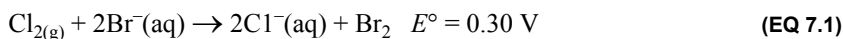

Objective

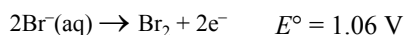
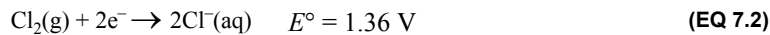
1. To set up galvanic cells, to identify electrodes and electrode processes, and to measure cell voltages.
2. To set up an electrolytic cell, to run it through charge and discharge cycles, and to identify electrodes and electrode processes during both parts of the cycle.
3. To use half-cell reactions and their values to write cell reactions and to calculate standard cell potentials for the galvanic cells prepared in the laboratory.
4. To set up and to operate concentration cells and to relate their cell voltages and electrochemical processes to the Nernst equation.

*Galvanic (Voltaic) Cells***Principles of Voltaic Cells**

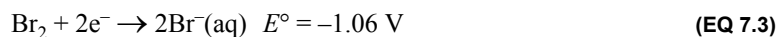
The standard cell potential E° for an oxidation-reduction reaction, such as



can be calculated from two half-cell potentials:



The first half-cell represents reduction (gain of electrons), and half-cells are commonly tabulated as reduction half-cells. The second half-cell represents oxidation (loss of electrons); at a reduction half-cell the sign of E° is reversed:



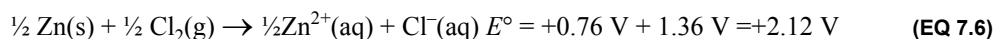
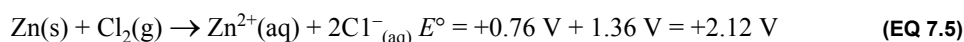
Thus E° for any cell reaction can be calculated by adding the reactions and E° values so that the electrons appear on opposite sides of the half reactions. The cell voltages E° refer to the voltages observed when all species are in their standard states (approximately 1M for species in solution and 1 atm pressure for gases). Most commonly, E° values are tabulated for 298 K.

Half-cell potentials can be calculated from cell potentials and from the convention that $E^\circ = 0$ V for the half-cell,



at all temperatures.

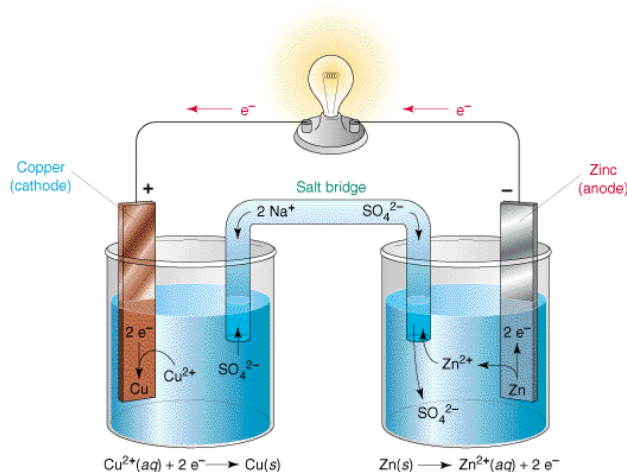
Electrode potentials are defined so that they do not depend on the number of molecules, ions, or electrons. This is why individual cells of the same kind, such as dry cells of penlight size AA, flashlight size D, or lantern size 6 all have the same $E^\circ = 1.5$ V. Thus, from the half-cell reactions above, the two following cell reactions have the same E° .



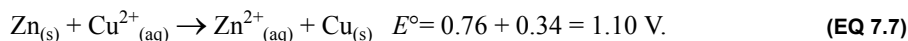
When a cell reaction is written so that E° is positive, the reaction will proceed spontaneously from left to right if all components are in standard states. The reaction can occur simply by mixing the reagents, or by separating the half-cells so that the potential can be measured. In the latter case the reaction actually occurs in the spontaneous direction, but very slowly since the voltmeter has a very high resistance to electric current. When the reagents are separated so that a measurable voltage is observed, the electrochemical cell is called a voltaic (or galvanic) cell.

It is useful to learn how to name all the components and processes occurring in a voltaic cell. Consider the example in Figure 7.1. The line notation for this cell is $\text{Zn}_{(\text{s})} | \text{Zn}^{2+}(1\text{M}) || \text{Cu}^{2+}(1\text{M}) | \text{Cu}_{(\text{s})}$.

