Solutions for Chapter 10 *End-of-Chapter Problems*

Problem 10.1.
(a) We have seen (Investigate This 10.2) that electrolysis of a dilute aqueous solution of an ionic compound (magnesium sulfate) produces a gas at both electrodes and a basic solution at the cathode and acidic solution at the anode, just as the problem statement says is observed here for a dilute aqueous NaCl solution. Thus, we might assume that the electrolysis half reactions are the same in this case as in the investigation:

cathode (reduction): $4H_2O(l) + 4e^-$ (from electrode) $\rightarrow 2H_2(g) + 4OH^-(aq)$

anode (oxidation): $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ (to electrode)
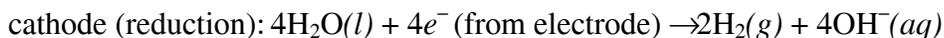
The gas produced at the anode is oxygen, which does not burn, so this is also consistent with the observations reported in the problem statement.

(b) In the concentrated aqueous NaCl solution, the cathode reaction produces a basic solution, so the half reaction is still probably the same as in the electrolysis of the dilute solution. At the anode, however, the gas produced causes a choking sensation when inhaled. The only elements present in the solution are H, O, Na, and Cl. The anode reaction is an oxidation and the most likely species to be oxidized (aside from water) is the chloride ion, $Cl^-(aq)$, in the solution. The product of the oxidation is chlorine gas, $Cl_2(g)$, which produces a choking sensation when inhaled. Solutions of chlorine gas also act as bleach, so the bleaching of the indicator dye color at the anode (reported in the problem statement) is consistent with this identification of the product. The reactions are:

cathode (reduction): $2H_2O(l) + 2e^-$ (from electrode) $\rightarrow H_2(g) + 2OH^-(aq)$

anode (oxidation): $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ (to electrode)
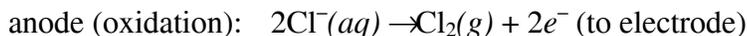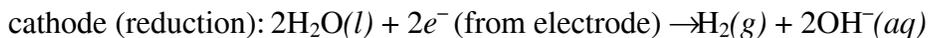
The ease of oxidation of water and chloride ion are similar with chloride being a bit easier to oxidize. When there is only a small amount of chloride in the solution, the large number of water molecules relative to chloride ions overwhelms the chloride and water is oxidized. When the concentration of chloride ion is large, it can compete successfully with water and is oxidized. At both concentrations, the gas at the anode is probably a mixture that contains both oxygen and chlorine, but in quite different proportions in the two cases.

Problem 10.2.
(a) When an aqueous solution of KI is electrolyzed, bubbles of gas are formed at the cathode and the solution around the anode becomes orange. The orange color at the anode appears to be $I_3^-(aq)$ (which the problem statement tells us is formed in a solution containing iodine, $I_2(aq)$, and iodide, $I^-(aq)$), so iodine, $I_2(aq)$, must have been produced at this electrode and reacted with $I^-(aq)$. Thus, the anodic reaction is probably the oxidation of $I^-(aq)$ to give $I_2(aq)$:

$2I^-(aq) \rightarrow I_2(aq) + 2e^-$
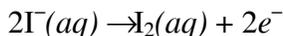
The cathodic reaction must be the reduction of water to yield hydrogen gas and hydroxide in solution:

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
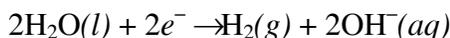
This is the reaction that occurs at the cathode in aqueous solution whenever there is no species present that is more easily reduced (such as some metal ions like Ag^+, Cu^{2+}, *etc.*) than water.

(b) A small amount of added sodium thiosulfate does not affect either electrode reaction directly and, as observed, gas (hydrogen) is still produced at the cathode as soon as electrolysis is begun. When iodine, $I_2(aq)$, is formed at the anode, however, it reacts rapidly with the thiosulfate and is not, at first, observed. After some time of electrolysis, enough $I_2(aq)$ has been produced to react with all the thiosulfate and the subsequent $I_2(aq)$ produced reacts with $I^-(aq)$ to form the $I_3^-(aq)$ color that is observed.

Problem 10.3.

(a) The half reaction at the cathode in the electrolysis of molten sodium chloride is

$$Na^+(melt) + e^- \rightarrow Na(l)$$
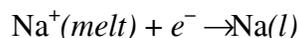
Twenty-three grams of sodium metal is one mole of sodium, so one mole of electrons are required for the electrolysis to produce of 23 g of $Na(l)$. Calculate the time required to pass one mole of electrons through the electrolysis cell at a current of 12 A:

$$1 \text{ mol electrons} = \frac{i \cdot t}{F} = \frac{(12 \text{ A}) \cdot (t)}{9.6485 \times 10^4 \text{ C} \cdot \text{mol}^{-1}}$$

$$t = 8.0 \times 10^3 \text{ s} = 2.2 \text{ hr}$$

(b) The half reaction at the cathode (reduction) is written in part (a). The oxidation half reaction at the anode to produce chlorine gas is:

$$2Cl^-(melt) \rightarrow Cl_2(g) + 2e^-$$

The net cell reaction is:

$$2Na^+(melt) + 2Cl^-(melt) \rightarrow 2Na(l) + Cl_2(g)$$
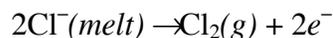
One mole of chlorine gas is produced for every two moles of sodium metal produced. Thus, one-half mole of chlorine gas, 35.5 g [= $(0.5 \text{ mol}) \cdot (71.0 \text{ g} \cdot \text{mol}^{-1})$], is produced during this electrolysis.

Problem 10.4.

(a)/(b) One of the reactions in the Dow process (production of pure magnesium metal by electrolysis of molten magnesium chloride) is the formation of Mg metal from Mg^{2+} ions:

$$Mg^{2+}(melt) + 2e^- \rightarrow Mg(l)$$
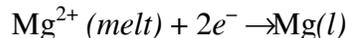
Since this is a reduction half-reaction, it takes place at the cathode. The other reaction is formation of Cl_2 gas from Cl^- ions:

$$2 Cl^-(melt) \rightarrow 2e^- + Cl_2(g)$$
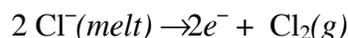
Since this is an oxidation half-reaction, it takes place at the anode.

(c) The net reaction in the Dow procell is:

$$2 Cl^-(aq) + Mg^{2+}(aq) \rightarrow Mg(l) + Cl_2(g)$$
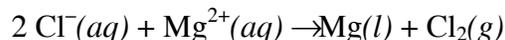
(d) The mass of magnesium metal produced by a 95,000-A current passed through a molten magnesium chloride cell for 8.0 hours is obtained by calculating the number of moles of electrons that pass through the cell and then the number moles and mass of magnesium metal from the stoichiometry of electrolysis in part (a):

$$\text{mol } e^- = \frac{(95000 \text{ A})(8.0 \text{ hr})(60 \text{ min} \cdot \text{hr}^{-1})(60 \text{ s} \cdot \text{min}^{-1})}{9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1}} = 2.8 \times 10^4 \text{ mol } e^-$$

$$2.8 \times 10^4 \text{ mol } e^- = (2.8 \times 10^4 \text{ mol } e^-)\left(\frac{1 \text{ mol Mg}}{2 \text{ mol } e^-}\right)\left(\frac{24 \text{ g Mg}}{1 \text{ mol Mg}}\right) = 3.4 \times 10^2 \text{ kg Mg}$$

(e) Solid salts do not conduct electricity, because the ions are fixed in place in the crystal lattice. Thus, the solid magnesium chloride must be melted, which requires a high temperature, in order to make its electrolysis possible.

Problem 10.5.
(a) The description of this gold electroplating system gives the reduction half reaction that occurs at the surface to be plated, so the object to be plated must be the cathode in the electroplating cell. The sheet of gold must be the anode, so the anode reaction is oxidation of gold, which enters the solution as the cyanide complex, $Au(CN)_4^-(aq)$. The electrode reactions are:

cathode (reduction): $Au(CN)_4^-(aq) + 3e^- \rightarrow Au(s) + 4CN^-(aq)$

anode (oxidation): $Au(s) + 4CN^-(aq) \rightarrow Au(CN)_4^-(aq) + 3e^-$
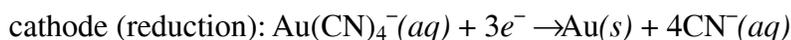
Note that the reactions are just the reverse of one another. As the electroplating is carried out, the concentration of the gold cyanide complex remains constant as the gold cation is reduced at the cathode and produced at the anode.

(b) Calculate the moles of gold deposited by a 2.5 A current passing through the electroplating cell for 7.5 minutes and convert to grams:

$$\text{mol Au} = {}^1\!/_3(\text{mol } e^-) = {}^1\!/_3\left(\frac{i \cdot t}{F}\right) = {}^1\!/_3\left(\frac{(2.5 \text{ A})(7.5 \text{ min})(60 \text{ s} \cdot \text{min}^{-1})}{9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1}}\right) = 3.9 \times 10^{-3} \text{ mol}$$

$$\text{mass Au} = (3.9 \times 10^{-3} \text{ mol})(197.0 \text{ g·mol}^{-1}) = 0.77 \text{ g}$$

(c) The ideal electroplating process would deposit 0.77 g [part (b)]. If only 0.65 g was deposited, the efficiency is $\left[\dfrac{(0.65 \text{ g})}{(0.77 \text{ g})}\right] \cdot 100\% = 84\%$.

Problem 10.6.
(a) The number of moles of electrons passed through the silver and cobalt cells in series is equal to the number of moles of Ag deposited, since one electron is required for each Ag atom.

$$\text{mol } e^- = \text{mol Ag} = (0.2789 \text{ g Ag})\left(\frac{1 \text{ mol Ag}}{107.87 \text{ g Ag}}\right) = 2.586 \times 10^{-3} \text{ mol}$$

(b) The ratio of the number of moles of electrons that pass through the cobalt cell [from part (a)] to the number of moles of cobalt deposited gives us the number of electrons required to reduce one atom of cobalt and hence the oxidation number of cobalt in the solution:

$$\text{mol Co} = (0.0502 \text{ g Co})\left(\frac{1 \text{ mol Co}}{58.93 \text{ g Co}}\right) = 8.52 \times 10^{-4} \text{ mol}$$

$$\frac{\text{mol } e^-}{\text{mol Co}} = \frac{2.586 \times 10^{-3} \text{ mol}}{8.52 \times 10^{-4} \text{ mol}} = 3.04$$

Thus, the oxidation number of the cobalt in the complex is +3.

Problem 10.7.
To determine how much time will it take to electroplate 0.0353 g of chromium from an aqueous potassium dichromate, $K_2Cr_2O_7$, solution, with a current of 0.125 A passing through the cell, we need to know how many electrons are required to reduce the Cr in $Cr_2O_7^{2-}$ ions to Cr metal. That is, we need to know the oxidation number of chromium in dichromate. The ion has a 2– charge and, recall from Chapter 6, that each of the oxygens can be assumed to have an oxidation number of –2, so the seven oxygens contribute an overall –14 oxidation number. The two chromiums must have a combined oxidation number of +12, in order to give the correct ionic charge. Therefore, each Cr has an oxidation number of +6. Each mole of Cr deposited requires six moles of electrons. The number of moles of Cr deposited is:

$$0.0353 \text{ g Cr} = (0.0353 \text{ g Cr})\left(\frac{1 \text{ mol Cr}}{52.00 \text{ g Cr}}\right) = 6.79 \times 10^{-4} \text{ mol Cr}$$

To get the time required, we express the required number of moles of electrons in terms of current, time, and the Faraday constant and solve for the time:

$$\text{mol } e^- = 6(6.79 \times 10^{-4} \text{ mol}) = \left(\frac{i \cdot t}{F}\right) = \left(\frac{(0.125 \text{ A})t}{9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1}}\right)$$

$$t = 3.14 \times 10^3 \text{ sec} = 52.4 \text{ min}$$

Problem 10.8.
(a) To find the current used by this electric company customer, we need to find the number of moles of electrons that entered the meter, divide by the time, and account for the percentage this current is of the total. The data we have are the mass of zinc deposited, 57 g, the time, 30 days, and the percentage of the current that passed through the meter, 8%. Since $Zn^{2+}(aq)$ is reduced to $Zn(s)$, two moles of electrons are required for each mole of zinc deposited:

$$57 \text{ g Zn} = (57 \text{ g Zn})\left(\frac{1 \text{ mol Zn}}{65.37 \text{ g Zn}}\right) = 0.87 \text{ mol Zn}$$

$$\text{mol } e^- = 2(0.87 \text{ mol}) = 1.74 \text{ mol } e^- \text{ (into the meter)}$$

This is the number of moles of electrons that are used by the meter, but is only 8% of the total moles of electrons that enter the house in 30 days; the total is:

$$\text{total mol } e^- = (1.74 \text{ mol } e^-)\left(\frac{100\%}{8\%}\right) = 21.8 \text{ mol } e^- \approx 22 \text{ mol } e^-$$

To find the average current (in ampere) used during the month, convert the total moles of electrons to coulombs (using the Faraday constant) and divide by the number of seconds in 30 days:

$$\text{current} = \frac{(22 \text{ mol})(9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1})}{(30 \text{ da})(24 \text{ hr} \cdot \text{da}^{-1})(60 \text{ min} \cdot \text{hr}^{-1})(60 \text{ s} \cdot \text{min}^{-1})} = 0.82 \text{ A}$$

(b) In order to operate, the cathode and anode in Edison's meter had to retain these identities during the entire time of the measurement, months and years. Since the current he supplied was direct current, this criterion was met. Now, however, with alternating current, the electrodes in an Edison meter would be changing identities sixty times per second. For half of each second,

one of the electrodes would be the cathode where Zn^{2+} is reduced to Zn and for the other half second would be the anode where Zn is oxidized to Zn^{2+}. The net effect would be no plating of the zinc, so the meter would be useless (as well as pretty inconvenient).

Problem 10.9.
We look at each of these unbalanced reactions to see which species on the left is oxidized (the anode reaction) and which reduced (the cathode reaction). All the species are metals and their cations, so it is easy to tell which are the oxidized forms (cations). The net cell reaction is then obtained by adding the two half reactions after each is multiplied by the appropriate stoichiometric factor to cancel the electrons. Reactions are shown as reversible, since we have no information about the direction of the reactions. The conventional cell notation is written with the anode on the left.

(a)   anode reaction: $Mn(s) \Leftrightarrow Mn^{2+}(aq) + 2e^-$

            cathode reaction: $Ti^{2+}(aq) + 2e^- \Leftrightarrow Ti(s)$

            net cell reaction: $Mn(s) + Ti^{2+}(aq) \ae Mn^{2+}(aq) + Ti(s)$

            cell notation: $Mn(s) \mid Mn^{2+}(aq) \parallel Ti^{2+}(aq) \mid Ti(s)$

(b)   anode reaction: $U(s) \Leftrightarrow U^{3+}(aq) + 3e^-$

            cathode reaction: $V^{2+}(aq) + 2e^- \Leftrightarrow V(s)$

            net cell reaction: $2U(s) + 3V^{2+}(aq) \Leftrightarrow 2U^{3+}(aq) + 3V(s)$

            cell notation: $U(s) \mid U^{3+}(aq) \parallel V^{2+}(aq) \mid V(s)$

(c)   anode reaction: $Zn(s) \Leftrightarrow Zn^{2+}(aq) + 2e^-$

            cathode reaction: $Ni^{2+}(aq) + 2e^- \Leftrightarrow Ni(s)$

            net cell reaction: $Zn(s) + Ni^{2+}(aq) \Leftrightarrow Zn^{2+}(aq) + Ni(s)$

            cell notation: $Zn(s) \mid Zn^{2+}(aq) \parallel Ni^{2+}(aq) \mid Ni(s)$

(d)   anode reaction: $Mg(s) \Leftrightarrow Mg^{2+}(aq) + 2e^-$

            cathode reaction: $Cr^{3+}(aq) + 3e^- \Leftrightarrow Cr(s)$

            net cell reaction: $3Mg(s) + 2Cr^{3+}(aq) \Leftrightarrow 3Mg^{2+}(aq) + 2Cr(s)$

            cell notation: $Mg(s) \mid Mg^{2+}(aq) \parallel Cr^{3+}(aq) \mid Cr(s)$

Problem 10.10.
The left-hand half of the line notation represents the anode reaction, so the metal shown there is oxidized to the cation in the anode reaction. The cation in the right-hand half of the line notation is reduced to the metal in the cathode reaction. The net cell reaction is then obtained by adding the two half reactions after each is multiplied by the appropriate stoichiometric factor to cancel the electrons and also canceling species, if any, that appear on both sides of the reaction equation.

(a)   anode reaction: $Cu(s) \Leftrightarrow Cu^{2+}(aq) + 2e^-$

            cathode reaction: $Cu^+(aq) + e^- \Leftrightarrow Cu(s)$

            net cell reaction: $2Cu^+(aq) \Leftrightarrow Cu(s) + Cu^{2+}(aq)$

(b)   anode reaction: $Co(s) \Leftrightarrow Co^{2+}(aq) + 2e^-$

cathode reaction: $Ag^+(aq) + e^- \Leftrightarrow Ag(s)$

net cell reaction: $Co(s) + 2Ag^+(aq) \Leftrightarrow Co^{2+}(aq) + 2Ag(s)$

(c)   anode reaction: $Al(s) \Leftrightarrow Al^{3+}(aq) + 3e^-$

cathode reaction: $Fe^{2+}(aq) + 2e^- \Leftrightarrow Fe(s)$

net cell reaction: $2Al(s) + 3Fe^{2+}(aq) \Leftrightarrow 2Al^{3+}(aq) + 3Fe(s)$

(d)   anode reaction: $Pb(s) \Leftrightarrow Pb^{2+}(aq) + 2e^-$

cathode reaction: $Cu^{2+}(aq) + 2e^- \Leftrightarrow Cu(s)$

net cell reaction: $Pb(s) + Cu^{2+}(aq) \Leftrightarrow Pb^{2+}(aq) + Cu(s)$

Problem 10.11.
In this manganese(II)-chromium(II) cell, the manganese electrode is negative, so electrons must be leaving the cell at this electrode. Since manganese metal is being oxidized (leaving its electrons behind to enter the external part of the circuit), the $Mn(s)–Mn^{2+}(aq)$ half cell must be the anode of the cell:

anode reaction: $Mn(s) \rightarrow Mn^{2+}(aq) + 2e^-$

cathode reaction: $Cr^{2+}(aq) + 2e^- \rightarrow Cr(s)$

net cell reaction: $Mn(s) + Cr^{2+}(aq) \rightarrow Mn^{2+}(aq) + Cr(s)$

cell notation: $Mn(s) \,|\, Mn^{2+}(aq) \,\|\, Cr^{2+}(aq) \,|\, Cr(s)$
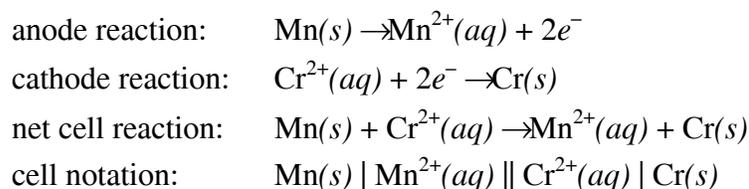
Since the positive charge increases in the anode half cell (as $Mn^{2+}(aq)$ cations are produced) and decreases in the cathode half cell (as cations are used up), the sulfate anions must migrate from the cathode to the anode half cell, in order to maintain charge neutrality in the solutions. Electrons are produced at the anode and used up at the cathode, so the flow of electrons in the wire connecting the electrodes is from the manganese metal electrode to the chromium metal electrode.

Problem 10.12.
(a) The observations described in this problem statement suggest that some product is darkening the surface of the Mg metal and that the concentration of Cu^{2+} is decreasing in the solution. (Solutions containing Cu^{2+} are blue and the color is fading.) A redox reaction that would account for these observations is:

$Cu^{2+}(aq) + Mg(s) \rightarrow Cu(s) + Mg^{2+}(aq)$
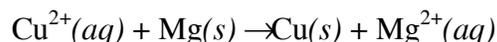
The darkening of the Mg surface is caused by the solid Cu reduced by the Mg metal at its surface. Mg^{2+} in solution is colorless, so we have no proof that it is being formed, but this reaction is analogous to the reaction between Cu and Ag^+ (Investigate This 6.62 and 10.14).

