12\,e^- \\ \hline 16\,H^+ + 2\,Cr_2O_7^{2-} + C_2H_5OH \rightarrow 4\,Cr^{3+} + 2\,CO_2 + 11\,H_2O \end{array}$$

$$0.03105\text{ L}\left(\frac{0.0600\text{ mol Cr}_2\text{O}_7^{\,2-}}{\text{L}}\right)\left(\frac{1\text{ mol C}_2\text{H}_5\text{OH}}{2\text{ mol Cr}_2\text{O}_7^{\,2-}}\right)\left(\frac{46.07\text{ g}}{\text{mol C}_2\text{H}_5\text{OH}}\right) = 0.0429\text{ g C}_2\text{H}_5\text{OH}$$

$$\frac{0.0429\text{ g C}_2\text{H}_5\text{OH}}{30.0\text{ g blood}} \times 100 = 0.143\%\ \text{C}_2\text{H}_5\text{OH}$$

108. $CH_3OH(l) + 3/2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)$ $\Delta G° = 2(-237) + (-394) - [-166] = -702$ kJ

The balanced half-reactions are:

$H_2O + CH_3OH \rightarrow CO_2 + 6\,H^+ + 6\,e^-$ and $O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$

For 3/2 mol O_2, 6 mol of electrons will be transferred (n = 6).

$$\Delta G° = -nFE°,\ \ E° = \frac{-\Delta G^{o}}{nF} = \frac{-(-702{,}000\text{ J})}{(6\text{ mol e}^-)(96{,}485\text{ C/mol e}^-)} = 1.21\text{ J/C} = 1.21\text{ V}$$

109. For C_2H_5OH, H has a +1 oxidation state, and O has a −2 oxidiation state. This dictates a −2 oxidation state for C. For CO_2, O has a −2 oxidiation state, so carbon has a +4 oxidiation state. Six moles of electrons are transferred per mole of carbon oxidized (C goes from −2 → +4). Two moles of carbon are in the balanced reaction, so n = 12.

$$w_{max} = -1320\text{ kJ} = \Delta G = -nFE,\ \ -1320 \times 10^3\text{ J} = -nFE = -(12\text{ mol e}^-)(96{,}485\text{ C/mol e}^-)E$$

E = 1.14 J/C = 1.14 V

110. For a concentration cell, $E^{o}_{cell} = 0$. Because the potential is negative, we want to perform the calculation with the nonspontaneous concentration cell reaction. This reaction is:

$$K^+_{outside} \rightarrow K^+_{inside}$$

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n}\log Q = \frac{-0.0591}{1}\log\frac{[K^+_{inside}]}{[K^+_{outside}]}$$

$$-70. \times 10^{-3}\text{ V} = \frac{-0.0591}{1}\log\frac{[K^+_{inside}]}{[K^+_{outside}]},\ \ \frac{[K^+_{inside}]}{[K^+_{outside}]} = 10^{1.18} = 15$$

The K^+ concentration inside the cell is approximately 15 times more concentrated as compared to the K^+ concentration outside the nerve cell.

111. $\Delta G° = [6 \text{ mol}(-394 \text{ kJ/mol}) + 6 \text{ mol}(-237 \text{ kJ/mol}] - [1 \text{ mol}(-911 \text{ kJ/mol} + 6 \text{ mol}(0)]$
$= -2875 \text{ kJ}$

Carbon is oxidized in this combustion reaction. In $C_6H_{12}O_6$, H has a +1 oxidation state, and oxygen has a −2 oxidation, so $6(x) + 12(+1) + 6(-2) = 0$, x = oxidation state of C in $C_6H_{12}O_6$ = 0. In CO_2, O has an oxidation state of −2, so $y + 2(-2) = 0$, y = oxidation state of C in CO_2 = +4. Carbon goes from the 0 oxidation state in $C_6H_{12}O_6$ to the +4 oxidation state in CO_2, so each carbon atom loses 4 electrons. Because the balanced reaction has 6 mol of carbon, 6(4) = 24 mol electrons are transferred in the balanced equation.

$$\Delta G° = -nFE°,\ E° = \frac{-\Delta G^o}{nF} = \frac{-(-2875 \times 10^3 \text{ J})}{(24 \text{ mol e}^-)(96{,}485 \text{ C/mol e}^-)} = 1.24 \text{ J/C} = 1.24 \text{ V}$$

112. For a spontaneous process, $E_{cell} > 0$. In each electron transfer step, we need to couple a reduction half-reaction with an oxidation half-reaction. To determine the correct order, each step must have a positive cell potential in order to be spontaneous. The only possible order for spontaneous electron transfer is:

Step 1:

$$\begin{array}{lr} \text{cyt a(Fe}^{3+}) + e^- \rightarrow \text{cyt a(Fe}^{2+}) & E = 0.385 \text{ V} \\ \text{cyt c(Fe}^{2+}) \rightarrow \text{cyt c(Fe}^{3+}) + e^- & -E = -0.254 \text{ V} \\ \hline \text{cyt a(Fe}^{3+}) + \text{cyt c(Fe}^{2+}) \rightarrow \text{cyt a(Fe}^{2+}) + \text{cyt c((Fe}^{3+}) & E_{cell} = 0.131 \text{ V} \end{array}$$

Step 2:

$$\begin{array}{lr} \text{cyt c(Fe}^{3+}) + e^- \rightarrow \text{cyt c(Fe}^{2+}) & E = 0.254 \text{ V} \\ \text{cyt b(Fe}^{2+}) \rightarrow \text{cyt b(Fe}^{3+}) + e^- & -E = -0.030 \text{ V} \\ \hline \text{cyt c(Fe}^{3+}) + \text{cyt b(Fe}^{2+}) \rightarrow \text{cyt c(Fe}^{2+}) + \text{cyt b((Fe}^{3+}) & E_{cell} = 0.224 \text{ V} \end{array}$$

Step 3 would involve the reduction half-reaction of cyt b(Fe^{3+}) + e^- → cyt b(Fe^{2+}) coupled with some oxidation half-reaction.

This is the only order that utilizes all three cytochromes and has each step with a positive cell potential. Therefore, electron transport through these cytochromes occurs from cyto-chrome a to chtochrome c to cytochrome b to some other substance and eventually to oxygen in O_2.

113. $$\frac{150. \times 10^3 \text{ g } C_6H_8N_2}{\text{h}} \times \frac{1 \text{ h}}{60 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} \times \frac{1 \text{ mol } C_6H_8N_2}{108.14 \text{ g } C_6H_8N_2} \times \frac{2 \text{ mol e}^-}{\text{mol } C_6H_8N_2} \times \frac{96{,}485 \text{ C}}{\text{mol e}^-}$$

$= 7.44 \times 10^4$ C/s, or a current of 7.44×10^4

114. Mercury is hazardous when it can be oxidized to the Hg_2^{2+} or Hg^{2+} ions. However, when mercury is in the solid elemental form having a zero oxidation state, it is relatively inert; it passes through the digestive system and is excreted before it can pose any risk. The reason Hg is relatively inert is because it is not easily oxidized. Only two oxidation potentials are listed in Table 18.1 that involve elemental mercury:

$$2\ Hg \rightarrow Hg_2^{2+} + 2e^- \qquad -E° = -0.80\ V$$

$$2\ Hg + 2\ Cl^- \rightarrow Hg2Cl2 + 2e^- \qquad -E° = -0.27\ V$$

Note that both these oxidation potentials are negative, indicating that these oxidations are fairly difficult to do. No oxidizing agents in the mouth or in the stomach have a reduction potential large enough to spontaneously oxidize mercury into its reactive and hazardous ions. So mercury in the solid elemental form is relatively inert because it is difficult to oxidize.

Note: Mercury in the vapor form is always hazardous, and specifically, inhalation of mercury vapor into the lungs is the most dangerous route of entry. Death often results from respiratory or kidney failure due to inhalation of mercury vapor.

Additional Exercises

115. The half-reaction for the SCE is:

$$Hg_2Cl_2 + 2\ e^- \rightarrow 2\ Hg + 2\ Cl^- \qquad E_{SCE} = 0.242\ V$$

For a spontaneous reaction to occur, E_{cell} must be positive. Using the standard reduction potentials in Table 18.1 and the given the SCE potential, deduce which combination will produce a positive overall cell potential.

a. $Cu^{2+} + 2\ e^- \rightarrow Cu \qquad E° = 0.34\ V$

$E_{cell} = 0.34 - 0.242 = 0.10$ V; SCE is the anode.

b. $Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad E° = 0.77\ V$

$E_{cell} = 0.77 - 0.242 = 0.53$ V; SCE is the anode.

c. $AgCl + e^- \rightarrow Ag + Cl^- \quad E° = 0.22\ V$

$E_{cell} = 0.242 - 0.22 = 0.02$ V; SCE is the cathode.

d. $Al^{3+} + 3\ e^- \rightarrow Al \qquad E° = -1.66\ V$

$E_{cell} = 0.242 + 1.66 = 1.90$ V; SCE is the cathode.

e. $Ni^{2+} + 2\ e^- \rightarrow Ni \qquad E° = -0.23\ V$

$E_{cell} = 0.242 + 0.23 = 0.47$ V; SCE is the cathode.

