Experiment 17

Electrochemical Cells and Thermodynamics

OBJECTIVE

To become familiar with some fundamentals of electrochemistry, including the Nernst equation, by constructing electrochemical (voltaic) cells and measuring their potentials at various temperatures. The quantities ΔG, ΔH, and ΔS are calculated from the temperature variation of the measured emf.

APPARATUS AND CHEMICALS

Apparatus

- DC voltmeter or potentiometer (to measure mV)
- emery cloth
- 600 mL beaker
- thermometer
- glass stirring rods (3)
- Bunsen burner and hose clamps (2)
- alligator clips and lead wires (2 sets)
- 50 mL test tubes (3)
- glass U-tubes (to fit large test tubes) (3)
- cotton
- ring stand, two iron rings, and wire gauze
- test tube clamps (2)

Chemicals

- 1 *M* $Pb(NO_3)_2$
- 1 *M* $SnCl_2$
- lead, tin, and copper strips or wire
- 1 *M* $Cu(NO_3)_2$
- 0.1 *M* KNO_3
- ice
- agar

DISCUSSION

BACKGROUND

Electrochemistry is that area of chemistry that deals with the relations between chemical changes and electrical energy. It is primarily concerned with oxidation-reduction phenomena. Chemical reactions can be used to produce electrical energy in cells that are referred to as *voltaic*, or galvanic, cells (🔗Section 20.3). Electrical energy, on the other hand, can be used to bring about chemical changes in what are termed *electrolytic* cells (🔗Section 20.9). In this experiment, you will investigate some of the properties of voltaic cells.

In principle, any spontaneous redox reaction can be used to produce electrical energy. This task can be accomplished by means of a voltaic cell, a device in which electron transfer takes place through an external circuit or pathway rather than directly between reactants. One such spontaneous reaction occurs when a strip of zinc is immersed in a solution containing Cu^{2+}. As the reaction proceeds, the blue color of the $Cu^{2+}(aq)$ ions begins to fade and metallic copper deposits on the zinc strip. At the same time, the zinc begins to dissolve. The redox reaction that occurs is given in Equation [1].

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s) \qquad [1]$$

Figure 17.1 shows a voltaic cell that utilizes the same reaction. The two solid metal strips connected by the external circuit are called electrodes (Figure 20.5). The electrode at which oxidation occurs is called the *anode*, and the electrode at which reduction occurs is called the *cathode*. The voltaic cell may be regarded as two "half-cells," one corresponding to the oxidation half-reaction and the other to the reduction half-reaction. Recall that a substance that loses electrons is said to be oxidized and a substance that gains electrons is said to be reduced. In the example below, Zn is oxidized and Cu^{2+} is reduced.

Anode (oxidation half-reaction) $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

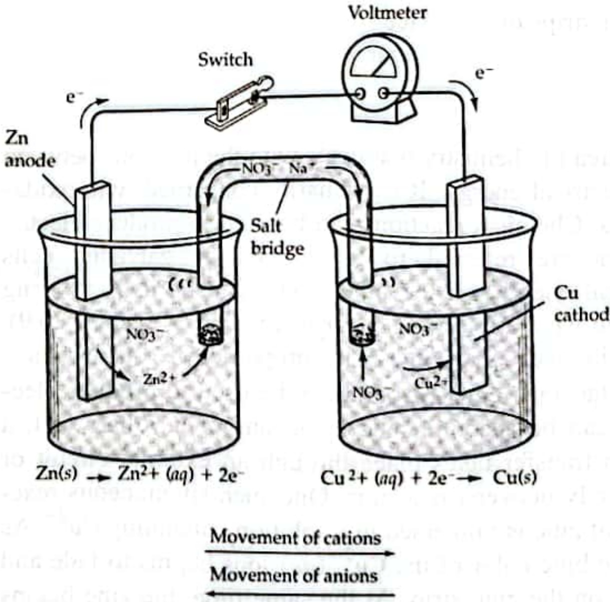
Cathode (oxidation half-reaction) $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Because Zn^{2+} ions are formed in one compartment and Cu^{2+} ions are depleted in the other compartment, a salt bridge is used to maintain electrical neutrality by allowing the migration of ions between these compartments.

The cell voltage, or electromotive force (*emf*), is indicated on the voltmeter in units of volts. The cell emf is also called the cell potential. The magnitude of the emf is a quantitative measure of the driving force or thermodynamic tendency for the reaction to occur. In general, the emf of a voltaic cell depends on the substances that make up the cell as well as on their concentration and temperature. Hence, it is a common practice to compare *standard cell potentials*, symbolized by E°_{cell} (Section 20.4). These potentials correspond to cell voltages under standard conditions: gases at 1 atm pressure; solutions at 1 *M* concentration and at 25 °C. For the Zn/Cu voltaic cell in Figure 17.1, the standard cell potential at 25 °C is 1.10 V.

$$Zn(s) + Cu^{2+}(aq, 1\,M) \longrightarrow Zn^{2+}(aq, 1\,M) + Cu(s) \qquad E^\circ_{cell} = 1.10\text{ V}$$

Recall that the superscript ° denotes standard state conditions (Section 20.4).



