EXPERIMENT C4: ELECTROCHEMISTRY

Learning Outcomes

Upon completion of this lab, the student will be able to:

1) Construct an electrochemical cell.
2) Measure the cell potential for an electrochemical cell.
3) Calculate the free energy change for an electrochemical cell using the measured cell potential value.

Introduction

Oxidation is the loss of electrons and reduction is the gain of electrons. These processes occur simultaneously in reactions referred to as redox reactions. A voltaic cell uses a spontaneous redox reaction to generate electrical energy. An electrolytic cell uses electrical energy to drive a non-spontaneous reaction.

Both of these cells use two electrodes that are placed in an electrolyte solution. The anode is the electrode where the oxidation half reaction takes place and the cathode is the electrode where the reduction half reaction takes place. Each half-reaction takes place in its own half-cell and the two half reactions are physically separated. An external circuit connects the half-cells and a salt bridge used to maintain electrical neutrality completes the circuit.

The potential difference between the anode and the cathode in a cell is known as the electromotive force or EMF of the cell. It is also referred to as the cell potential and is denoted the symbol E_{cell}.

Consider for instance a cell constructed using zinc and copper electrodes. The standard reduction potentials for these two electrodes are given below.

$Zn^{2+}_{(aq)} + 2e^{-} \rightarrow Zn_{(s)}$ $E°_{RED} = -0.76$ V
$Cu^{2+}_{(aq)} + 2e^{-} \rightarrow Cu_{(s)}$ $E°_{RED} = +0.34$ V

A spontaneous redox reaction will result when the electrode with the higher reduction potential undergoes reduction reaction. Since the copper electrode has the higher reduction potential, it is the electrode that becomes reduced and is therefore at the cathode and consequently the zinc electrode is at the anode.

The two half reactions and the overall cell reaction in this instance may be written as follows:

Cathode: $Cu^{2+}_{(aq)} + 2e^{-} \rightarrow Cu_{(s)}$
Anode: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^{-}$

Overall: $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

The cell potential, $E°_{cell}$ is given by:

$$E°_{cell} = E°_{RED}(\text{cathode}) - E°_{RED}(\text{anode}) \qquad \text{Equation 1}$$

According to Equation 1, the cell potential for the electrochemical cell that results in a spontaneous redox reaction using zinc and copper electrodes is given by:

$$E°_{cell} = 0.34 - (-0.76) = 1.10 \text{ V}$$

A schematic representation of this cell is given below in Figure 1.

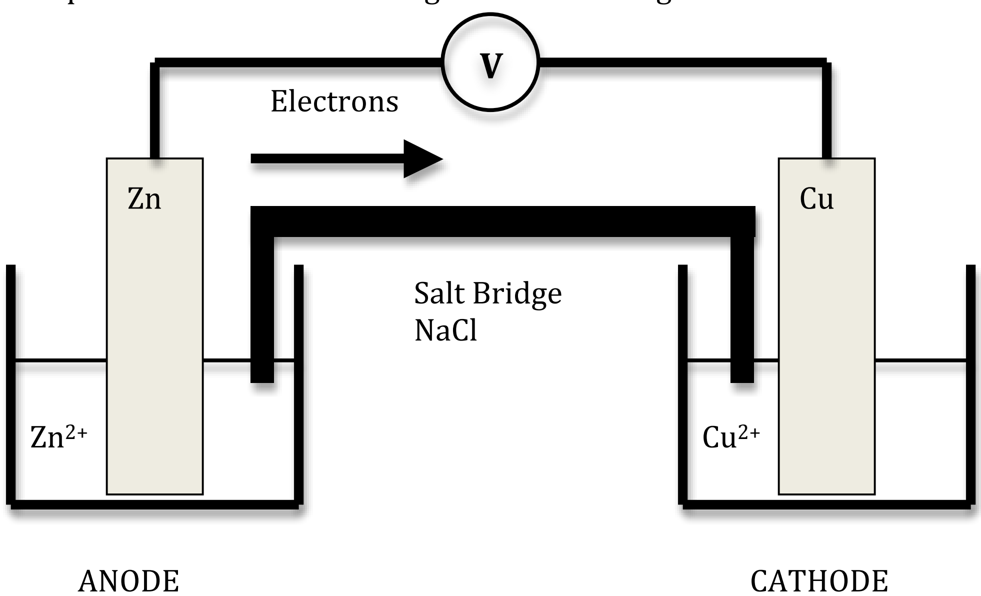

FIGURE 1: ELECTROCHEMICAL CELL

The line diagram for the electrochemical cell shown in Figure 1 is written as follows:

$$Zn|Zn^{2+}||Cu^{2+}|Cu$$

Under standard conditions, the molarities of the electrolyte solutions are assumed to be 1M and the standard temperature is assumed to be room temperature, 25°C or 298 K. The cell potential calculated under these conditions is the standard cell potential $E°_{cell}$ given by Equation 1.