FIGURE 7.1



The cell reaction is



For every zinc atom oxidized, one copper ion is reduced and two electrons flow through the wire. Since both beakers must maintain a neutral charge, ions must flow through the Na_2SO_4 salt bridge;

either a zinc ion from right to left, or a sulfate ion from left to right. In actuality, of course, both Zn^{2+} and SO_4^{2-} migrate into the salt bridge, and Na^+ and SO_4^{2-} migrate out of it. After many hours of operation, the salt bridge will contain many ions from both beakers; but for each electron passed through the wire, one net charge will transfer between beakers to maintain electrical neutrality. Note the following points:

1. The sulfate ion can be replaced by any other anion that does not precipitate Zn^{2+} or Cu^{2+} or otherwise participate in a reaction: Cl^- or NO_3^- can be used.
2. The copper electrode can be replaced by an inert, conducting substance such as platinum, gold, or carbon (graphite). In any case, copper metal will be deposited on the cathode.
3. The two independent half-cells connected by a salt bridge can simply be mixed together. If this is done, the reaction will proceed essentially to completion. Separation into two half-cells is merely a convenient way of illustrating how useful the half-cell concept is.

Voltaic Cells Procedure

Part A. Before setting up pairs of half-cells, make a complete cell of the type shown in Figure 7.1. We will use zinc nitrate and copper(II) nitrate instead of the sulfates as shown in the Figure.

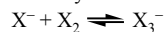
1. Place 30 mL of 0.1M $\text{Zn}(\text{NO}_3)_2$ solution and 30 mL of 0.1 M $\text{Cu}(\text{NO}_3)_2$ solution in separate 100 mL beakers.
2. Obtain a zinc strip and a copper strip from the storage shelf: clean both sides of the copper strip with sandpaper.
3. Obtain a salt bridge from the stockroom.
4. Insert the strips in the solutions of their own ions. Label the diagram with the appropriate electrode names, processes, and signs.
5. Obtain a voltmeter from your instructor. Identify its positive and negative terminals. Attach it to the appropriate electrodes (do not guess) and read the voltage.
6. Now short-circuit the cell with a single piece of wire with alligator clips at each end. What chemical reaction is taking place? Which way are electrons flowing? Record in your notebook any physical change occurring that confirms that the chemical reaction is taking place?
7. Set the cell-aside, leaving it short-circuited. until the end of the period. Before leaving the laboratory, disconnect the short circuit. note the physical condition of the electrodes and the color of the solution. and read the voltage across the electrodes with the voltmeter.

Part B. Your instructor will assign students to prepare two or three labeled 100 mL beakers representing each of the following half-cells (each should contain 25 to 30 mL of total solution). If low-impedance voltmeters are used, 1M solutions may be required.

TABLE 7.1

0.1 M Zn(NO ₃) ₂ solution, Zn electrode
0.1 M Cu(NO ₃) ₂ solution, Cu electrode (make six beakers if necessary)
0.1 M Cd(NO ₃) ₂ solution, Cd electrode
0.1 M Pb(NO ₃) ₂ solution, Pb electrode
0.1 M Br ₂ solution, 0.1 M KBr solution, ^a Pt electrode ^b
0.1 M I ₂ solution, 0.1 M KI solution, Pt electrode
0.1 M AgNO ₃ solution, Ag electrode

a. Actually contains halogen, mostly as a complex ion from the equilibrium



b. Use Pt foil for the electrode. The wire does not have enough surface area.

Proceed systematically to set up cells to measure the potentials of the reactions listed in Table 7.1 on page 38. (Your instructor will tell you which cells to set up if there is not time to do them all.)

For each voltaic cell refer to “Questions and Data Interpretation” on page 43 for data work-up.

When you have finished this experiment, return all the metal electrodes to the appropriate containers. Salt bridges should be stored for future use in large beakers partly filled with 0.1 M KNO₃ solution.