(b) This is a sketch of an electrochemical cell that would take advantage of the reaction in part (a) to provide a flow of electrons in an external circuit plus its cathodic and anodic half reactions, net cell reaction, and line notation are:

anode reaction: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

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

net cell reaction: $Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$

cell notation $Mg(s) \,|\, Mg^{2+}(aq) \,\|\, Cu^{2+}(aq) \,|\, Cu(s)$
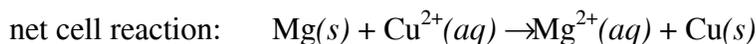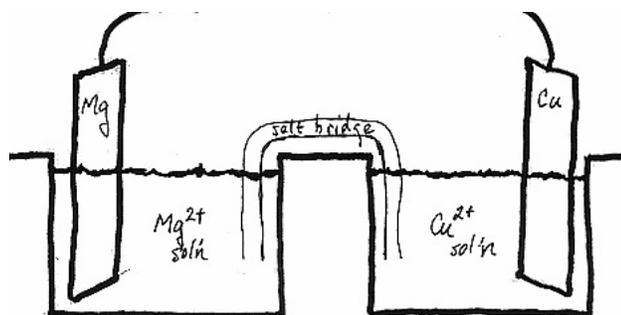
Problem 10.13.
(a) The observations described in this problem statement suggest that chromium metal can react with iron(II) cations to reduce the cations to iron metal (the dark deposit on the metal surface). Concomitantly, chromium metal atoms must be oxidized to chromium(III) cations. A cell that can take advantage of this spontaneous reaction is a chromium metal-chromium(III) cation anode and iron(II) cation-iron metal cathode connected by a salt bridge:
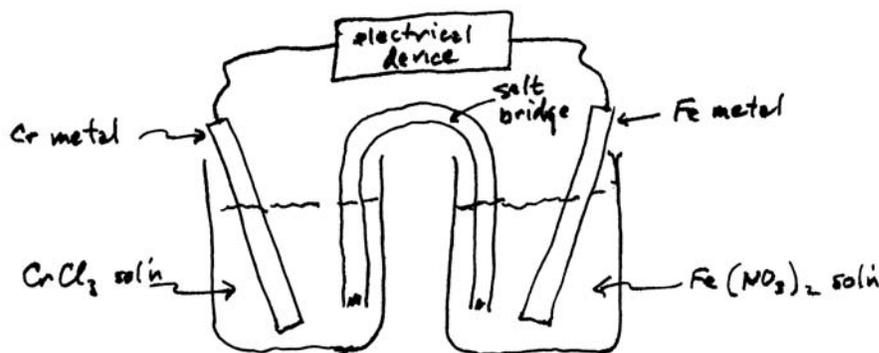
(b) The half reactions and net cell reaction for this cell are:

anode reaction: $Cr(s) \rightarrow Cr^{3+}(aq) + 3e^-$

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

net cell reaction: $2Cr(s) + 3Fe^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Fe(s)$
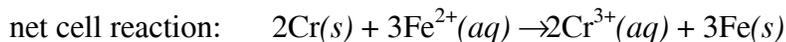
(c) The line notation for this cell is:

$Cr(s) \,|\, Cr^{3+}(aq) \,\|\, Fe^{2+}(aq) \,|\, Fe(s)$
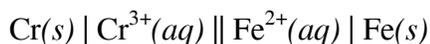
The rationale for the anode and cathode reactions is given in part (a) and the conventional cell notation follows naturally with the anode written on the left.

Problem 10.14.
(a) In order to maintain the neutrality of the solutions around the electrodes in an electrochemical cell, ions have to move in the solutions, as in Figure 10.4. If electrons are drawn too quickly

from the cell, the ions may not be able to move fast enough to prevent charge separation or polarization of the cell. Charge separation like this always opposes the flow of electrons (since the separation is set up by the reactions that cause the flow). If the polarization becomes too great, the flow of electrons falls to an unusable level and the battery appears to have "run down," that is, come to equilibrium. Allowing the battery to rest for some time gives the ions inside a chance to move and eliminate the charge separation. The battery can then be used again, because the opposing charge separation is no longer present.
(b) The slow movement of ions inside the battery is exactly the condition that will favor polarization, if the reactions are required to go quickly to produce a lot of electrons.

Problem 10.15.
(a) Since the zinc metal electrode in these simple galvanic cells loses mass, the zinc atoms must be being oxidized to zinc cations, so the zinc electrode is the anode of the cell. A reduction reaction must be going on at the copper electrode (cathode). Water is the common ingredient in all the cells discussed in the problem, so it is likely to be water that is reduced. We know that the reduction of water produces hydrogen gas, so this fits with the observed production of hydrogen gas at the copper cathode. The half reactions are:

$$\text{anode (zinc) reaction:} \qquad Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

$$\text{cathode (copper) reaction:} \quad 2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

(b) The net cell reaction is:

$$Zn(s) + 2H_2O(l) \rightarrow Zn^{2+}(aq) + H_2(g) + 2OH^-(aq)$$

(c) The line notation for the cell is:
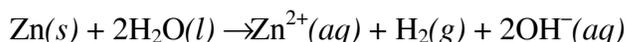
$$Zn(s)\,|Zn^{2+}(aq),\ \text{ionic solution in } H_2O(l),\ OH^-(aq)\,|H_2(g)\,|Cu(s)$$
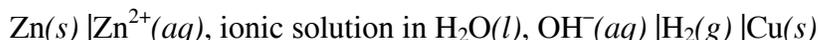
The choice of anode and cathode for this cell is described in part (a). Note that the cell has no salt bridge since the two electrodes are in the same solution. An aqueous ionic solution is specified, since the water is required as a reactant and the ions as charge carriers to complete the circuit within the cell.

Problem 10.16.
(a) Consider an electrochemical cell in which a zinc and carbon electrode dip into the same solution and chlorine gas bubbles into the cell solution and reacts at the surface of a graphite (carbon) electrode. The cell is based on this spontaneous reaction:

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

The half reactions are:

$$\text{oxidation (anode):} \quad Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

$$\text{reduction (cathode):} Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$$
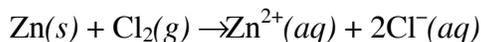
(b) The zinc electrode is the anode in this cell, since, as shown in part (a), the oxidation reaction occurs at that electrode. The carbon electrode is the cathode, since the electrons are furnished to the chlorine molecules to reduce them to chloride ions as they bubble against its surface.
(c) Initially, the cell solution can be essentially any aqueous ionic solution (to provide charge carriers). As the cell reaction proceeds, $Zn^{2+}(aq)$ and $Cl^-(aq)$ ions are produced in a one-to-two ratio and the solution becomes a solution of zinc chloride dissolved in the aqueous ionic solution, which is shown in this sketch of the cell and its line notation:

$Zn(s) \,|\, Zn^{2+}(aq),\, Cl^-(aq),$ aqueous ionic solution $|\, Cl_2(g) \,|\, C(s)$
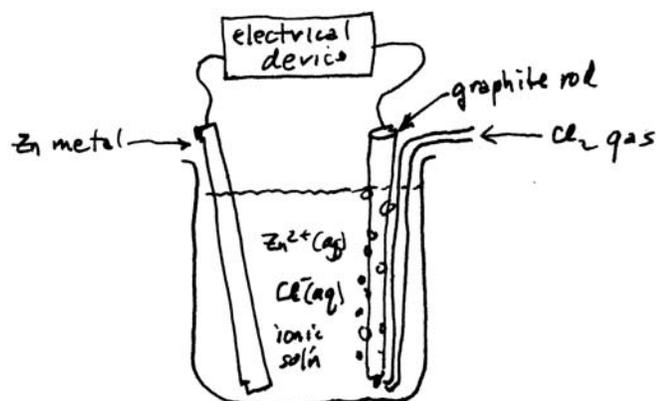
(d) Electrons move from the anode to the cathode in the external part of the circuit, so they move from the zinc to the carbon electrode.

(e) The number of moles of electrons required to produce a 0.12 A current for exactly 7 days is:

$$\text{mol } e^- = \frac{i \cdot t}{F} = \frac{(0.12 \text{ A})(7 \text{ day})(24 \text{ hr} \cdot \text{day}^{-1})(60 \text{ min} \cdot \text{hr}^{-1})(60 \text{ s} \cdot \text{min}^{-1})}{9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1}}$$

$$\text{mol } e^- = 0.75 \text{ mol}$$

One mole of chlorine molecules requires two moles of electrons for its reduction, so 0.38 mol [= 0.5·(0.75 mol)] of chlorine molecules is required to produce the current in this case.

Problem 10.17.

The measured voltage of an electrochemical cell made by connecting a $Fe^{2+}|Fe$ half cell with a $Pb^{2+}|Pb$ half cell is positive when the anode input from the voltmeter is connected to the lead metal electrode. The Pb electrode is the anode, so oxidation of $Pb(s)$ to $Pb^{2+}(aq)$ must be occurring at this electrode. The cell reaction consistent with this observation is:

$$Pb(s) + Fe^{2+}(aq) \rightarrow Pb^{2+}(aq) + Fe(s)$$
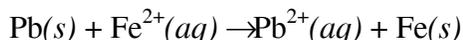
You could test the direction of this reaction by immersing a clean piece of Pb metal in a solution of Fe^{2+}. Discoloration of the Pb surface is an indication that some reaction is occurring to affect the Pb. You could test the solution after some time to see whether it contains Pb^{2+} ions. You could also place a very tiny sliver of Pb in Fe^{2+} solution to see if it disappears. In all cases, you need to do control experiments with water and with alkali metal solutions of the anions, to be sure that it is the Fe^{2+} that is responsible for your observations.

Problem 10.18.

Both cell reactions shown involve the silver-silver ion half reaction, so they can be combined to cancel the silver species, leaving the desired cell reaction:

$$\begin{array}{ll} Ni(s) + 2Ag^+(aq) \Leftrightarrow Ni^{2+}(aq) + 2Ag(s) & E^\circ = 1.03 \text{ V} \\ -[Cu(s) + 2Ag^+(aq) \Leftrightarrow Cu^{2+}(aq) + 2Ag(s) & E^\circ = 0.46 \text{ V}] \\ \hline Ni(s) + Cu^{2+}(aq) \Leftrightarrow Ni^{2+}(aq) + Cu(s) & E^\circ = 0.57 \text{ V} \end{array}$$
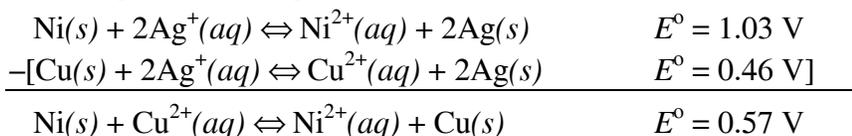
Problem 10.19.
(a) When a clean strip of lead is placed in a 0.2 M aqueous solution of silver nitrate, the surface of the metal in contact with the solution soon turns dark and then small silvery needles begin to grow on the surface. This behavior is similar to what you observe when a strip of copper metal is immersed in an aqueous solution of silver nitrate (Investigate This 6.62 and 10.14.). What will happen if a strip of copper is placed in a solution of lead nitrate? What will happen if a strip of lead is placed in a solution of copper nitrate? We know that both copper metal and lead metal reduce silver cations to silver metal while themselves being oxidized to copper(II) and lead(II) cations, respectively. Unless both metals have the same potential to bring about this reduction, one of them will be able to reduce cations of the other. That is, either lead metal can reduce copper(II) cations or copper metal can reduce lead(II) cations, but we do not know which. Thus, we cannot predict what will happen in the two experiments proposed.

(b) The cell data given show that the potentials for lead and copper to reduce silver cations are not the same. The potential of the cell with lead as the anode is more positive, so lead has the greater ability to reduce silver cations. We can subtract the copper-silver cell from the lead-silver cell to get the potential and cell notation for the lead-copper cell:

$$Pb(s)\,|\,Pb^{2+}(aq,\,0.2\text{ M})\,\|\,Ag^{+}(aq,\,0.2\text{ M})\,|\,Ag(s) \qquad E = 0.90\text{ V}$$
$$\underline{-\,[Cu(s)\,|\,Cu^{2+}(aq,\,0.2\text{ M})\,\|\,Ag^{+}(aq,\,0.2\text{ M})\,|\,Ag(s) \qquad\quad E = 0.44\text{ V}]}$$
$$Pb(s)\,|\,Pb^{2+}(aq,\,0.2\text{ M})\,\|\,Cu^{2+}(aq,\,0.2\text{ M})\,|\,Cu(s) \qquad E = 0.46\text{ V}$$
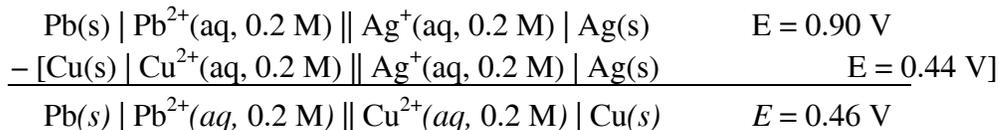
(c) With the knowledge from part (b), we see that the oxidation of lead metal by copper(II) cations (or equivalently, the reduction of copper(II) cations by lead metal) is a favored process (positive cell potential), so now we can answer part (a). The reduction of copper(II) cations by lead metal is the process that will occur. The surface of a piece of lead dipped into a solution of copper(II) cations should darken as finely divided copper metal deposits on the surface. The initially blue solution of $Cu^{2+}(aq)$ will get lighter as the concentration of the cation decreases.

Problem 10.20.
(a) The negative measured potential is an indication that the voltmeter is connected incorrectly to the cell. That is, the lead electrode is the cathode and the nickel electrode is the anode. Thus, we can write:

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

cathode reaction: $Pb^{2+}(aq) + 2e^{-} \rightarrow Pb(s)$

net cell reaction: $Ni(s) + Pb^{2+}(aq) \rightarrow Ni^{2+}(aq) + Pb(s)$

cell notation: $Ni(s)\,|\,Ni^{2+}(aq)\,\|\,Pb^{2+}(aq)\,|\,Pb(s)$
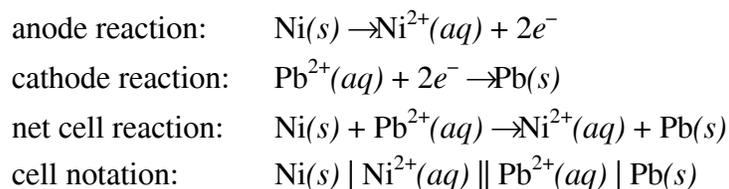
(b) The favored reaction in this system is the reduction of lead(II) ion by nickel metal. Therefore, placing a strip of lead metal in a nickel(II) cation solution will result in no reaction. The lead strip will get wet, but no other changes will be observed.

Problem 10.21.
From Appendix C, we find the standard reduction potentials for copper and magnesium ions and combine the half reactions and standard reduction potentials to get the cell reaction and standard cell potential for the cell sketched in Problem 10.12:

$$Cu^{2+} + 2e^- \Leftrightarrow Cu \qquad\qquad E^\circ = 0.337 \text{ V}$$
$$-\{Mg^{2+} + 2e^- \Leftrightarrow Mg\} \qquad E^\circ = -(-2.38 \text{ V})$$
$$\overline{Cu^{2+} + Mg \Leftrightarrow Cu + Mg^{2+} \qquad E^\circ = 2.72 \text{ V}}$$
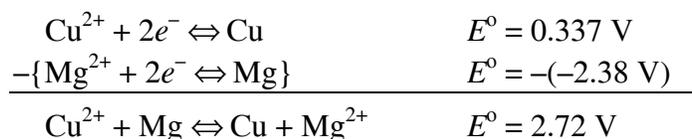
Problem 10.22.

(a) In Appendix B, we find that the standard reduction potentials are 0.799 V for the $Ag^+|Ag$ half cell and –0.41 V for the $Fe^{2+}|Fe$ half cell. Thus, the more positive silver reaction will proceed as written as a reduction and the iron reaction will proceed in reverse as an oxidation. The iron metal in the $Fe^{2+}|Fe$ half cell will be the anode and the silver metal in the $Ag^+|Ag$ half cell will be the cathode of this cell. The assumption we make to get these predictions is that the *sign* of the potential for the actual cell (with concentrations that might not be standard concentrations) will be the same as the sign of the standard cell potential. Since the standard cell potential is so large [see part (b)], it is unlikely that any reasonable concentrations in the half cells will change its sign. The line notation for this cell is:

$$Fe(s) \,|\, Fe^{2+}(aq) \,\|\, Ag^+(aq) \,|\, Ag(s)$$
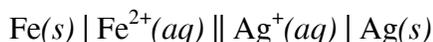
(b) To get the net cell reaction, combine the half-cell reactions appropriately to cancel out electrons. To get the standard cell potential from the standard reduction potentials, use the equation from Figure 10.9.

$$2 \cdot [Ag^+(aq) + e^- \rightarrow Ag(s)]$$
$$- [Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)]$$
$$\overline{\quad Fe(s) + 2Ag^+(aq) \rightarrow Fe^{2+}(aq) + 2Ag(s)\quad}$$

$$E^\circ = E^\circ(Ag^+, Ag) - E^\circ(Fe^{2+}, Fe) = 0.799 \text{ V} - (-0.41 \text{ V}) = 1.20 \text{ V}$$
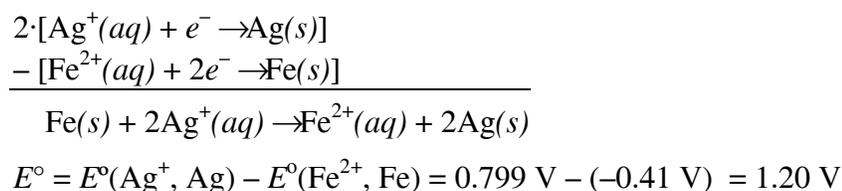
Problem 10.23.

The table of standard reduction potentials in Appendix B is labeled showing that the strongest reducing agents (the species on the right-hand side of the reduction half reaction) are those at the end of the list, that is, those whose formation has the most negative standard reduction potential. This makes sense, since the driving force to go in reverse (giving up electrons and reducing other species) is the largest. The half reactions and standard reduction potentials of interest in this problem are:

$$Al^{3+}(aq) + 3e^- \rightarrow Al(s) \qquad E^\circ = -1.66 \text{ V}$$
$$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s) \qquad E^\circ = -2.76 \text{ V}$$
$$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s) \qquad E^\circ = -2.38 \text{ V}$$
$$Na^+(aq) + e^- \rightarrow Na(s) \qquad E^\circ = -2.71 \text{ V}$$
$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \qquad E^\circ = -0.763 \text{ V}$$
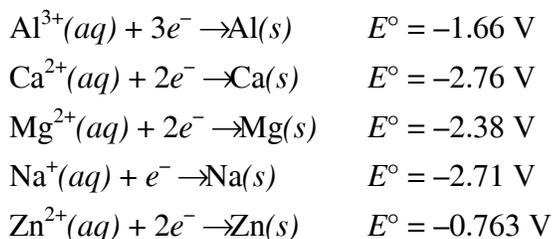
Thus the order of increasing strength as reducing agents (and increasing $|E^\circ|$) is:

Zn < Al < Mg < Na < Ca (with Na and Ca being very nearly the same)

Problem 10.24.

The table of standard reduction potentials in Appendix B is labeled showing that the strongest oxidizing agents (the species on the left-hand side of the reduction half reaction) are those at the

beginning of the list, that is, those whose reaction has the most positive standard reduction potential. This makes sense, since the driving force to go as written (taking up electrons and oxidizing other species) is the largest. The half reactions and standard reduction potentials of interest in this problem are:

$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$ $\qquad\qquad E° = 1.06$ V

$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $\qquad\qquad E° = 1.359$ V

$F_2(g) + 2e^- \rightarrow 2F^-(aq)$ $\qquad\qquad E° = 2.87$ V

$I_2(s) + 2e^- \rightarrow 2I^-(aq)$ $\qquad\quad E° = 0.5355$ V

$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ $\quad E° = 1.230$ V
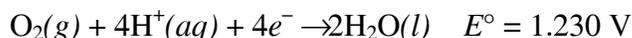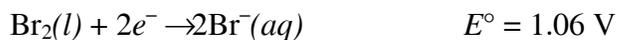
Thus the order of increasing strength as oxidizing agents (and increasing $E°$) is:

$I_2 < Br_2 < O_2 < Cl_2 < F_2 < Cl_2$

Problem 10.25.
(a) Chromium metal, $Cr(s)$, reduces lead(II) ion, $Pb^{2+}(aq)$ to lead metal, $Pb(s)$. The reduction half reaction of lead(II) cation has a more positive standard reduction potential than that for the reduction half reaction of chromium(III), so the process is spontaneous with this net cell reaction and standard cell potential:

$2Cr(s) + 3Pb^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Pb(s)$
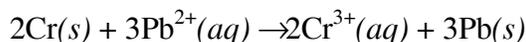
$E° = E°(Pb^{2+}, Pb) - E°(Cr^{3+}, Cr) = -0.13$ V $- (-0.74$ V$) = 0.61$ V

(b) In basic solution, mercury metal, $Hg(l)$, reduces cadmiun hydroxide, $Cd(OH)_2(s)$, to cadmium metal, $Cd(s)$, and forms mercury(II) oxide, $HgO(s)$. The reduction half reaction of mercury(II) oxide to mercury metal has a more positive standard reduction potential than that for the reduction half reaction of cadmium hydroxide to cadmium metal. The process in the statement is not spontaneous. In basic solution, $HgO(s)$ oxidizes $Cd(s)$ to $Cd(OH)_2(s)$ and forms $Hg(l)$ with this net cell reaction and standard cell potential:

$Cd(s) + HgO(s) + H_2O(l) \rightarrow Cd(OH)_2(s) + Hg(l)$
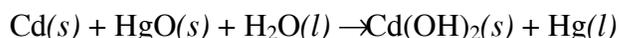
$E° = E°(HgO, Hg) - E°(Cd(OH)_2, Cd) = 0.098$ V $- (-0.81$ V$) = 0.91$ V

(c) Nickel(II) ion, $Ni^{2+}(aq)$, is reduced to nickel metal, $Ni(s)$, by hydrogen gas, $H_2(g)$ in acidic solution. The reduction half reaction of hydronium ion to hydrogen gas has a more positive standard reduction potential than that for the reduction half reaction of nickel cation to nickel metal. The process in the statement is not spontaneous. In acidic solution, $H_3O^+(aq)$ oxidizes $Ni(s)$ to $Ni^{2+}(aq)$ and forms $H_2(g)$ with this net cell reaction and standard cell potential:

$Ni(s) + 2H_3O^+(aq) \rightarrow Ni^{2+}(aq) + H_2(g) + 2H_2O(l)$
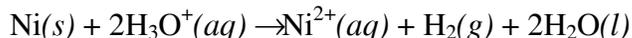
$E° = E°(H_3O^+, H_2) - E°(Ni^{2+}, Ni) = 0.000$ V $- (-0.23$ V$) = 0.23$ V

(d) Sodium metal, $Na(s)$, reduces water, $H_2O(l)$, at pH 7 to form hydrogen gas $H_2(g)$. The reduction half reaction of water (hydronium ion) at pH 7 has a more positive standard reduction potential than that for the reduction half reaction of sodium cation, so the process is spontaneous with this net cell reaction and standard cell potential:

$2Na(s) + 2H_3O^+(aq) \rightarrow 2Na^+(aq) + H_2(g) + 2H_2O(l)$

$E°' = E°'(H_3O^+, H_2) - E°(Ni^{2+}, Ni) = -0.414$ V $- (-2.71$ V$) = 2.30$ V

Problem 10.26.
(a) We interpret what is going on according to the changes in color observed upon mixing the solutions and write the redox reaction, if any, that occurs in each case.

