

EXPERIMENT IV

Oxidation-Reduction Reactions

PURPOSE: Determine the cell voltage for several oxidation-reduction reactions and determine how concentration and pH affect the potential (free energy) of these reactions.

INTRODUCTION:

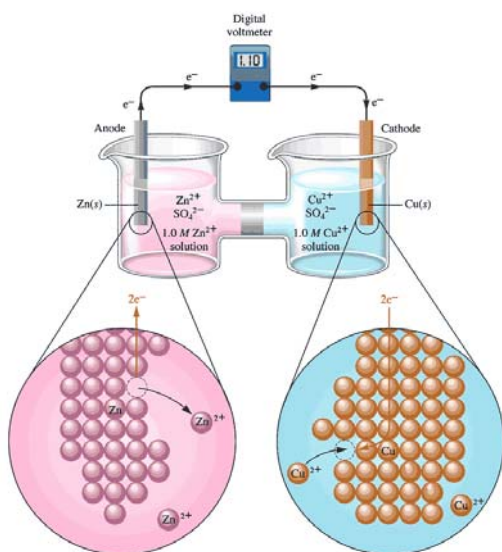
This experiment is related to material that will be covered in lecture over the next few weeks. The goal of the exercises is to provide practical experience with electrochemical cells, to give some background knowledge for the concepts and calculations introduced in lecture.

To accomplish this, you will:

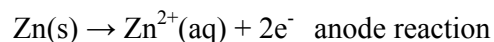
- Construct an electrochemical cell
- Learn to use your pH meter is a voltmeter;
- Measure the cell voltages of several electrochemical cells;
- Determine the effect of pH on cell voltage;
- Determine the effect of concentration on cell voltage;
- Determine K_{sp} for a salt by an electrochemical approach

Part 1: Building an Electrochemical Cell

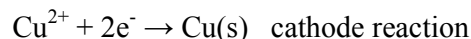
An electrochemical cell consists of two half-cells connected via an external circuit and an internal electrolyte (salt bridge). An electrochemical cell allowed to run spontaneously is referred to as a **galvanic cell**. In a galvanic cell, the anode material (usually a metal) will oxidize more readily than the cathode material. The classic example is the zinc/copper cell depicted below.



Zinc oxidizes more readily than copper. Therefore the anode reaction is:



The electrons given off by zinc at the anode travel through the external circuit to the copper cathode. At the cathode the excess electrons reduce copper ions to copper metal.



If the galvanic cell is allowed to reach equilibrium most of the Cu^{2+} ions will have been plated out on the copper cathode, and the zinc anode will have been partially corroded away. At equilibrium the potential of the cell will be zero. A charged galvanic cell will exhibit a positive potential. We can

measure this potential by placing a voltmeter between the anode and cathode in the external circuit. The voltmeter not only measures the potential, it also drastically slows down the flow of electrons. This enables a stable voltage to be measured.

The portable pH meter you have been using is really a voltmeter. When attached to a pH electrode the instrument measures the difference in potential between a silver/silver chloride half-cell and a proton concentration cell (more on this later). When you calibrate the pH meter using pH 4, 7 and 10 buffer solutions, you are really setting the reference potential for the electrochemical cell. Potential, like enthalpy or free energy, doesn't have an absolute value. It must always be referenced to some reproducible standard state. From here on out, we will refer to potential using the symbol \mathcal{E} . Therefore any measurement is understood to mean $\mathcal{E} - \mathcal{E}_{\text{ref}}$ (potential relative to the reference potential).

Most often we are interested in the difference in potential between two half cells; let's call them R and B for red and black. Then the voltmeter will measure:

$$\mathcal{E}_{\text{R}} - \mathcal{E}_{\text{ref}} - (\mathcal{E}_{\text{B}} - \mathcal{E}_{\text{ref}}) = \mathcal{E}_{\text{R}} - \mathcal{E}_{\text{B}} \quad \text{Eq. 1}$$

The following procedure will help you to build an electrochemical cell and measure its cell voltage (potential).