▲**FIGURE 17.1** A complete and functioning voltaic cell using a salt bridge to complete the electrical circuit.

The cell potential is the difference between two electrode potentials, one associated with the cathode and the other associated with the anode. By convention, the potential associated with each electrode is chosen to be the potential for reduction to occur at that electrode. Thus, standard electrode potentials are tabulated for reduction reactions, and they are denoted by the symbol, E°_{red}. The cell potential is given by the standard reduction potential of the cathode reaction, E°_{red} (cathode), *minus* the standard reduction potential of the anode reaction, E°_{red} (anode) as follows:

$$E^\circ_{cell} = E^\circ_{red}\,(\text{cathode}) - E^\circ_{red}\,(\text{anode}) \qquad [2]$$

Because it is not possible to directly measure the potential of an isolated half-cell reaction, the standard hydrogen reduction half-reaction, in which $H^+(aq)$ is reduced to $H_2(g)$ under standard conditions, has been selected as a reference (Section 20.4). It has been assigned a standard reduction potential of exactly 0 V.

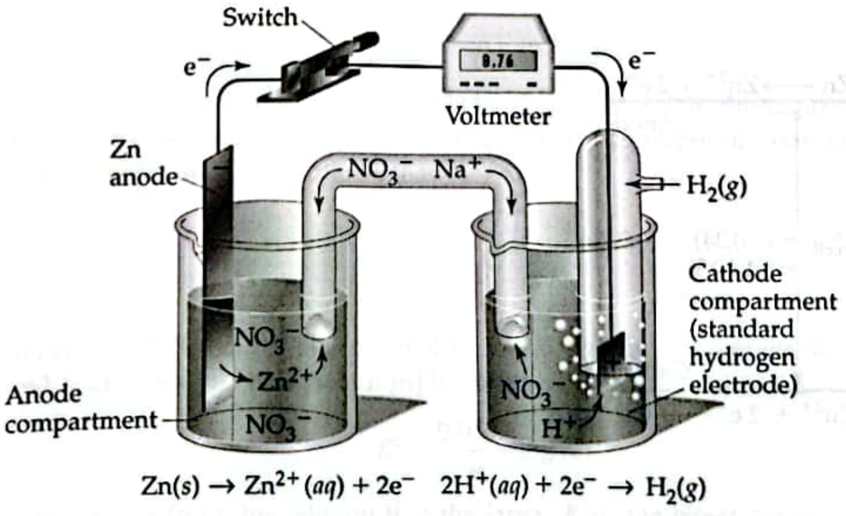
$$2H^+(aq,\ 1\ M) + 2e^- \longrightarrow H_2(g,\ 1\ \text{atm}) \qquad E^\circ_{red} = 0\ \text{V}$$

An electrode designed to produce this half-reaction is called the standard hydrogen electrode (SHE). Figure 17.2 shows a voltaic cell using a SHE and a standard Zn^{2+}/Zn electrode. The spontaneous reaction occurring in this cell is the oxidation of Zn and the reduction of H^+.

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

The standard cell potential for this cell is 0.76 V. By using the defined standard reduction potential of H^+ ($E^\circ_{red} = 0$ V) and Equation [2], you can determine the standard reduction potential for the Zn^{2+}/Zn half-reaction as follows:

$$E^\circ_{cell} = E^\circ_{red}\,(\text{cathode}) - E^\circ_{red}\,(\text{anode})$$
$$0.76\ \text{V} = 0\ \text{V} - E^\circ_{red}\,(\text{anode})$$
$$E^\circ_{red}\,(\text{anode}) = -0.76\ \text{V}$$



▲**FIGURE 17.2** Voltaic cell using a standard hydrogen electrode.

Thus, a standard reduction potential of −0.76 V can be assigned to the reduction of Zn^{2+} to Zn as follows:

$$Zn^{2+}(aq,\ 1\ M) + 2e^- \longrightarrow Zn(s) \qquad E^\circ_{red} = -0.76\ V$$

Notice that the reaction is written as a reduction even though it is "running in reverse" as an oxidation in the cell in Figure 17.2. Whenever you assign a potential to a half-cell reaction, you write the reaction as a reduction reaction.

Standard reduction potentials for other half-reactions can be established in a manner similar to that used for the $Zn^{2+} \mid Zn$ half-reaction. The table in Appendix H lists some standard reduction potentials. Example 17.1 illustrates how this method can be used to determine the standard reduction potential for the $Cu^{2+} \mid Cu$ half-reaction.