(i) yellow green + colorless →orange solution: Br_2 is formed in the solution
$$Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$$
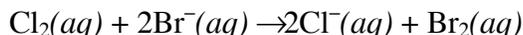
(ii) yellow green + colorless →red solution: I_2 is formed in the solution
$$Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$$
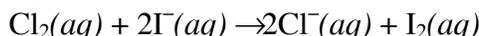
(iii) orange + colorless →orange solution: no apparent reaction
$$Br_2(aq) + 2Cl^-(aq) \rightarrow 2Br^-(aq) + Cl_2(aq) \text{ DOES NOT OCCUR}$$
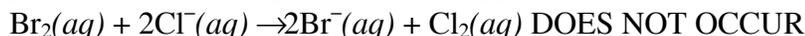
(iv) orange + colorless →red solution: I_2 is formed in the solution
$$Br_2(aq) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(aq)$$
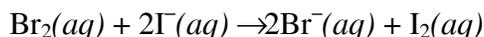
The standard reduction potentials for these three halogens are:
$$Cl_2(aq) + 2e^- \Leftrightarrow 2Cl^-(aq) \quad E° = 1.359 \text{ V}$$
$$Br_2(aq) + 2e^- \Leftrightarrow 2Br^-(aq) \quad E° = 1.087 \text{ V}$$
$$I_2(aq) + 2e^- \Leftrightarrow 2I^-(aq) \quad E° = 0.536 \text{ V}$$
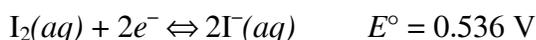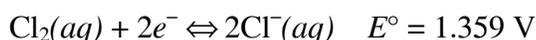
The strongest oxidizing agent (reactant with the most positive reduction potential) is Cl_2, which can oxidize both bromide and iodide to the halogen molecule (zero oxidation number), as shown in reactions (i) and (ii). Bromine cannot oxidize chloride; the bromine reduction potential is lower than that for the chlorine half reaction. Thus, mixture (iii) gave no apparent reaction. Bromine can oxidize iodide and this is shown in case (iv).

(b) Since the reduction potential for iodine is lower than that for chlorine, iodine cannot oxidize chloride. This would be the reverse of reaction (ii) and we know from the experimental results that reaction (ii) is the favored direction. If you mixed a red $I_2/I^-(aq)$ solution with a colorless $Cl^-(aq)$ solution the resulting mixture would retain the red color, as no reaction would occur.

(c) Since the reduction potential for chlorine is greater than that for bromine, chlorine can oxidize bromide. Thus, if you bubble chlorine gas, $Cl_2(g)$, into an aqueous solution of sodium bromide, $NaBr(aq)$ [which contains $Br^-(aq)$], the initially clear, colorless solution will become orange as $Br_2(aq)$ is produced and forms $Br_2/Br^-(aq)$. This is the reverse of reaction (iii) in part (a), which we found experimentally does not procede as proposed. Now we see why and predict that the reverse reaction, $2Br^-(aq) + Cl_2(aq) \rightarrow Br_2(aq) + 2Cl^-(aq)$, will be observed (and it is).

Problem 10.27.
The data in Appendix B show that oxygen gas is a stronger oxidant than elemental bromine, so it should be possible, in acidic solution, to oxidize bromide ion to bromine by bubbling oxygen through a brine solution containing bromide ion:
$$4Br^-(aq) + O_2(g) + 4H^+(aq) \rightarrow 2Br_2(l) + 2H_2O(l)$$
$$E° = E°(O_2, H_2O) - E°(Br_2, Br^-) = 1.229 \text{ V} - (1.087 \text{ V}) = 0.142 \text{ V}$$
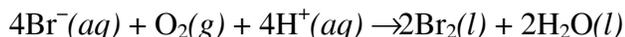
This reaction is apparently relatively slow (possibly because the interaction of the gaseous oxygen with the ions in solution is inefficient), so this is not a commercially useful way to extract the bromine.

Problem 10.28.
The assumptions we have to make to get an estimate of the cell potential for the reaction between molten aluminum chloride, $AlCl_3$, and sodium metal are rather bold and difficult to justify, but will probably rationalize the *direction* of the reaction. Assume that $AlCl_3$ is ionized to Al^{3+} and Cl^- in its liquid, and that the aluminum ion acts as if it is in aqueous solution. Assume that we can ignore the formation of the solid sodium chloride and make our analysis as though the product is sodium ion in aqueous solution. Obviously, these assumptions are all suspect, but the only data we have in Appendix B are for aqueous solutions. We have to use them to see what they predict, knowing that the actual system is quite different. In these reactions, the state of the species has been omitted, because of the great uncertainty about what it is in this system:

$$Al^{3+} + 3e^- \Leftrightarrow Al \qquad E^o = -1.66 \text{ V}$$
$$\underline{-3\{Na^+ + e^- \Leftrightarrow Na\} \qquad E^o = -(-2.71 \text{ V})}$$
$$Al^{3+} + 3Na \Leftrightarrow Al + 3Na^+ \quad E^o = 1.05 \text{ V}$$
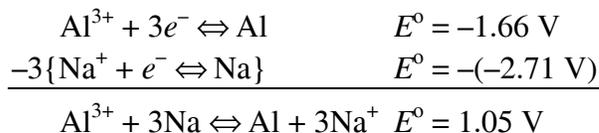
The cell potential is favorable for this reaction. Formation of solid products that probably separate from the molten reaction mixture will also favor the formation of the products. This reaction is not one that can be run readily on a large scale, so the amount of pure aluminum metal available before the end of the nineteenth century was small. (Nowadays, aluminum beverage cans are so inexpensive and ubiquitous that you might even be tempted to discard them rather than recycle. Resist the temptation; it is still the case that a great deal of energy is required to reduce aluminum ions to aluminum metal, as its reduction potential shows, and recycling saves this energy—as well as the metal.)

Problem 10.29.
(a) The reduction half reaction of chlorine gas to chloride anion has a more positive standard reduction potential, 1.359 V, than that for the reduction half reaction of zinc cation to zinc metal, –0.763 V. Therefore, in a cell made by placing a sheet of zinc metal, $Zn(s)$, in an aqueous solution of zinc sulfate, $ZnSO_4(aq)$, that is connected by a salt bridge to an aqueous solution of sodium chloride, $NaCl(aq)$, containing a coil of platinum wire, $Pt(s)$, over which chlorine gas, $Cl_2(g)$, is bubbled, the platinum electrode in contact with the chlorine gas and chloride ion solution will be the cathode (where chlorine gas is reduced) and the zinc electrode will be the anode (where zinc metal is oxidized to zinc cation).

(b) The explanation for these half reactions is in part (a):

anode reaction: $\quad Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

cathode reaction: $\quad Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$

net cell reaction: $\quad Zn(s) + Cl_2(g) \rightarrow Zn^{2+}(aq) + 2Cl^-(aq)$
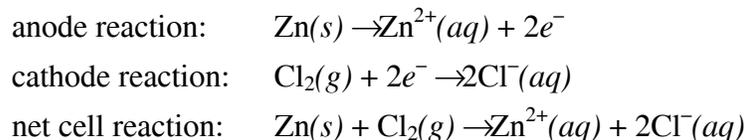
(c) The line notation for the cell and its standard potential are:

$Zn(s) \,|\, Zn^{2+}(aq) \,\|\, Cl^-(aq) \,|\, Cl_2(g) \,|\, Pt(s)$

$E^o = E^o(Cl_2, Cl^-) - E^o(Zn^{2+}, Zn) = 1.359 \text{ V} - (-0.763 \text{ V}) = 2.122 \text{ V}$
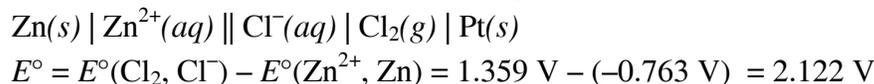
Problem 10.30.
(a) The relevant reduction half reactions and their combination for the net reaction for the titration of $Fe^{2+}(aq)$ with $MnO_4^-(aq)$ are:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$
$$\underline{-5 \cdot [Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)\,]}$$
$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$$
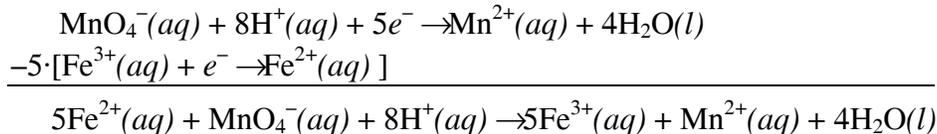
(b) The standard cell potential for the reactions in part (a) is:

$E° = E°(MnO_4^-, Mn^{2+}) - E°(Fe^{3+}, Fe^{2+}) = 1.507\ V - (0.771\ V) = 0.736\ V$

(c) Since the permanganate reduction from Mn(VII) to Mn(II) is a five electron change and the oxidation of iron(II) to iron(III) is a one electron change, it takes one-fifth, 0.200, mol of permanganate to oxidize 1.000 mol of iron. Or, put the other way, one mole of permanganate reacts with five moles of iron(II). If 23.46 mL of 0.0200 M KMnO$_4$(aq) is required to titrate a sample containing iron(II) ion, the number of moles of iron in the sample is:

mol Mn(VII) = (0.02346 L)(0.0200 mol·L^{-1}) = 4.69×10^{-4} mol

mol Fe(II) = [4.69×10^{-4} mol Mn(VII)]$\left(\dfrac{5 \text{ mol Fe(II)}}{1 \text{ mol Mn(VII)}} \right)$ = 2.35×10^{-3} mol Fe(II)

Problem 10.31.
(a) The relevant reduction half reactions and their combination to give the net reaction producing chlorine gas by dropping hydrochloric acid solution, HCl(aq), onto crystals of potassium permanganate, KMnO$_4$(s) are:

$$2 \cdot [MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)]$$
$$\underline{-5 \cdot [Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)]}$$
$$10Cl^-(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 5Cl_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$$
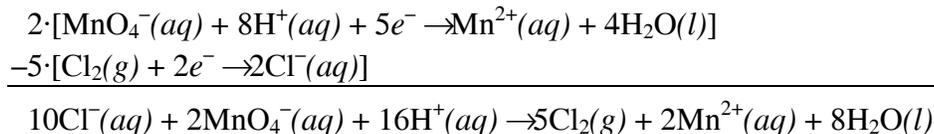
(b) The standard cell potential for this reaction is:

$E° = E°(MnO_4^-, Mn^{2+}) - E°(Cl_2, Cl^-) = 1.507\ V - (1.359\ V) = 0.148\ V$

Problem 10.32.
(a) Will reaction occur between the pair of reactants Fe^{3+}(aq) and Br$^-$(aq)? The standard reduction potential for the iron(III) cation to iron(II) cation half reaction, 0.771 V, is more negative than that for the elemental bromine to bromide anion half reaction, 1.087 V, so no reaction will occur between Fe^{3+}(aq) and Br$^-$(aq).

(b) Will reaction occur between the pair of reactants Fe^{3+}(aq) and I$^-$(aq)? The standard reduction potential for the iron(III) cation to iron(II) cation half reaction, 0.771 V, is more positive than that for the elemental iodine to iodide anion half reaction, 0.5355 V, so reaction can occur between Fe^{3+}(aq) and I$^-$(aq). The net reaction and its standard cell potential are:

$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(s)$

$E° = E°(Fe^{3-}, Fe^{2+}) - E°(I_2, I^-) = 0.771\ V - (0.5355\ V) = 0.235\ V$
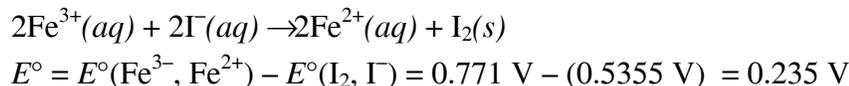
(c) Will reaction occur between the pair of reactants Fe^{2+}(aq) and Br$_2$(aq)? The standard reduction potential for the elemental bromine to bromide anion half reaction, 1.087 V, is more positive than that for the iron(III) cation to iron(II) cation half reaction 0.771 V, so reaction can occur between Fe^{2+}(aq) and Br$_2$(aq). The net reaction and its standard cell potential are:

$Br_2(aq) + 2Fe^{2+}(aq) \rightarrow 2Br^-(aq) + 2Fe^{3+}(aq)$
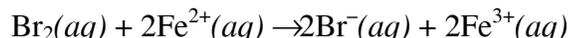
$$E° = E°(Br_2, Br^-) - E°(Fe^{3+}, Fe^{2+}) = 1.087 \text{ V} - (0.771 \text{ V}) = 0.316 \text{ V}$$

(d) Will reaction occur between the pair of reactants $Fe^{2+}(aq)$ and $Ag^+(aq)$? The standard reduction potential for the silver cation to silver metal half reaction, 0.799 V, is more positive than that for the iron(III) cation to iron(II) cation half reaction, 0.771 V, so reaction can occur between $Fe^{2+}(aq)$ and $Ag^+(aq)$. The net reaction and its standard cell potential are:
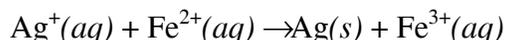
$$Ag^+(aq) + Fe^{2+}(aq) \rightarrow Ag(s) + Fe^{3+}(aq)$$
$$E° = E°(Ag^+, Ag) - E°(Fe^{3+}, Fe^{2+}) = 0.799 \text{ V} - (0.771 \text{ V}) = 0.028 \text{ V}$$

Problem 10.33.
(a) Will the reaction, $Cu^{2+}(aq) + H_2O_2(aq) \rightarrow Cu(s) + O_2(g)$, occur? The standard reduction potential for the copper(II) cation to copper metal half reaction, 0.337 V, is more negative than that for the elemental oxygen to hydrogen peroxide half reaction, 0.69 V, so no reaction will occur between $Cu^{2+}(aq)$ and $H_2O_2(aq)$.

(b) Will the reaction, $Cu(s) + NO_3^-(aq) + H^+(aq) \rightarrow Cu^{2+}(aq) + NO(g)$, occur? The standard reduction potential for the nitrate cation to nitric oxide half reaction, 0.955 V, is more positive than that for the copper(II) cation to copper metal half reaction, 0.337 V, so reaction can occur between $Cu(s)$ and $NO_3^-(aq)$ in acidic solution. The balanced net reaction and its standard cell potential are:
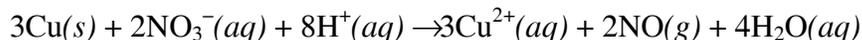
$$3Cu(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Cu^{2+}(aq) + 2NO(g) + 4H_2O(aq)$$
$$E° = E°(NO_3^-, NO) - E°(Cu^{2+}, Cu) = 0.955 \text{ V} - (0.337 \text{ V}) = 0.618 \text{ V}$$

(c) Will the reaction, $MnO_2(s) + I^-(aq) \rightarrow Mn^{2+}(aq) + I_2(aq)$, occur? The standard reduction potential for the manganese dioxide to manganese(II) cation half reaction, 1.230 V, is more positive than that for the elemental iodine to iodide ion half reaction, 0.5355 V, so reaction can occur between $MnO_2(s)$ and $I^-(aq)$ in acidic solution. The balanced net reaction and its standard cell potential are:
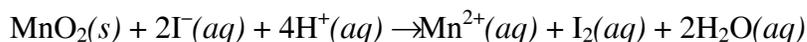
$$MnO_2(s) + 2I^-(aq) + 4H^+(aq) \rightarrow Mn^{2+}(aq) + I_2(aq) + 2H_2O(aq)$$
$$E° = E°(MnO_2, Mn^{2+}) - E°(I_2, I^-) = 1.230 \text{ V} - (0.5355 \text{ V}) = 0.694 \text{ V}$$

(d) Will the reaction, $Cr_2O_7^{2-}(aq) + CH_3CH_2OH(aq) + H^+(aq) \rightarrow Cr^{3+}(aq) + CH_3CHO(aq)$, occur? The standard reduction potential for the dichromate anion to chromium(III) cation half reaction, 1.36 V, is more positive than that shown for the ethanal (acetaldehyde) to ethanol half reaction, –0.20 V, so reaction can *probably* occur between $Cr_2O_7^{2-}(aq)$ and $CH_3CH_2OH(aq)$. The ambiguity in this case arises because the potential for the dichromate reduction is given for acidic solution, with pH = 0, and the ethanal potential is for the reaction at pH = 7. Le Chatelier's principle predicts that the ethanal reduction potential will become more positive (closer to that of the dichromate reduction) as the pH decreases, since the reaction involves hydronium ions as reactants. The difference between the two potentials is so large that this effect is not likely to change our prediction of the direction of the overall reaction. This reaction is, in fact, the basis for the Breathalyzer® test for alcohol in a person's breath, so it does work and goes in the direction we write here. The balanced net reaction and its standard cell potential are:
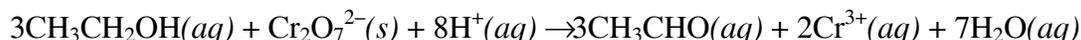
$$3CH_3CH_2OH(aq) + Cr_2O_7^{2-}(s) + 8H^+(aq) \rightarrow 3CH_3CHO(aq) + 2Cr^{3+}(aq) + 7H_2O(aq)$$
$$E° = E°(Cr_2O_7^{2-}, Cr^{3+}) - E°(\text{ethanal, ethanol}) = 1.36 \text{ V} - [> (-0.20 \text{ V})] = < 1.56 \text{ V}$$

Problem 10.34.

(a) For the cell reaction, $Zn(s) + Pb^{2+}(aq) \rightarrow Zn^{2+}(aq) + Pb(s)$, use the measured cell potential, 0.660 V, to find the free energy change (with $n = 2$, since the reaction is a two-electron transfer) per mole of reaction:

$$\Delta G_{reaction} = -nFE = -2 \cdot (9.6485 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(0.660 \text{ V}) = -127.4 \text{ kJ} \cdot \text{mol}^{-1}$$

The reaction is spontaneous. The free energy change is negative and the cell potential is positive, either of which can be taken as an indication of spontaneity.

(b) The negative of the free energy change gives the maximum amount of work that can be done by the cell on its surroundings. In part (a) we calculated the free energy change for a mole of reaction (equivalent in this case to a mole of zinc metal reacting). Thus, for the reaction of 0.125 mol $Zn(s)$:

$$\text{maximum work} = -(0.125 \text{ mol})(-127.4 \text{ kJ} \cdot \text{mol}^{-1}) = 15.9 \text{ kJ}$$

(c) For every mole of $Zn(s)$ that reacts a mole of $Pb(s)$ is formed, so 0.125 mol of lead metal forms when the work in part (b) is produced:

$$\text{mass Pb}(s) = (0.125 \text{ mol})(207.2 \text{ g} \cdot \text{mol}^{-1}) = 25.9 \text{ g}$$

Problem 10.35.

(a) In a copper-zinc cell, **e**ach Zn atom that goes into solution as Zn^{2+} leaves behind two electrons for the external circuit. Therefore, the number of moles of electrons produced is twice the number of moles of Zn that react. The molar mass of Zn is 65.37 g·mol^{-1} and the mass of Zn that has reacted in the cell described here is 270.7 g (= 486.5 − 215.8). The moles of Zn reacted and e^- produced are:

$$\text{mol Zn reacted} = (270.7 \text{ g})\left(\frac{1 \text{ mol Zn}}{65.37 \text{ g Zn}}\right) = 4.141 \text{ mol Zn}$$

$$\text{mol } e^- \text{ produced} = 2(\text{mol Zn}) = 8.282 \text{ mol } e^-$$

(b) The Faraday constant, F, is the amount of charge on one mole of electrons, so the total charge transferred during the lifetime of this cell is:

$$\text{charge transferred} = (8.282 \text{ mol})(96485 \text{ C} \cdot \text{mol}^{-1}) = 7.991 \times 10^5 \text{ C}$$

To get the amount of work that could be produced by this amount of charge, we need to know the cell potential, E, for this cell. Figure 10.6 shows a copper-zinc cell with a cell potential of 1.10 V (with 0.10 M solutions for both metal ions). From the data in Appendix B we find that the standard cell potential is:

$$E° = E°(Cu^{2+}, Cu) - E°(Zn^{2+}, Zn) = 0.337 \text{ V} - (-0.763 \text{ V}) = 1.100 \text{ V}$$

It looks like 1.10 V is a reasonable approximation for the cell potential to get an estimate of the work that the cell can produce. (If you jump ahead to Problem 10.74, you find that one version of a cell like this, often called a Daniell cell, has an intial potential of 1.15 V that decreases slowly over its lifetime.)

$$\text{work} = (\text{charge transferred})(\text{cell potential}) = (7.991 \times 10^5 \text{ C})(1.10 \text{ V}) \approx 8.8 \times 10^2 \text{ kJ}$$

(Note that this is enough energy to lift a loaded moving van to the top of a one-story building.)