Procedure 1: (performed by each group)

Chemicals: 50 mL of a 0.2 M acetic acid/0.2 M sodium acetate buffer
Copper (II) sulfate*pentahydrate - $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
Nickel (II) sulfate*heptahydrate - $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$
Copper wire
Nickel wire
Distilled Water
Tap water

Apparatus: pH meter with alligator clip connector
2 glass-frit electrode tubes
1 ring stand with utility clamp
2 Clean 25-mL volumetric flasks
1 Clean 50-mL beaker or large test tube
1 500-mL beaker (for rinse)
1 wash bottle with distilled water
2 dropper pipet.
400 grit emory paper

[1] Using the acetate buffer prepare 25 mL of a copper (II) sulfate solution using ~ 0.25 g of copper (II) sulfate*pentahydrate in a 25 mL volumetric flask. The amount of salt is approximately 1/2 of the contents of the vial. You don't need to use exactly 0.25 g, but you should know the amount you used. This is solution **Cu-A**.

[2] Using the acetate buffer prepare 25 mL of a nickel (II) sulfate solution using ~ 0.25 g of nickel (II) sulfate*heptahydrate in a 25 mL volumetric flask. The amount of salt is approximately 1/2 of the contents of the vial. You don't need to use exactly

0.25 g, but you should know the amount you used. This is solution **Ni-A**.

[3] Determine the molarities of the **Cu-A** and **Ni-A** solutions. You must include the waters of hydration in your calculations. (ex. For $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ water accounts for ~ 35% of the mass of the hydrate).

[4] Obtain 2 glass-frit electrode tubes and mount them tip down on a ring stand using a utility clamp. Label them Cu and Ni, respectively.

[5] Using a dropper pipet fill the Cu electrode tube $\frac{3}{4}$ full with the copper (II) sulfate solution.

[6] Using a new dropper pipet fill the Ni electrode tube $\frac{3}{4}$ full with the nickel (II) sulfate solution.

[7] Obtain a piece of copper wire and nickel wire approximately twice the length of the electrode tubes. Gently rub any tarnish off with a piece of emory paper and place them half way into their respective electrode tubes. You have now constructed a $\text{Cu}|\text{Cu}^{2+}$ and a $\text{Ni}|\text{Ni}^{2+}$ half cell. (Since the nickel wire is thin, bend it in half then place the elbow in the electrode tube.)

[8] Attach the alligator clip connector to the pH meter. Connect the red clip to the copper wire and black clip to the two ends of the nickel wire. Be sure the two leads aren't touching each other and that they are not touching any metal. A little care and ingenuity here will save you problems later on.

[9] Now you're ready to connect the two half cells to complete a circuit. Pour some distilled water into a clean 50-mL beaker. Lower the fritted ends of the two half cells into the water. To complete the circuit, turn the pH meter on and set the mode to mV. Record what you observe in Table 1. Turn the voltmeter off when you are done.

[10] Repeat step [9] using tap water rather than distilled water. Record what you observe in Table 1. Turn the voltmeter off when you are done.

[11] Repeat step [9] using some of the acetate buffer solution instead of water. Record the voltage in mV in Table 1. Turn the voltmeter off when you are done.

[12] Remove the two half cells from the acetate buffer. Remove the wires from the half cells, wipe them clean with some kimwipe and place their ends directly into the acetate buffer. Making sure the wires don't touch, record the potential between the two metals in Table 1.

[13] Save the $\text{Cu}|\text{Cu}^{2+}$ and $\text{Ni}|\text{Ni}^{2+}$ half cells for Part 2 of the lab.

[14] Save the **Cu-A** and **Ni-A** solutions for subsequent parts of the lab.

Analysis 1:

Q1: Determine the molarities of the CuSO_4 and NiSO_4 solutions.

Q2: What is the purpose of rubbing the wires with the emory paper?