EXAMPLE 17.1

The cell in Figure 17.1 may be represented by the following cell notation:

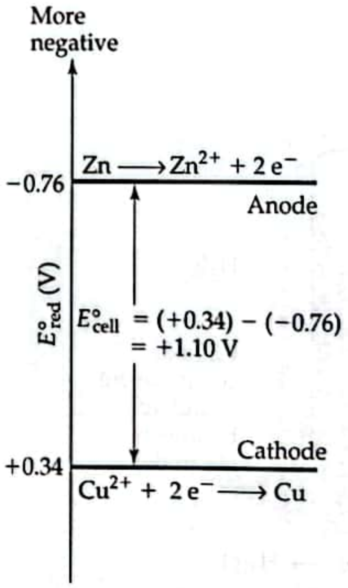
$$Zn \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu$$

The single bar represents the phase separation of the electrode from the solution. The double bar represents the salt bridge. The cell notation is generally written as | Anode || Cathode |. Given that E°_{cell} for this cell is 1.10 V, the Zn electrode is the anode, and the standard reduction potential of Zn^{2+} is −0.76 V, calculate the E°_{red} for the reduction of Cu^{2+} to Cu.

$$Cu^{2+}(aq,\ 1\ M) + 2e^- \longrightarrow Cu(s)$$

SOLUTION: Use Equation [2] and the information provided. See Figure 17.3.

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



▲FIGURE 17.3 Half-cell potentials and standard cell potential for the Zn-Cu voltaic cell.

The free-energy change, ΔG, associated with a chemical reaction is a measure of the driving force or spontaneity of the process. If the free-energy change of a process is negative, the reaction will occur spontaneously in the direction indicated by the chemical equation (Section 20.5).

The cell potential of a redox process is related to the free-energy change as follows:

$$\Delta G = -nFE \qquad [3]$$

In this equation, F is Faraday's constant, the electrical charge on 1 mol of electrons is

$$1F = 96{,}485\frac{\text{C}}{\text{mol e}^-} = 96{,}485\frac{\text{J}}{\text{V-mol e}^-}$$

and n represents the number of moles of electrons transferred in the reaction. When both reactants and products are in their standard states, Equation [3] takes the following form:

$$\Delta G^\circ = -nFE^\circ \qquad [4]$$

EXAMPLE 17.2

Calculate the standard free-energy change associated with the redox reaction $2\text{Ce}^{4+} + \text{Tl}^{+} \longrightarrow 2\text{Ce}^{3+} + \text{Tl}^{3+}$ ($E^\circ = 0.450$ V). Would this reaction occur spontaneously under standard conditions?

SOLUTION:

$$\begin{aligned}\Delta G^\circ &= -nFE^\circ \\ &= -(2 \text{ mol e}^-)\left(\frac{96{,}485 \text{ J}}{\text{V-mol e}^-}\right)(0.450 \text{ V}) \\ &= -86.9\times10^3 \text{ J} \\ &= -86.9 \text{ kJ}\end{aligned}$$

Because $\Delta G^\circ < 0$, this reaction would occur spontaneously.

The standard free-energy change of a chemical reaction is also related to the equilibrium constant for the reaction as follows:

$$\Delta G^\circ = -RT \ln K \qquad [5]$$

where R is the gas law constant (8.314 J/K-mol) and T is the temperature in Kelvin. Consequently, E° is also related to the equilibrium constant. From Equations [4] and [5], it follows that

$$-nFE^\circ = -RT \ln K$$

$$E^\circ = \frac{RT}{nF}\ln K \qquad [6]$$

When $T = 298$ K, $\ln K$ is converted to $\log K$, and the appropriate values of R and F are substituted, Equation [6] becomes

$$E^\circ = \frac{0.0592}{n}\log K \qquad [7]$$

You can see from this relation that the larger K is, the larger the standard cell potential will be.

In practice, most voltaic cells are not likely to be operating under standard state conditions. It is possible, however, to calculate the cell emf, E, under nonstandard state conditions with a knowledge of $E°$, temperature, and concentrations of reactants and products as follows:

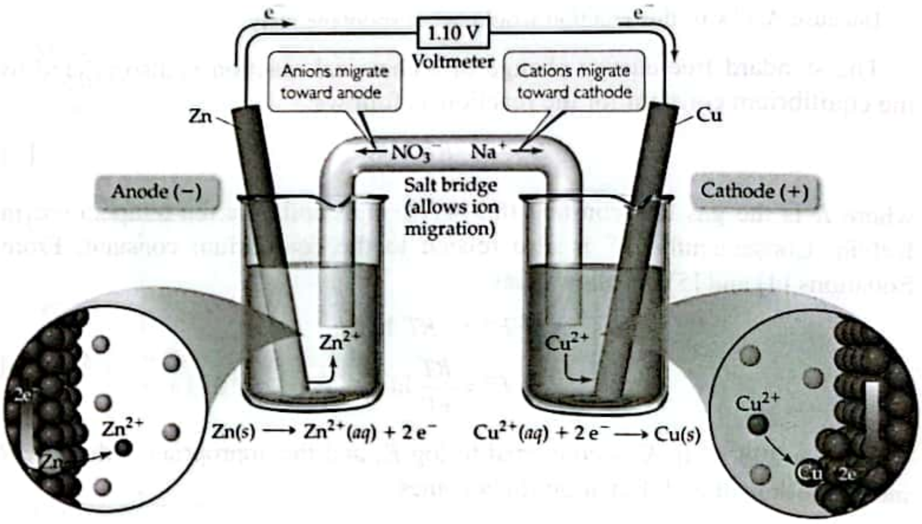
$$E = E° - \frac{0.0592}{n} \log Q \qquad [8]$$

Q is called the reaction quotient; it has the form of an equilibrium constant expression, but the concentrations used to calculate Q are not equilibrium concentrations. The relationship given in Equation [8] is referred to as the Nernst equation (see Example 17.3) (🔗Section 20.6).

Now consider the operation of the cell shown in Figure 17.1 in more detail. Earlier you saw that the reaction

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

is spontaneous. Consequently, it has a positive electrochemical potential ($E° = 1.10$ V) and a negative free energy ($\Delta G° = -nFE°$). As this reaction occurs, Cu^{2+} will be reduced and deposited as copper metal onto the copper electrode. The electrode at which reduction occurs is called the cathode. Simultaneously, zinc metal from the zinc electrode will be oxidized and go into solution as Zn^{2+}. The electrode at which oxidation occurs is called the anode. Effectively, then, electrons will flow in the external wire from the zinc electrode through the voltmeter to the copper electrode and be given up to copper ions in solution. These copper ions will be reduced to copper metal and plate out on the copper electrode. Concurrently, zinc metal will give up electrons to become Zn^{2+} ions in solution. These Zn^{2+} ions will diffuse through the salt bridge into the copper solution and replace the Cu^{2+} ions that are being removed. See Figure 17.4.



▲**FIGURE 17.4** Voltaic cell indicating movement of electrons and ions.

EXAMPLE 17.3

Calculate the cell potential for the cell

$$\mathrm{Zn}\,|\,\mathrm{Zn}^{2+}(0.60\ M)\,||\,\mathrm{Cu}^{2+}(0.20\ M)\,|\,\mathrm{Cu}$$

given the following:

$$\mathrm{Cu}(aq)^{2+} + \mathrm{Zn}(s) \longrightarrow \mathrm{Cu}(s) + \mathrm{Zn}(aq)^{2+} \qquad E^\circ = 1.10\ \mathrm{V}$$

(HINT: Recall that Q includes expressions for species in solution but not for pure solids.)

SOLUTION:

$$\begin{aligned} E &= E^\circ - \frac{0.0592}{n}\log\frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Cu}^{2+}]} \\ &= 1.10\ \mathrm{V} - \frac{0.0592}{2}\log\frac{[0.60]}{[0.20]} \\ &= 1.10 - 0.014 \\ &= 1.086 \\ &= 1.09\ \mathrm{V} \end{aligned}$$

You can see that changes in concentrations have small effects on the cell emf because of the log term in the above equation.

A list of the properties of electrochemical cells and some definitions of related terms are given in Table 17.1.

Chemists have developed a shorthand notation for electrochemical cells, as shown in Example 17.1. The notation for the Cu-Zn cell that explicitly shows concentrations is as follows:

$$\underset{\substack{\text{Anode}\\ \text{(oxidation)}}}{\mathrm{Zn}\,|\,\mathrm{Zn}^{2+}(xM)}\,||\,\underset{\substack{\text{Cathode}\\ \text{(reduction)}}}{\mathrm{Cu}^{2+}(yM)\,|\,\mathrm{Cu}}$$

In this notation, the anode (oxidation half-cell) is written on the left and the cathode (reduction half-cell) is written on the right.

Your objective in this experiment is to construct a set of three electrochemical cells and to measure their cell potentials. With a knowledge of two half-cell potentials and the cell potentials obtained from your measurements, you will calculate the other half-cell potentials and the equilibrium constants for the reactions. By measuring the cell potential as a function of temperature, you may also determine the thermodynamic constants, ΔG, ΔH, and ΔS, for the reactions. This can be done with the aid of Equation [9].

$$\Delta G = \Delta H - T\Delta S \qquad [9]$$

ΔG may be obtained directly from measurements of the cell potential using the following relationship:

$$\Delta G = -nFE$$

TABLE 17.1 Summary of Properties of Electrochemical Cells and Some Definitions

Voltaic cells: $E > 0$, $\Delta G < 0$; reaction spontaneous, K large (greater than 1)
Electrolytic cells: $E < 0$, $\Delta G > 0$; reaction nonspontaneous, K small (less than 1)
Anode: electrode at which oxidation occurs
Cathode: electrode at which reduction occurs
Oxidizing agent: species accepting electrons to become reduced
Reducing agent: species donating electrons to become oxidized

A plot of ΔG versus temperature in Kelvin will give $-\Delta S$ as the slope and ΔH as the intercept. A more accurate measure of ΔH can be obtained, however, by substituting ΔG and ΔS back into Equation [9] and calculating ΔH.