Problem 10.36.
(a) In the cell described in this problem, the cell potential is positive when the anode lead from a digital voltmeter is connected to the platinum wire, so the platinum wire is the anode of the cell and the reaction there must be the oxidation of hydrogen gas (bubbled over the wire) to hydronium ions. The cathode must be the silver wire and the cathode reaction must be the reduction of the silver cation in solid silver chloride to silver metal with the release of chloride anion into the solution. The line notation for this cell is:

$$\text{Pt} \mid H_2(g, \text{ 1 bar}) \mid H^+(aq, \text{ 1 M}), Cl^-(aq, \text{ 1 M}) \mid AgCl(s) \mid Ag(s)$$
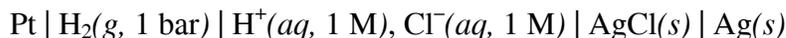
(b) The rationale for the choices of reaction are given in part (a) and based on the makeup of the cell and the identity of the anode. The reduction half reactions and cell reaction are:

$$\text{anode reaction:} \quad 2H^+(aq) + 2e^- \rightarrow H_2(g)$$

$$\text{cathode reaction:} \quad AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$$

$$\text{net cell reaction:} \quad H_2(g) + 2AgCl(s) \rightarrow 2H^+(aq) + 2Ag(s) + 2Cl^-(aq)$$
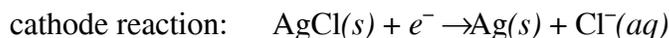
(c) All of the species in the cell are present at their standard concentrations (or pressure), so the measured potential, 0.22 V, is the standard potential, $E°$, for this cell and the standard free energy change for one mole of cell reaction is:

$$\Delta G°_{reaction} = -nFE° = -2 \cdot (9.6485 \times 10^4 \text{ C·mol}^{-1})(0.22 \text{ V}) = -42 \text{ kJ·mol}^{-1}$$

The free energy change is for one mole of hydrogen gas and two moles of silver chloride solid reacting as shown in the net cell reaction, which involves two moles of electrons.

(d) The anode of this cell is the standard hydrogen electrode, SHE, which, by definition, has a reduction potential of zero volts. Other reduction potentials are determined by measuring the cell potential of a cell made by combining the appropriate half cell with the SHE (taken as the anode). This is the way this cell is set up, so the standard reduction potential for the AgCl|Ag electrode is 0.22 V, which is the value you find (to two significant figures) in Appendix B.

Problem 10.37.
(a) In the reaction, $O_2(g) + 2H_2S(aq) \Leftrightarrow 2H_2O(l) + 2S(s)$, the oxygen atoms in O_2 are being reduced from an oxidation number of zero to an oxidation number of –2 in water. The opposite is the case for sulfur atoms, which are being oxidized from an oxidation number of –2 to 0. The reduction half reactions for O_2 and for S are:

$$O_2(g) + 4H^+(aq) + 4e^- \Leftrightarrow 2H_2O(l)$$

$$S(s) + 2H^+(aq) + 2e^- \Leftrightarrow H_2S(aq)$$
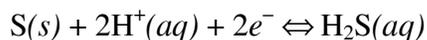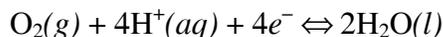
The hydronium ions cancel out when the two half reactions are combined (first minus double the second) to give the overall reaction.

(b) The standard cell potential for the reaction can be calculated from the standard free energy given for the reaction:

$$E° = -\frac{\Delta G°}{nF} = -\frac{\left(-418.8 \times 10^3 \text{ J·mol}^{-1}\right)}{4\left(96485 \text{ C·mol}^{-1}\right)} = 1.085 \text{ V}$$

Problem 10.38.
(a) The redox reaction between oxalic acid and permanganate ion is:

$$5HOOCCOOH(s) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$$
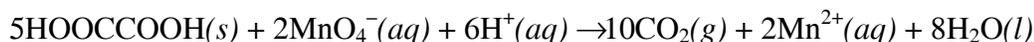
The standard free energy change for this redox reaction is:

$$\Delta G°_{rxn} = (10 \text{ mol})\Delta G°_f(CO_2) + (2 \text{ mol})\Delta G°_f(Mn^{2+}) + (8 \text{ mol})\Delta G°_f(H_2O)$$
$$- (5 \text{ mol})\Delta G°_f(HOOCCOOH) - (2 \text{ mol})\Delta G°_f(MnO_4^-) - (6 \text{ mol})\Delta G°_f(H^+)$$

$$\Delta G°_{rxn} = 10(-394.36 \text{ kJ}) + 2(-223 \text{ kJ}) + 8(-237.13 \text{ kJ})$$
$$- 5(-697.9 \text{ kJ}) - 2(-425 \text{ kJ}) - 6(0 \text{ kJ})$$

$$\Delta G°_{rxn} = -1.95 \times 10^3 \text{ kJ}$$

The reaction, with this very high negative standard free energy change, is definitely spontaneous under standard conditions.

(b) The standard cell potential for this reaction is obtained by rearranging $-\Delta G°_{rxn} = nFE°$ to solve for $E°$. The value of n is 10 in this case because two permanganate anions [containing manganese(VII)] are reduced to two manganese(II) cations.

$$E° = \frac{-\Delta G°_{rxn}}{nF} = \frac{1.95 \times 10^6 \text{ J}}{10 \cdot (9.6485 \times 10^4 \text{ C} \cdot \text{mol}^{-1})} = 2.02 \text{ V}$$

(c) From part (b), we know the standard cell potential for the reaction that involves the oxidation of oxalic acid by permanganate and we can find the standard reduction potential for the permanganate anion reduction, 1.507 V, in Appendix B. These values can be combined to find the standard reduction potential for the reduction of carbon dioxide gas to oxalic acid:

$$2CO_2(g) + 2H^+(aq) + 2e^- \Leftrightarrow HOOCCOOH(s):$$
$$E° = 2.02 \text{ V} = E°(MnO_4^-, Mn^{2+}) - E°(CO_2, \text{oxalic acid}) = 1.507 \text{ V} - E°(CO_2, \text{oxalic acid})$$
$$E°(CO_2, \text{oxalic acid}) = -0.51 \text{ V}$$

Problem 10.39.
For each of these cells, we write the cathodic and anodic half cell reactions (as reductions), the net cell reaction, the standard cell potential (from the reduction potentials in Appendix B), and the standard free energy change (from $\Delta G°_{rxn} = -nFE°$).

(a) $Cr(s) | Cr^{2+}(aq) \| Cr^{3+}(aq) | Cr(s)$

cathodic: $2 \cdot [Cr^{3+}(aq) + 3e^- \Leftrightarrow Cr(s)]$

anodic: $-3 \cdot [Cr^{2+}(aq) + 2e^- \Leftrightarrow Cr(s)]$

net reaction: $Cr(s) + 2Cr^{3+}(aq) \Leftrightarrow 3Cr^{2+}(aq)$
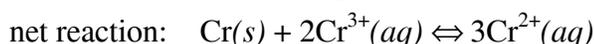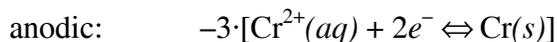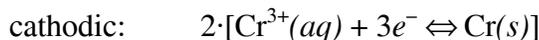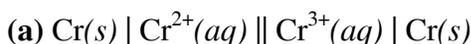
$E° = E°(Cr^{3+}, Cr) - E°(Cr^{2+}, Cr) = -0.74 \text{ V} - (-0.89 \text{ V}) = 0.15 \text{ V}$

$\Delta G°_{rxn} = -nFE° = -6 \cdot (9.6485 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(0.15 \text{ V}) = -87 \text{ kJ} \cdot \text{mol}^{-1}$

(b) $Pt(s) | Fe^{3+}(aq), Fe^{2+}(aq) \| Cr_2O_7^{2-}(aq), Cr^{3+}(aq) | Pt(s)$

cathodic: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \Leftrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

anodic: $-6 \cdot [Fe^{3+}(aq) + e^- \Leftrightarrow Fe^{2+}(aq)]$

net reaction: $6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \Leftrightarrow 6Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$
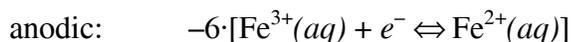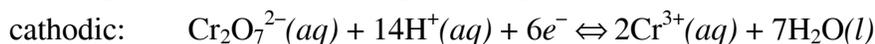
$E° = E°(Cr_2O_7^{2-}, Cr^{3+}) - E°(Fe^{3+}, Fe^{2+}) = 1.36 \text{ V} - (0.771 \text{ V}) = 0.59 \text{ V}$

$\Delta G°_{rxn} = -nFE° = -6 \cdot (9.6485 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(0.59 \text{ V}) = -3.4 \times 10^2 \text{ kJ} \cdot \text{mol}^{-1}$

(c) $Zn(s) \mid Zn^{2+}(aq) \parallel Fe^{2+}(aq) \mid Fe(s)$

        cathodic: $Fe^{2+}(aq) + 2e^- \Leftrightarrow Fe(s)$

        anodic: $-[Zn^{2+}(aq) + 2e^- \Leftrightarrow Zn(s)]$

        net reaction: $Zn(s) + Fe^{2+}(aq) \Leftrightarrow Zn^{2+}(aq) + Fe(s)$
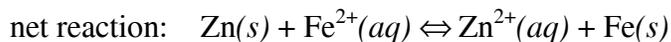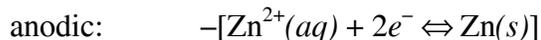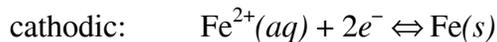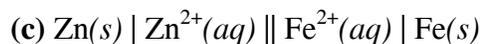
        $E° = E°(Fe^{2+}, Fe) - E°(Zn^{2+}, Zn) = -0.41 \text{ V} - (-0.763 \text{ V}) = 0.35 \text{ V}$

        $\Delta G°_{rxn} = -nFE° = -2 \cdot (9.6485 \times 10^4 \text{ C·mol}^{-1})(0.35 \text{ V}) = -68 \text{ kJ·mol}^{-1}$

(d) $Hg(l) \mid Hg_2Cl_2(s) \mid Cl^-(aq) \parallel Hg_2^{2+}(aq) \mid Hg(l)$

        cathodic: $Hg_2^{2+}(aq) + 2e^- \Leftrightarrow 2Hg(l)$

        anodic: $-[Hg_2Cl_2(s) + 2e^- \Leftrightarrow 2Hg(l) + 2Cl^-(aq)]$

        net reaction: $Hg_2^{2+}(aq) + 2Cl^-(aq) \Leftrightarrow Hg_2Cl_2(s)$
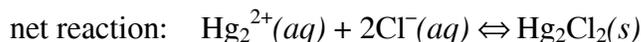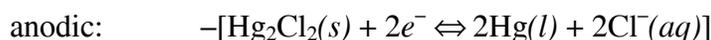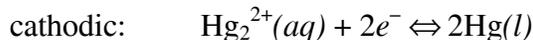
        $E° = E°(Hg_2^{2+}, Hg) - E°(Hg_2Cl_2, Hg) = 0.796 \text{ V} - (0.268 \text{ V}) = 0.528 \text{ V}$

        $\Delta G°_{rxn} = -nFE° = -2 \cdot (9.6485 \times 10^4 \text{ C·mol}^{-1})(0.528 \text{ V}) = -101.9 \text{ kJ·mol}^{-1}$

Note that the net reaction in this case, part (d), is not a redox reaction. It is a precipitation reaction and the substantial negative standard free energy change suggests that mercury(I) chloride, $Hg_2Cl_2(s)$, is quite insoluble. This insolubility is what drives the reaction in the cell.

Problem 10.40.
(a) The standard reduction potential for the copper(II) cation to copper metal half reaction, 0.337 V, is more positive than that for the iron(II) cation to iron metal half reaction, –0.41 V, so copper(II) cation will be reduced to copper metal and iron metal will be oxidized to iron(II) cation in the cell described in this problem. The loss of atoms from the iron metal will result in its losing mass. Addition of the copper metal to the copper electrode will increase its mass.

(b) Iron(II) cations are produced in the iron half cell, so the metal ion concentration will increase in this half cell.

(c) Use the standard reduction potentials (which are given at 298 K) to get the initial (standard) cell potential:

        $E° = E°(Cu^{2+}, Cu) - E°(Fe^{2+}, Fe) = 0.337 \text{ V} - (-0.41 \text{ V}) = 0.75 \text{ V}$

Consider what happens to each reduction half reaction, as the reaction proceeds:

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

        anode: $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$
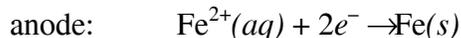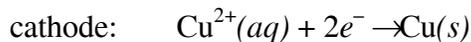
In the copper half cell, the concentration of copper(II) declines, so the reduction potential becomes less positive. In the iron half cell, the concentration of iron(II) increases, so the reduction potential becomes more positive. (Use Le Chatelier's principle to make these predictions.) The result is that the reduction potentials for the half reactions approach one another as the more positive becomes less positive and the less positive becomes more positive. Thus, the cell potential, the difference between these two reduction potentials becomes less and less as the cell reaction goes on. Ultimately, the reduction potentials will come to the same value and the cell potential will become zero. Equilibrium will have been reached. Dead cells are at equilibrium.

Problem 10.41.

(a) The cell notation, Ni*(s)* | Ni^{2+}*(aq,* 0.1 M*)* ‖ Fe^{3+}*(aq,* 0.1 M*)* , Fe^{2+}*(aq,* 0.1 M*)* | Pt*(s)*, implies that Ni, the left-hand electrode, is the anode. The measured positive potential means that this is correct, since the assumption we have to make is that the anode input to the voltmeter was connected to the Ni metal electrode. Thus, oxidation of Ni occurs at the Ni electrode and reduction of Fe^{3+} at the Pt cathode:

$$2Fe^{3+} + Ni \rightarrow 2Fe^{2+} + Ni^{2+}$$
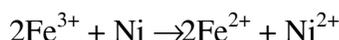
(b) Since Fe^{2+} is a product of the reaction, increasing its concentration has the effect of shifting the reaction back toward the reactants (to reduce the effect of the disturbacne, the addition of a reaction product—Le Chatelier's principle). This shift will decrease the cell potential, since the shift is in a direction to lower the driving force for the cell reaction.

(c) Ni^{2+} is also a product of the reaction, so increasing its concentration will have the same directional effect as for the addition of Fe^{2+} in part (b), that is, decreasing the cell potential.

(d) If a strip of nickel metal is immersed in an equimolar aqueous solution of Fe^{3+} and Fe^{2+} ions, we would you expect, on the basis of the cell reaction we have written, some of the Ni metal to react and go into solution as Ni^{2+} ions while twice as many moles of Fe^{3+} are reduced to Fe^{2+}. Thus, you would expect to find Ni^{2+} in the solution with the amount of Fe^{3+} reduced by two moles for every mole of Ni^{2+} present and the amount of Fe^{2+} increased by two moles for every mole of Ni^{2+}.

Problem 10.42.

(a) For this cell, Cd*(s)* | Cd^{2+}*(aq,* ?? M*)* ‖ Ni^{2+}*(aq,* 1.0 M*)* | Ni*(s)*, the measured cell potential, *E*, is 0.225 V at 298 K. The cadmium metal electrode is the anode in this cell, so cadmium metal is being oxidized to cadmium cation. The cathodic reaction must be the reduction of nickel(II) cation to nickel metal. The half reactions (as reductions) and net cell reaction are:

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

anodic: $Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$

net reaction: $Cd(s) + Ni^{2+}(aq) \rightarrow Cd^{2+}(aq) + Ni(s)$
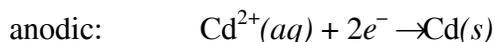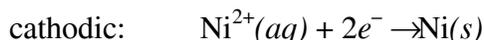
(b) The standard cell potential is the difference between the cathodic and anodic standard reduction potentials:

$$E° = E°(Ni^{2+}, Ni) - E°(Cd^{2+}, Cd) = -0.23 \text{ V} - (-0.40 \text{ V}) = 0.17 \text{ V}$$

(c) If the cadmium cation concentration were 1 M, the cell potential would be the standard cell potential (because the nickel(II) cation concentration is 1 M as well). The cell potential is more positive than the standard potential, so the net reaction has a greater driving force than if all concentrations were 1 M. Since cadmium cation is a product of the cell reaction, Le Chatelier's principle predicts that its concentration is lower than 1 M, as this would make the driving force for reaction greater, as observed. Use the measured potential for the cell, 0.225 V, the standard cell potential from part (b), and the known concentration of nickel(II) cation, 1.0 M, in the Nernst equation to get a numerical value for the unknown cadmium cation concentration:

$$E = 0.225 \text{ V} = E° - \frac{(0.05916 \text{ V})}{n} \log Q = 0.17 \text{ V} - \frac{(0.05916 \text{ V})}{2} \log\left(\frac{(Cd^{2+})}{(Ni^{2+})}\right)$$

$$-\frac{2 \cdot (0.225\ \text{V})}{0.05916\ \text{V}} = \log\left(\frac{(Cd^{2+})}{(Ni^{2+})}\right) = \log\left(\frac{(Cd^{2+})}{1}\right) = \log(Cd^{2+}) = -1.86$$

$$(Cd^{2+}) = 0.014$$

The concentration of cadmium ion is 0.014 M. This numerical result is consistent with the directional reasoning based on Le Chatelier's principle.

(d) We know that the equilibrium constant for the reaction is related to the standard cell potential:

$$\ln K = \frac{nFE^\circ}{RT} = \frac{2 \cdot (9.6485 \times 10^4\ \text{C} \cdot \text{mol}^{-1})(0.17\ \text{V})}{(8.314\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298\ \text{K})} = 13.2 \qquad \therefore K = 5.4 \times 10^5$$

Problem 10.43.
For the cell of interest, $Pt(s) \mid H_2(g) \mid H^+(aq),\ SO_4^{2-}(aq) \mid PbSO_4(s) \mid Pb(s)$, the columns in this table are labeled with the effect of each change on the cell potential.

change in the cell	increase	decrease	no effect
increase in pH of the solution	X		
dissolving Na_2SO_4 in the solution		X	
increase in size of the Pb electrode			X
decrease in H_2 gas pressure		X	
addition of water to the solution	X		
increase in the amount of $PbSO_4$			X
dissolving a bit of NaOH in the solution	X		

To analyze the results of the changes, use the net cell reaction:

$$H_2(g) + PbSO_4(s) \rightarrow 2H^+(aq) + Pb(s) + SO_4^{2-}(aq)$$
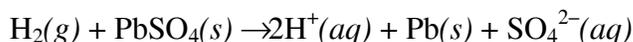
The first and last changes both decrease the concentration of hydronium ion, $H^+(aq)$, which is a product of the reaction. Le Chatelier's principle predicts that the system will react to this disturbance by forming more hydronium ion, which drives the reaction toward products and increases the cell potential. Similarly, addition of water reduces the concentrations of both hydronium ion and sulfate anion. Since these are products, the reaction will be driven toward products, thus increasing the cell potential. Changing the amount of a pure solid in an equilibrium system has no effect on the reaction quotient because the dimensionless concentration ratio is unchanged. Thus increasing either the lead or the lead sulfate has no effect on the cell potential. Adding sulfate anion increases the concentration of a product and the system will respond by decreasing its concentration, that is, the reaction proceeds in reverse, which decreases the cell potential. Finally, a decrease in the hydrogen gas pressure is a decrease in the "concentration" of a reactant and the system responds by increasing the amount of hydrogen, that is, the reaction proceeds in reverse, which decreases the cell potential.

Problem 10.44.
For the cell of interest, $Cu(s) \mid Cu^{2+}(aq) \parallel Cr_2O_7^{2-}(aq),\ Cr^{3+}(aq),\ H^+(aq) \mid Pt(s)$, the columns in this table are labeled with the effect of each change on the cell potential.

change in the cell	increase	decrease	no effect
decrease in pH in the Cr solution	X		
decrease in size of the Cu electrode			X
addition of water to the Cu solution	X		
addition of water to the Cr solution		X	
dissolving $Cr(NO_3)_3$ in the Cr solution		X	
dissolving $K_2Cr_2O_7$ in the Cr solution	X		

To analyze the results of the changes, use the net cell reaction:

$$3Cu(s) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 3Cu^{2+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$$
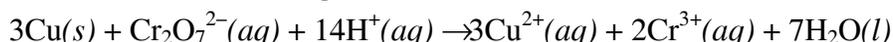
Decreasing the pH in the chromium half cell increases the hydronium ion concentration. Hydronium ion is a reactant, so the system responds by reacting to decrease its concentration. The reaction is driven toward products, thus increasing the cell potential. Note that this can be a very large effect since the concentration of hydronium ion in the reaction quotient is raised to the 14th power. The size or amount of any solid reactant or product has no effect on the reaction quotient, because its dimensionless concentration ratio is unaffected. Thus decreasing the size of the copper electrode (as long as it is not decreased to zero) has no effect on the cell potential. Addition of water to the copper half cell decreases the concentration of copper(II) cation, a reaction product. The system responds by making more copper(II) cation, thus driving the reaction toward products and increasing the cell potential. Addition of water to the chromium half cell is a more difficult change to analyze, since it decreases the concentrations of both reactants, $Cr_2O_7^{2-}(aq)$ and $H^+(aq)$, and a product, $Cr^{3+}(aq)$. To figure out what will happen, we consider how the reaction quotient for this reaction will be affected and how its change will affect the cell potential, via the Nernst equation:

$$E = E^\circ - \frac{(0.05916\ V)}{n} \log Q = E^\circ - \frac{(0.05916\ V)}{6} \log\left(\frac{(Cu^{2+})^3 (Cr^{3+})^2}{(Cr_2O_7^{2-})(H^+)^{14}} \right)$$

The overwhelming effect of the hydronium ion concentration raised to the 14th power is the major factor here. A small decrease in the concentration of hydronium ion will cause a large increase in the numerical value of Q, because it cannot be wholly compensated by the concomitant decrease in the concentration of the chromium(III) cation, which is only raised to the 2nd power in the numerator. Thus, the $\log Q$ term will increase and this will make the negative term on the right hand side of the equation more negative, thus decreasing E. Addition of more chromium(III) cation (the fifth change in the table) to the chromium half cell increases the concentration of a reaction product. The system responds by reacting in reverse to decrease this concentration, thus driving the reaction toward reactants and decreasing the cell potential. The last change, addition of more dichromate anion to the chromium half cell, increases the concentration of one of the reactants. The system responds by reacting to decrease its concentration, so the reaction is driven toward products, thus increasing the cell potential.