116. The potential oxidizing agents are NO_3^- and H^+. Hydrogen ion cannot oxidize Pt under either condition. Nitrate cannot oxidize Pt unless there is Cl^- in the solution. Aqua regia has both Cl^- and NO_3^-. The overall reaction is:

$$(NO_3^- + 4\,H^+ + 3\,e^- \rightarrow NO + 2\,H_2O) \times 2 \qquad E° = 0.96\text{ V}$$
$$(4\,Cl^- + Pt \rightarrow PtCl_4^{2-} + 2\,e^-) \times 3 \qquad -E° = -0.755\text{ V}$$

$$12\,Cl^-(aq) + 3\,Pt(s) + 2\,NO_3^-(aq) + 8\,H^+(aq) \rightarrow 3\,PtCl_4^{2-}(aq) + 2\,NO(g) + 4\,H_2O(l) \qquad E^o_{cell} = 0.21\text{ V}$$

117. $Ag^+(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + 2\,Ag(s)$ $E^o_{cell} = 0.80 - 0.34\text{ V} = 0.46\text{ V}$; a galvanic cell produces a voltage as the forward reaction occurs. Any stress that increases the tendency of the forward reaction to occur will increase the cell potential, whereas a stress that decreases the tendency of the forward reaction to occur will decrease the cell potential.

a. Added Cu^{2+} (a product ion) will decrease the tendency of the forward reaction to occur, which will decrease the cell potential.

b. Added NH_3 removes Cu^{2+} in the form of $Cu(NH_3)_4^{2+}$. Because a product ion is removed, this will increase the tendency of the forward reaction to occur, which will increase the cell potential.

c. Added Cl^- removes Ag^+ in the form of AgCl(s). Because a reactant ion is removed, this will decrease the tendency of the forward reaction to occur, which will decrease the cell potential.

d. $Q_1 = \dfrac{[Cu^{2+}]_0}{[Ag^+]_0^2}$; as the volume of solution is doubled, each concentration is halved.

$$Q_2 = \frac{1/2\,[Cu^{2+}]_0}{(1/2\,[Ag^+]_0)^2} = \frac{2[Cu^{2+}]_0}{[Ag^+]_0^2} = 2Q_1$$

The reaction quotient is doubled because the concentrations are halved. Because reactions are spontaneous when $Q < K$, and because Q increases when the solution volume doubles, the reaction is closer to equilibrium, which will decrease the cell potential.

e. Because Ag(s) is not a reactant in this spontaneous reaction, and because solids do not appear in the reaction quotient expressions, replacing the silver electrode with a platinum electrode will have no effect on the cell potential.

118.

$$(Al^{3+} + 3\,e^- \rightarrow Al) \times 2 \qquad E° = -1.66\text{ V}$$
$$(M \rightarrow M^{2+} + 2\,e^-) \times 3 \qquad -E° = ?$$

$$3\,M(s) + 2\,Al^{3+}(aq) \rightarrow 2\,Al(s) + 3\,M^{2+}(aq) \qquad E^o_{cell} = -E° - 1.66\text{ V}$$

$\Delta G° = -nFE^o_{cell}$, $-411 \times 10^3\text{ J} = -(6\text{ mol e}^-)(96{,}485\text{ C/mol e}^-)E^o_{cell}$, $E^o_{cell} = 0.71\text{ V}$

$E^o_{cell} = -E° - 1.66\text{ V} = 0.71\text{ V}$, $-E° = 2.37$ or $E° = -2.37$

From Table 18.1, the reduction potential for $Mg^{2+} + 2\ e^- \rightarrow Mg$ is −2.37 V, which fits the data. Hence, the metal is magnesium.

119. a. $\Delta G° = \sum n_p \Delta G^o_{f,\,products} - \sum n_r \Delta G^o_{f,\,reactants} = 2(-480.) + 3(86) - [3(-40.)] = -582\ kJ$

From oxidation numbers, n = 6. $\Delta G° = -nFE°$, $E° = \dfrac{-\Delta G^o}{nF} = \dfrac{-(-582{,}000\ J)}{6(96{,}485)\ C} = 1.01\ V$

$$\log K = \frac{nE^o}{0.0591} = \frac{6(1.01)}{0.0591} = 102.538,\ K = 10^{102.538} = 3.45 \times 10^{102}$$

b.

$$\begin{array}{ll} (2\ e^- + Ag_2S \rightarrow 2\ Ag + S^{2-}) \times 3 & E^o_{Ag_2S} = ? \\ (Al \rightarrow Al^{3+} + 3\ e^-) \times 2 & -E° = 1.66\ V \\ \hline 3\ Ag_2S(s) + 2\ Al(s) \rightarrow 6\ Ag(s) + 3\ S^{2-}(aq) + 2\ Al^{3+}(aq) & E^o_{cell} = 1.01\ V = E^o_{Ag_2S} + 1.66V \end{array}$$

$$E^o_{Ag_2S} = 1.01\ V - 1.66\ V = -0.65\ V$$

120. $Zn \rightarrow Zn^{2+} + 2\ e^-$ $-E° = 0.76\ V$; $Fe \rightarrow Fe^{2+} + 2\ e^-$ $-E° = 0.44\ V$

It is easier to oxidize Zn than Fe, so the Zn would be preferentially oxidized, protecting the iron of the *Monitor's* hull.

121. Aluminum has the ability to form a durable oxide coating over its surface. Once the HCl dissolves this oxide coating, Al is exposed to H^+ and is easily oxidized to Al^{3+}; i.e., the Al foil disappears after the oxide coating is dissolved.

122. Only statement e is true. The attached metals that are more easily oxidized than iron are called sacrificial metals. For statement a, corrosion is a spontaneous process, like the ones harnessed to make galvanic cells. For statement b, corrosion of steel is the oxidation of iron coupled with the reduction of oxygen. For statement c, cars rust more easily in high-moisture areas (the humid areas) because water is a reactant in the reduction half-reaction as well as providing a medium for ion migration (a salt bridge of sorts). For statement d, salting roads adds ions to the corrosion process, which increases the conductivity of the aqueous solution and, in turn, accelerates corrosion.

123. Consider the strongest oxidizing agent combined with the strongest reducing agent from Table 18.1:

$$\begin{array}{ll} F_2 + 2\ e^- \rightarrow 2\ F^- & E° = 2.87\ V \\ (Li \rightarrow Li^+ + e^-) \times 2 & -E° = 3.05\ V \\ \hline F_2(g) + 2\ Li(s) \rightarrow 2\ Li^+(aq) + 2\ F^-\ (aq) & E^o_{cell} = 5.92\ V \end{array}$$

The claim is impossible. The strongest oxidizing agent and strongest reducing agent when combined only give an E^o_{cell} value of about 6 V.

124. $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$; oxygen goes from the zero oxidation state to the −2 oxidation state in H_2O. Because 2 mol of O are in the balanced reaction, n = 4 moles of electrons transferred.

a. $E^{o}_{cell} = \dfrac{0.0591}{n}\log K = \dfrac{0.0591}{4}\log(1.28 \times 10^{83}),\ E^{o}_{cell} = 1.23\ V$

$\Delta G° = -nFE^{o}_{cell} = -\ (4\ mol\ e^-)(96{,}485\ C/mol\ e^-)(1.23\ J/C) = -4.75 \times 10^5\ J = -475\ kJ$

b. Because the moles of gas decrease as reactants are converted into products, ΔS° will be negative (unfavorable). Because the value of ΔG° is negative, ΔH° must be negative to override the unfavorable ΔS° (ΔG° = ΔH° − TΔS°).

c. $\Delta G = w_{max} = \Delta H - T\Delta S$. Because ΔS is negative, as T increases, ΔG becomes more positive (closer to zero). Therefore, w_{max} will decrease as T increases.

125. $O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$ $\qquad E° = 0.40\ V$

$(H_2 + 2\ OH^- \rightarrow 2\ H_2O + 2\ e^-) \times 2$ $\qquad -E° = 0.83\ V$

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$ $\qquad E^{o}_{cell} = 1.23\ V = 1.23\ J/C$

Because standard conditions are assumed, $w_{max} = \Delta G°$ for 2 mol H_2O produced.