EXAMPLE 17.4

For the voltaic cell

$$\mathrm{Pb}\,|\,\mathrm{Pb}^{2+}(1\,M)\,||\,\mathrm{Cu}^{2+}(1\,M)\,|\,\mathrm{Cu}$$

the following data were obtained:

$$E = 0.464\ \mathrm{V} \qquad T = 298\ \mathrm{K}$$
$$E = 0.468\ \mathrm{V} \qquad T = 308\ \mathrm{K}$$
$$E = 0.473\ \mathrm{V} \qquad T = 318\ \mathrm{K}$$

Calculate ΔG, ΔH, and ΔS for this cell.

SOLUTION:

$$\Delta G = -nFE$$

At 298 K,

$$\Delta G = -(2\ \mathrm{mol\ e^-})(96{,}485\ \mathrm{J/V\text{-}mol\ e^-})(0.464\ \mathrm{V})(1\ \mathrm{kJ}/1000\ \mathrm{J})$$
$$= -89.5\ \mathrm{kJ}$$

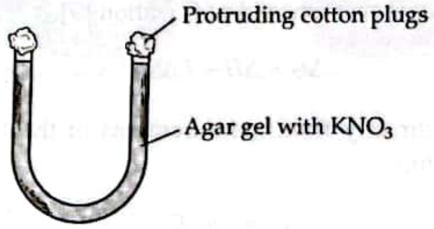
At 308 K,

$$\Delta G = -(2\ \mathrm{mol\ e^-})(96{,}485\ \mathrm{J/V\text{-}mol\ e^-})(0.468\ \mathrm{V})(1\ \mathrm{kJ}/1000\ \mathrm{J})$$
$$= -90.3\ \mathrm{kJ}$$

At 318 K,

$$\Delta G = -(2\ \mathrm{mol\ e^-})(96{,}485\ \mathrm{J/V\text{-}mol\ e^-})(0.473\ \mathrm{V})(1\ \mathrm{kJ}/1000\ \mathrm{J})$$
$$= -91.3\ \mathrm{kJ}$$

Because $\Delta G = \Delta H - T\Delta S$, a plot of ΔG versus T in Kelvin gives $\Delta H = -64.2$ kJ/mol and $\Delta S = 85.0$ J/mol-K.



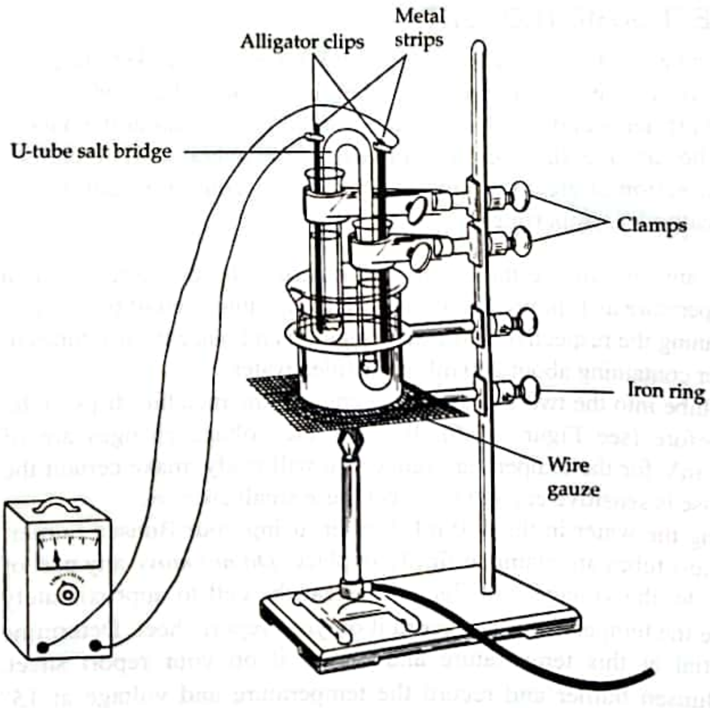
▲**FIGURE 17.5** U-tube salt bridge.