FIGURE 7.2 Example Diagram

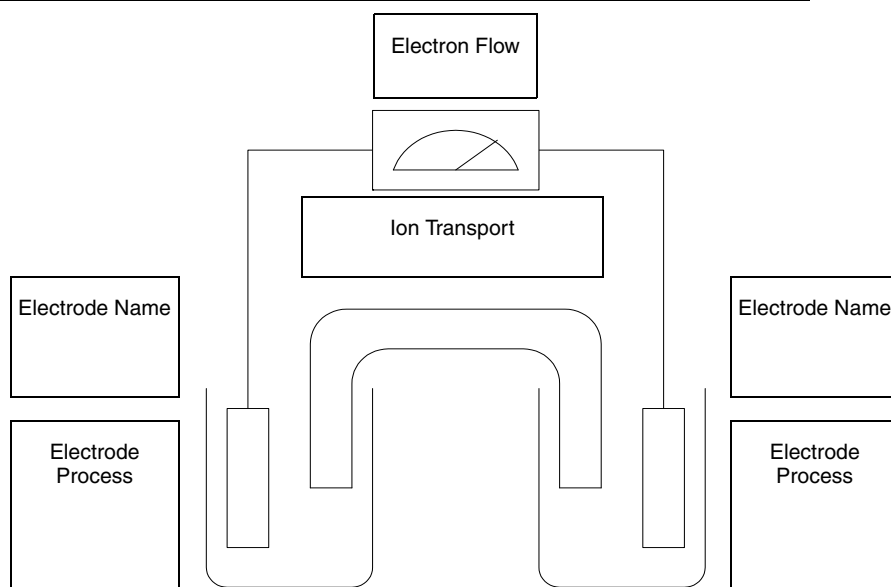


TABLE 7.2

	Left Side	Right Side
Diagram #1	Pb Pb(NO ₃) ₂	Cu Cu(NO ₃) ₂
Diagram #2	Cd Cd(NO ₃) ₂	Cu Cu(NO ₃) ₂
Diagram #3	Pt Br ₂ , Br ⁻	Cu Cu(NO ₃) ₂
Diagram #4	Pt I ₂ , I ⁻	Cu Cu(NO ₃) ₂
Diagram #5	Ag AgNO ₃	Cu Cu(NO ₃) ₂
Diagram #6	Pt Br ₂ , Br ⁻	I ₂ , I ⁻ Pt

Electrolytic Cells

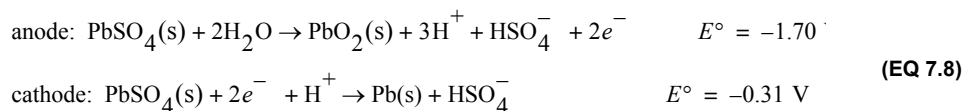
Electrolytic Cells Principles

Electrochemical cells include various types:

- Galvanic (voltaic) cells are used to produce electricity from a chemical reaction for which $E^\circ > 0$.
- Concentration cells
- Fuel cells are galvanic cells that produce electricity from a chemical reaction in which the reactants can be supplied continually
- Electrolytic cells, in which an external voltage source forces an electrochemical reaction to occur. Such cells are used to electroplate metals (e.g. silver plating jewelry or purifying copper). A battery being charged is also an electrolytic cell.

A lead storage cell is an example of the last-mentioned type of cell. During charging it functions as an electrolytic cell as energy is pumped in; during discharge this energy is extracted. Lead storage cells are important commercially: they are inexpensive, reliable, efficient, and can be reused many times. Their only real drawback is their energy density on a weight basis; lead is so dense that lead batteries are very heavy.

If two lead electrodes are immersed in H₂SO₄ solution the lead is oxidized. The product, PbSO₄, is relatively insoluble in H₂SO₄ solution, and it covers the lead electrodes. If these PbSO₄-coated electrodes are then subjected to an external voltage source greater than 2 V, the following reactions occur during the electrolysis:

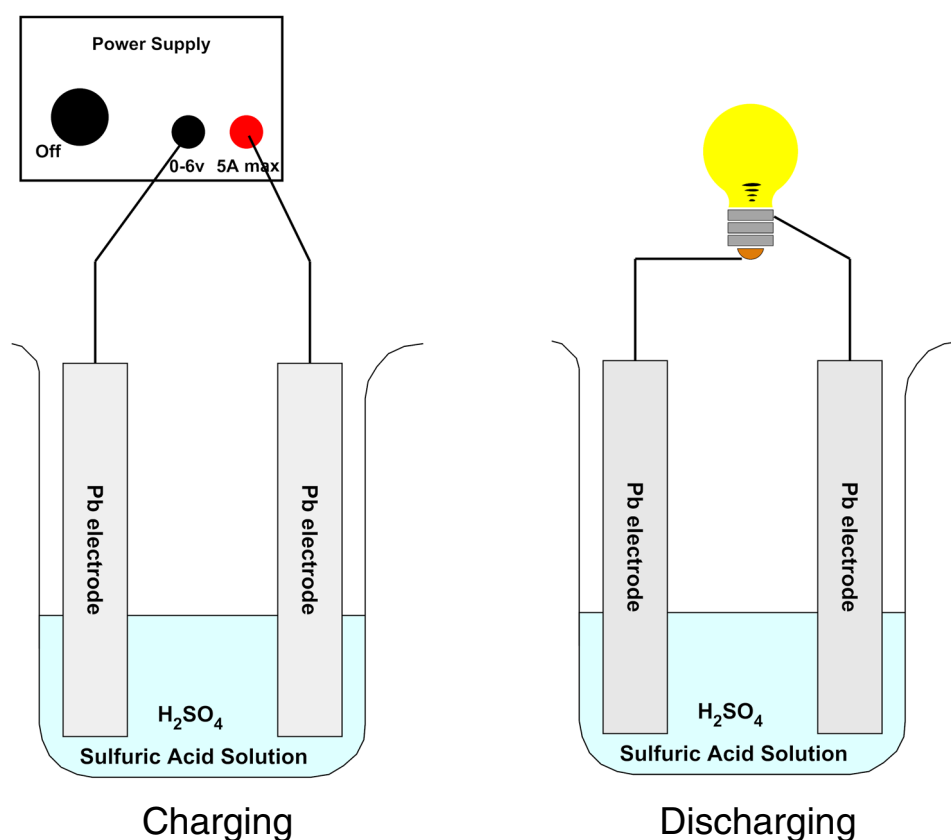


Note that the definitions of anode (site of oxidation) and cathode (site of reduction) are the same as in a voltaic cell, but the sign assigned to the electrodes is different. Since electrons are being pumped in during the electrolysis process, the negative electrode is now the cathode. During discharge, the cell reactions are reversed; the cell is a voltaic cell; the positive electrode becomes the cathode (as it is in any voltaic cell.).

Electrolytic Cell Procedure

1. Take two lead electrodes and clean them with sandpaper. Place them carefully in a test tube and add concentrated H_2SO_4 until the acid level is just below the point at which the copper wires are attached. Write the reaction that occurs in your lab notebook.
2. Pour approximately 75 mL of 3 M H_2SO_4 into a 200 mL beaker and place a paper towel in the beaker with the acid.
3. Place the lead electrodes into the beaker, and use the alligator clips to connect them to the power supply as in the “Charging” diagram in Figure 7.3.
4. Use your voltmeter to adjust the charging voltage to approximately 3 volts.
5. Charge for 1 minute and measure the voltage with the voltmeter. After the voltage has been measured, briefly discharge the battery by touching the leads together for a moment.

FIGURE 7.3



6. Charge the battery in 30 second intervals and check the burn-time with the small lightbulb provided. That is, charge for 30 s then time the discharge with the bulb, then charge for 1 minute and time the discharge with the bulb. Repeat this until you complete a charge cycle of 5 minutes of charging time.
7. Make a graph of run-time vs. charge time. Is this a linear relationship?
8. Now, choose a variable to investigate. Design an experiment to investigate this variable and how it affects the run-time of the battery.

For this cell refer to “Questions and Data Interpretation” on page 43 for data work-up.

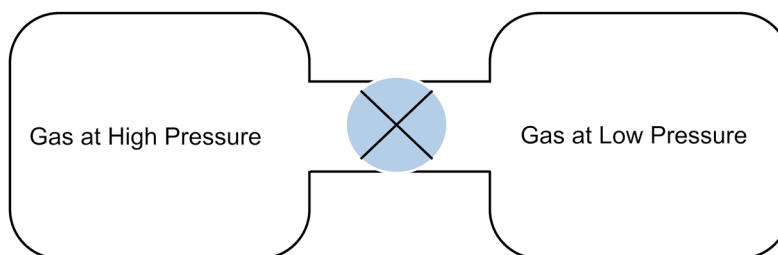
Concentration Cells

Concentration Cell Principles

In this experiment you will observe the effects of varying the concentration of a species participating in an electrochemical oxidation-reduction reaction both in a qualitative (Le Châtelier) and quantitative (Nernst equation) fashion.

If two identical cylinders contain the same gas at different pressures, and if the cylinders are connected, gas will flow from the cylinder at higher pressure to the one at lower pressure (Figure 7.4). If a gas turbine is connected between the cylinders, the system will turn the turbine and produce useful work until the pressures are equal.