$\Delta G° = -nFE^{o}_{cell} = -(4\ mol\ e^-)(96{,}485\ C/mol\ e^-)(1.23\ J/C) = -475{,}000\ J = -475\ kJ$

For 1.00×10^3 g H_2O produced, w_{max} is:

$$1.00 \times 10^3\ g\ H_2O \times \frac{1\ mol\ H_2O}{18.02\ g\ H_2O} \times \frac{-475\ kJ}{2\ mol\ H_2O} = -13{,}200\ kJ = w_{max}$$

The work done can be no larger than the free energy change. The best that could happen is that all of the free energy released would go into doing work, but this does not occur in any real process because there is always waste energy in a real process. Fuel cells are more efficient in converting chemical energy into electrical energy; they are also less massive. The major disadvantage is that they are expensive. In addition, $H_2(g)$ and $O_2(g)$ are an explosive mixture if ignited; much more so than fossil fuels.

126. Cadmium goes from the zero oxidation state to the +2 oxidation state in $Cd(OH)_2$. Because 1 mol of Cd appears in the balanced reaction, n = 2 mol electrons transferred. At standard conditions:

$$w_{max} = \Delta G° = -nFE°,\quad w_{max} = -(2\ mol\ e^-)(96{,}485\ C/mol\ e^-)(1.10\ J/C) = -2.12 \times 10^5\ J = -212\ kJ$$

127. $(CO + O^{2-} \rightarrow CO_2 + 2\ e^-) \times 2$

$O_2 + 4\ e^- \rightarrow 2\ O^{2-}$

$2\ CO + O_2 \rightarrow 2\ CO_2$

$$\Delta G = -nFE, \quad E = \frac{-\Delta G^o}{nF} = \frac{-(-380 \times 10^3 \text{ J})}{(4 \text{ mol e}^-)(96{,}485 \text{ C/mol e}^-)} = 0.98 \text{ V}$$

128. If the metal M forms 1+ ions, then the atomic mass of M would be:

$$\text{mol M} = 150.\text{ s} \times \frac{1.25 \text{ C}}{\text{s}} \times \frac{1 \text{ mol e}^-}{96{,}485 \text{ C}} \times \frac{1 \text{ mol M}}{1 \text{ mol e}^-} = 1.94 \times 10^{-3} \text{ mol M}$$

$$\text{Atomic mass of M} = \frac{0.109 \text{ g M}}{1.94 \times 10^{-3} \text{ mol M}} = 56.2 \text{ g/mol}$$

From the periodic table, the only metal with an atomic mass close to 56.2 g/mol is iron, but iron does not form stable 1+ ions. If M forms 2+ ions, then the atomic mass would be:

$$\text{mol M} = 150.\text{ s} \times \frac{1.25 \text{ C}}{\text{s}} \times \frac{1 \text{ mol e}^-}{96{,}485 \text{ C}} \times \frac{1 \text{ mol M}}{2 \text{ mol e}^-} = 9.72 \times 10^{-4} \text{ mol M}$$

$$\text{Atomic mass of M} = \frac{0.109 \text{ g M}}{9.72 \times 10^{-4} \text{ mol M}} = 112 \text{ g/mol}$$

Cadmium has an atomic mass of 112.4 g/mol and does form stable 2+ ions. Cd^{2+} is a much more logical choice than Fe^+.

129. The oxidation state of gold in $Au(CN)_2^-$ is +1. Each mole of gold produced requires 1 mol of electrons gained (+1 → 0). The only oxygen containing reactant is H_2O. Each mole of oxygen goes from −2 → 0 oxidation states as H_2O is converted into O_2. One mole of O_2 contains 2 mol O, so 4 mol of electrons are lost when 1 mol O_2 is formed. In order to balance the electrons, we need 4.00 mol of gold for every mole of O_2 produced or 0.250 mol O_2 for every 1.00 mol of gold formed.

130. In the electrolysis of aqueous sodium chloride, H_2O is reduced in preference to Na^+, and Cl^- is oxidized in preference to H_2O. The anode reaction is $2\ Cl^- \rightarrow Cl_2 + 2\ e^-$, and the cathode reaction is $2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$. The overall reaction is:

$$2\ H_2O(l) + 2\ Cl^-(aq) \rightarrow Cl_2(g) + H_2(g) + 2\ OH^-(aq)$$

From the 1 : 1 mol ratio between Cl_2 and H_2 in the overall balanced reaction, if 257 L of $Cl_2(g)$ is produced, then 257 L of $H_2(g)$ will also be produced because moles and volume of gas are directly proportional at constant T and P (see Chapter 5 of text).

131. $$\text{Mol e}^- = 50.0 \text{ min} \times \frac{60 \text{ s}}{\text{min}} \times \frac{2.50 \text{ C}}{\text{s}} \times \frac{1 \text{ mol e}^-}{96{,}485 \text{ C}} = 7.77 \times 10^{-2} \text{ mol e}^-$$

$$\text{Mol Ru} = 2.618 \text{ g Ru} \times \frac{1 \text{ mol Ru}}{101.1 \text{ g Ru}} = 2.590 \times 10^{-2} \text{ mol Ru}$$

$$\frac{\text{Mol e}^-}{\text{Mol Ru}} = \frac{7.77\times10^{-2}\ \text{mol e}^-}{2.590\times10^{-2}\ \text{mol Ru}} = 3.00\text{; the charge on the ruthenium ions is +3.}$$

$(Ru^{3+} + 3\ e^- \rightarrow Ru)$

132. $15\ \text{kWh} = \frac{15000\ \text{J h}}{\text{s}} \times \frac{60\ \text{s}}{\text{min}} \times \frac{60\ \text{min}}{\text{h}} = 5.4 \times 10^7\ \text{J or } 5.4 \times 10^4\ \text{kJ}$ (Hall-Heroult process)

To melt 1.0 kg Al requires: $1.0 \times 10^3\ \text{g Al} \times \frac{1\ \text{mol Al}}{26.98\ \text{g}} \times \frac{10.7\ \text{kJ}}{\text{mol Al}} = 4.0 \times 10^2\ \text{kJ}$

It is feasible to recycle Al by melting the metal because, in theory, it takes less than 1% of the energy required to produce the same amount of Al by the Hall-Heroult process.

133. a. Species present: Na^+, SO_4^{2-}, and H_2O. From the potentials, H_2O is the most easily oxidized and the most easily reduced species present. The reactions are:

Cathode: $2\ H_2O + 2\ e^- \rightarrow H_2(g) + 2\ OH^-$; anode: $2\ H_2O \rightarrow O_2(g) + 4\ H^+ + 4\ e^-$

b. When water is electrolyzed, a significantly higher voltage than predicted is necessary to produce the chemical change (called overvoltage). This higher voltage is probably great enough to cause some SO_4^{2-} to be oxidized instead of H_2O. Thus the volume of O_2 generated would be less than expected, and the measured volume ratio would be greater than 2 : 1.

Challenge Problems

134. a. HCl(aq) dissociates to $H^+(aq) + Cl^-(aq)$. For simplicity, let's use H^+ and Cl^- separately.

$H^+ \rightarrow H_2$ $\qquad$ $Fe \rightarrow HFeCl_4$

$(2\ H^+ + 2\ e^- \rightarrow H_2) \times 3$ $\qquad$ $(H^+ + 4\ Cl^- + Fe \rightarrow HFeCl_4 + 3\ e^-) \times 2$

$$6\ H^+ + 6\ e^- \rightarrow 3\ H_2$$
$$2\ H^+ + 8\ Cl^- + 2\ Fe \rightarrow 2\ HFeCl_4 + 6\ e^-$$
$$\overline{8\ H^+ + 8\ Cl^- + 2\ Fe \rightarrow 2\ HFeCl_4 + 3\ H_2}$$

or $8\ HCl(aq) + 2\ Fe(s) \rightarrow 2\ HFeCl_4(aq) + 3\ H_2(g)$

b. $IO_3^- \rightarrow I_3^-$ $\qquad$ $I^- \rightarrow I_3^-$

$3\ IO_3^- \rightarrow I_3^-$ $\qquad$ $(3\ I^- \rightarrow I_3^- + 2\ e^-) \times 8$

$3\ IO_3^- \rightarrow I_3^- + 9\ H_2O$

$16\ e^- + 18\ H^+ + 3\ IO_3^- \rightarrow I_3^- + 9\ H_2O$

$$16\ e^- + 18\ H^+ + 3\ IO_3^- \rightarrow I_3^- + 9\ H_2O$$
$$24\ I^- \rightarrow 8\ I_3^- + 16\ e^-$$
$$\overline{18\ H^+ + 24\ I^- + 3\ IO_3^- \rightarrow 9\ I_3^- + 9\ H_2O}$$