PROCEDURE

Before setting up pairs of half-cells, make a complete cell of the type shown in Figure 17.1 in the following manner illustrated in Figure 17.6: Place 30 mL of 1 M $Pb(NO_3)_2$ and 30 mL of 1 M $Cu(NO_3)_2$ in separate large test tubes. Obtain a lead strip and a copper strip and clean the surfaces of each with emery cloth or sandpaper. Boil 100 mL of 0.1 M KNO_3. Remove this solution from the heat and add to the boiling solution 1 g of agar, stirring constantly until all of the agar dissolves. Invert a U-tube and fill the U-tube with this solution before it cools, leaving about a half inch of air space at each end of the U-tube as shown in Figure 17.5. The cotton plugs must protrude from the ends of the U-tube. Construct two additional agar-filled U-tubes in the same manner. Place a U-tube in the test tubes as a salt bridge, as shown in Figure 17.6.

Insert the lead strip into the $Pb(NO_3)_2$ solution and the copper strip into the $Cu(NO_3)_2$ solution. Obtain a voltmeter and attach the positive lead to the copper strip and the negative lead to the lead strip using alligator clips. Read the voltage. Check that the alligator clips make good contact with the metal strips. Record this voltage and the temperature of the cells on your report sheet. If your measured potential is negative, reverse the wire connection. Now construct the following cells and measure their voltages in the same manner.

$$\mathrm{Sn}\,|\,\mathrm{Sn}^{2+}(1\,M)\,||\,\mathrm{Cu}^{2+}(1\,M)\,|\,\mathrm{Cu}$$
$$\mathrm{Pb}\,|\,\mathrm{Pb}^{2+}(1\,M)\,||\,\mathrm{Sn}^{2+}(1\,M)\,|\,\mathrm{Sn}$$



▲**FIGURE 17.6** Electrochemical reaction apparatus.

GIVE IT SOME THOUGHT

a. In the cells you constructed, which half-reaction occurs at the anode?
b. Which half reaction occurs at the cathode?
c. Explain your choice.
d. In each of these cells, do you observe a spontaneous reaction?
e. How can you observe this experimentally?

GIVE IT SOME THOUGHT

Consider the cell illustrated in Figure 17.4

a. Do the concentrations of $Cu^{2+}(aq)$ and $Zn^{2+}(aq)$ increase, decrease, or remain the same as the reaction proceeds?
b. Does the mass of the $Cu(s)$ and $Zn(s)$ increase, decrease, or remain the same as the reaction proceeds?
c. Why do the concentrations and masses change?

Record the voltage and temperature of each cell on your report sheet. From the measured voltages, calculate the half-cell potentials for the lead and tin half-cells and the equilibrium constants for these two reactions. In these calculations, use $E° = 0.34$ V for the $Cu^{2+} | Cu$ couple.

GIVE IT SOME THOUGHT

Describe a voltaic cell consistent with Figure 17.1 by sketching each voltaic cell. In your sketch, label the anode and cathode compartments and indicate the half-reaction occurring at the anode and the cathode, the overall cell reaction, the overall cell potential, the direction of electron flow, and the ions present in the anode and cathode compartments.

Now choose any one of the three cells and measure the cell potential as a function of temperature as follows: Insert the metal strips into each of two 50 mL test tubes containing the respective 1 *M* cation solution and place the test tubes in a 600 mL beaker containing about 200 mL of distilled water.

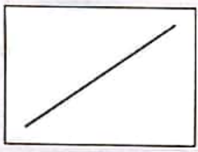
Place the U-tube into the two test tubes and connect the metallic strips to the voltmeter as before (see Figure 17.6). Because the voltage changes are of the order of 30 mV for the temperature range you will study, make certain the voltmeter you use is sensitive enough to detect these small changes.

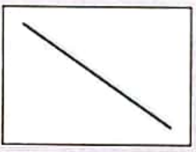
Begin heating the water in the 600 mL beaker, using your Bunsen burner. Make sure the test tubes are clamped firmly in place. *Do not move* any part of the cell; if you do, the voltage will fluctuate. Heat the cell to approximately 70 °C. Measure the temperature and record it on your report sheet. Determine the cell potential at this temperature and record it on your report sheet. Remove the Bunsen burner and record the temperature and voltage at 15° intervals as the cell cools to room temperature. Finally, replace the beaker of water with a beaker containing an ice-water mixture, being careful not to move the test tubes and their contents. After the cell has been in the ice-water mixture for about 10 min, measure the temperature of the ice-water mixture in the 600 mL beaker and record it and the cell potential. You have determined the cell potential at various temperatures. Calculate ΔG for the cell at each of these temperatures and plot ΔG versus temperature on the graph paper provided. The slope of the plot is $-\Delta S$. From the values of ΔG and ΔS, calculate ΔH at 298 K. If time permits, determine the temperature dependence of E for another cell.

GIVE IT SOME THOUGHT

a. Which variable would you plot on the x- and y-axis on your graph?

b. Rearrange Equation [9] ($\Delta G = \Delta H - T\Delta S$) into $y = mx + b$.
Which of the following graphs should yours resemble?