Q3: What is the purpose of adding the acetate buffer between the two half cells?

Q4: Why did the potential change when the wires were immersed directly in the acetate buffer?

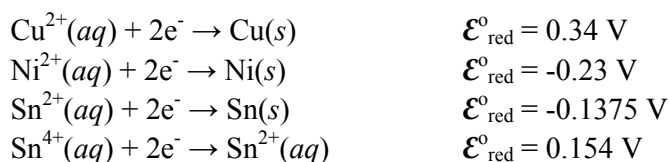
Table 1: Potential of Cu/Ni Cell

Electrolyte	Potential (mV)	Observation
Distilled water		
Tap water		
Acetate buffer		
Wires in buffer		

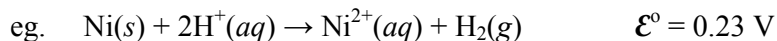
Part 2: Potential of Galvanic Cells

If the two half-cells of an electrochemical cell each have a 1.0 M solution of metal ions, the measured voltage will be the standard potential, \mathcal{E}° . In the case of copper and zinc, $\mathcal{E}^\circ = 1.10$ V. This is too large for our pH meters to handle. Therefore, you will be working with nickel, tin and copper.

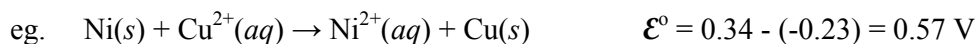
The standard potential for a galvanic cell can be calculated using a table of standard reduction potentials. Standard reduction potentials indicate the voltage one would measure if a galvanic cell were constructed using the material in question as the cathode half-cell and the normal hydrogen electrode (NHE) as the anode half-cell, each at 1.0 M cation concentration. Standard reduction potentials for Cu^{2+} , Ni^{2+} , Sn^{2+} and Sn^{4+} are given below.



The negative signs in this table indicate that relative to hydrogen, these would actually be anode reactions if run as galvanic cells.



To determine the standard potential for any galvanic cell, we simply subtract the reduction potential of the anode reaction from that of the cathode reaction.



Standard potentials are useful for predicting the anode and cathode reactions of an electrochemical cell. As is the case for the Cu/Ni cell, the cathode reaction will have the larger reduction potential. In general, however; measured cell potentials differ from the standard values owing to a variety of factors including: temperature, pH, concentration and the presence of other species in solution. In the following procedure you will explore the effect of some of these factors. In practice, the deviation away from standard cell potentials is used as a sensitive analytical tool for measuring these attributes.

Procedure 2: (performed by each group)

Chemicals: Solution **Cu-A** from Part 1
Solution **Ni-A** from Part 1
50 mL of a 0.1 N sulfuric acid solution
50 mL of a 0.2 M acetic acid/0.2 M sodium acetate buffer
50 mL of a 0.2 M ammonia/0.2 M ammonium chloride buffer
Tin (II) sulfate - SnSO_4
Copper wire
Nickel wire
Tin wire (solder)

Apparatus: pH meter with alligator clip connector
pH electrode
2 glass-frit electrode tubes
1 ring stand with utility clamp
3 Clean 50-mL beakers or large test tubes
1 500-mL beaker (for rinse)
1 wash bottle with distilled water
2 dropper pipets.
400 grit emory paper