Problem 10.45.

(a) The standard potential for the quinhydrone-silver cell is obtained by subtracting the standard reduction potential for the anode reaction (quinhydrone) from the standard potential for the cathode reaction (silver):

$$E° = E°(Ag^+, Ag) - E°(Qu, H_2Qu) = 0.799 \text{ V} - (0.699 \text{ V}) = 0.100 \text{ V}$$

(b) Write the Nernst equation (at 298 K) for the net cell reaction with the known values for E, $E°$, and concentrations and solve for the unknown hydronium ion concentration:

$$Pt(s) \mid H_2Qu(aq, c), Qu(aq, c), H_3O^+(pH) \parallel Ag^+(aq, 0.10 \text{ M}) \mid Ag(s)$$

$$H_2Qu(aq) + 2Ag^+(aq) \rightarrow Qu(aq) + 2H^+(aq) + 2Ag(s)$$
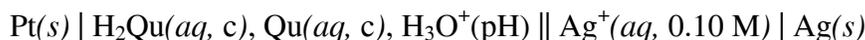
$$0.256 \text{ V} = 0.100 \text{ V} - \frac{(0.05916 \text{ V})}{2} \log\left(\frac{(Qu)(H^+)^2}{(H_2Qu)(Ag^+)^2}\right)$$

$$0.156 \text{ V} = -\frac{(0.05916 \text{ V})}{2} \log\left(\frac{(c)(H^+)^2}{(c)(0.10)^2}\right) = -\frac{(0.05916 \text{ V})}{2}[2 \cdot \log(H^+) - 2 \cdot \log(0.10)]$$

$$-\log(H^+) = pH = \left(\frac{0.156 \text{ V}}{0.05916 \text{ V}}\right) - \log(0.10) = 3.64$$

Problem 10.46.

(a) The line notation for the cell with net reaction, $Zn(s) + Hg_2^{2+}(aq) \Leftrightarrow Zn^{2+}(aq) + 2Hg(l)$, is:

$$Zn \mid Zn^{2+}(aq) \parallel Hg_2^{2+}(aq) \mid Hg(l)$$

(b) Substitute the known values, $[Hg_2^{2+}(aq)] = 0.010 \text{ M}$, $[Zn^{2+}(aq)] = 0.50 \text{ M}$, and $E = 1.51 \text{ V}$, into the Nernst equation (at 298 K) and solve to find $E°$ for the cell reaction:

$$1.51 \text{ V} = E° - \frac{(0.05916 \text{ V})}{2} \log\left(\frac{(Zn^{2+})}{(Hg_2^{2+})}\right)$$

$$E° = 1.51 \text{ V} + \frac{(0.05916 \text{ V})}{2} \log\left(\frac{0.50}{0.010}\right) = 1.51 \text{ V} + 0.05 \text{ V} = 1.56 \text{ V}$$

(You can check this result using the standard reduction potentials in Appendix B.) To get the equilibrium constant, substitute $E°$ in:

$$\ln K = \frac{nE°}{0.05916 \text{ V}} = \frac{2 \cdot (1.56 \text{ V})}{0.05916 \text{ V}} = 52.7; \qquad \therefore K = 8.0 \times 10^{22}$$

(c) The equilibrium constant for the reaction is quite large, so the equilibrium lies very far to the side of the products. Thus, almost no zinc cations will be reduced by the addition of mercury to a solution containing 1.0 M zinc cations. Assuming that there is a negligible change in the concentration of zinc cations, we can use K to calculate the tiny concentration of mercury(I) dication, $Hg_2^{2+}(aq)$, that will be formed.

$$K = 8.0 \times 10^{22} = \left(\frac{(Zn^{2+})}{(Hg_2^{2+})}\right) = \left(\frac{1.0}{(Hg_2^{2+})}\right); \quad (Hg_2^{2+}(aq)) = 1.3 \times 10^{-23}$$

$$[Hg_2^{2+}(aq)] = 1.3 \times 10^{-23} \text{ M}$$

This tiny concentration confirms that very little reaction occurs, so $[Zn^{2+}(aq)] = 1.0$ M is an excellent approximation.

Problem 10.47.
 (a) For the cell, $Sn(s) \mid Sn^{2+}(aq, 0.10 \text{ M}) \parallel Sn^{4+}(aq, 0.010 \text{ M}) , Sn^{2+}(aq, 1.0 \text{ M}) \mid Pt(s)$, the anodic and cathodic half reactions (as reductions) and the net cell reaction are:

anode: $Sn^{2+}_{an}(aq) + 2e^- \Leftrightarrow Sn(s)$

cathode: $Sn^{4+}(aq) + 2e^- \Leftrightarrow Sn^{2+}_{cath}(aq)$

cell reaction: $Sn(s) + Sn^{4+}(aq) \Leftrightarrow Sn^{2+}_{an}(aq) + Sn^{2+}_{cath}(aq)$
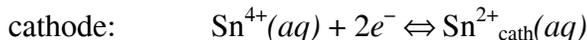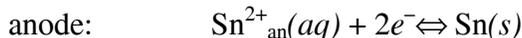
Here, for the moment, we distinguish between tin(II) ion on the anode and cathode sides of the cell, since they do not mix with one another. The reaction quotient and its numeric value are:

$$Q = \frac{\left(Sn^{2+}_{an}(aq)\right)\left(Sn^{2+}_{cath}(aq)\right)}{\left(Sn^{4+}(aq)\right)} = \frac{(0.10)(1.0)}{(0.010)} = 10.$$

(b) Use the Nernst equation with our known values of E from the problem statement and Q from part (a) to get $E°$ and $\Delta G°_{rxn}$:

$$E = 0.25 \text{ V} = E° - \frac{0.059 \text{ V}}{n}\log Q = E° - \frac{0.059 \text{ V}}{2}\log(10); \qquad E° = 0.28 \text{ V}$$

$$\Delta G°_{rxn} = -nFE° = -2(96485 \text{ C·mol}^{-1})(0.28 \text{ V}) = 5.4 \times 10^4 \text{ J·mol}^{-1} = 54 \text{ kJ·mol}^{-1}$$

(c) The equilibrium constant expression is written for the reaction as though all species are together in the same solution:

$$K = \frac{\left(Sn^{2+}(aq)\right)^2}{\left(Sn^{4+}(aq)\right)}$$

The equilibrium constant is obtained either from $E°$ or $\Delta G°_{reaction}$; from $E°$:

$$\ln K = \frac{nFE°}{RT} = \frac{2\left(96485 \text{ C·mol}^{-1}\right)(0.28 \text{ V})}{\left(8.314 \text{ J·mol}^{-1}\cdot K^{-1}\right)(298K)} = 21.8$$

$$K = e^{21.8} = 2.9 \times 10^9$$

(d) The cell potential (and free energy change) for the reaction of tin metal with tin(IV) are favorable, so we expect that tin metal added to the tin(IV) solution will react to reduce most of the tin(IV) to tin(II). If all the tin(IV) reacts, an equivalent number of moles of tin metal must be oxidized to tin(II). There are 2.5×10^{-4} mol [= (0.050 L)(0.005 M)] of tin(IV) which can react with 0.03 g of tin [= $(2.5 \times 10^{-4}$ mol)(119 g·mol^{-1})]. Thus there is tin metal remaining in the solution, so we can use our equilibrium constant, which is written for a reaction solution that contains tin(IV) and tin(II) in equilibrium with tin metal. The equilibrium constant is so large that we can probably assume that "all" the tin in solution is tin(II) and use the equilibrium constant expression to calculate the tiny concentration of tin(IV) remaining. The concentration of tin(II) is 0.010 M, because it includes the original tin present as tin(IV) plus the equivalent amount formed by oxidation of the tin metal. The concentration of tin(IV), $[Sn^{4+}(aq)]$, is numerically equivalent to $(Sn^{4+}(aq))$:

$$(Sn^{4+}(aq)) = \frac{\left(Sn^{2+}(aq)\right)}{K} = \frac{(0.010)^2}{2.9 \times 10^9} = 3.4 \times 10^{-14}$$

Our assumption that essentially all of the tin(IV) has reacted is justified. The solution contains almost all tin(II) with only a minuscule amount of tin(IV) remaining.

Problem 10.48.
[NOTE: This problem should be moved to the next section (assigned after Section 10.7 has been introduced), because part (c) is most easily done by applying the Nernst equation to the half cell reaction, which is done in Section 10.7.]

(a) When a saturated calomel electrode (S.C.E.), $E = 0.241$ V, is connected to a $Co^{2+}|Co$ half cell in which the concentration of Co^{2+} is 0.050 M, the measured cell potential at 298 K is 0.561 V and the cobalt half cell is the anode. The cell potential is the difference between the cathode reduction potential and the anode reduction potential. Since the cobalt half cell is the anode we can write:

$$E = 0.561 \text{ V} = E(\text{S.C.E.}) - E(Co^{2+}, Co) = 0.241 \text{ V} - E(Co^{2+}, Co)$$
$$E(Co^{2+}, Co) = -0.320 \text{ V}$$

(b) The net cell reaction for this cell is:

$$Co(s) + 2Hg(l) + 2Cl^-(\textit{saturated aqueous KCl solution}) \Leftrightarrow Co^{2+}(aq) + Hg_2Cl_2(s)$$

The free energy change for the cell reaction, under the conditions stated, is:

$$\Delta G_{rxn} = -nFE = -2 \cdot (9.6485 \times 10^4 \text{ C·mol}^{-1})(0.561 \text{ V}) = -108.3 \text{ kJ·mol}^{-1}$$

(c) Applying the Nernst equation (at 298 K) to the cobalt half cell reduction reaction and reduction potential for the cell here gives the standard reduction potential and thence the standard free energy change:

$$E(Co^{2+}, Co) = -0.320 \text{ V} = E°(Co^{2+}, Co) - \frac{(0.05916 \text{ V})}{2} \log\left(\frac{1}{(Co^{2+})}\right)$$

$$E°(Co^{2+}, Co) = -0.320 \text{ V} + \frac{(0.05916 \text{ V})}{2} \log\left(\frac{1}{0.050}\right) = -0.282 \text{ V}$$

$$\Delta G°_{rxn} = -nFE° = -2 \cdot (9.6485 \times 10^4 \text{ C·mol}^{-1})(-0.282 \text{ V}) = 54.4 \text{ kJ·mol}^{-1}$$

Problem 10.49.
(a) The half reactions (as reductions) in mercury cells can be represented as:

$$ZnO(s) + H_2O(l) + 2e^- \Leftrightarrow Zn(s) + 2OH^-(aq)$$
$$HgO(s) + H_2O(l) + 2e^- \Leftrightarrow Hg(l) + 2HO^-(aq)$$
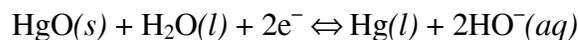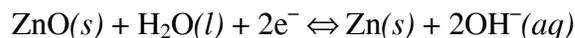
The problem states that Zn is the anode and, since oxidation occurs at the anode, the first reaction must be going in reverse as an oxidation in the cell. The cell reaction is the first half reaction subtracted from the second which gives (with redundant species cancelled out):

$$Zn(s) + HgO(s) \Leftrightarrow ZnO(s) + Hg(l)$$
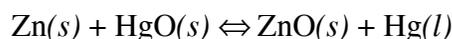
(b) As the product concentrations get higher, Le Chatelier's principle suggests that the system will respond in a way to decrease the effect of the change, that is, by reacting to use up the products. The reaction would go in reverse (or not go forward as forcefully as before the change)

and this would decrease the driving force for the reaction, which shows up as a decrease in the cell potential. (This argument has to be made with care and used cautiously because Le Chatelier's principle really applies to equilibrium systems and cells producing a potential are not at equilibrium.) For the mercury cell, you see that the cell reaction involves only solids and a pure elemental liquid. The concentrations (or activities) of these species do not change as they are produced or used up. Only when one or the other of the reactants, Zn and HgO, is used up (or almost used up) does the cell potential decline.

(c) The reaction quotient for the cell reaction in part (a) is:

$$Q = \frac{(Hg(l))(ZnO(s))}{(HgO(s))(Zn(s))} = \frac{1\cdot 1}{1\cdot 1} = 1$$

The dimensionless concentration ratio for pure solids and liquids is unity, so this substitution gives a constant reaction quotient of unity. The logarithm of unity is zero, so the cell potential does not vary until the reactants are almost used up in the cell.

Problem 10.50.

(a) The net cell reaction, $Al(s) + Fe^{3+}(aq) \Leftrightarrow Al^{3+}(aq) + Fe(s)$, is given in the problem statement. The corresponding Q is:

$$Q = \frac{(Al^{3+}(aq))(Fe(s))}{(Al(s))(Fe^{3+}(aq))} = \frac{(Al^{3+}(aq))}{(Fe^{3+}(aq))}$$

The dimensionless concentration ratio for pure solids and liquids is unity, so $(Al(s))$ and $(Fe(s))$ are both unity, which leaves us with only the aqueous ionic concentrations in Q.

(b) Use the Nernst equation (at 298 K) and the cell potential and concentration data to get $E°$ and, hence, $\Delta G°_{reaction}$:

$$1.59 \text{ V} = E° - \frac{(0.05916 \text{ V})}{3} \log\left(\frac{(Al^{3+}(aq))}{(Fe^{3+}(aq))}\right)$$

$$E° = 1.59 \text{ V} + \frac{(0.05916 \text{ V})}{3} \log\left(\frac{0.250}{0.0050}\right) = 1.59 \text{ V} + 0.03 \text{ V} = 1.62 \text{ V}$$

$$\Delta G°_{rxn} = -nFE° = -3\cdot(9.6485 \times 10^4 \text{ C·mol}^{-1})(1.62 \text{ V}) = -469 \text{ kJ·mol}^{-1}$$

(c) The equilibrium constant expression is identical to the expression for Q (at equilibrium) in part (a). The equilibrium constant at 298 K can be obtained from either $E°$ or $\Delta G°_{rxn}$:

$$\ln K = \frac{nE°}{0.05916 \text{ V}} = \frac{3\cdot(1.62 \text{ V})}{0.05916 \text{ V}} = 82.2; \qquad \therefore K = 4.8 \times 10^{35}$$

(d) Although the thermite reaction occurs between solid aluminum metal and solid iron(III) oxide, $2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(l)$, the redox chemistry is the same as that analyzed in parts (a)–(c). We can estimate the standard free energy change by assuming it is the same as we calculated in part (b), taking into account that the thermite reaction involves two moles of aluminum metal and our calculation was for only one mole in the cell reaction. Therefore, the free energy of the thermite reaction would be approximately –940 kJ for every two moles of molten iron metal produced or –470 kJ for one mole of iron. Free energy is related to the thermal energy of the reaction by $\Delta G = \Delta H - T\Delta S$. The reaction of interest involves three moles of solids as reactants and produces a mole of solid and two moles of liquid products. Thus, the entropy

change is probably positive but not very large, so the $T\Delta S$ term is relatively small. To a rough approximation, it's likely that $\Delta G \approx \Delta H$. This means that there would be somewhat more than five times as much energy released by the reaction as are needed to melt the iron (about 81 kJ·mol^{-1}). It certainly makes sense that molten iron is produced and the reaction is sometimes used to make small amounts of molten iron to weld iron (steel) pieces together.

Problem 10.51.
(a) To find the cell potential (at 298 K) for Mg(s) | Mg$^{2+}(aq,$ 0.60 M$)$ || Cu$^{2+}(aq,$ 0.60 M$)$ | Cu(s), use the standard reduction potentials from Appendix B to find $E°$ and then the Nernst equation to get E for the conditions here:

$$E° = E°(Cu^{2+}, Cu) - E°(Mg^{2+}, Mg) = 0.377 \text{ V} - (-2.38 \text{ V}) = 2.76 \text{ V}$$

$$E = 2.76 \text{ V} - \frac{(0.05916 \text{ V})}{2}\log\left(\frac{(Mg^{2+}(aq))}{(Cu^{2+}(aq))}\right) = 2.76 \text{ V} - (0.02958 \text{ V})\cdot\log\left(\frac{0.60}{0.60}\right)$$

$$E = 2.76 \text{ V}$$

(b) At equilibrium, the cell potential (and the free energy change for the change from reactants to products at their equilibrium concentrations) is zero. This is the criterion for equilibrium in an electrochemical cell. The state of equilibrium will be reached, only if enough magnesium metal is present for the reaction to go as far as necessary to reach equilibrium with some left over. Although the "concentration" of the solids does not appear in the reaction quotient, the reaction depends upon their presence.

(c) The equilibrium criterion is $E = 0$, so substitute into the Nernst equation and solve for $(Mg^{2+}(aq))/(Cu^{2+}(aq)) = [Mg^{2+}(aq)]/[Cu^{2+}(aq)]$:

$$0 = 2.76 \text{ V} - \frac{(0.05916 \text{ V})}{2}\log\left(\frac{(Mg^{2+}(aq))}{(Cu^{2+}(aq))}\right)_{eq}$$

$$\log\left(\frac{(Mg^{2+}(aq))}{(Cu^{2+}(aq))}\right)_{eq} = 93.3 \qquad \therefore \left(\frac{(Mg^{2+}(aq))}{(Cu^{2+}(aq))}\right)_{eq} = 2 \times 10^{93}$$

At equilibrium "all" the copper(II) ions have been reduced to copper metal.

Problem 10.52.
(a) The line notation and net reaction for a zinc-chlorine cell are:

Zn(s) | Zn$^{2+}(aq,$ sat'd ZnCl$_2$), Cl$^-(aq,$ sat'd ZnCl$_2$) | Cl$_2(g, P)$ | Pt(s),

Zn(s) + Cl$_2(g, P) \Leftrightarrow$ Zn$^{2+}(aq,$ sat'd ZnCl$_2$) + 2Cl$^-(aq,$ sat'd ZnCl$_2$)
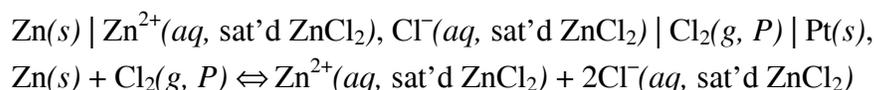
Use the standard reduction potentials from Appendix B to determine the standard cell potential (at 298 K):

$$E° = E°(Cl_2, Cl^-) - E°(Zn^{2+}, Zn) = 1.359 \text{ V} - (-0.763 \text{ V}) = 2.122 \text{ V}$$

(b) The reaction quotient for this cell reaction is:

$$Q = \frac{(Zn^{2+}(aq, \text{ sat'd } ZnCl_2))(Cl^-(aq, \text{ sat'd } ZnCl_2))^2}{(Cl_2(g, P))}$$

(c) Use the Nernst equation with $E°$ from part (a) and to get the cell potential under the solution conditions specified in the problem statement. The stoichiometry of zinc chloride dissolution gives solution concentrations of $[Zn^{2+}(aq, \text{ sat'd } ZnCl_2)] = 3$ M and $[Cl^-(aq, \text{ sat'd } ZnCl_2)] = 6$ M, and the chlorine gas pressure is 1.0 bar.

$$E = 2.122 \text{ V} - \frac{(0.05916 \text{ V})}{2} \log \frac{(3)(6)^2}{(1)} = 2 \text{ V}$$

The uncertainty in the concentrations and nonideality of these concentrated solutions suggest that one significant figure in this result is about the best we can justify.

(d) The work available per mole of cell reaction (equivalent to one mole of $Zn(s)$ reacting) is:

$$w_{elec} \text{ [J·mol}^{-1}\text{]} = nFE = 2 \cdot (9.6485 \times 10^4 \text{ C·mol}^{-1})(2 \text{ V}) = 4 \times 10^2 \text{ kJ·mol}^{-1}$$

To get 75 kJ of work, we need 0.2 mol $[= (75 \text{ kJ})/(4 \times 10^2 \text{ kJ·mol}^{-1})]$ of $Zn(s)$ to react. The reaction requires one mole of chlorine gas for each mole of zinc metal, so 0.2 mol of $Cl_2(g)$ is also required.