Dispose of the solutions in the test tubes and the agar containing U-tubes in the designated waste container.

Name ______________________________ Desk ______________

Date ______________ Laboratory Instructor ______________

Electrochemical Cells and Thermodynamics | 17 Pre-lab Questions

Before beginning this experiment in the laboratory, you should be able to answer the following questions.

1. Define the following terms: *faraday*, *salt bridge*, *anode*, *cathode*, *voltaic cell*, and *electrolytic cell.*

2. Write a chemical equation for the reaction that occurs in the following cell: $\mathrm{Cu} \mid \mathrm{Cu}^{2+}(aq) \parallel \mathrm{Ag}^{+}(aq) \mid \mathrm{Ag}$.

3. Given the following E's, calculate the standard-cell potential for the cell in question 2.

$$\mathrm{Cu}^{2+}(aq) + 2e^{-} \longrightarrow \mathrm{Cu}(s) \qquad E° = +0.34\ \mathrm{V}$$
$$\mathrm{Ag}^{+}(aq) + e^{-} \longrightarrow \mathrm{Ag}(s) \qquad E° = +0.80\ \mathrm{V}$$

4. Calculate the voltage of the following cell:

$$\mathrm{Zn} \mid \mathrm{Zn}^{2+}(0.10\,M) \parallel \mathrm{Cu}^{2+}(0.20\,M) \mid \mathrm{Cu}$$

5. Calculate the cell potential, the equilibrium constant, and the free-energy change for

$$\mathrm{Ca}(s) + \mathrm{Mn}^{2+}(aq)(1\,M) \rightleftharpoons \mathrm{Ca}^{2+}(aq)(1\,M) + \mathrm{Mn}(s)$$

given the following $E°$ values:

$$\mathrm{Ca}^{2+}(aq) + 2e^{-} \longrightarrow \mathrm{Ca}(s) \qquad E° = -2.87\ \mathrm{V}$$
$$\mathrm{Mn}^{2+}(aq) + 2e^{-} \longrightarrow \mathrm{Mn}(s) \qquad E° = -1.18\ \mathrm{V}$$

6. Would you normally expect ΔH° to be positive or negative for a voltaic cell? Justify your answer.

7. Predict whether the following reactions are spontaneous.

$Pd(aq)^{2+} + H_2(g) \longrightarrow Pd(s) + 2H(aq)^+$

$Pd(aq)^{2+} + 2e^- \longrightarrow Pd(s)$
$E^\circ = 0.987\ V$

$Sn(aq)^{4+} + H_2(g) \longrightarrow Sn(aq)^{2+} + 2H^+$

$Sn(aq)^{4+} + 2e^- \longrightarrow Sn(aq)^{2+}$
$E^\circ = 0.154\ V$

$Ni(aq)^{2+} + H_2(g) \longrightarrow Ni(s) + 2H(aq)^+$

$Ni(aq)^{2+} + 2e^- \longrightarrow Ni(s)$
$E^\circ = -0.250\ V$

$Cd(aq)^{2+} + H_2(g) \longrightarrow Cd(s) + 2H(aq)^+$

$Cd(aq)^{2+} + 2e^- \longrightarrow Cd(s)$
$E^\circ = -0.403\ V$

From your answers, decide which of the above metals could be reduced by hydrogen.

8. Identify the oxidizing agents and reducing agents in the reactions in question 7.

Name ____________________ Desk ____________________

Date ____________________ Laboratory Instructor ____________________

REPORT SHEET

Electrochemical Cells and Thermodynamics

EXPERIMENT

17

	Shorthand cell designation	*Temperature (℃)*	*E cell (measured)*	*ΔG (calculated)*	*K_{eq} (calculated)*
1.					
2.					
3.					

Show calculations for $\Delta G°$ and K_{eq} for an exemplary pair. For Pb | Pb^{2+} || Sn^{2+} | Sn:

	Half-cell equation	*E half-cell (calculated)*
1.		
2.		
3.		

Effect of Temperature on Cell Potential

Cell designation: E (measured)	*Temperature (°C)*	*Temperature (K)*	*ΔG (calculated)*

ΔS determined from the slope of a plot of ΔG versus T ____________________

$\Delta H°$ calculated at 298 K ____________________ (show calculations)

Is the cell reaction endothermic or exothermic? ______________________

QUESTIONS

1. Write the net ionic equations that occur in the following cells:

   $Pb \mid Pb(NO_3)_2 \parallel AgNO_3 \mid Ag$

   $Zn \mid ZnCl_2 \parallel Pb(NO_3)_2 \mid Pb$

   $Pb \mid Pb(NO_3)_2 \parallel NiCl_2 \mid Ni$

2. Which of the following reactions will have the larger emf under standard conditions? Why?

$$CuSO_4(aq) + Pb(s) \rightleftharpoons PbSO_4(s) + Cu(s)$$
$$Cu(NO_3)_2(aq) + Pb(s) \rightleftharpoons Pb(NO_3)_2(aq) + Cu(s)$$