- [1] Using 0.1 N sulfuric acid prepare 25 mL of a tin (II) sulfate solution using ~ 0.1 g of tin (II) sulfate in a clean 50 mL beaker. The tin solution will appear cloudy since some of the tin (II) sulfate is being converted to insoluble tin (II) hydroxide and insoluble SnO_2 . Label this solution **Sn-L** for low pH.
- [2] Using the acetate buffer prepare 25 mL of a tin (II) sulfate solution using ~ 0.1 g of tin (II) sulfate in a clean 50 mL beaker. The tin solution will appear cloudy since some of the tin (II) sulfate is being converted to insoluble tin (II) hydroxide and insoluble SnO_2 . Label this solution **Sn-M** for medium pH.
- [3] Using the ammonia buffer prepare 25 mL of a tin (II) sulfate solution using ~ 0.1 g of tin (II) sulfate in a clean 50 mL beaker. The tin solution will appear cloudy since some of the tin (II) sulfate is being converted to insoluble tin (II) hydroxide and insoluble SnO_2 . Label this solution **Sn-H** for high pH.
- [4] Calibrate the pH meter using the pH electrode and the standard buffer solutions. As you do this, switch the pH meter to millivolts using the mode switch and record the voltage at a pH of 4, 7 and 10.
- [5] Measure the pH of the three tin solutions and record the associated millivolt readings.
- [6] Mount the $\text{Cu}|\text{Cu}^{2+}$ half cell tip down on a ring stand using a utility clamp.
- [7] Obtain a small piece of tin solder and gently rub off any tarnish with emory paper.
- [8] Lower the fritted end of the copper half cell into the beaker containing the **Sn-L**

solution. Connect the red alligator clip to the copper wire. Connect the black alligator clip to the piece of tin solder.

[9] Complete the circuit by turning the pH meter on and dipping the end of the tin solder into the tin solution. Record the potential in Table 3. Turn the voltmeter off when you are done.

[10] Disconnect the copper half cell from the red alligator clip. Remove the copper half cell from the tin solution and rinse it with distilled water.

[11] Repeat steps [6 - 10] using the Ni|Ni²⁺ half cell.

[12] Repeat steps [6 – 11] with the **Sn-M** and **Sn-H** solutions. Be sure to wipe the tin solder clean between solutions.

[13] Empty the solutions from the copper and nickel half cells, rinse out the tubes several times with distilled water.

[14] Save the **Cu-A** and **Ni-A** solutions for subsequent parts of the lab.

Analysis 2:

Table 2: Description of Tin solutions

Solution	Appearance	pH	pH (mV)
Sn-L			
Sn-M			
Sn-H			

Q1: What was the difference in appearance of solution **Sn-L**, **Sn-M** and **Sn-H**.

Q2: What were the voltages corresponding to pH 4.0, 7.0 and 10.0?

Q3: Calculate the standard potentials for the {Ni|Ni²⁺||Cu²⁺|Cu}, {Sn|Sn²⁺||Cu²⁺|Cu} and {Ni|Ni²⁺||Sn²⁺|Sn} electrochemical cells use the reduction potentials given above.

Q4: Fill in the potential measurements into Table 3. If you measured a negative potential record it as such. In the last three spaces of Table 3, calculate the potential for the Ni|Ni²⁺||Cu²⁺|Cu cell using the difference between the Sn|Sn²⁺||Cu²⁺|Cu and Sn|Sn²⁺||Ni²⁺|Ni values.

$$\mathcal{E}_{\text{Ni/Cu}} = \mathcal{E}_{\text{Sn/Cu}} - \mathcal{E}_{\text{Sn/Ni}}$$

Q5: How does the value for \mathcal{E} of Ni|Ni²⁺||Cu²⁺|Cu from Table 3 agree with that measured in Part 1?

Table 3: Potential of Galvanic Cells

Sample	Potential (mV)
Sn Sn ²⁺ Cu ²⁺ Cu (Sn-L)	
Sn Sn ²⁺ Cu ²⁺ Cu (Sn-M)	
Sn Sn ²⁺ Cu ²⁺ Cu (Sn-H)	
Sn Sn ²⁺ Ni ²⁺ Ni (Sn-L)	
Sn Sn ²⁺ Ni ²⁺ Ni (Sn-M)	
Sn Sn ²⁺ Ni ²⁺ Ni (Sn-H)	
Ni Ni ²⁺ Cu ²⁺ Cu (Sn-L)	
Ni Ni ²⁺ Cu ²⁺ Cu (Sn-L)	
Ni Ni ²⁺ Cu ²⁺ Cu (Sn-L)	

Part 3: Concentration Dependence of the Cell Potential

In Part 2 you measured the cell potential of various galvanic cells. As you may have noticed, the potential you measured agreed with the standard potential, \mathcal{E}° , in sign and order of magnitude, but surely wasn't exactly on. (Okay, for some of you it was pretty far off.). Other than the inevitable errors associated with laboratory work, there was a fundamental reason why the expected and measured potentials didn't match; cell potential is concentration dependent. To illustrate this, let's consider the redox reaction for the Ni/Cu cell again.