However, if the concentrations of the electrolyte solutions are different from 1M, the non-standard cell potential, E, is calculated using the Nernst Equation, given in Equation 2.

$$E = E^{\circ} - \frac{0.0592}{n}\log Q \qquad \text{Equation 2}$$

In Equation 2, “n” is the number of electrons transferred from the anode to the cathode in the redox process and Q is the reaction quotient. In the example shown above for the zinc/copper electrochemical cell, n = 2 and Q is obtained from the overall cell equation.

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

The free energy change for a redox reaction is related to the cell potential according to Equation 3 below.

$$\Delta G = -nFE \qquad \text{Equation 3}$$

In Equation 3, ΔG is the free energy change and “F” is the Faraday’s constant (96,485 Coulombs/mol).

Experimental Design

Several electrochemical cells will be constructed and the cell potential of each cell will be measured using a voltmeter. The free energy change of the cell will then be calculated from the measured value of the cell potential.

Reagents and Supplies

Zinc, copper, and silver electrodes, 0.2 M solutions of Zn^{2+}, Cu^{2+}, Ag^{+}, 2 M ammonium nitrate

Electrochemical cell kit (from the stockroom)

(See posted Material Safety Data Sheets)

Procedure

1. Obtain an Electrochemical Cell kit from the stockroom. Make sure that the electrodes are sanded.

2. Construct the cell using the following procedure:

    a. Insert the two medicine droppers into the two holes of the provided rubber stopper.

    b. Place a small piece of cotton plug at the tip of each medicine dropper.

    c. Place the electrode inside the medicine dropper and surround the electrode with the appropriate electrolyte solution.

    d. Place the medicine dropper and the stopper set up on a plastic cup containing aqueous ammonium nitrate solution.

    e. The entire set up should look similar to that shown in Figure 2 below.

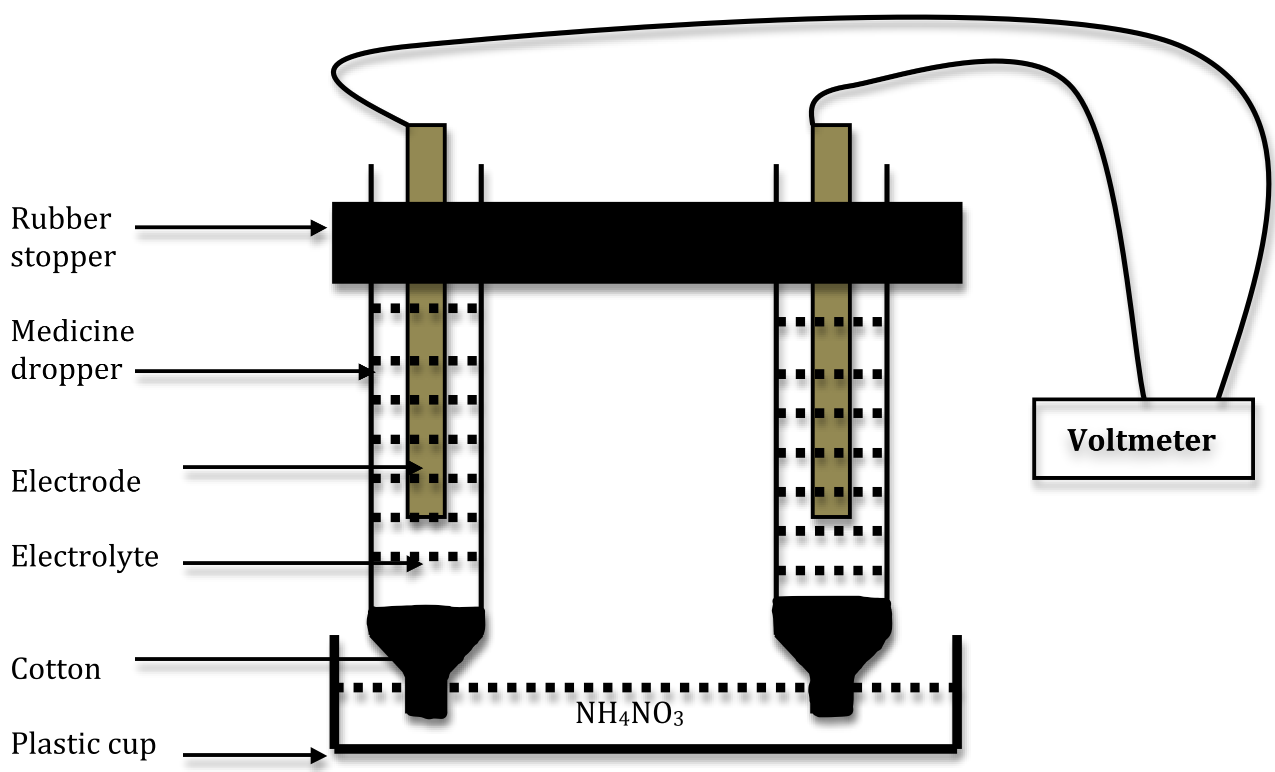

FIGURE 2: ELECTROCHEMICAL CELL, LABORATORY SETUP

f. Construct each cell shown in Table 1 below.