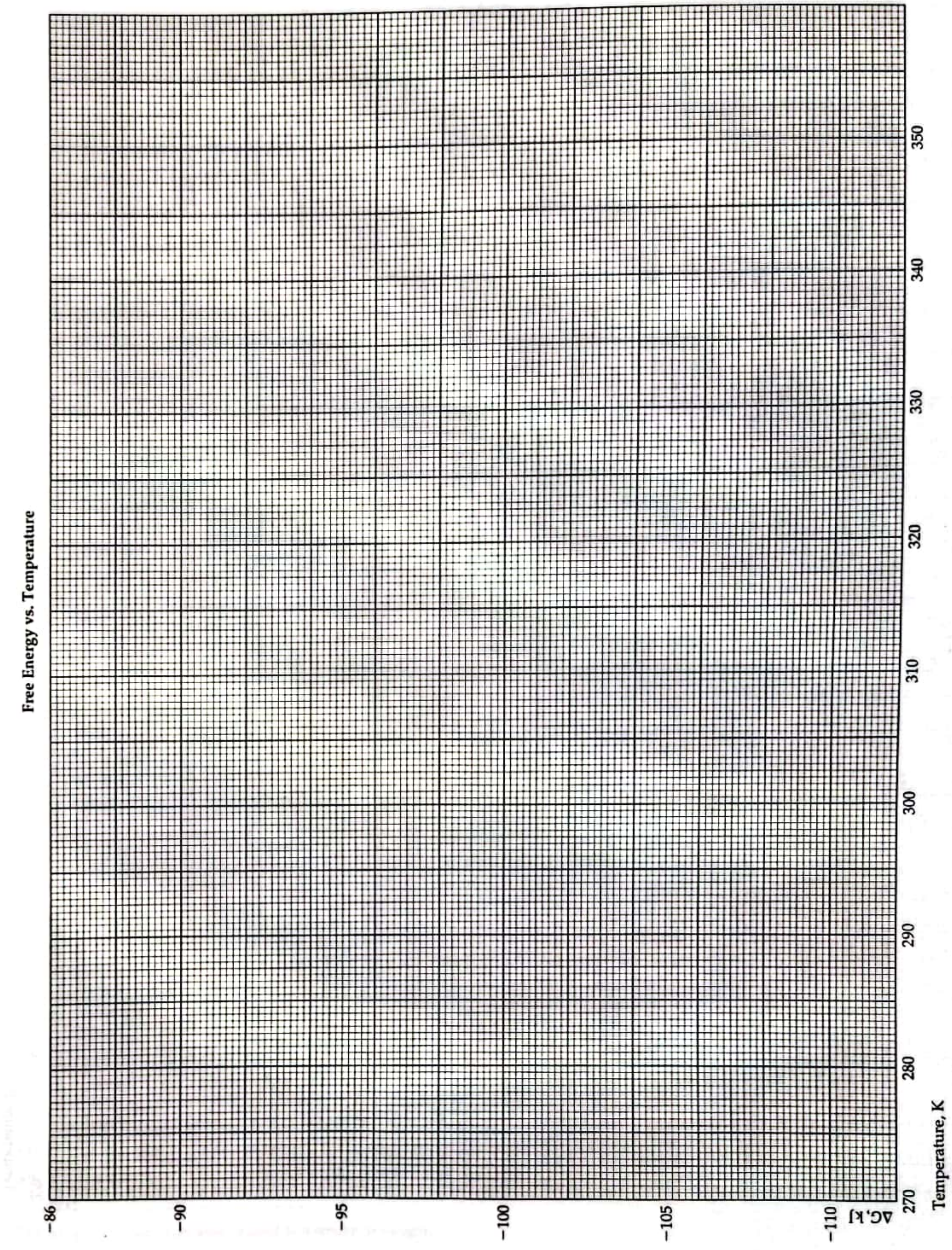
3. Calculate ΔG for the reaction in Example 17.3.

4. Voltages listed in textbooks and handbooks are given as *standard cell potentials* (voltages). What is meant by a standard cell? Were the cells constructed in this experiment standard cells? Why or why not?

5. As a standard voltaic cell runs, it "discharges" and the cell potential decreases with time. Explain.

6. Using standard potentials given in the appendices, calculate the standard cell potentials and the equilibrium constants for the following reactions:

$$Cu(s) + 2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$$
$$Zn(s) + Fe^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Fe(s)$$


Free Energy vs. Temperature
ΔG, kJ
−86
−90
−95
−100
−105
−110
Temperature, K
270
280
290
300
310
320
330
340
350