Reducing: $6\ H^+(aq) + 8\ I^-(aq) + IO_3^-(aq) \rightarrow 3\ I_3^-(aq) + 3\ H_2O(l)$

c. $(\mathrm{Ce^{4+}} + \mathrm{e^-} \rightarrow \mathrm{Ce^{3+}}) \times 97$

$$\mathrm{Cr(NCS)_6^{4-}} \rightarrow \mathrm{Cr^{3+}} + \mathrm{NO_3^-} + \mathrm{CO_2} + \mathrm{SO_4^{2-}}$$

$$54\ \mathrm{H_2O} + \mathrm{Cr(NCS)_6^{4-}} \rightarrow \mathrm{Cr^{3+}} + 6\ \mathrm{NO_3^-} + 6\ \mathrm{CO_2} + 6\ \mathrm{SO_4^{2-}} + 108\ \mathrm{H^+}$$

Charge on left $= -4$. Charge on right $= +3 + 6(-1) + 6(-2) + 108(+1) = +93$. Add 97 $\mathrm{e^-}$ to the product side, and then add the two balanced half-reactions with a common factor of 97 $\mathrm{e^-}$ transferred.

$$54\ \mathrm{H_2O} + \mathrm{Cr(NCS)_6^{4-}} \rightarrow \mathrm{Cr^{3+}} + 6\ \mathrm{NO_3^-} + 6\ \mathrm{CO_2} + 6\ \mathrm{SO_4^{2-}} + 108\ \mathrm{H^+} + 97\ \mathrm{e^-}$$

$$97\ \mathrm{e^-} + 97\ \mathrm{Ce^{4+}} \rightarrow 97\ \mathrm{Ce^{3+}}$$

$$97\ \mathrm{Ce^{4+}(aq)} + 54\ \mathrm{H_2O(l)} + \mathrm{Cr(NCS)_6^{4-}(aq)} \rightarrow 97\ \mathrm{Ce^{3+}(aq)} + \mathrm{Cr^{3+}(aq)} + 6\ \mathrm{NO_3^-(aq)} + 6\ \mathrm{CO_2(g)} + 6\ \mathrm{SO_4^{2-}(aq)} + 108\ \mathrm{H^+(aq)}$$

This is very complicated. A check of the net charge is a good check to see if the equation is balanced. Left: Charge $= 97(+4) -4 = +384$. Right: Charge $= 97(+3) + 3 + 6(-1) + 6(-2) + 108(+1) = +384$.

d. $\mathrm{CrI_3} \rightarrow \mathrm{CrO_4^{2-}} + \mathrm{IO_4^-}$ $\qquad$ $\mathrm{Cl_2} \rightarrow \mathrm{Cl^-}$

$(16\ \mathrm{H_2O} + \mathrm{CrI_3} \rightarrow \mathrm{CrO_4^{2-}} + 3\ \mathrm{IO_4^-} + 32\ \mathrm{H^+} + 27\ \mathrm{e^-}) \times 2$ $\qquad$ $(2\ \mathrm{e^-} + \mathrm{Cl_2} \rightarrow 2\ \mathrm{Cl^-}) \times 27$

Common factor is a transfer of 54 $\mathrm{e^-}$.

$$54\ \mathrm{e^-} + 27\ \mathrm{Cl_2} \rightarrow 54\ \mathrm{Cl^-}$$

$$32\ \mathrm{H_2O} + 2\ \mathrm{CrI_3} \rightarrow 2\ \mathrm{CrO_4^{2-}} + 6\ \mathrm{IO_4^-} + 64\ \mathrm{H^+} + 54\ \mathrm{e^-}$$

$$32\ \mathrm{H_2O} + 2\ \mathrm{CrI_3} + 27\ \mathrm{Cl_2} \rightarrow 54\ \mathrm{Cl^-} + 2\ \mathrm{CrO_4^{2-}} + 6\ \mathrm{IO_4^-} + 64\ \mathrm{H^+}$$

Add 64 $\mathrm{OH^-}$ to both sides and convert 64 $\mathrm{H^+}$ into 64 $\mathrm{H_2O}$.

$$64\ \mathrm{OH^-} + 32\ \mathrm{H_2O} + 2\ \mathrm{CrI_3} + 27\ \mathrm{Cl_2} \rightarrow 54\ \mathrm{Cl^-} + 2\ \mathrm{CrO_4^{2-}} + 6\ \mathrm{IO_4^-} + 64\ \mathrm{H_2O}$$

Reducing gives:

$$64\ \mathrm{OH^-(aq)} + 2\ \mathrm{CrI_3(s)} + 27\ \mathrm{Cl_2(g)} \rightarrow 54\ \mathrm{Cl^-(aq)} + 2\ \mathrm{CrO_4^{2-}(aq)} + 6\ \mathrm{IO_4^-(aq)} + 32\ \mathrm{H_2O(l)}$$

e. $\mathrm{Ce^{4+}} \rightarrow \mathrm{Ce(OH)_3}$

$(\mathrm{e^-} + 3\ \mathrm{H_2O} + \mathrm{Ce^{4+}} \rightarrow \mathrm{Ce(OH)_3} + 3\ \mathrm{H^+}) \times 61$

$$\mathrm{Fe(CN)_6^{4-}} \rightarrow \mathrm{Fe(OH)_3} + \mathrm{CO_3^{2-}} + \mathrm{NO_3^-}$$

$$\mathrm{Fe(CN)_6^{4-}} \rightarrow \mathrm{Fe(OH)_3} + 6\ \mathrm{CO_3^{2-}} + 6\ \mathrm{NO_3^-}$$

There are 39 extra O atoms on right. Add 39 $\mathrm{H_2O}$ to left; then add 75 $\mathrm{H^+}$ to right to balance $\mathrm{H^+}$.

$$39\ \mathrm{H_2O} + \mathrm{Fe(CN)_6^{4-}} \rightarrow \mathrm{Fe(OH)_3} + 6\ \mathrm{CO_3^{2-}} + 6\ \mathrm{NO_3^-} + 75\ \mathrm{H^+}$$

Net charge = 4– $\qquad$ Net charge = 57+

Add 61 $\mathrm{e^-}$ to the product side, and then add the two balanced half-reactions with a common factor of 61 $\mathrm{e^-}$ transferred.

$$\begin{aligned} 39\ H_2O + Fe(CN)_6^{4-} &\rightarrow Fe(OH)_3 + 6\ CO_3^{-} + 6\ NO_3^{-} + 75\ H^+ + 61\ e^- \\ 61\ e^- + 183\ H_2O + 61\ Ce^{4+} &\rightarrow 61\ Ce(OH)_3 + 183\ H^+ \end{aligned}$$

$$\overline{222\ H_2O + Fe(CN)_6^{4-} + 61\ Ce^{4+} \rightarrow 61\ Ce(OH)_3 + Fe(OH)_3 + 6\ CO_3^{2-} + 6\ NO_3^{-} + 258\ H^+}$$

Adding 258 OH^- to each side and then reducing gives:

$$\begin{aligned} 258\ OH^-(aq) + Fe(CN)_6^{4-}(aq) + 61\ Ce^{4+}(aq) \rightarrow 61\ Ce(OH)_3(s) + Fe(OH)_3(s) \\ + 6\ CO_3^{2-}(aq) + 6\ NO_3^-(aq) + 36\ H_2O(l) \end{aligned}$$

135. $\Delta G° = -nFE° = \Delta H° - T\Delta S°,\ E° = \dfrac{T\Delta S°}{nF} - \dfrac{\Delta H°}{nF}$

If we graph E° versus T we should get a straight line ($y = mx + b$). The slope of the line is equal to $\Delta S°/nF$, and the y intercept is equal to $-\Delta H°/nF$. From the preceding equation, E° will have a small temperature dependence when $\Delta S°$ is close to zero.

136. a. We can calculate $\Delta G°$ from $\Delta G° = \Delta H° - T\Delta S°$ and then E° from $\Delta G° = -nFE°$, or we can use the equation derived in Exercise 135. For this reaction, n = 2 (from oxidation states).

$$E^{o}_{-20} = \frac{T\Delta S^{o} - \Delta H^{o}}{nF} = \frac{(253\ \text{K})(263.5\ \text{J/K}) + 315.9 \times 10^3\ \text{J}}{(2\ \text{mol e}^-)(96{,}485\ \text{C/mol e}^-)} = 1.98\ \text{J/C} = 1.98\ \text{V}$$

b. $$E_{-20} = E_{-20} - \frac{RT}{nF}\ln Q = 1.98\ \text{V} - \frac{RT}{nF}\ln\frac{1}{[H^+]^2[HSO_4^-]^2}$$

$$E_{-20} = 1.98\ \text{V} - \frac{(8.3145\ \text{J/K} \bullet \text{mol})(253\text{K})}{(2\ \text{mol e}^-)(96{,}485\ \text{C/mol e}^-)}\ln\frac{1}{(4.5)^2(4.5)^2} = 1.98\ \text{V} + 0.066\ \text{V}$$

$$= 2.05\ \text{V}$$

c. From Exercise 67, E = 2.12 V at 25°C. As the temperature decreases, the cell potential decreases. Also, oil becomes more viscous at lower temperatures, which adds to the difficulty of starting an engine on a cold day. The combination of these two factors results in batteries failing more often on cold days than on warm days.