If a piece of metallic nickel were placed into a beaker containing Cu²⁺ ions, the nickel would be oxidized from Ni⁰ to Ni²⁺, while copper would plate out as copper metal. This is simply the forward reaction. On the other hand, if copper metal were placed in a solution containing only Ni²⁺, a tiny fraction of the Nickel would be reduced, while a tiny amount of copper would be oxidized; that is, the reverse reaction would occur. Either way, the reaction mixture will move toward equilibrium, as predicted by Le Chatelier's principle.

Carrying out the reaction in an electrochemical cell simply slows down the approach to equilibrium. At equilibrium; however, the cell potential would drop to zero, just as the free energy difference goes to zero at equilibrium. The cell potential depends on how close to equilibrium a redox reaction has become; that is, it is concentration dependent.

The concentration dependence of the cell potential is given by the Nernst Equation

$$E = E^\circ - \frac{RT}{nF} \ln(Q) \quad \text{Eq. 2}$$

Here \mathcal{E}° is the standard potential (1.0 M solutions), \mathcal{E} is the potential at the concentrations

giving rise to the reaction quotient, Q , n is the moles of electrons transferred from reducing agent to the oxidant per mole of reaction, and F is Faraday's constant = 96,485 C/mol e^- .

At 25 °C we group the constants, and convert natural log to log base 10 to give:

$$E = E^\circ - \frac{0.0591}{n} \log(Q) \quad \text{Eq. 3}$$

As an example: an electrochemical with 0.10 M Ni^{2+} in the anode compartment and 1.00 M Cu^{2+} in the cathode compartment would exhibit a cell potential of:

$$E = 0.57 - \frac{0.0591}{2} \log\left(\frac{0.10}{1.00}\right) = 0.60 \text{ V}$$

Since the concentration of the anode compartment has been diluted, relative to the cathode compartment, the cell has been shifted away from equilibrium relative to standard states. Being farther from equilibrium, the cell potential is increased.

In a concentration cell, the anode and cathode compartments differ in concentration but not in the type of substance present. At equilibrium, the concentrations in the two cells must be equal. Diluting one cell, will force ions from the concentrated cell to the dilute one. The driving force for this process can be measured as a cell voltage. For this concentration cell Eq. 3 becomes:

$$E = \frac{-0.0591}{n} \log\left(\frac{\text{anode concentration}}{\text{cathode concentration}}\right) \quad \text{Eq. 4}$$

$E^\circ = 0$ since both compartments have the same substance. In this part you will verify Eq. 4 for the Cu/Cu^{2+} concentration cell.

Procedure 3: (performed by each group)

Chemicals: 100 mL of a 0.2 M acetic acid/0.2 M sodium acetate buffer
20 mL of 0.500 M sulfuric acid, $\text{H}_2\text{SO}_4(aq)$
Copper (II) sulfate*pentahydrate - $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
Copper wire

Apparatus: pH meter with alligator clip connector
1 glass frit electrode tube
1 ring stand with utility clamp
1 100-mL graduated cylinder
1 25-mL volumetric flask
2 10-mL graduated pipets
7 clean 20-mL test tubes, or 50 mL beakers
1 clean 250-mL beakers
1 500-mL beaker (for rinse)
1 wash bottle with distilled water
1 dropper pipet.

[1] Obtain 100 mL of the acetic acid / acetate buffer in a clean 250-mL beaker.