FIGURE 7.4

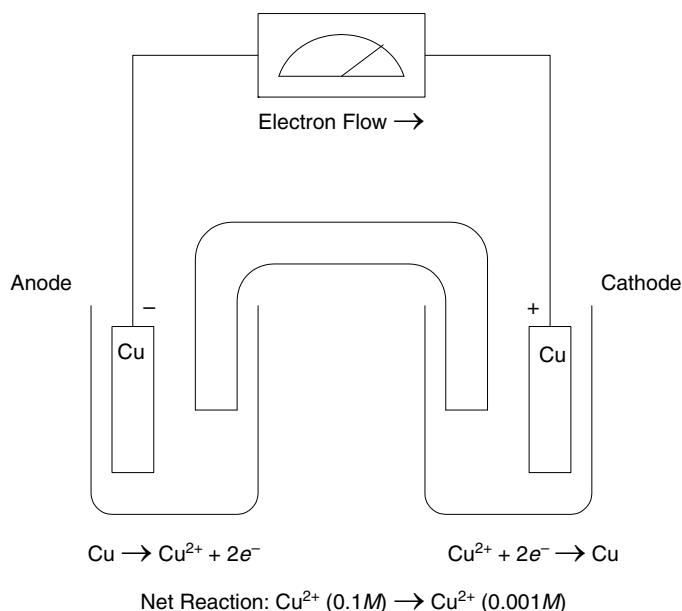


A parallel situation exists when two half-cells differing only in the concentration of one species are connected by a salt bridge

This cell, a concentration cell as in Figure 7.5 on page 42, will undergo the two half-reactions shown until (like the gas cylinders in Figure 7.4) the concentrations of Cu^{2+} (like the gas pressures) are equal. Actually, the activities of Cu^{2+} must be identical, but it is not a bad approximation to consider the solutions ideal, with concentrations equaling activities.

Refer to “Questions and Data Interpretation” on page 43 for data work-up.

FIGURE 7.5



When an electrochemical cell contains species that are not at unit activities (approximately 1 *M* for dissolved species and 1 atm for gases), the cell voltage, *E*, can be found from the **Nernst equation**. For the hypothetical reaction



Equation 7.10 can be written.

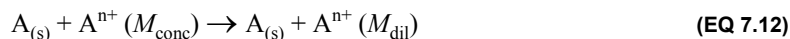
$$E = E^{\circ} - R \frac{T}{nF} \ln \frac{[C]^p [D]^q}{[A]^r [B]^s} \quad (\text{EQ 7.10})$$

where *R* = the gas constant, 8.314 J/molK; *T* = temperature (in kelvins); *n* = number of electrons transferred for the species indicated in the equation; and *F* = Faraday's constant, 96487 C/mol or 96487 J/Vmol.

When the temperature is 298.15 K and natural logarithms are converted to common logarithms (In *x* = 2.303 log₁₀ *x*), Equation 7.10 becomes,

$$E = E^{\circ} - \frac{0.0592}{n} \log \frac{[C]^p [D]^q}{[A]^r [B]^s} \quad (\text{EQ 7.11})$$

In a concentration cell the reaction is simply the equivalent of mixing the more concentrated solution with the more dilute solution:



Since the two half-reactions are the same, $E^{\circ}_{\text{anode}} = E^{\circ}_{\text{cathode}}$, so that $E^{\circ} = 0$ and the Nernst equation becomes simply

$$E = -\frac{0.0592}{n} \log \frac{[A^{n+} M_{\text{dil}}]}{[A^{n+} M_{\text{conc}}]} \quad (\text{EQ 7.14})$$

Concentration Cell Procedure

- Set up a simple concentration cell by using a Cu 0.1M Cu(NO₃)₂ half-cell such as that prepared for the “Voltaic Cells Procedure” on page 37, and a second half-cell prepared as follows.
 - Take 25 to 30 mL (the same volume as before) of 0.1 M KNO₃ solution and add exactly 1 drop of 0.1 M Cu(NO₃)₂ solution to this solution.
 - Clean a Cu strip with sandpaper and insert it into the beaker. Connect the two half-cells by a salt bridge and measure the cell voltage.
- Now add 11 drops of 0.1 M Na₂S solution to the second, more dilute, half-cell. Since CuS is very insoluble, the addition of Na₂S has the effect of decreasing [Cu²⁺] to an extremely small value.
- Measure the cell voltage again. Diagram the cell as with the others, labeling the electrode signs and processes. Measure the temperature of the solutions.