137.
$$\begin{aligned} (Ag^+ + e^- \rightarrow Ag) \times 2 \qquad & E° = 0.80\ \text{V} \\ Pb \rightarrow Pb^{2+} + 2\ e^- \qquad & -E° = -(-0.13) \end{aligned}$$

$$\overline{2\ Ag^+ + Pb \rightarrow 2\ Ag + Pb^{2+} \qquad E^{o}_{cell} = 0.93\ \text{V}}$$

$$E = E° - \frac{0.0591}{n}\log\frac{[Pb^{2+}]}{[Ag^+]^2},\ 0.83\ \text{V} = 0.93\ \text{V} - \frac{0.0591}{n}\log\frac{(1.8)}{[Ag^+]^2}$$

$$\log\frac{(1.8)}{[Ag^+]^2} = \frac{0.10(2)}{0.0591} = 3.4,\ \frac{(1.8)}{[Ag^+]^2} = 10^{3.4},\ [Ag^+] = 0.027\ M$$

$$Ag_2SO_4(s) \rightleftharpoons 2\,Ag^+(aq) + SO_4^{2-}(aq) \quad K_{sp} = [Ag^+]^2[SO_4^{2-}]$$

Initial	s = solubility (mol/L)	0	0
Equil.		$2s$	s

From problem: $2s = 0.027\ M$, $s = 0.027/2$

$K_{sp} = (2s)^2(s) = (0.027)^2(0.027/2) = 9.8 \times 10^{-6}$

138. a. $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \quad E^{\circ}_{cell} = 1.10\ V$

$$E_{cell} = 1.10\ V - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E_{cell} = 1.10\ V - \frac{0.0591}{2}\log\frac{0.10}{2.50} = 1.10\ V - (-0.041\ V) = 1.14\ V$$

b. $$10.0\ h \times \frac{60\ min}{h} \times \frac{60\ s}{min} \times \frac{10.0\ C}{s} \times \frac{1\ mol\ e^-}{96{,}485\ C} \times \frac{1\ mol\ Cu}{2\ mol\ e^-} = 1.87\ mol\ Cu\ produced$$

The Cu^{2+} concentration decreases by 1.87 mol/L, and the Zn^{2+} concentration will increase by 1.87 mol/L.

$[Cu^{2+}] = 2.50 - 1.87 = 0.63\ M$; $[Zn^{2+}] = 0.10 + 1.87 = 1.97\ M$

$$E_{cell} = 1.10\ V - \frac{0.0591}{2}\log\frac{1.97}{0.63} = 1.10\ V - 0.015\ V = 1.09\ V$$

c. $$1.87\ mol\ Zn\ consumed \times \frac{65.38\ g\ Zn}{mol\ Zn} = 122\ g\ Zn$$

Mass of electrode = 200. – 122 = 78 g Zn

$$1.87\ mol\ Cu\ formed \times \frac{63.55\ g\ Cu}{mol\ Cu} = 119\ g\ Cu$$

Mass of electrode = 200. + 119 = 319 g Cu

d. Three things could possibly cause this battery to go dead:

(1) All the Zn is consumed.
(2) All the Cu^{2+} is consumed.
(3) Equilibrium is reached ($E_{cell} = 0$).

We began with 2.50 mol Cu^{2+} and 200. g Zn × 1 mol Zn/65.38 g Zn = 3.06 mol Zn. Cu^{2+} is the limiting reagent and will run out first. To react all the Cu^{2+} requires:

$$2.50 \text{ mol } Cu^{2+} \times \frac{2 \text{ mol } e^-}{\text{mol } Cu^{2+}} \times \frac{96{,}485 \text{ C}}{\text{mol } e^-} \times \frac{1 \text{ s}}{10.0 \text{ C}} \times \frac{1 \text{ h}}{3600 \text{ s}} = 13.4 \text{ h}$$

For equilibrium to be reached: $E = 0 = 1.10 \text{ V} - \dfrac{0.0591}{2} \log \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$

$$\frac{[Zn^{2+}]}{[Cu^{2+}]} = K = 10^{2(1.10)/0.0591} = 1.68 \times 10^{37}$$

This is such a large equilibrium constant that virtually all the Cu^{2+} must react to reach equilibrium. So the battery will go dead in 13.4 hours.

139.

$$\begin{array}{ll} 2\,H^+ + 2\,e^- \rightarrow H_2 & E° = 0.000 \text{ V} \\ Fe \rightarrow Fe^{2+} + 2e^- & -E° = -(-0.440\text{V}) \\ \hline 2\,H^+(aq) + Fe(s) \rightarrow H_2(g) + Fe^{3+}(aq) & E^{o}_{cell} = 0.440 \text{ V} \end{array}$$

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n} \log Q, \text{ where } n = 2 \text{ and } Q = \frac{P_{H_2} \times [Fe^{3+}]}{[H^+]^2}$$

To determine K_a for the weak acid, first use the electrochemical data to determine the H^+ concentration in the half-cell containing the weak acid.

$$0.333 \text{ V} = 0.440 \text{ V} - \frac{0.0591}{2} \log \frac{1.00 \text{ atm}(1.00 \times 10^{-3}\ M)}{[H^+]^2}$$

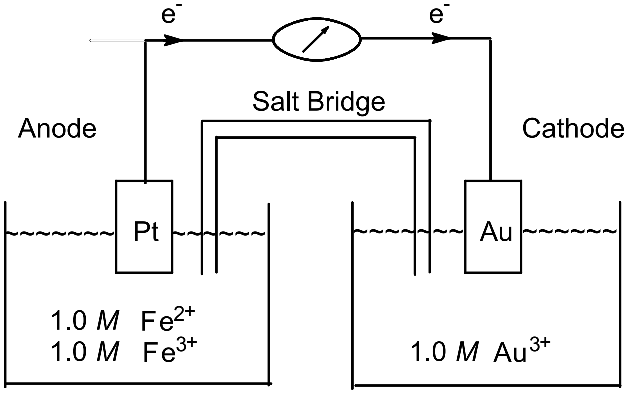
$$\frac{0.107(2)}{0.0591} = \log \frac{1.0 \times 10^{-3}}{[H^+]^2}, \quad \frac{1.0 \times 10^{-3}}{[H^+]^2} = 10^{3.621} = 4.18 \times 10^3, \quad [H^+] = 4.89 \times 10^{-4}\ M$$

Now we can solve for the K_a value of the weak acid HA through the normal setup for a weak acid problem.

	HA(aq)	⇌	H^+(aq)	+	A^-(aq)	$K_a = \dfrac{[H^+][A^-]}{[HA]}$
Initial	1.00 *M*		~0		0	
Equil.	$1.00 - x$		x		x	

$$K_a = \frac{x^2}{1.00 - x}, \text{ where } x = [H^+] = 4.89 \times 10^{-4}\ M, \quad K_a = \frac{(4.89 \times 10^{-4})^2}{1.00 - 4.89 \times 10^{-4}} = 2.39 \times 10^{-7}$$

140. a. Nonreactive anions are present in each half-cell to balance the cation charges.



b. $Au^{3+}(aq) + 3\ Fe^{2+}(aq) \rightarrow 3\ Fe^{3+}(aq) + Au(s)$ $E^\circ_{cell} = 1.50 - 0.77 = 0.73$ V

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log Q = 0.73\ V - \frac{0.0591}{3}\log\frac{[Fe^{3+}]^3}{[Au^{3+}][Fe^{2+}]^3}$$

Because $[Fe^{3+}] = [Fe^{2+}] = 1.0\ M$: $0.31\ V = 0.73\ V - \frac{0.0591}{3}\log\frac{1}{[Au^{3+}]}$

$$\frac{3(-0.42)}{0.0591} = -\log\frac{1}{[Au^{3+}]},\ \log[Au^{3+}] = -21.32,\ [Au^{3+}] = 10^{-21.32} = 4.8 \times 10^{-22}\ M$$

$Au^{3+} + 4\ Cl^- \rightleftharpoons AuCl_4^-$; because the equilibrium Au^{3+} concentration is so small, assume $[AuCl_4^-] \approx [Au^{3+}]_0 \approx 1.0\ M$, i.e., assume K is large, so the reaction essentially goes to completion.

$$K = \frac{[AuCl_4^-]}{[Au^{3+}][Cl^-]^4} = \frac{1.0}{(4.8\times10^{-22})(0.10)^4} = 2.1 \times 10^{25};\ \text{assumption good (K is large).}$$

141. a. $E_{cell} = E_{ref} + 0.05916\ pH$, $0.480\ V = 0.250\ V + 0.05916\ pH$

$$pH = \frac{0.480 - 0.250}{0.05916} = 3.888;\ \text{uncertainty} = \pm1\ mV = \pm\ 0.001\ V$$

$$pH_{max} = \frac{0.481 - 0.250}{0.05916} = 3.905;\quad pH_{min} = \frac{0.479 - 0.250}{0.05916} = 3.871$$

Thus, if the uncertainty in potential is ±0.001 V, then the uncertainty in pH is ±0.017, or about ±0.02 pH units. For this measurement, $[H^+] = 10^{-3.888} = 1.29 \times 10^{-4}\ M$. For an error of +1 mV, $[H^+] = 10^{-3.905} = 1.24 \times 10^{-4}\ M$. For an error of −1 mV, $[H^+] = 10^{-3.871} = 1.35 \times 10^{-4}\ M$. So the uncertainty in $[H^+]$ is $\pm0.06 \times 10^{-4}\ M = \pm6 \times 10^{-6}\ M$.

b. From part a, we will be within ±0.02 pH units if we measure the potential to the nearest ±0.001 V (±1 mV).