[2] Obtain 20 mL of 0.5 M sulfuric acid in a 100-mL graduated cylinder.

- [3] Fill a wash bottle with distilled water.
- [4] Calibrate the pH meter with the pH electrode and temperature probe attached.
- [5] Determine the pH of the acetate buffer. Using the 0.5 M sulfuric acid, lower the pH of the acetate buffer to pH = 4.2.
- [6] Attach the alligator clip connector to the pH meter to record a redox potential. Attach copper wire to both alligator clips; 1 red lead and 1 black lead.
- [7] Obtain a glass-frit electrode tube.
- [8] Using the pH = 4.2 buffer prepared in step [5], prepare 25 mL of a copper (II) sulfate solution using ~ 0.50 g, of copper (II) sulfate*pentahydrate in a 25 mL volumetric flask. You don't need to use exactly 0.50 g, but you should know the amount you used. This is your reference solution, **Cu-R**.
- [9] Place 10.0 mL of the **Cu-R** solution in a clean test tube, and also add the **Cu-R** solution 3/4-full in the glass frit electrode tube. Place the electrode tube in the vial of solution, tip down.
- [10] Place the end of the red lead in the reference electrode, and the end of the black lead in the solution in the beaker. Record a voltage. This is the **bias** voltage for your electrochemical cell, $\mathcal{E}_{\text{bias}}$.
- [11] Add 5-mL of the **Cu-R** solution to a second test tube. To this, add 5-mL of the pH = 4.2 buffer. You should now have a copper sulfate solution that has been diluted by a factor of 2.
- [12] Rinse the tip of the black lead and of the reference electrode with distilled water and wipe dry. Then record the potential of the diluted copper sulfate solution. The reference electrode and red lead remain as before.
- [13] Repeat steps [11] & [12] six more times, successively diluting the previous solution by a factor of 2. By the end, you should have a total of 8 measurements ranging from full strength to a 1/128 dilution.
- [14] When finished rinse your electrode tube several times with distilled water. Discard all solutions in the container specified by your instructor.

Analysis 3:

Q1: Determine the molarity of copper sulfate for the solutions in your dilution series and place the values in Table 4.

Q2: Record the measured cell potentials (in mV) in Table 4 for the various dilutions vs. the red-lead cathode.

Q3: Subtract the bias voltage (first entry in Table 4) from the measured voltages and place the result in the correct cell potential column of Table 4.

Q4: With the undiluted solution as the cathode solution, determine $\log\left(\frac{[\text{Cu}^{2+}]_{\text{anode}}}{[\text{Cu}^{2+}]_{\text{cathode}}}\right)$

and place the values in Table 4.

Q5: Make a graph of corrected cell potential vs. $\log\left(\frac{[\text{Cu}^{2+}]_{\text{anode}}}{[\text{Cu}^{2+}]_{\text{cathode}}}\right)$. On the same graph, plot the relationship. $E = -29.55 \log\left(\frac{[\text{Cu}^{2+}]_{\text{anode}}}{[\text{Cu}^{2+}]_{\text{cathode}}}\right)$, the Nernst equation with $n = 2$.

Q6: Over what range of dilutions is the Nernst equation valid? Give a plausible reason for the observed deviation from the Nernst equation (if any).

Table 4: Cu/Cu²⁺ Concentration Cell

Dilution Factor	[CuSO ₄] in mol/L = [Cu ²⁺] _{anode}	Cell potential (mV)	Cell potential Corrected (mV)	$\log\left(\frac{[\text{Cu}^{2+}]_{\text{anode}}}{[\text{Cu}^{2+}]_{\text{cathode}}}\right)$
1			0 mV	
1/2				
1/4				
1/8				
1/16				
1/32				
1/64				
1/128				

Part 4: Electrochemical Determination of K_{sp}.