(e) The concentrations of the ions are unchanged after 75 kJ of work is produced by this cell. The reaction mixture is saturated with $ZnCl_2(s)$. The $Zn^{2+}(aq)$ and $Cl^-(aq)$ produced (in the stoichiometric 1:2 ratio) by the reaction simply react to form more $ZnCl_2(s)$, since the solution is saturated and already contains the maximum possible concentrations of these ions.

Problem 10.53.
(a) In the cell represented as $Zn(s) | ZnO(s) | KOH(aq, 40\%) | Ag_2O(s) | Ag(s)$, the cathodic reaction is reduction of silver(I) in solid silver(I) oxide to silver metal:

$$Ag_2O(s) + H_2O(aq) + 2e^- \Leftrightarrow 2Ag(s) + 2OH^-(aq)$$
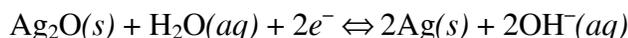
(b) The anodic half reaction (written as an oxidation) is the oxidation of zinc metal to Zn(II) in solid zinc(II) oxide:

$$Zn(s) + 2OH^-(aq) \Leftrightarrow ZnO(s) + H_2O(aq) + 2e^-$$

(c) Combining the half reactions in parts (a) and (b) gives the net cell reaction:

$$Zn(s) + Ag_2O(s) \Leftrightarrow ZnO(s) + 2Ag(s)$$

(d) The KOH electrolyte solution is not represented in the net cell reaction in part (c) but is required to provide the mobile charge carriers, $OH^-(aq)$ anions, that complete the electrical circuit in the cell. This is like the aluminum-air cell in Worked Example 10.29.

Problem 10.54.
The reduction potential for methylene blue reduction, $MB^+(aq) + H^+(aq) + 2e^- \Leftrightarrow MBH(aq)$, should vary as the pH of the half reaction is varied. This table gives reduction potential data for methylene blue at different pH's.

pH	0	1	2	3	4	5	6	7	8	9	10
E, V	0.53	0.47	0.38	0.29	0.21	013	0.07	0.01	–0.03	–0.07	–0.11

Hydronium ion is a reactant in the methylene blue, MB, reduction reaction (10.93). As the pH at which the half reaction occurs is increased (hydronium ion concentration decreased), a reactant concentration is decreased. We would predict that the system would respond to reduce the effect

of the change by not going forward as forcefully and therefore that the reduction potential would decrease with increasing pH. The table shows that this is what occurs.

Problem 10.55.
[NOTE: To be consistent with our nomenclature throughout the rest of the text, the formula for hypochlorous acid should be written HOCl, to make clear that the H is bonded to the O; this is an oxyacid.]

(a) Hypochlorous acid, HOCl, is a strong oxidizing agent:

$$2HOCl(aq) + 2H^+(aq) + 2e^- \Leftrightarrow Cl_2(g) + 2H_2O(l) \quad E^\circ = 1.630 \text{ V}$$
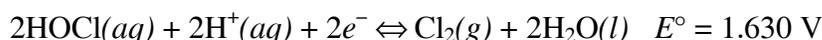
Two other components of a bleach solution are oxidizable by hypochlorous acid, chloride ion and water:

$$Cl_2(g) + 2e^- \Leftrightarrow 2Cl^-(aq) \qquad\qquad\qquad E^\circ = 1.359 \text{ V}$$

$$O_2(g) + 4H^+(aq) + 4e^- \Leftrightarrow 6H_2O(l) \qquad\qquad E^\circ = 1.229$$

Oxidation of water would produce oxygen gas, which is not "hazardous." Oxidation of chloride ion would produce chlorine gas, which is toxic and, hence, "hazardous." Reduction of hypochlorous acid also produces chlorine. It seems likely that the reaction to "produce a hazardous gas" referred to on the warning label is the one with chloride:

$$HOCl(aq) + H^+(aq) + Cl^-(aq) \Leftrightarrow Cl_2(g) + H_2O(l) \quad E^\circ = 0.271 \text{ V}$$
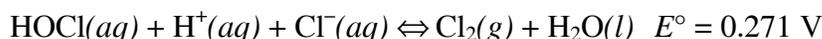
(Although both oxidation reactions are favored, the oxidation of chloride is fast and the oxidation of water is slow, which is why you can make solutions of hypochlorite.) The standard free energy change for one mole of this reaction is:

$$\Delta G^\circ = -nFE^\circ = -(1)(96485 \text{ C·mol}^{-1})(0.271 \text{ V}) = -26.1 \text{ kJ}$$

The value of n is one, because only one electron is transferred in the net reaction (from Cl^- with an oxidation number of -1 to the Cl with an oxidation number $+1$ in HClO, to give them both an oxidation number of zero in the Cl_2 product).

(b) The equilibrium constant expression and equilibrium constant for the net redox reaction are:

$$K = \frac{(Cl_2(g))(H_2O(l))}{(HOCl(aq))(H^+(aq))(Cl^-(aq))} = \frac{(Cl_2(g))}{(HOCl(aq))(H^+(aq))(Cl^-(aq))}$$

$$\ln K = \frac{nE^\circ}{0.05916 \text{ V}} = \frac{1 \cdot (0.271 \text{ V})}{0.05916 \text{ V}} = 4.58; \quad \therefore K = 98$$

(c) Apply the Nernst equation (at 298 K) to the net redox reaction with $(H^+(aq)) = 10^{-14}$ (pH 14) and all other species still at their standard concentrations:

$$E(\text{pH } 14) = E^\circ - \frac{(0.05916 \text{ V})}{n} \log \frac{(Cl_2(g))}{(HOCl(aq))(H^+(aq))(Cl^-(aq))}$$

$$E(\text{pH } 14) = 0.271 \text{ V} - \frac{(0.05916 \text{ V})}{1} \log \frac{(1)}{(1)(10^{-14})(1)} = -0.557 \text{ V}$$

This potential, $E(\text{pH } 14) = -0.557$ V, is the standard cell potential for the reaction in basic solution, where $[OH^-(aq)] = 1.00$ is the standard condition. In basic solution (at pH 14) the reaction is quite unfavorable, as written. Under these conditions, chlorine dissolved in the basic solution reacts with itself to form hypochlorite anion, $ClO^-(aq)$, and chloride ion (which is pretty

much how bleach is made and why the solution contains the chloride ion necessary for the reaction in part (a) – under acidic conditions).

(d) In basic solution, the concentration of hydronium ion is low. Hydronium ion is a reactant in the net reaction, so lowering its concentration, lowers the driving force of the reaction, as we saw in part (c). We can use the Nernst equation again to get the cell potential when the hydronium ion concentration is 10^{-8} M (pH 8) as in a bottle of bleach, and all other species are still at approximately unit activity.

$$E(\text{pH } 8) = E° - \frac{(0.05916 \text{ V})}{n} \log \frac{(\text{Cl}_2(g))}{(\text{HOCl}(aq))(\text{H}^+(aq))(\text{Cl}^-(aq))}$$

$$E(\text{pH } 8) = 0.271 \text{ V} - \frac{(0.05916 \text{ V})}{1} \log \frac{(1)}{(1)(10^{-8})(1)} = -0.202 \text{ V}$$

Thus, making the solution basic makes the reaction unfavorable. Furthermore, in basic solution, the HOCl reacts with hydroxide ion to lose its proton, so its concentration also gets quite small, which decreases the cell potential even more. We could use the K_a for HClO to find out how much lower, but there is no need to do that for this problem.

Problem 10.56.
(a) For this cell, Pb*(s)* | Pb^{2+}*(aq, 1.0 M)* ‖ H$^+$*(aq, 1.0 M)* | H$_2$*(g, 1 bar)* | Pt*(s)*, the standard cell potential is:

$$E° = E°(\text{H}^+, \text{H}_2) - E°(\text{Pb}^{2+}, \text{Pb}) = 0 \text{ V} - (-0.13 \text{ V}) = 0.13 \text{ V}$$

(b) Use K_{sp} and the solubility product expression for PbSO$_4$*(s)* to find the concentration of lead(II) ion in equilibrium with [SO$_4$*(aq)*] = 0.50 M:

$$K_{sp} = 6.3 \times 10^{-7} = (\text{Pb}^{2+}(aq))(\text{SO}_4(aq)) = (\text{Pb}^{2+}(aq))(0.50)$$
$$(\text{Pb}^{2+}(aq)) = 1.3 \times 10^{-6}$$

(c) Substitute the value for (Pb^{2+}*(aq)*) from part (b) in the Nernst equation for the lead ion-lead metal half cell reduction potential to find the reduction potential after enough sulfate ion has been added to the lead ion solution in the cell in part (a) to make [SO$_4$*(aq)*] = 0.50 M:

$$E(\text{Pb}^{2+}, \text{Pb}) = E°(\text{Pb}^{2+}, \text{Pb}) - \frac{(0.05916 \text{ V})}{2} \log \frac{(\text{Pb}(s))}{(\text{Pb}^{2+}(aq))}$$

$$E(\text{Pb}^{2+}, \text{Pb}) = -0.13 \text{ V} - \frac{(0.05916 \text{ V})}{2} \log \frac{1}{1.3 \times 10^{-6}} = -0.30 \text{ V}$$

(d) Since the cell in part (a) is set up with the SHE as the cathode, the cell potential is the negative of the reduction potential for the lead ion-lead metal half cell, that is, $E = 0.30$ V in this case. Note that, since oxidation occurs in the lead ion-lead metal half cell, the potential of the cell increases, larger driving force, as the concentration of the product, lead ion, decreases. This is in accord with Le Chatelier's principle.

Problem 10.57.
Use the Nernst equation to determine the standard cell potential from the measured cell potential and the conditions in the Clark cell:

Zn*(s)* | Zn^{2+}*(aq, 0.100 M)*, SO$_4$$^{2-}$*(aq)* | Hg$_2SO_4$*(s)* | Hg*(l)*

$$Zn(s) + Hg_2SO_4(s) \Leftrightarrow Zn^{2+}(aq) + 2Hg(l) + SO_4^{2-}(aq)$$

$$1.435 \text{ V} = E° - \frac{(0.05916 \text{ V})}{2} \log\left(\frac{(Zn^{2+}(aq))(Hg(l))^2(SO_4^{2-}(aq))}{(Zn(s))(Hg_2SO_4(s))} \right)$$

$$E° = (1.435 \text{ V}) + \frac{(0.05916 \text{ V})}{2} \log\left(\frac{(0.100)(1)^2(0.100)}{(1)(1)} \right) = 1.376 \text{ V}$$

The standard cell potential is the difference between the desired standard reduction potential, $E°(Hg_2SO_4, Hg)$, and the standard zinc reduction potential, $E°(Zn^{2+}, Zn)$:

$$E° = 1.376 \text{ V} = E°(Hg_2SO_4, Hg) - E°(Zn^{2+}, Zn)$$

$$E°(Hg_2SO_4, Hg) = (1.376 \text{ V}) + (-0.763 \text{ V}) = 0.613 \text{ V}$$

Problem 10.58.

(a) The NAD^+ reaction with ethanol and its standard cell potential (pH 7) are:

$$NAD^+(aq) + CH_3CH_2OH(aq) \Leftrightarrow NADH(aq) + CH_3CHO(aq) + H^+(aq) \quad E°´ = -0.12 \text{ V}$$

We can get the standard free energy change at pH 7, $\Delta G°´$, from the standard cell potential at pH 7:

$$\Delta G°´ = -nFE°´ = -(2)(96485 \text{ C·mol}^{-1})(-0.12 \text{ V}) = 23 \text{ kJ·mol}^{-1}$$

The positive free energy and negative cell potential both show that the reaction, in the direction written, is not favored under standard conditions at pH 7.

(b) The reaction quotient for this reaction (at pH 7 which is accounted for already) is:

$$Q´ = \frac{(NADH)(CH_3CHO)}{(NAD^+)(CH_3CH_2OH)}$$

The equilibrium constant for the reaction is less than one; $K´_{eq} < 1$, because $\Delta G°´ > 0$. The addition of a reagent that reacts with the aldehyde, CH_3CHO, lowers its concentration, so $Q´$, after addition of this reagent, is smaller than $K´_{eq}$ in this solution with added reagent. Both $\ln K´_{eq}$ and $\ln Q´$ are negative (< 0), but $\ln Q´$ is smaller (more negative). The equation for the free energy is:

$$\Delta G´ = \Delta G°´ + RT\ln Q´$$

The negative logarithmic term will make $\Delta G´$ smaller than $\Delta G°´$ and could even make $\Delta G´$ negative. Note that it is not necessary that $\Delta G´$ become negative to make the analysis for ethanol work. As the aldehyde reacts with the added reagent, more reaction of ethanol with NAD^+ is required to try to restore equilibrium conditions, even if they are not very favorable for product formation. The newly produced aldehyde can react with more reagent and more reaction will have to occur to replace it. As this process continues, the NADH product is building up. If an excess of the reagent that reacts with aldehyde is present, the reaction above will be forced to continue producing aldehyde until the ethanol is essentially used up and an equivalent amount of NADH produced to measure spectrophotometrically.

(c) H_3O^+ is a product of the reaction, so raising the pH [decreasing the $(H_3O^+(aq)]$ will have the affect of decreasing $\Delta G´$ and possibly even making it negative. The problem is that the enzyme, alcohol dehydrogenase, might not be active at a higher pH; it could be denatured.

Problem 10.59.
(a) The electrode reactions and net cell reaction for zinc and platinum electrodes implanted in our oxygenated and ionic body fluids are:

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

cathodic $O_2(aq) + 2H^+(aq) + 2e^- \rightarrow H_2O(aq)$

net reaction: $Zn(s) + O_2(aq) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2O(aq)$

(b) The standard cell potential for this net reaction under biological conditions (pH 7) is:

$E^{\circ\prime} = E^{\circ\prime}(O_2, H_2O) - E^{\circ}(Zn^{2+}, Zn) = 0.816 \text{ V} - (-0.763 \text{ V}) = 1.579 \text{ V}$

(c) The amount of charge (moles of electrons) available from 4.5 g of zinc metal is equal to twice the number of moles of zinc metal, since each atom oxidized produces two electrons:

$$\text{mol } e^- = 2\left(\frac{4.5 \text{ g}}{65.37 \text{ g} \cdot \text{mol}^{-1}} \right) = 0.138 \text{ mol}$$

Convert moles of electrons to coulombs, and calculate the amount of time current would flow at 35×10^{-6} A to equal this many coulombs:

number coulombs $= (0.138 \text{ mol})(9.6485 \times 10^4 \text{ C} \cdot \text{mol}^{-1}) = 1.33 \times 10^4 \text{ C}$

$1.33 \times 10^4 \text{ C} = (35 \times 10^{-6} \text{ A}) \cdot t \qquad \therefore t = 3.8 \times 10^8 \text{ s} = 4.4 \times 10^3 \text{ day} = 12 \text{ yr}$

Twelve years is a reasonable length of time for an implant to last before maintenance (or replacement) is required.

Problem 10.60.
(a) We can use standard reduction potentials and standard free energies of formation to find the standard free energy changes for each of these three reactions and their sum:

(i) $NO_3^-(aq) + 4H^+(aq) + 3e^- \Leftrightarrow NO(g) + 2H_2O(l)$

(ii) $NO(g) + \frac{1}{2}O_2(g) \Leftrightarrow NO_2(g)$

(iii) $H_2O(l) \Leftrightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$

(iv) $NO_3^-(aq) + 2H^+(aq) + e^- \Leftrightarrow NO_2(g) + H_2O(l)$

$\Delta G^{\circ}_i = -nFE^{\circ}_i = - 3 \cdot (9.6485 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(0.955 \text{ V}) = -276 \text{ kJ} \cdot \text{mol}^{-1}$

$\Delta G^{\circ}_{ii} = \Delta G^{\circ}_f(NO_2) - \Delta G^{\circ}_f(NO) - \frac{1}{2}\Delta G^{\circ}_f(O_2)$

$\Delta G^{\circ}_{ii} = (5 \quad \text{kJ} \cdot \text{mol}^{-1}) - (86.55 \text{ kJ} \cdot \text{mol}^{-1}) - \frac{1}{2}(0 \text{ kJ} \cdot \text{mol}^{-1}) = -35 \text{ kJ} \cdot \text{mol}^{-1}$

$\Delta G^{\circ}_{iii} = -nFE^{\circ}_{iii} = - 2 \cdot (9.6485 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(-1.229 \text{ V}) = 237 \text{ kJ} \cdot \text{mol}^{-1}$

Note that the potential used for half reaction (iii) is the negative of the standard reduction potential, because the reaction is written in reverse as an oxidation. The sum of these standard free energy changes is the standard free energy change for half reaction (iv):

$\Delta G^{\circ}_{iv} = (-276 \text{ kJ} \cdot \text{mol}^{-1}) + (-35 \text{ kJ} \cdot \text{mol}^{-1}) + (237 \text{ kJ} \cdot \text{mol}^{-1}) = -74 \text{ kJ} \cdot \text{mol}^{-1}$

(b) Get the standard cell potential for half reaction (iv) from its standard free energy change in part (a):

$$E^\circ_{iv} = -\frac{\Delta G^o_{iv}}{nF} = -\frac{(-74 \times 10^3 \text{ J} \cdot \text{mol}^{-1})}{1 \cdot (9.6485 \times 10^4 \text{ C} \cdot \text{mol}^{-1})} = 0.77 \text{ V}$$

Problem 10.61.
(a) The reaction of interest must be oxidation of chloride anion, by the manganese(IV) in manganese(IV) dioxide, $MnO_2(s)$, to produce the desired chlorine gas. In this process, the manganese(IV) is reduced, probably to manganese(II), $Mn^{2+}(aq)$, which is the lowest oxidation state of manganese ion in the solution. The net redox reaction is:

$$2Cl^-(aq) + MnO_2(s) + 4H^+(aq) \rightarrow Cl_2(g) + Mn^{2+}(aq) + 2H_2O(aq)$$

(b) The standard cell potential for this reaction is:

$$E^\circ = E^\circ(MnO_2, Mn^{2+}) - E^\circ(Cl_2, Cl^-) = 1.230 \text{ V} - (1.359 \text{ V}) = -0.129 \text{ V}$$

The reaction has a negative standard cell potential, which indicates that it is not spontaneous under standard conditions.

(c) Use the Nernst equation to find the reduction potentials if $[H^+(aq)] = [Cl^-(aq)] = 6$ M, and all other concentrations are still standard concentrations:

$$E(Cl_2, Cl^-) = E^\circ(Cl_2, Cl^-) - \frac{(0.05916 \text{ V})}{2} \log \frac{(Cl^-(aq))^2}{(Cl_2(g))}$$

$$E(Cl_2, Cl^-) = 1.359 \text{ V} - \frac{(0.05916 \text{ V})}{2} \log \frac{6^2}{1} = 1.313 \text{ V}$$

$$E(MnO_2, Mn^{2+}) = E^\circ(MnO_2, Mn^{2+}) - \frac{(0.05916 \text{ V})}{2} \log \frac{(Mn^{2+}(aq))(H_2O(aq))}{(MnO_2(s))(H^+(aq))^4}$$

$$E(MnO_2, Mn^{2+}) = 1.230 \text{ V} - \frac{(0.05916 \text{ V})}{2} \log \frac{1 \cdot 1}{1 \cdot 6^4} = 1.322 \text{ V}$$

The cell potential for the reaction in 6 M HCl is:

$$E = E(MnO_2, Mn^{2+}) - E(Cl_2, Cl^-) = 1.322 \text{ V} - (1.313 \text{ V}) = 0.009 \text{ V}$$

The reaction is spontaneous (but without a large driving force) when 6 M HCl is used as the reactant. Higher concentrations of the acid would provide a more positive cell potential and more driving force. Once again, we need to be aware that these calculations based on ideal behavior for solutions at high concentrations are liable to be inaccurate and provide only directional information. In particular, the activity of water in this solution is probably less than one, which will further increase $E(MnO_2, Mn^{2+})$ and the cell potential.

Problem 10.62.
(a) The reaction of vanillin with Benedict's reagent transforms the aldehyde carbon into a carboxylic acid carbon:

In this basic solution the carboxylic acid group transfers its proton to hydroxide ion, so it is shown as a carboxylate anion in this reaction equation. (If the solution is basic enough, at least

some of the protons from the phenolic –OH group will also be transferred to hydroxide, but this is not shown here.)

(b) Although vanillin does give a positive Benedict's test and there is almost surely vanillin in the bottle of vanilla extract, you can't be positive about this, just from the Benedict's test. The reason is that the mixture contains corn syrup, last ingredient on the list. Corn syrup is derived from corn starch and contains glucose and other reducing sugars, as well as longer chain molecules that make the liquid "syrupy." The positive Benedict's test can be caused by these sugars as well as by the vanillin.