Questions and Data Interpretation

Voltaic Cells Data

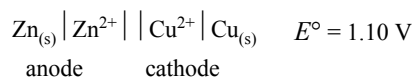
Part A. Chemical reaction in the single-cell setup (Figure 7.1):

- Label all electrodes, processes, and signs in Figure 7.1. Show the direction of electron flow and initial cell voltage
- Record the appearance of cell after discharge, and explanation of this appearance.
- Record the final cell voltage. Explain why it has changed. If it is not zero, explain why it will eventually become zero.

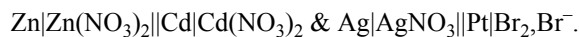
Part B. For each pair of half-cells label all items shown in Figure 7.2: electrode names, direction of electron flow, half-cell reactions, and ion transport across the salt bridge. Show the observed voltage and the voltmeter signs for each cell. Reproduce this drawing in your laboratory notebook for each cell. Use the handout to report the findings that you recorded in your notebook.

Voltaic Cells Data Interpretation

- For each cell in “Part B” on page 37 calculate E° from a textbook table of half-cell potentials. Compare your values with those observed. If all your solutions were 0.1 M, the net difference between your observed E and E° should be negligible.
- The cell in Figure 7.1 on page 36 can be described as follows:



Calculate the cell potential of the following cells, using *both* your data and a textbook table of half-cell potentials. Include signs for each E°



Note: E° is positive if electrons flow from left to right in the external wire. Here vertical lines represent a phase boundary, and double vertical lines represent a salt bridge.

Voltaic Cells Questions

1. Is it necessary for you to take into account how many electrons are transferred per atom or ion when calculating a cell potential E°_{cell} ?
2. Would the cell voltage change significantly if the right-hand half-cells contained twice their volume of a solution of the same concentration? Why? What if each electrode were made from cylindrical wires instead of flat sheets?
3. Why do you suppose your observed cell voltages are usually less than calculated E° values? (Do not assume that meter inaccuracy is a satisfactory reason.)

Electrolytic Cell Data

1. What is the voltage of the Pb cell after steps 1-5 in the procedure, "Electrolytic Cell Procedure" on page 40 has been completed?
2. Does the run-time vs. charge time graph appear to be linear? How did you assess the linearity?
3. Briefly describe the variable that you investigated and how it affected burn time.
4. During discharge of a lead storage cell, does $[\text{H}_2\text{SO}_4]$ increase or decrease? How can the density (or specific gravity) of the solution indicate the state of discharge of the cell? '
5. If Na_2SO_4 were used instead of H_2SO_4 could the cell function? What if HNO_3 were substituted for H_2SO_4 ? Why? (Hint: Consult a solubility table.)
6. Re-write the table below in your report, and fill in the blanks:

TABLE 7.3

Cell Type	Process	ΔG°	Negative Electrode	Positive Electrode
Voltaic	Discharge	Less than 0 (Spontaneous)	Anode (Oxidation)	Cathode ()
Electrolytic	()	() than 0 ()	() ()	() ()

Concentration Cell Data

1. Record the cell voltage and observed changes in the cell upon addition of the Na_2S solution. Record the voltage after the addition of the Na_2S solution. Be sure to diagram the cell as in each of the previous parts: showing electrode signs, electrode processes, etc.
2. One drop has a volume of about 0.05 mL, thus the concentration of Cu^{2+} in the dilute half-cell is about $(0.05 \text{ mL}/25 \text{ mL})(0.1 \text{ M}) = 2 \times 10^{-4} \text{ M}$. Use Equation 7.14 to calculate it at 298 K and compare it with your observed value. Why might they differ?
3. After adding 11 drops (0.5 mL) of Na_2S solution, $[\text{S}^{2-}]$ is about $(0.5 \text{ mL}/25 \text{ mL})(0.1 \text{ M}) = 2 \times 10^{-3} \text{ M}$. Calculate $[\text{Cu}^{2+}]$ from the solubility product constant:

$$K_{\text{sp}} = 8 \times 10^{-37} = [\text{Cu}^{2+}][\text{S}^{2-}] \quad (\text{EQ 7.15})$$

Then calculate E and again compare it with the E observed after you added Na_2S solution to the dilute Cu^{2+} half-cell.

4. Suppose you had solutions 1 M in $\text{Hg}(\text{NO}_3)_2$ and Na_2S available. $K_{\text{sp}} \text{HgS} = 1.6 \times 10^{-34}$. What is the highest E you could achieve with a $\text{Hg}-\text{Hg}^{2+}$ concentration cell? What would be the constituents of each half-cell? Neglect the fact that S^{2-} hydrolyzes extensively in water.