142. a. From Table 18.1: $2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$ $E° = -0.83\ V$

$$E^o_{cell} = E^o_{H_2O} - E^o_{Zr} = -0.83\ V + 2.36\ V = 1.53\ V$$

Yes, the reduction of H_2O to H_2 by Zr is spontaneous at standard conditions since $E^o_{cell} > 0$.

b.
$$\begin{array}{l} (2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-) \times 2 \\ Zr + 4\ OH^- \rightarrow ZrO_2{\bullet}H_2O + H_2O + 4\ e^- \\ \hline 3\ H_2O(l) + Zr(s) \rightarrow 2\ H_2(g) + ZrO_2{\bullet}H_2O(s) \end{array}$$

c. $\Delta G° = -nFE° = -(4\ \text{mol e}^-)(96{,}485\ \text{C/mol e}^-)(1.53\ \text{J/C}) = -5.90 \times 10^5\ \text{J} = -590.\ \text{kJ}$

$$E = E° - \frac{0.0591}{n}\log Q;\ \text{at equilibrium, } E = 0 \text{ and } Q = K.$$

$$E° = \frac{0.0591}{n}\log K,\ \log K = \frac{4(1.53)}{0.0591} = 104,\ K \approx 10^{104}$$

d. $$1.00 \times 10^3\ \text{kg Zr} \times \frac{1000\ \text{g}}{\text{kg}} \times \frac{1\ \text{mol Zr}}{91.22\ \text{g Zr}} \times \frac{2\ \text{mol H}_2}{\text{mol Zr}} = 2.19 \times 10^4\ \text{mol H}_2$$

$$2.19 \times 10^4\ \text{mol H}_2 \times \frac{2.016\ \text{g H}_2}{\text{mol H}_2} = 4.42 \times 10^4\ \text{g H}_2$$

$$V = \frac{nRT}{P} = \frac{(2.19 \times 10^4\ \text{mol})(0.08206\ \text{L atm/K} \bullet \text{mol})(1273\ \text{K})}{1.0\ \text{atm}} = 2.3 \times 10^6\ \text{L H}_2$$

e. Probably yes; less radioactivity overall was released by venting the H_2 than what would have been released if the H_2 had exploded inside the reactor (as happened at Chernobyl). Neither alternative is pleasant, but venting the radioactive hydrogen is the less unpleasant of the two alternatives.

143. a.
$$\begin{array}{ll} (Ag^+ + e^- \rightarrow Ag) \times 2 & E° = 0.80\ V \\ Cu \rightarrow Cu^{2+} + 2\ e^- & -E° = -0.34\ V \\ \hline 2\ Ag^+(aq) + Cu(s) \rightarrow 2\ Ag(s) + Cu^{2+}(aq) & E^o_{cell} = 0.46\ V \end{array}$$

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log Q,\ \text{where } n = 2 \text{ and } Q = \frac{[Cu^{2+}]}{[Ag^+]^2}.$$

To calculate E_{cell}, we need to use the K_{sp} data to determine $[Ag^+]$.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \quad K_{sp} = 1.6 \times 10^{-10} = [Ag^+][Cl^-]$$

		Ag^+	Cl^-
Initial	s = solubility (mol/L)	0	0
Equil.		s	s

$K_{sp} = 1.6 \times 10^{-10} = s^2$, $s = [Ag^+] = 1.3 \times 10^{-5}$ mol/L

$$E_{cell} = 0.46\text{ V} - \frac{0.0591}{2}\log\frac{2.0}{(1.3 \times 10^{-5})^2} = 0.46\text{ V} - 0.30 = 0.16\text{ V}$$

b. $Cu^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons Cu(NH_4)_4{}^{2+}(aq) \quad K = 1.0 \times 10^{13} = \dfrac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4}$

Because K is very large for the formation of $Cu(NH_3)_4{}^{2+}$, the forward reaction is dominant. At equilibrium, essentially all the 2.0 *M* Cu^{2+} will react to form 2.0 *M* $Cu(NH_3)_4{}^{2+}$. This reaction requires 8.0 *M* NH_3 to react with all the Cu^{2+} in the balanced equation. Therefore, the moles of NH_3 added to 1.0-L solution will be larger than 8.0 mol since some NH_3 must be present at equilibrium. In order to calculate how much NH_3 is present at equilibrium, we need to use the electrochemical data to determine the Cu^{2+} concentration.

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n}\log Q,\ 0.52\text{ V} = 0.46\text{ V} - \frac{0.0591}{2}\log\frac{[Cu^{2+}]}{(1.3 \times 10^{-5})^2}$$

$$\log\frac{[Cu^{2+}]}{(1.3 \times 10^{-5})^2} = \frac{-0.06(2)}{0.0591} = -2.03,\ \frac{[Cu^{2+}]}{(1.3 \times 10^{-5})^2} = 10^{-2.03} = 9.3 \times 10^{-3}$$

$[Cu^{2+}] = 1.6 \times 10^{-12} = 2 \times 10^{-12}$ *M*

(We carried extra significant figures in the calculation.)

Note: Our assumption that the 2.0 *M* Cu^{2+} essentially reacts to completion is excellent because only 2×10^{-12} *M* Cu^{2+} remains after this reaction. Now we can solve for the equilibrium $[NH_3]$.

$$K = 1.0 \times 10^{13} = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4} = \frac{(2.0)}{(2 \times 10^{-12})[NH_3]^4},\ [NH_3] = 0.6\ M$$

Because 1.0 L of solution is present, 0.6 mol NH_3 remains at equilibrium. The total moles of NH_3 added is 0.6 mol plus the 8.0 mol NH_3 necessary to form 2.0 *M* $Cu(NH_3)_4{}^{2+}$. Therefore, 8.0 + 0.6 = 8.6 mol NH_3 was added.

144. Standard reduction potentials can only be manipulated and added together when electrons in the reduction half-reaction exactly cancel with the electrons in the oxidation half-reaction. We will solve this problem by applying the equation $\Delta G° = -nFE°$ to the half-reactions.

$M^{3+} + 3\,e^- \rightarrow M \quad \Delta G° = -nFE° = -3(96{,}485)(0.10) = -2.9 \times 10^4$ J

Because M and e^- have $\Delta G_f^o = 0$: $-2.9 \times 10^4 \text{ J} = -\Delta G^o_{f,\,M^{3+}}$, $\Delta G^o_{f,\,M^{3+}} = 2.9 \times 10^4$ J

$M^{2+} + 2\,e^- \rightarrow M \quad \Delta G° = -nFE° = -2(96{,}485)(0.50) = -9.6 \times 10^4$ J

$-9.6 \times 10^4 \text{ J} = -\Delta G^o_{f,\,M^{2+}}$, $\Delta G^o_{f,\,M^{2+}} = 9.6 \times 10^4$ J

$M^{3+} + e^- \rightarrow M^{2+} \qquad \Delta G° = 9.6 \times 10^4 \text{ J} - (2.9 \times 10^4 \text{ J}) = 6.7 \times 10^4$ J

$$E° = \frac{-\Delta G^o}{nF} = \frac{-(6.7 \times 10^4)}{(1)(96{,}485)} = -0.69 \text{ V}; \quad M^{3+} + e^- \rightarrow M^{2+} \quad E° = -0.69 \text{ V}$$

145. $2\,Ag^+(aq) + Ni(s) \rightarrow Ni^{2+}(aq) + Ag(s)$; the cell is dead at equilibrium (E = 0).

$E^o_{cell} = 0.80 \text{ V} + 0.23 \text{ V} = 1.03$ V

$$0 = 1.03 \text{ V} - \frac{0.0591}{2}\log K, \quad K = 7.18 \times 10^{34}$$

K is very large. Let the forward reaction go to completion.