Problem 10.63.
(a) The reactions involved in the analysis of bleach are:

(1) $HClO(aq) + 3I^-(aq) + H^+(aq) \Leftrightarrow Cl^-(aq) + I_3^-(aq) + H_2O(l)$

(2) $I_3^-(aq) + 2S_2O_3^{2-}(aq) \Leftrightarrow 3I^-(aq) + S_4O_6^{2-}(aq)$

The first reaction is the reduction of chlorine in hypochlorous acid from an oxidation number of +1 to chloride ion with and oxidation number of –1. Appendix B does not give a reduction potential for this reaction, so we have to calculate it by combining two half reactions that give the overall half reaction of interest:

(3) $2HClO(aq) + 2H^+(aq) + 2e^- \Leftrightarrow Cl_2(g) + 2H_2O(l)$ $\qquad E°_3 = 1.630$ V

(4) $Cl_2(g) + 2e^- \Leftrightarrow 2Cl^-(aq)$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad E°_4 = 1.359$ V

(5) $2HClO(aq) + 2H^+(aq) + 4e^- \Leftrightarrow 2Cl^-(aq) + 4H_2O(l)$ $\quad E°_5 = ?$

The approach we use to get the unknown reduction potential for half reaction (5) is to calculate it using the free energies of the reactions:

$$-n_5FE°_5 = \Delta G°_5 = \Delta G°_3 + \Delta G°_4 = -n_3FE°_3 - n_4FE°_4$$

Half reaction (5), written as the sum of two other half reactions, involves four electrons, so its potential is:

$$E°_5 = \frac{-\Delta G_5^o}{n_5F} = \frac{n_3FE_3^o + n_4FE_4^o}{n_5F} = \frac{n_3E_3^o + n_4E_4^o}{n_5} = \frac{2(1.630 \text{ V}) + 2(1.359 \text{ V})}{4}$$

$E°_5 = 1.495$ V

NOTE: This last equation is general. You can determine the reduction potential of any half reaction that is the sum of two or more other half reactions by using a weighted combination of their reduction potentials. The n in the denominator is the sum of the n values for the half reactions that are combined.

The reaction sequence in the problem involves three half reactions [with reaction (5) written in its conventional simplest form with the smallest possible set of integer stoichiometric coefficients]:

(5) $HClO(aq) + H_3O^+(aq) + 2e^- \Leftrightarrow Cl^-(aq) + 2H_2O(l)$ $\qquad E°_5 = 1.495$ V

(6) $I_3^-(aq) + 2e^- \Leftrightarrow 3I^-(aq)$ $\qquad\qquad\qquad\qquad\qquad\qquad E°_6 = 0.5355$ V

(7) $S_4O_6^{2-}(aq) + 2e^- \Leftrightarrow 2S_2O_3^{2-}(aq)$ $\qquad\qquad\qquad\qquad E°_7 = 0.09$ V

Since the iodine (triiodide) reduction potential is intermediate between the other two, iodide, I^- *(aq)*, can be oxidized by hypochlorous acid and, in turn, the iodine (triiodide) product can

oxidize thiosulfate. Thus, reaction (6) is the coupling reaction in this sequence. The cell potentials for reactions (1) and (2) are:

$$E°_1 = E°_5 - E°_6 = (1.495 \text{ V}) - (0.5355 \text{ V}) = 0.959 \text{ V}$$
$$E°_2 = E°_6 - E°_7 = (0.5355 \text{ V}) - (0.09 \text{ V}) = 0.45 \text{ V}$$

Just as we reasoned, both are favored.

(b) The iodine (triiodide)-iodide half reaction couples the other two. The necessary property for coupling is that the reduction potential for the coupling reaction be intermediate between the other two. This is the basis for the reasoning in part (a). It also has to be the case that the reactions are quantitative and go essentially to "completion." The equilibria have to lie far toward the products. The cell potentials, in this case, give equilibrium constants of about 10^{32} and 10^{15}.

(c) The net reaction is the sum of reactions (1) and (2) and, as you see, the reactant and product in the coupling reaction do not appear in the net reaction:

(1) $HClO(aq) + 3I^-(aq) + H^+(aq) \Leftrightarrow Cl^-(aq) + I_3^-(aq) + H_2O(l)$
(2) $I_3^-(aq) + 2S_2O_3^{2-}(aq) \Leftrightarrow 3I^-(aq) + S_4O_6^{2-}(aq)$
_____

(8) $HClO(aq) + 2S_2O_3^{2-}(aq) + H^+(aq) \Leftrightarrow Cl^-(aq) + S_4O_6^{2-}(aq) + H_2O(l)$

(d) Net reaction (8) shows that the equivalent of one mole of hypochlorous acid reacts with two moles of thiosulfate ion. We can use this equivalence to work backward from the number of moles of thiosulfate ion reacted in the analysis to the number of moles of hypochlorous acid in the sample:

$$\text{mol } S_2O_3^{2-} \text{ reacted} = (32.56 \times 10^{-3} \text{ L})(0.200 \text{ M}) = 6.51 \times 10^{-3} \text{ mol } S_2O_3^{2-}$$

$$\text{mol HClO reacted} = (6.51 \times 10^{-3} \text{ mol } S_2O_3^{2-})\left(\frac{1 \text{ mol HClO}}{2 \text{ mol } S_2O_3^{2-}}\right) = 3.26 \times 10^{-3} \text{ mol}$$

The concentration of hypochlorite in the bleach is the same as the concentration of hypochlorous acid found in the analysis reaction:

$$\text{conc'n of ClO}^- = \text{conc'n of HClO} = \frac{3.26 \times 10^{-3} \text{ mol}}{5.00 \times 10^{-3} \text{ L}} = 0.652 \text{ M}$$

Problem 10.64.
(a) Two reactions that are important in considering the silver mirror or Tollens' test for aldehydes are:

(1) $2Ag^+(aq) + RCHO(aq) + 3OH^-(aq) \Leftrightarrow 2Ag(s) + RCOO^-(aq) + 2H_2O(l)$
(2) $2Ag^+(aq) + 2OH^-(aq) \Leftrightarrow Ag_2O(s) + H_2O(l) \quad K \approx 10^{16}$

Equation (2) represents the precipitation reaction for $Ag_2O(s)$. The solubility product for the dissolution of $Ag_2O(s)$, the reverse of reaction equation (2), is:

$$K_{sp} = (Ag^+(aq))^2(OH^-(aq))^2 = 10^{-16}$$

Recall that, when a reaction is reversed, the equilibrium constant for the reversed reaction is the inverse of that for the forward reaction. In the Tollen's solution with pH = 12 (pOH = 2), the $(OH^-(aq)) = 10^{-2}$. Substituting for $(OH^-(aq))$ in the solubility product equation and solving gives $(Ag^+(aq)) = 10^{-6}$. An $Ag^+(aq)$ concentration of 10^{-6} M is the highest concentration of silver ion that can be present in the solution without precipitating as the oxide.

(b) Use the Nernst equation to calculate $E(Ag^+,Ag)$ from $E°(Ag^+,Ag) = 0.799$ V and, from part (a), $(Ag^+(aq)) = 10^{-6}$:

$$E(Ag^+,Ag) = E°(Ag^+,Ag) - \left(\frac{0.05916 \text{ V}}{1}\right)\log\left(\frac{1}{(Ag^+(aq))}\right)$$

$$E(Ag^+,Ag) = (0.799 \text{ V}) - \left(\frac{0.05916 \text{ V}}{1}\right)\log\left(\frac{1}{10^{-6}}\right) = (0.799 \text{ V}) - (0.355 \text{ V}) = 0.444 \text{ V}$$

(The uncertainties in the solubility product, the hydroxide ion concentration, and, hence, the silver ion concentration certainly do not justify three significant figures in this cell potential, but the conclusion in part (c) is unaffected, even if this value is only good to one significant figure.)

(c) To get the minimum value for the cell potential for reaction (1), when RCHO is glucose, we combine $E(Ag^+,Ag)$ with $E_{\text{gluconate,glucose}}$. Recall equation (10.85):

$$RCOO^-(aq) + 2H_2O(l) + 2e^- \Leftrightarrow RCHO(aq) + 3OH^-(aq) \quad E^{o'}_{\text{gluconate,glucose}} = -0.44 \text{ V}$$

The reduction potential here is for pH = 7. As we argued in the text, $E_{\text{gluconate,glucose}}$ will be more negative at higher pH where the concentration of $OH^-(aq)$ is higher and drives the reaction even further toward the left, that is, makes the oxidation of glucose even more favorable. Thus, the minimum value for the oxidation of glucose by silver ion in Tollens reagent is:

$$E = E(Ag^+,Ag) - E_{\text{gluconate,glucose}} = (0.444 \text{ V}) - (-0.44\text{V}) = 0.88 \text{ V}$$

For reaction (1), two moles of electrons are transferred from glucose to silver for every mole of glucose that reacts, so the minimum free energy change, $-nFE$, for the reaction is:

$$\Delta G = -2 \cdot (9.6485 \times 10^4 \text{ C} \cdot \text{mol}^{-1}) \cdot (0.88 \text{ V}) = -1.7 \times 10^2 \text{ kJ} \cdot \text{mol}^{-1}$$

Problem 10.65.
The standard reduction potentials, $E°'$, for the cytochromes in the electron transport pathway in mitochondria are given alphabetically in this list.

cytochrome	$E°'$, V
a	0.29
a_3	0.55
b	0.077
c	0.254
c_1	0.22

The order of the cytochromes in the electron transport pathway, from the one that oxidizes ubiquinol to the one that is oxidized by oxygen, is the order from weakest to strongest oxidizing agent, since the weakest one must oxidize ubiquinol and then be reoxidized by the next and so on until the last one is oxidized by oxygen. The order of increasing oxidizing power (of the oxidized cytochrome) is: $b < c_1 < c < a < a_3$.

Problem 10.66.
(a) Appendix B gives the half reactions and reduction potentials (at pH 7, physiological conditions) for the two half reactions that make up reaction (i), the reduction of 3-phosphoglycerate, 3PG (a carboxylate, $RCOO^-$), to glyceraldehyde-3-phosphate, G3P (an aldehyde, RCHO), by NADPH:

$$RCOO^- + 3H^+ + 2e^- \Leftrightarrow RCHO + H_2O \qquad\qquad E^{\circ\prime} = -0.55 \text{ V}$$
$$-\{NADP^+ + H^+ + 2e^- \Leftrightarrow NADPH\} \qquad\qquad -E^{\circ\prime} = 0.32 \text{ V}$$
$$RCOO^- + 2H^+ + NADPH \Leftrightarrow RCHO + NADP^+ + H_2O \qquad E^{\circ\prime} = -0.23 \text{ V}$$

The negative cell potential means that the reaction is not favored, as written. The standard free energy change, $\Delta G^{\circ\prime} = -(2)(96485 \text{ C·mol}^{-1})(-0.23 \text{ V}) = 44 \text{ kJ·mol}^{-1}$ (of reaction), is positive.

(b) From Appendix B, the two half reactions that make up reaction (iii), reduction of 1,3-diphosphoglycerate, 1,3-DPG ($RCOO\text{-}PO_3^{2-}$) by NADPH, are:

$$RCOO\text{-}PO_3^{2-} + 2H_3O^+ + 2e^- \Leftrightarrow RCHO + HOPO_3^{2-} + 2H_2O \qquad\qquad E^{\circ\prime} = -0.29 \text{ V}$$
$$-\{NADP^+ + H_3O^+ + 2e^- \Leftrightarrow NADPH + H_2O\} \qquad\qquad -E^{\circ\prime} = 0.32 \text{ V}$$
$$RCOO\text{-}PO_3^{2-} + NADPH + H_3O^+ \Leftrightarrow RCHO + NADP^+ + HOPO_3^{2-} + H_2O \quad E^{\circ\prime} = 0.03 \text{ V}$$

The standard free energy change, $\Delta G^{\circ\prime} = -(2)(96485 \text{ C·mol}^{-1})(0.03 \text{ V}) = -6 \text{ kJ·mol}^{-1}$ (of reaction), is small, but negative.

(c) The net reaction for the pathway in part (b) of the problem is the sum of the two reactions:

$$(2) \quad RCOO^- + ATP^{4-} \Leftrightarrow RCOO\text{-}PO_3^{2-} + ADP^{3-}$$
$$(3) \quad RCOO\text{-}PO_3^{2-} + NADPH + H^+ \Leftrightarrow RCHO + NADP^+ + HOPO_3^{2-}$$
$$RCOO^- + ATP^{4-} + NADPH + H^+ \Leftrightarrow RCHO + ADP^{3-} + NADP^+ + HOPO_3^{2-}$$

The standard free energy change for the net reaction is the sum of the standard free energy changes for reactions (2)—given as 19 kJ·mol^{-1} in the problem statement—and (3):

$$\Delta G^{\circ\prime} = 19 \text{ kJ·mol}^{-1} + (-6 \text{ kJ·mol}^{-1}) \approx 13 \text{ kJ·mol}^{-1}$$

The free energy is somewhat positive, so the net reaction is not favored in the direction written.

(d) We get the [G3P]/[3PG] ratio at equilibrium for each case by using $\Delta G^{\circ\prime}$ to get the equilibrium constant and substituting the cellular conditions of the reaction, [ATP]/[ADP] = 10; [NADPH]/[NADP$^+$] = 10; and [HOPO$_3^{2-}$] = 10^{-2} M, into the equilibrium constant expression.

For reaction (i):

$$\ln K_i = -\frac{\Delta G^{\circ\prime}}{RT} = -18 = \ln\left(\frac{[G3P][NADP^+]}{[3PG][NADPH]}\right)_{eq}$$

$$1.5 \times 10^{-8} = \left(\frac{[G3P][NADP^+]}{[3PG][NADPH]}\right)_{eq} = \left(\frac{[G3P]}{[3PG]}\right)_{eq}\left(\frac{[NADP^+]}{[NADPH]}\right)_{eq}$$

$$\left(\frac{[G3P]}{[3PG]}\right)_{eq} = 1.5 \times 10^{-8}\left(\frac{[NADPH]}{[NADP^+]}\right)_{eq} = 1.5 \times 10^{-8}(10) = 1.5 \times 10^{-7}$$

For the combination of reactions in part (b) of the problem:

$$\ln K_{(b)} = -\frac{\Delta G^{\circ\prime}}{RT} = -5.2 = \ln\left(\frac{[G3P][ADP^{3-}][NADP^+][HOPO_3^{2-}]}{[3PG][ATP^{4-}][NADPH]}\right)_{eq}$$

$$5.5 \times 10^{-3} = \left(\frac{[G3P]\left[ADP^{3-}\right]\left[NADP^+\right]\left[HOPO_3^{2-}\right]}{[3PG]\left[ATP^{4-}\right][NADPH]} \right)_{eq}$$

$$\left(\frac{[G3P]}{[3PG]} \right)_{eq} = 5.5 \times 10^{-3} \left(\frac{[NADPH]}{\left[NADP^+\right]} \right)_{eq} \left(\frac{\left[ATP^{4-}\right]}{\left[ADP^{3-}\right]} \right)_{eq} \left(\frac{1}{\left[HOPO_3^{2-}\right]} \right)_{eq}$$

$$\left(\frac{[G3P]}{[3PG]} \right)_{eq} = 5.5 \times 10^{-3}(10)(10)(100) = 55$$

The indirect pathway in part (b) can provide almost 400 million times more of the desired product, G3P, glyceraldehyde-3-phosphate, than the direct pathway. This is because the overall free energy change for the indirect pathway, although unfavorable, is less than one-third as large as that for the direct pathway. Phosphorylation of the acid requires a large input of free energy, but produces a product whose reduction is favored. A substantial part of the free energy for the phosphorylation is provided by the reaction with ATP to transfer a phosphate group to the acid.

(e) The reactions in part (b) are coupled in the sense that we can imagine the hydrolysis free energy for ATP is used to drive the net reactions. Although reaction (2) occurs directly, when catalyzed by the appropriate enzyme, we can think of it as being the sum of two reactions:

$$RCOO^- + HOPO_3^{2-} + H_3O^+ \Leftrightarrow RCOO\text{-}PO_3^{2-} + 2H_2O$$

$$ATP^{4-} + 2H_2O \Leftrightarrow ADP^{3-} + HOPO_3^{2-} + H_3O^+$$

Under physiological conditions, $\Delta G^{\circ\prime}$ for the first reaction is about 49 kJ·mol^{-1} and for the second about –30 kJ·mol^{-1}. Therefore, the direct reaction has $\Delta G^{\circ\prime} \approx 19$ kJ·mol^{-1}. This is another example of the way in which the hydrolysis free energy of ATP is "coupled" to other reactions to provide a more favorable free energy change for an overall reaction, including the pathway here.

Problem 10.67.
(a) The cell described in the problem is set up for measuring half cell reduction potentials relative to the SHE, so the cell potential is the reduction potential for the silver half cell with the silver ion concentration controlled by the solubility of AgSCN*(s)* in a solution that is 0.10 M in SCN$^-$*(aq)*. Use the Nernst equation to find the silver ion concentration from the measured cell potential 0.45 V with the SHE as the anode:

$$0.45 \text{ V} = E^\circ (Ag^+, Ag) - \frac{(0.05916 \text{ V})}{1} \log \frac{(Ag(s))}{(Ag^+(aq))} = 0.799 \text{ V} - \frac{(0.05916 \text{ V})}{1} \log \frac{(1)}{(Ag^+(aq))}$$

$$\log \frac{(1)}{(Ag^+(aq))} = \frac{(0.799 \text{ V}) - (0.45 \text{ V})}{0.05916 \text{ V}} = 5.9; \qquad (Ag^+(aq)) = 1.3 \times 10^{-6}$$

$$[Ag^+(aq)] = 1.3 \times 10^{-6} \text{ M}$$

(b) The solubility product expression and solubility product for silver thiocyanate are:

$$K_{sp} = (Ag^+(aq))(SCN^-(aq)) = (1.3 \times 10^{-6})(0.10 \text{ M}) = 1.3 \times 10^{-7}$$

Problem 10.68.
(a) The half reaction in a half cell that contains Ag(s), AgCl(s), and Cl⁻(aq) is the sum of the silver ion-silver half reaction and the solubility reaction for solid silver chloride:

$$Ag^+(aq) + e^- \Leftrightarrow Ag(s)$$
$$\underline{AgCl(s) \Leftrightarrow Ag^+(aq) + Cl^-(aq)}$$
$$AgCl(s) + e^- \Leftrightarrow Ag(s) + Cl^-(aq)$$

(b) Use the standard reduction potential for the silver ion-silver half reaction to get $\Delta G°(Ag^+, Ag)$ for the first half reaction in part (a) and the solubility product for silver chloride to get $\Delta G°(AgCl\ K_{sp})$ for the solubility reaction:

$$\Delta G°(Ag^+, Ag) = -nFE° = -(1)(9.6485 \times 10^4\ C\cdot mol^{-1})(0.799\ V) = -77.1\ kJ\cdot mol^{-1}$$

$$\Delta G°(AgCl\ K_{sp}) = -RTlnK_{sp} = -(8.314\ J\cdot K^{-1}\cdot mol^{-1})\cdot(298\ K)\cdot ln(1.8 \times 10^{-10}) = 55.6$$
kJ·mol⁻¹

The standard free energy change for the silver chloride-silver half reaction is the sum of these two values:

$$\Delta G°(AgCl, Ag) = \Delta G°(Ag^+, Ag) + \Delta G°(AgCl\ K_{sp})$$

$$\Delta G°(AgCl, Ag) = (-77.1\ kJ\cdot mol^{-1}) + (55.6\ kJ\cdot mol^{-1}) = -21.5\ kJ\cdot mol^{-1}$$

(c) Use $\Delta G°(AgCl, Ag)$ to calculate °(AgCl, Ag):

$$°(AgCl, Ag) = -\frac{\Delta G°(AgCl, Ag)}{nF} = -\frac{(-21.5 \times 10^3\ J\cdot mol^{-1})}{(1)(9.6485 \times 10^4 C\cdot mol^{-1})} = 0.223\ V$$

This value is identical, within the precision of the data, to the one in Appendix B. The reduction potential for this half-cell reaction is the information that is usually used to calculate the solubility product for silver chloride (and other solubility products) by the reverse of the reasoning for this problem.