Cell Number	Cell Notations
1	$Zn|Zn^{2+}(0.20M)||Cu^{2+}(0.20M)|Cu$
2	$Cu|Cu^{2+}(0.20M)||Ag^{+}(0.20M)|Ag$
3	$Zn|Zn^{2+}(0.20M)||Ag^{+}(0.20M)|Ag$
4	$Zn|Zn^{2+}(0.20M)||Cu^{2+}(0.010M)|Cu$
5	$Zn|Zn^{2+}(0.010M)||Cu^{2+}(0.20M)|Cu$
6	$Zn|Zn^{2+}(0.20M)||Ag^{+}(0.010M)|Ag$
7	$Zn|Zn^{2+}(0.010M)||Ag^{+}(0.20M)|Ag$

g. NOTE: In cells 1, 2, and 3 the 0.2 M solutions of electrolytes provided may be used as is.

h. NOTE: In cells 4 – 7, 0.01 M solutions of electrolytes are needed. In order to prepare these solutions, add ONE drop of 0.2 M solution to 19 drops of deionized water.

i. NOTE: Replace the cotton and NH_4NO_3 for each cell.

3. Measure the cell potential of each constructed electrochemical cell to the nearest millivolt.

4. Repeat the entire experiment to obtain a duplicate set of readings.

5. Discard all the waste into a large waste beaker. Empty the contents of the waste beaker into a waste container provided by the instructor.

Data Table

Cell Number	**E_{cell} (V)**	
	Trial 1	**Trial 2**
1		
2		
3		
4		
5		
6		
7		

Data Analysis

1. **<u>Calculation of theoretical values of E_{cell} & ΔG:</u>** For each write the cathode and anode half-reactions and the overall reactions. Refer to tables of standard reduction potentials and calculate the standard cell potential. Using Equation 2, calculate the non-standard cell potential E, based on the concentrations used in the experiment. Also calculate ΔG for each cell using Equation 3. Cell number 1 is shown below as an example.

<u>Cell Number 1: Zn|Zn^{2+}(0.20M)||Cu^{2+}(0.20M)|Cu</u>

Cathode:	$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$	$E°_{RED} = +0.34$ V
Anode:	$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$	$E°_{RED} = -0.76$ V
Overall:	$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$	$E°_{cell} = 0.34 - (-0.76) = 1.10$ V

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{0.20}{0.20} = 1$$

$$E = E^\circ - \frac{0.0592}{n}\log Q = 1.10 - \frac{0.0592}{2}\log(1) = 1.10V$$

$\Delta G = -nFE = -2 \times 96485 \times 1.10 = -212267$ J/mol $= -212$ kJ/mol

<u>Cell Number 2: Cu|Cu^{2+}(0.20M)||Ag^+(0.20M)|Ag</u>

Cell Number 3: $Zn|Zn^{2+}(0.20M)||Ag^{+}(0.20M)|Ag$

Cell Number 4: $Zn|Zn^{2+}(0.20M)||Cu^{2+}(0.010M)|Cu$

Cell Number 5: $Zn|Zn^{2+}(0.010M)||Cu^{2+}(0.20M)|Cu$

<u>Cell Number 6: $Zn|Zn^{2+}(0.20M)||Ag^{+}(0.010M)|Ag$</u>

<u>Cell Number 7: $Zn|Zn^{2+}(0.010M)||Ag^{+}(0.20M)|Ag$</u>

2. Determine the experimental value of ΔG for each cell using Equation 2 and the experimental value of E_{cell} (average from two trials).

Cell Number	**Experimental ΔG kJ/mol**
1	
2	
3	
4	
5	
6	
7	
8	

3. Enter the experimental (average from two trials) and theoretical values of E_{cell} and ΔG for each cell and calculate the percent error in the experimental value in each case.

Cell Number	E_{cell}, V (experimental)	E_{cell} V (calculated)	ΔG, kJ/mol (experimental)	ΔG, kJ/mol (calculated)	Percent error
1					
2					
3					
4					
5					
6					
7					

4. Using the zinc/copper cell diagram shown in Figure 1 as an example, draw labeled diagrams for the other two cells used in this experiment.

Copper/Silver Cell

Zinc/Silver Cell