$2\,Ag^+ + Ni \rightarrow Ni^{2+} + 2\,Ag \qquad K = [Ni^{2+}]/[Ag^+]^2 = 7.18 \times 10^{34}$

Before	1.0 *M*	1.0 *M*
After	0 *M*	1.5 *M*

Now solve the back-equilibrium problem.

$2\,Ag^+ + Ni \rightleftharpoons Ni^{2+} + 2\,Ag$

Initial	0		1.5 *M*
Change	$+2x$	←	$-x$
Equil.	$2x$		$1.5 - x$

$$K = 7.18 \times 10^{34} = \frac{1.5 - x}{(2x)^2} \approx \frac{1.5}{(2x)^2}; \text{ solving, } x = 2.3 \times 10^{-18}\,M. \quad \text{Assumptions good.}$$

$[Ag^+] = 2x = 4.6 \times 10^{-18}\,M$; $[Ni^{2+}] = 1.5 - 2.3 \times 10^{-18} = 1.5\,M$

146. a. $Ag_2CrO_4(s) + 2\,e^- \rightarrow 2\,Ag(s) + CrO_4^{2-}(aq) \qquad E° = 0.446$ V

$Hg_2Cl_2 + 2\,e^- \rightarrow 2\,Hg + 2\,Cl^- \qquad E_{SCE} = 0.242$ V

SCE will be the oxidation half-reaction with $E_{cell} = 0.446 - 0.242 = 0.204$ V.

$\Delta G = -nFE_{cell} = -2(96{,}485)(0.204)\text{J} = -3.94 \times 10^4 \text{ J} = -39.4$ kJ

b. In SCE, we assume all concentrations are constant. Therefore, only CrO_4^{2-} appears in the Q expression, and it will appear in the numerator since CrO_4^{2-} is produced in the reduction half-reaction. To calculate E_{cell} at nonstandard CrO_4^{2-} concentrations, we use the following equation.

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{2}\log[CrO_4^{2-}] = 0.204\text{ V} - \frac{0.0591}{2}\log[CrO_4^{2-}]$$

c. $E_{cell} = 0.204 - \frac{0.0591}{2}\log(1.00 \times 10^{-5}) = 0.204\text{ V} - (-0.148\text{ V}) = 0.352\text{ V}$

d. $0.504\text{ V} = 0.204\text{ V} - (0.0591/2)\log[CrO_4^{2-}]$

$\log[CrO_4^{2-}] = -10.152$, $[CrO_4^{2-}] = 10^{-10.152} = 7.05 \times 10^{-11}\ M$

e.
$$\begin{array}{lr} Ag_2CrO_4 + 2\,e^- \rightarrow 2\,Ag + CrO_4^{2-} & E^{o}_{c} = 0.446\text{ V} \\ (Ag \rightarrow Ag^+ + e^-) \times 2 & -E^{o}_{a} = -0.80\text{ V} \\ \hline Ag_2CrO_4(s) \rightarrow 2\,Ag^+(aq) + CrO_4^{-}(aq) & E^{o}_{cell} = -0.35\text{ V};\quad K = K_{sp} = ? \end{array}$$

$$E^{o}_{cell} = \frac{0.0591}{n}\log K_{sp},\ \log K_{sp} = \frac{(-0.35\text{ V})(2)}{0.0591} = -11.84,\ K_{sp} = 10^{-11.84} = 1.4 \times 10^{-12}$$

147.
$$\begin{array}{lr} (Ag^+ + e^- \rightarrow Ag) \times 2 & E^{o}_{c} = 0.80\text{ V} \\ Cd \rightarrow Cd^{2+} + 2\,e^- & -E^{o}_{a} = 0.40\text{ V} \\ \hline 2\,Ag^+(aq) + Cd(s) \rightarrow Cd^{2+}(aq) + 2\,Ag(s) & E^{o}_{cell} = 1.20\text{ V} \end{array}$$

Overall complex ion reaction:

$Ag^+(aq) + 2\,NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq)$ $\quad K = K_1K_2 = 2.1 \times 10^3(8.2 \times 10^3) = 1.7 \times 10^7$

Because K is large, we will let the reaction go to completion and then solve the back-equilibrium problem.

	Ag^+	+	$2\,NH_3$	⇌	$Ag(NH_3)_2^+$	$K = 1.7 \times 10^7$
Before	1.00 *M*		15.0 *M*		0	
After	0		13.0		1.00	New initial
Change	x		$+2x$	←	$-x$	
Equil.	x		$13.0 + 2x$		$1.00 - x$	

$$K = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2};\quad 1.7 \times 10^7 = \frac{1.00 - x}{x(13.0 + 2x)^2} \approx \frac{1.00}{x(13.0)^2}$$

Solving: $x = 3.5 \times 10^{-10}\ M = [Ag^+]$; assumptions good.

$$E = E° - \frac{0.0591}{2}\log\frac{[Cd^{2+}]}{[Ag^+]^2} = 1.20\text{ V} - \frac{0.0591}{2}\log\left[\frac{1.0}{(3.5 \times 10^{-10})^2}\right]$$

E = 1.20 – 0.56 = 0.64 V

148. a.

$$\begin{array}{lr} 3 \times (e^- + 2\,H^+ + NO_3^- \rightarrow NO_2 + H_2O) & E^\circ = 0.775\ V \\ 2\,H_2O + NO \rightarrow NO_3^- + 4\,H^+ + 3\,e^- & -E^\circ = -0.957\ V \\ \hline 2\,H^+(aq) + 2\,NO_3^-(aq) + NO(g) \rightarrow 3\,NO_2(g) + H_2O(l) & E^\circ_{cell} = -0.182\ V \quad K = ? \end{array}$$

$$\log K = \frac{E^\circ}{0.0591} = \frac{3(-0.182)}{0.0591} = -9.239,\ K = 10^{-9.239} = 5.77 \times 10^{-10}$$

b. Let C = concentration of HNO_3 = $[H^+]$ = $[NO_3^-]$.

$$5.77 \times 10^{-10} = \frac{P^3_{NO_2}}{P_{NO} \times [H^+]^2 \times [NO_3^-]^2} = \frac{P^3_{NO_2}}{P_{NO} \times C^4}$$

If 0.20% NO_2 by moles and P_{total} = 1.00 atm:

$$P_{NO_2} = \frac{0.20\ mol\ NO_2}{100.\ mol\ total} \times 1.00\ atm = 2.0 \times 10^{-3}\ atm;\ P_{NO} = 1.00 - 0.0020 = 1.00\ atm$$

$$5.77 \times 10^{-10} = \frac{(2.0 \times 10^{-3})^3}{(1.00)C^4},\ C = 1.9\ M\ HNO_3$$

Integrative Problems

149. a.

$$\begin{array}{lr} (In^+ + e^- \rightarrow In) \times 2 & E^\circ = -0.126\ V \\ In^+ \rightarrow In^{3+} + 2\,e^- & -E^\circ = 0.444\ V \\ \hline 3\,In^+ \rightarrow In^{3+} + 2\,In & E^\circ_{cell} = 0.318 \end{array}$$

$$\log K = \frac{nE^\circ}{0.0591} = \frac{2(0.318)}{0.0591} = 10.761,\ K = 10^{10.761} = 5.77 \times 10^{10}$$

b. $\Delta G^\circ = -nFE^\circ = -(2\ mol\ e^-)(96{,}485\ C/mol\ e^-)(0.318\ J/C) = -6.14 \times 10^5\ J = -61.4\ kJ$

$$\Delta G^\circ_{rxn} = -61.4\ kJ = [2(0) + 1(-97.9\ kJ] - 3\,\Delta G^\circ_{f,\,In^+},\ \Delta G^\circ_{f,\,In^+} = -12.2\ kJ/mol$$

150. $E^\circ_{cell} = 0.400\ V - 0.240\ V = 0.160\ V;\ E = E^\circ - \frac{0.0591}{n}\log Q$

$$0.180 = 0.160 - \frac{0.0591}{n}\log(9.32 \times 10^{-3}),\ 0.020 = \frac{0.120}{n},\ n = 6$$

Six moles of electrons are transferred in the overall balanced reaction. We now have to figure out how to get 6 mol e^- into the overall balanced equation. The two possibilities are to have ion charges of +1 and +6 or +2 and +3; only these two combinations yield a 6 when common multiples are determined when adding the reduction half-reaction to the oxidation half-reaction. Because N forms +2 charged ions, M must form for +3 charged ions. The overall cell reaction can now be determined.

$$\begin{array}{ll} (M^{3+} + 3\,e^- \rightarrow M) \times 2 & E^\circ = 0.400\text{ V} \\ \quad (N \rightarrow N^{2+} + 2\,e^-) \times 3 & -E^\circ = -0.240\text{ V} \\ \hline 2\,M^{3+} + 3\,N \rightarrow 3\,N^{2+} + 2\,M & E^\circ_{\text{cell}} = 0.160\text{ V} \end{array}$$

$$Q = 9.32 \times 10^{-3} = \frac{[N^{2+}]_0^{\,3}}{[M^{3+}]_0^{\,2}} = \frac{(0.10)^3}{[M^{3+}]^2},\ [M^{3+}] = 0.33\ M$$

$$w_{max} = \Delta G = -nFE = -6(96{,}485)(0.180) = -1.04 \times 10^5\text{ J} = -104\text{ kJ}$$

The maximum amount of work this cell could produce is 104 kJ.