Problem 10.69.
(a) The measured cell potential, E, for this cell is 0.608 V at 298 K:

Ag(s) | AgBr(s) | Br⁻(aq, 0.050 M) ‖ Ag⁺(aq, 0.200 M) | Ag(s)

The measured cell potential is the difference between the cathode and anode half-cell potentials:

$$E = 0.608\ V = E(Ag^+, Ag) - E(AgBr, Ag)$$

Each half-cell potential can be expressed in terms of the Nernst equation and the resulting expression solved for $E°(AgBr, Ag)$ (which solves part (b) of the problem):

$$0.608\ V = \left[E°(Ag^+, Ag) - \frac{(0.05916\ V)}{1}log\left(\frac{(Ag(s))}{(Ag^+(aq))}\right)\right]$$
$$- \left[E°(AgBr, Ag) - \frac{(0.05916\ V)}{1}log\left(\frac{(Ag(s))(Br^-(aq))}{(AgBr(s))}\right)\right]$$

$$0.608 \text{ V} = \left[(0.799 \text{ V}) - \frac{(0.05916 \text{ V})}{1} \log\left(\frac{1}{0.200} \right) \right]$$

$$- \left[E^\circ(\text{AgBr, Ag}) - \frac{(0.05916 \text{ V})}{1} \log\left(\frac{1 \cdot (0.050)}{1} \right) \right]$$

$E^\circ(\text{AgBr, Ag}) = 0.073 \text{ V}$

Convert this standard half-cell reduction potential to the standard free energy change for the reaction and subtract the standard free energy change for the silver ion-silver half-cell reaction to get the standard free energy of the solubility reaction (the reverse of the procedure in Problem 10.68) and hence the solubility product:

$$\Delta G^\circ(\text{AgBr, Ag}) = -nFE^\circ = -(1)(9.6485 \times 10^4 \text{ C·mol}^{-1})(0.073 \text{ V}) = -7.0 \text{ kJ·mol}^{-1}$$

$$\Delta G^\circ(\text{Ag}^+, \text{Ag}) = -nFE^\circ = -(1)(9.6485 \times 10^4 \text{ C·mol}^{-1})(0.799 \text{ V}) = -77.1 \text{ kJ·mol}^{-1}$$

Therefore,

$$\Delta G^\circ(\text{AgBr } K_{sp}) = \Delta G^\circ(\text{AgBr, Ag}) - \Delta G^\circ(\text{Ag}^+, \text{Ag}) = (-7.0 \text{ kJ·mol}^{-1}) - (-77.1 \text{ kJ·mol}^{-1})$$

$$\Delta G^\circ(\text{AgBr } K_{sp}) = 70.1 \text{ kJ·mol}^{-1} = -RT\ln K_{sp} = -(8.314 \text{ J·K}^{-1}\text{·mol}^{-1})\cdot(298 \text{ K})\cdot\ln K_{sp}$$

$$K_{sp} = 5.1 \times 10^{-13}$$

(b) See part (a): $E^\circ(\text{AgBr, Ag}) = 0.073 \text{ V}$

Problem 10.70.
(a) The anodic half cell is the one containing the silver ion complex with thiosulfate dianion, $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}(aq$, from the dissolved $\text{Na}_2\text{S}_2\text{O}_3\cdot5\text{H}_2\text{O}$, so the cell described in the problem is:

$$\text{Ag}(s) \,|\, \text{Ag}^+(aq), \text{Ag}(\text{S}_2\text{O}_3)_2^{3-}(aq), \text{S}_2\text{O}_3^{2-}(aq) \,\|\, \text{Ag}^+(aq, 0.050 \text{ M}) \,|\, \text{Ag}(s)$$

(b) To get the equilibrium constant for complex formation, we need the equilibrium values for $(\text{Ag}^+(aq))$, $(\text{S}_2\text{O}_3^{2-}(aq))$, and $(\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}(aq))$ in the complex-forming solution. We can use the cell potential to find $(\text{Ag}^+(aq))$ in the anodic half cell:

$$E = 0.618 \text{ V} = E^\circ - \frac{(0.05916 \text{ V})}{1} \log \frac{(\text{Ag}^+(aq, \text{ anode}))}{(\text{Ag}^+(aq, \text{ cathode}))}$$

$$0.618 \text{ V} = (0.000 \text{ V}) - \frac{(0.05916 \text{ V})}{1} \log \frac{(\text{Ag}^+(aq, \text{ anode}))}{0.050}$$

$$(\text{Ag}^+(aq)) = 1.8 \times 10^{-12}$$

The number of moles of $\text{Na}_2\text{S}_2\text{O}_3\cdot5\text{H}_2\text{O}$ in the anodic half cell and the concentration of $\text{S}_2\text{O}_3^{2-}(aq)$ that would be present in the absence of reaction is:

$$\text{mol Na}_2\text{S}_2\text{O}_3\cdot5\text{H}_2\text{O} = \frac{(0.500 \text{ g})}{(248 \text{ g} \cdot \text{mol}^{-1})} = 2.02 \times 10^{-3} \text{ mol}$$

$$[\text{S}_2\text{O}_3^{2-}(aq)] = \frac{2.02 \times 10^{-3} \text{ mol}}{0.0100 \text{ L}} = 0.202 \text{ M}$$

Some of this thiosulfate dianion is used by the reaction to form the complex;

$$\text{Ag}^+(aq) + 2\text{S}_2\text{O}_3^{2-}(aq) \Longleftrightarrow \text{Ag}(\text{S}_2\text{O}_3)_2^{3-}(aq)$$

Essentially all of the silver ion initially present has reacted to form the complex (almost none is left uncomplexed), so $[Ag(S_2O_3)_2^{3-}(aq)] = 0.050$ M. The ratio of thiosulfate dianion to silver ion reacting is 2:1, so 0.100 M thiosulfate has reacted, leaving $[S_2O_3^{2-}(aq)] = 0.102$ M in the complex-forming solution. The equilibrium constant for complex formation is:

$$K = \frac{(Ag(S_2O_3)_2^{2-}(aq))}{(Ag^+(aq))(S_2O_3^{2-}(aq))^2} = \frac{0.050}{(1.8 \times 10^{-12})(0.102)^2} = 2.7 \times 10^{12}$$

(c) The half reaction of interest, $Ag(S_2O_3)_2^{3-}(aq) + e^- \Leftrightarrow Ag(s) + 2S_2O_3^{2-}(aq)$, is the difference between the half reaction for silver ion reduction to silver metal and the complexation reaction whose equilibrium constant we calculated in part (b).

$$Ag^+(aq) + e^- \Leftrightarrow Ag(s)$$
$$\underline{-[Ag^+(aq) + 2S_2O_3^{2-}(aq) \Leftrightarrow Ag(S_2O_3)_2^{3-}(aq)]}$$
$$Ag(S_2O_3)_2^{3-}(aq) + e^- \Leftrightarrow Ag(s) + 2S_2O_3^{2-}(aq)$$

Convert the standard reduction potential for the silver ion-silver half reaction and the equilibrium constant in part (b) to the standard free energy changes for these reactions and subtract them to get the standard free energy change for the half reaction of interest:

$$\Delta G°(Ag^+, Ag) = -nFE° = -(1)(9.6485 \times 10^4 \text{ C·mol}^{-1})(0.799 \text{ V}) = -77.1 \text{ kJ·mol}^{-1}$$

$$\Delta G°(Ag(S_2O_3)_2^{3-} \text{ formation}) = -RT\ln K = -(8.314 \text{ J·K}^{-1}\text{·mol}^{-1})·(298 \text{ K})·\ln(2.7 \times 10^{12})$$

$$\Delta G°(Ag(S_2O_3)_2^{3-} \text{ formation}) = -70.9 \text{ kJ·mol}^{-1}$$

$$\Delta G°(Ag(S_2O_3)_2^{3-}, Ag) = \Delta G°(Ag^+, Ag) - \Delta G°(Ag(S_2O_3)_2^{3-} \text{ formation})$$

$$\Delta G°(Ag(S_2O_3)_2^{3-}, Ag) = -77.1 \text{ kJ·mol}^{-1} - (-70.9 \text{ kJ·mol}^{-1}) = -6.2 \text{ kJ·mol}^{-1}$$

Convert this standard free energy to the standard reduction potential for the reaction:

$$°(Ag(S_2O_3)_2^{3-}, Ag) = -\frac{\Delta G°(Ag(S_2O_2)_2^{2-}, Ag)}{nF} = -\frac{(-6.2 \times 10^3 \text{ J·mol}^{-1})}{(1)(9.6485 \times 10^4 \text{C·mol}^{-1})} = 0.064 \text{ V}$$

Problem 10.71.
(a) Write and solve the Nernst equation for the cell potential as a function of pH for this cell and cell reaction:

$$Pt(s) \,|\, H_2(g, \text{ 1 bar}) \,|\, H^+(aq, \text{ pH}) \,\|\, Cl^-(aq, \text{ 1.00 M}) \,|AgCl(s)\,|\, Ag(s)$$
$$H_2(g) + 2AgCl(s) \Leftrightarrow 2H^+(aq) + Cl^-(aq) + 2Ag(s)$$

The cell is set up with a hydrogen electrode as the anode, so the standard potential for the cell is the standard reduction potential for the silver chloride-silver metal half cell, $E° = 0.222$ V:

$$E = (0.222 \text{ V}) - \frac{(0.05916 \text{ V})}{2}\log\frac{(Ag(s))^2(H^+(aq))^2(Cl^-(aq))^2}{(AgCl(s))^2(H_2(g))}$$

All of the dimensionless concentration ratios in Q are unity, except $(H^+(aq))$, the variable of interest:

$$E = (0.222 \text{ V}) - \frac{(0.05916 \text{ V})}{2}\log(H^+(aq))^2 = (0.799 \text{ V}) - (0.05916 \text{ V})·\log(H^+(aq))$$

$$E = (0.222 \text{ V}) + (0.05916 \text{ V})·pH$$

This is the equation of a straight line with an intercept of 0.222 V at pH 0 and a positive slope of 0.05916 V per pH unit:

The cell potential increases with pH, which is what you expect from the cell reaction in which $H^+(aq)$ is a product. Increasing pH means decreasing ($H^+(aq)$) and Le Chatelier's principle predicts that the reaction proceed in a direction to try to increase ($H^+(aq)$), that is, toward products, which increases the cell potential.

(b) You can either read the pH from the graph at $E = 0.435$ V, as shown (poorly) on the graph above, or (better) use the linear equation to calculate pH:

$$pH = \frac{(0.435\ \text{V}) - (0.222\ \text{V})}{0.05916\ \text{V}} = 3.60$$

Problem 10.72.
(a) The half reaction for reduction of methylene blue and Nernst equation corresponding to the half reaction are:

$$E = E° - 0.059\log Q = (0.053\ \text{V}) - \frac{0.059\ \text{V}}{2}\log\left[\frac{(MBH(aq))}{(MB^+(aq))(H^+(aq))^2}\right]$$

(b) The data in Problem 10.54 are E *vs*. pH for this half cell. In order to plot the data to see whether they obey the Nernst equation, we have to rewrite the Nernst equation, so we have the reduction potential as a function of pH:

$$E = (0.053\ \text{V}) - \frac{0.059\ \text{V}}{2}\log\left[\frac{(MBH(aq))}{(MB^+(aq))}\right] - \frac{0.059\ \text{V}}{2}\log\left[\frac{1}{(H^+(aq))^2}\right]$$

$$E = -\,(0.059\ \text{V})\text{pH} + (0.053\ \text{V}) - \frac{0.059\ \text{V}}{2}\log\left[\frac{\left(\text{MBH}(aq)\right)}{\left(\text{MB}^+(aq)\right)}\right]$$

This form of the Nernst equation indicates that E should vary linearly with pH (if the ratio of the methylene blue forms, $\dfrac{\left(\text{MBH}(aq)\right)}{\left(\text{MB}^+(aq)\right)}$, is constant as pH changes) and the slope of the line should be –0.059 V. The data give this plot:

The data do not give a linear dependence over the entire pH range, although the values at high and low pH seem to fall on straight (but different) lines. Neither line has a slope of $-\,0.059$ V, so the data do not obey the Nernst equation. It is hard to justify saying that the data at either high or low pH are consistent with the Nernst equation. The intercept of the plot at pH 0 is $E°$ for this half cell, if the $(\text{MBH})/(\text{MB}^+)$ ratio is unity, so $\log[(\text{MBH})/(\text{MB}^+)] = 0$. The value for $E°$ in Appendix B is 0.054 V, which is essentially the same as the intercept here and implies that $(\text{MBH})/(\text{MB}^+) = 1$ under the conditions of the measurements reported in Problem 10.54. On the other hand, the value for $E°´$ in Appendix B is 0.01 V, the same as in these data at pH 7. The difference between the pH 0 and pH 7 values, 0.52 V, is not consistent with the Nernst equation, which would predict a difference of 0.41 V [$= 7\cdot(0.05916\ \text{V})$].

(c) The oxidized form of methylene blue has a positive charge that is shown on one of the nitrogens in the structure. However, we know that electrons in the pi-electron system of a molecule like methylene blue are delocalized over the whole molecule. [You can, for example, write an equivalent form of the Lewis structure in part (a) with the positive charge on the right-hand N atom.] This also spreads the positive charge out over the molecule, so the molecule, as a whole, repels other positive charges and is a weaker base than the reduced form, which is electrically neutral.

If solutions are prepared with equal amounts of the oxidized and reduced forms of methylene blue, we might expect the $(\text{MBH})/(\text{MB}^+)$ ratio to be unity; $\log[(\text{MBH})/(\text{MB}^+)]$ would be zero in the E *vs.* pH equation. However, if MBH reacts as a base to give MBH_2^+ (or even MBH_3^{2+}), the concentration of MBH decreases, the logarithm becomes negative and the last term in the equation becomes positive. This effect would increase E, make the reduction more positive, than if the acid-base reaction did not occur. This seems to be what we observe in the

figure at low pH where the potential increases faster than expected from the Nernst equation (which does not account for the "loss" of MBH). Although MB^+ also acts as a base, it is a weaker base than MBH, so is not as much affected by the changes in pH. Because the MBH is more affected by changes in the pH, the ratio is less than unity at low pH. The problem with this explanation is that it contradicts the reasoning in part (b), which suggests that the (MBH)/(MB$^+$) ratio is unity at pH 0. The several discrepancies between the experimental data and predictions from the Nernst equation for the simple reaction written in part (a) suggest that the reaction is not that simple and that the values for $E°$ and $E°´$ may not actually reflect concentration conditions that are standard in this half cell.

At high pH, both MB^+ and MBH should be in their base forms and we might expect the Nernst equation to be obeyed. However, the potential decreases more slowly than predicted by the Nernst equation. This is the result we would observe if the (MBH)/(MB$^+$) ratio is greater than one. It could be the case that the positive MB^+ molecule reacts with the increasing amounts of OH^- in the solutions (to form some sort of neutral adduct or complex) and is "lost" from the solution.

Problem 10.73.

(a) To keep track of which concentration is which, use (H$^+$*inter*) for the hydronium ion concentration in the intermembrane space and (H$^+$*matrix*) for the hydronium ion concentration in the matrix (with a pH one unit greater than in the intermembrane space). This is a concentration cell, so the standard cell potential is zero. Write the cell reaction as H$^+$*inter* →H$^+$*matrix*. Focus on the transfer of one unit of charge (one hydronium ion) from the intermembrane side of the membrane to the matrix, so $n = 1$ in the Nernst equation:

$$E = - (0.05916 \text{ V}) \cdot \log \frac{\left(H^+ (matrix) \right)}{\left(H^+ (inter) \right)} = - (0.05916 \text{ V}) \cdot \log \frac{10^{-(pH + 1)}}{10^{-pH}}$$

$$E = - (0.05916 \text{ V}) \cdot \log(10^{-1}) = 0.059 \text{ V}$$

The cell potential is positive, so transfer of hydronium ions from the intermembrane space to the matrix is favorable.

(b) The free energy change for this transfer of hydronium ions is:

$$\Delta G = -nFE = - 1 \cdot (9.6485 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(0.059 \text{ V}) = -5.7 \text{ kJ} \cdot \text{mol}^{-1}$$

(c) The spontaneous direction of hydronium ion transfer should be from the side of the membrane with the higher concentration to that with the lower. The intermembrane space has the higher hydronium ion concentration (its pH is lower), so transfer from the intermembrane space to the matrix, as envisioned in the reaction written in part (a), is spontaneous. The positive cell potential and negative free energy for this transfer are consistent with this direction.

Problem 10.74.

(a) Since the zinc electrode is the anode (where oxidation occurs) the cell reaction is:

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

The work done by an electrodchemical cell is nFE, where, in this case, $n = 2$, since two moles of electrons are transferred from Zn to Cu^{2+} for each mole of Zn oxidized. Thus:

$$\text{work (1 mol reaction)} = 2 \cdot (9.6485 \times 10^4 \text{ C} \cdot \text{mol}^{-1}) \cdot (1.15 \text{ V}) = 222 \text{ kJ} \cdot \text{mol}^{-1}$$

(b) Since $Zn^{2+}(aq)$ is produced in the upper layer, its concentration increases there. $Cu^{2+}(aq)$ is used up in the bottom layer by the electrochemical reaction, but more $CuSO_4(s)$ dissolves to take its place and keep the solution saturated, so the $Cu^{2+}(aq)$ remains unchanged as the cell does work, but more $SO_4^{2-}(aq)$ is added to the solution. Either some of the $Zn^{2+}(aq)$ has to leave the upper layer or $SO_4^{2-}(aq)$ has to leave the bottom layer (probably both occur) to maintain the electrical neutrality of the upper and lower solutions. As we have said, the $CuSO_4(s)$ dissolves to keep the concentration of $Cu^{2+}(aq)$ approximately constant.

(c) As the cell discharges, the concentration of $Zn^{2+}(aq)$ builds up in the upper layer. $Zn^{2+}(aq)$ is a product of the electrochemical reaction, and its build up is a disturbance to the system. Although the system is not at equilibrium, we can use Le Chatelier's principle to help understand how the reaction will be affected by this disturbance. If the system adjusts to reduce the stress it will adjust in such a way as to reduce the amount of $Zn^{2+}(aq)$ formed. The reaction will have less driving force to go in the direction written and, thus, a decreasing cell potential, as is observed when the cell is used.

Problem 10.75.
(a) The cell reaction in the Daniell cell is:

$$Zn(s) + Cu^{2+}(aq) \Leftrightarrow Zn^{2+}(aq) + Cu(s)$$

We can use the Nernst equation to determine the ratio, $(Zn^{2+}(aq))/(Cu^{2+}(aq))$, that will give the observed cell potential:

$$1.15\ V = 1.10\ V - \frac{(0.05916\ V)}{2}\log\left[\frac{(Zn^{2+}(aq))}{(Cu^{2+}(aq))}\right]$$

$$\log\left[\frac{(Zn^{2+}(aq))}{(Cu^{2+}(aq))}\right] = -1.69$$

$$\left[\frac{(Zn^{2+}(aq))}{(Cu^{2+}(aq))}\right] = 0.020$$

The upper, $Zn^{2+}(aq)$, solution is quite a bit more dilute than the lower, $Cu^{2+}(aq)$, solution.

(b) The density of the copper sulfate solution is $1.27\ g\cdot mL^{-1}$, so one liter of the copper sulfate solution has a mass of 1270 g. Assume that one liter of solution is one liter of water plus enough $CuSO_4$ to give the observed density. (This assumption will probably somewhat underestimate the concentration.) One liter of water has a mass of 1000 g. The extra 270 g in the solution must be $CuSO_4$. This is $(270\ g)/(159.6\ g\cdot mol^{-1}) = 1.69$ mol of $CuSO_4$ in one liter of solution. The copper sulfate solution is 1.69 M. From part (a), we know the ratio of concentrations, so, for the initial concentration of zinc cation in the cell, we have:

$$0.020 = \left[\frac{(Zn^{2+}(aq))}{(Cu^{2+}(aq))}\right] = \left[\frac{(Zn^{2+}(aq))}{1.69}\right]$$

$$(Zn^{2+}(aq)) = 0.034; \qquad .[Zn^{2+}(aq)] = 0.034\ M$$

(c) In Problem 10.6, we found that 270.7 g (= 4.140 mol) of zinc had gone into solution as $Zn^{2+}(aq)$ in a cell that we are now told is a Daniell cell. In 2.5 L of solution, this amount of zinc would give $[Zn^{2+}(aq)] = 1.7\ M \left[= \frac{(4.140\ mol)}{(2.5\ L)}\right]$. To this, we should add the initial

concentration of zinc cation, but it is so low, part (b), that it does not change this final concentration.

(d) To get the cell potential of the used cell, we once again apply the Nernst equation and substitute the concentrations of $Zn^{2+}(aq)$ (= 1.7 M) and $Cu^{2+}(aq)$ (= 1.69 M):

$$E = 1.10 \text{ V} - \frac{(0.05916 \text{ V})}{2} \log\left[\frac{1.7}{1.69}\right] = 1.10 \text{ V}$$

As you see, the cell potential has not declined too much and Problem 10.6 indicated that the zinc electrode had not been used up. However, the cell is probably no longer useful because the high concentration of the upper solution has increased its density, so the solutions can begin to mix and destroy the separation of the half reactions that makes it possible to get electrical work from the cell. It's time to recycle the cell solutions, put in fresh solutions and a fresh zinc electrode, and use the cell again.

Problem 10.76.
(a) A major advantage of this set up with a porous glass disc for ions to migrate through (instead of a salt bridge) is alluded to in the problem statement. You do not need to construct a salt bridge. The ions in the half-cell solutions carry the charge through the solutions, so no extra ions are added. A disadvantage is that ions from the two half cells mix in this cell as they move to maintain charge neutrality. If the ions in the two half cells react with one another, the cell potential could be affected and the cell could become inoperable.
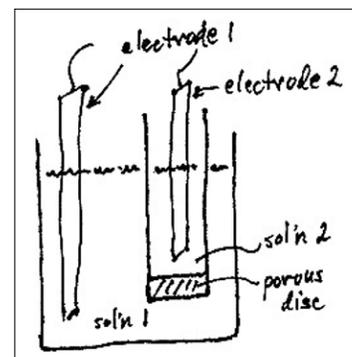
(b) Metal-metal ion half cells could work well in this set up, if the anion is the same in both half cells and the solutions do not diffuse too rapidly through the porous glass disc. (The original design of the Daniell cell shown in Problem 10.74 used this sort of set up.)

(c) Metal-metal ion half cells with different anions might not work so well, especially if the anion in one half cell reacts with the metal ion or anion in the other half cell.

Problem 10.77.
The term "fuel cells" is generally applied to electrochemical cells in which a "fuel" gives up electrons with the ultimate acceptor being oxygen, usually from the air. The overall reaction that occurs is the same as would occur in the combustion of the fuel in air with no production of electric potential or electric current. In the aluminum-air cell, the fuel, aluminum metal, gives up its electrons to oxygen, as shown in reaction equation (10.46). This is similar to the reaction that occurs when pure aluminum metal is exposed to air and almost immediately forms a thin coat of aluminum oxide, which protects the metal from further reaction with the air and is the reason that aluminum is such a useful metal for a variety of purposes, even though the pure metal is very reactive. The fuel you would have to carry around, in case the cell ran out, is pieces of aluminum, which will be quite safe for both you and your surroundings.