151. Chromium(III) nitrate [Cr(NO$_3$)$_3$] has chromium in the +3 oxidation state.

$$1.15\text{ g Cr} \times \frac{1\text{ mol Cr}}{52.00\text{ g}} \times \frac{3\text{ mol e}^-}{\text{mol Cr}} \times \frac{96{,}485\text{ C}}{\text{mol e}^-} = 6.40 \times 10^3\text{ C of charge}$$

For the Os cell, 6.40×10^3 C of charge also was passed.

$$3.15\text{ g Os} \times \frac{1\text{ mol Os}}{190.2\text{ g}} = 0.0166\text{ mol Os};\ 6.40 \times 10^3\text{ C} \times \frac{1\text{ mol e}^-}{96{,}485\text{ C}} = 0.0663\text{ mol e}^-$$

$$\frac{\text{Mol e}^-}{\text{Mol Os}} = \frac{0.0663}{0.0166} = 3.99 \approx 4$$

This salt is composed of Os^{4+} and NO$_3^-$ ions. The compound is Os(NO$_3$)$_4$, osmium(IV) nitrate.

For the third cell, identify X by determining its molar mass. Two moles of electrons are transferred when X^{2+} is reduced to X.

$$\text{Molar mass} = \frac{2.11\text{ g X}}{6.40 \times 10^3\text{ C} \times \frac{1\text{ mol e}^-}{96{,}485\text{ C}} \times \frac{1\text{ mol X}}{2\text{ mol e}^-}} = 63.6\text{ g/mol}$$

This is copper (Cu), which has an electron configuration of [Ar]4s^{1}3d^{10}.

Marathon Problems

152. a.

$$\begin{array}{ll} Cu^{2+} + 2\,e^- \rightarrow Cu & E^\circ = 0.34\text{ V} \\ \quad V \rightarrow V^{2+} + 2\,e^- & -E^\circ = 1.20\text{ V} \\ \hline Cu^{2+}(aq) + V(s) \rightarrow Cu(s) + V^{2+}(aq) & E^\circ_{\text{cell}} = 1.54\text{ V} \end{array}$$

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n}\log Q, \text{ where n = 2 and } Q = \frac{[V^{2+}]}{[Cu^{2+}]} = \frac{[V^{2+}]}{1.00\,M}.$$

To determine E_{cell}, we must know the initial $[V^{2+}]$, which can be determined from the stoichiometric point data. At the stoichiometric point, moles H_2EDTA^{2-} added = moles V^{2+} present initially.

$$\text{Mol } V^{2+} \text{ present initially} = 0.5000\text{ L} \times \frac{0.0800\text{ mol } H_2EDTA^{2-}}{\text{L}} \times \frac{1\text{ mol } V^{2+}}{\text{mol } H_2EDTA^{2-}}$$

$$= 0.0400\text{ mol } V^{2+}$$

$$[V^{2+}]_0 = \frac{0.0400\text{ mol } V^{2+}}{1.00\text{ L}} = 0.0400\,M$$

$$E_{cell} = 1.54\text{ V} - \frac{0.0591}{2}\log\frac{0.0400}{1.00} = 1.54\text{ V} - (-0.0413) = 1.58\text{ V}$$

b. Use the electrochemical data to solve for the equilibrium $[V^{2+}]$.

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n}\log\frac{[V^{2+}]}{[Cu^{2+}]}, \quad 1.98\text{ V} = 1.54\text{ V} - \frac{0.0591}{2}\log\frac{[V^{2+}]}{1.00\,M}$$

$$[V^{2+}] = 10^{-(0.44)(2)/0.0591} = 1.3 \times 10^{-15}\,M$$

$$H_2EDTA^{2-}(aq) + V^{2+}(aq) \rightleftharpoons VEDTA^{2-}(aq) + 2\,H^{+}(aq) \qquad K = \frac{[VEDTA^{2-}][H^{+}]^2}{[H_2EDTA^{2-}][V^{2+}]}$$

In this titration reaction, equal moles of V^{2+} and H_2EDTA^{2-} are reacted at the stoichiometric point. Therefore, equal moles of both reactants must be present at equilibrium, so $[H_2EDTA^{2-}] = [V^{2+}] = 1.3 \times 10^{-15}\,M$. In addition, because $[V^{2+}]$ at equilibrium is very small compared to the initial 0.0400 *M* concentration, the reaction essentially goes to completion. The moles of $VEDTA^{2-}$ produced will equal the moles of V^{2+} reacted (= 0.0400 mol). At equilibrium, $[VEDTA^{2-}]$ = 0.0400 mol/(1.00 L + 0.5000 L) = 0.0267 *M*. Finally, because we have a buffer solution, the pH is assumed not to change, so $[H^{+}] = 10^{-10.00} = 1.0 \times 10^{-10}\,M$. Calculating K for the reaction:

$$K = \frac{[VEDTA^{2-}][H^{+}]^2}{[H_2EDTA^{2-}][V^{2+}]} = \frac{(0.0267)(1.0 \times 10^{-10})^2}{(1.3 \times 10^{-15})(1.3 \times 10^{-15})} = 1.6 \times 10^{8}$$

c. At the halfway point, 250.0 mL of H_2EDTA^{2-} has been added to 1.00 L of 0.0400 *M* V^{2+}. Exactly one-half the 0.0400 mol of V^{2+} present initially has been converted into $VEDTA^{2-}$. Therefore, 0.0200 mol of V^{2+} remains in 1.00 + 0.2500 = 1.25 L solution.

$$E_{cell} = 1.54\text{ V} - \frac{0.0591}{2}\log\frac{[V^{2+}]}{[Cu^{2+}]} = 1.54 - \frac{0.0591}{2}\log\frac{(0.0200/1.25)}{1.00}$$

$$E_{cell} = 1.54 - (-0.0531) = 1.59\text{ V}$$

153. Begin by choosing any reduction potential as 0.00 V. For example, let's assume

$B^{2+} + 2\,e^- \rightarrow B \qquad E° = 0.00\text{ V}$

From the data, when B/B^{2+} and E/E^{2+} are together as a cell, E° = 0.81 V.

$E^{2+} + 2\,e^- \rightarrow E$ must have a potential of −0.81 V or 0.81 V since E may be involved in either the reduction or the oxidation half-reaction. We will arbitrarily choose E to have a potential of −0.81 V.

Setting the reduction potential at −0.81 for E and 0.00 for B, we get the following table of potentials.

$B^{2+} + 2\,e^- \rightarrow B$	0.00 V
$E^{2+} + 2\,e^- \rightarrow E$	−0.81 V
$D^{2+} + 2\,e^- \rightarrow D$	0.19 V
$C^{2+} + 2\,e^- \rightarrow C$	−0.94 V
$A^{2+} + 2\,e^- \rightarrow A$	−0.53 V

From largest to smallest:

$D^{2+} + 2\,e^- \rightarrow D$	0.19 V
$B^{2+} + 2\,e^- \rightarrow B$	0.00 V
$A^{2+} + 2\,e^- \rightarrow A$	−0.53 V
$E^{2+} + 2\,e^- \rightarrow E$	−0.81 V
$C^{2+} + 2\,e^- \rightarrow C$	−0.94 V

$A^{2+} + 2\,e^- \rightarrow A$ is in the middle. Let's call this 0.00 V. The other potentials would be:

$D^{2+} + 2\,e^- \rightarrow D$	0.72 V
$B^{2+} + 2\,e^- \rightarrow B$	0.53 V
$A^{2+} + 2\,e^- \rightarrow A$	0.00 V
$E^{2+} + 2\,e^- \rightarrow E$	−0.28 V
$C^{2+} + 2\,e^- \rightarrow C$	−0.41 V

Of course, since the reduction potential of E could have been assumed to 0.81 V instead of −0.81 V, we can also get:

$C^{2+} + 2\,e^- \rightarrow C$	0.41 V
$E^{2+} + 2\,e^- \rightarrow E$	0.28 V
$A^{2+} + 2\,e^- \rightarrow A$	0.00 V
$B^{2+} + 2\,e^- \rightarrow B$	−0.53 V
$D^{2+} + 2\,e^- \rightarrow D$	−0.72 V

One way to determine which table is correct is to add metal C to a solution with D^{2+} and metal D to a solution with C^{2+}. If D comes out of solution, the first table is correct. If C comes out of solution, the second table is correct.