In part 3 you saw that the cell potential of a concentration cell increases when the anode compartment is diluted. Because of this, electrochemical probes can be used as a sensitive measuring device for very low concentrations of dissolved ions. The glass membrane of a pH electrode represents an application of this principle. [H⁺] as low as 10⁻¹⁴ M can be detected because it represents a large concentration difference compared to the strong acid contained in the electrode. Similar principles are used in designing ion-selective electrodes. As an example, a calcium electrode represents a concentration cell, with a known concentration of calcium internal to the electrode. When the potential is measured between the calcium electrode and an analyte solution, rapid determination of the Ca²⁺ concentration can be affected. One of the most reliable ways of obtaining a known concentration of an ion is to take advantage of the K_{sp} of a sparingly soluble salt. Provided that some precipitate is present, the concentration of the solution surrounding the precipitate will always have the same concentration because of the solubility equilibrium of the salt and its dissolved ions.

Most salts of oxalic acid are only sparingly soluble. K_{sp} values vary from 10⁻⁵ to 10⁻¹⁵. In this experiment you will use a procedure similar to that used in Part 3 to determine the pK_{sp} of copper (II) oxalate (CuC₂O₄).

Procedure 4: (performed by each group)

Chemicals: 120 mL of a 0.2 M acetic acid/0.2 M sodium acetate buffer

Sodium oxalate

Copper (II) sulfate*pentahydrate - $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Nickel wire

Apparatus: pH meter with alligator clip connector

1 glass frit electrode tube

1 ring stand with utility clamp

1 100-mL graduated cylinder

1 50-mL volumetric flask

1 1-mL volumetric pipet

2 10-mL graduated pipets

1 clean 50 mL beaker

6 clean 20-mL glass vials, or 50 mL beakers

1 clean 250-mL beakers

1 500-mL beaker (for rinse)

1 wash bottle with distilled water

1 dropper pipet.

- [1] Obtain 120 mL of the acetic acid / acetate buffer in a clean 250-mL beaker.
- [2] Prepare 25 mL of 0.3 M sodium oxalate by adding ~ 1.0 g of sodium oxalate to deionized water. Refer to this as **D0**.
- [3] Fill a wash bottle with distilled water.
- [4] Attach the alligator clip connector to the pH meter to record a redox potential. Attach copper wire to both alligator clips; 1 red lead and 1 black lead.
- [5] Obtain a glass-frit electrode tube.
- [6] Using the acetate buffer, prepare 50 mL of a copper (II) sulfate solution using ~ 0.50 g, of copper (II) sulfate*pentahydrate in a 50 mL volumetric flask. You don't need to use exactly 0.50 g, but you should know the amount you used. This is your reference solution, **Cu-R**.
- [7] Determine the molarity of the **Cu-R** solution.
- [8] We now need to perform some serial dilutions of the sodium oxalate solution to determine the effect of oxalate concentration on the potential of a $\text{Cu}|\text{Cu}^{2+}$ concentration cell. Start by cleaning 4 test tubes. Label them D1, D2, D3 and D4.
- [9] Combine 10 mL of 0.3 M sodium oxalate solution (**D0**) with 10 mL of acetate buffer in test tube D1. Next combine 10 mL of solution D1 with 10 mL of acetate buffer in test tube D2. Next combine 10 mL of solution D2 with 10 mL of acetate buffer in test tube D3. Finally combine 10 mL of solution D3 with 10 mL of acetate buffer in test tube D4.

- [10] Add solution **Cu-R** $\frac{3}{4}$ full in the glass frit electrode tube.
- [11] Place 10.0 mL of the **Cu-R** solution in a clean 50-mL beaker. Place the electrode tube in the beaker of solution, tip down.
- [12] Place the end of the red lead in the reference electrode, and the end of the black lead in the solution in the beaker. Record a voltage. This is the **bias** voltage for your electrochemical cell, $\mathcal{E}_{\text{bias}}$.
- [13] Add 10-mL of **D0** to the beaker of **Cu-R** solution used in step [11]. You should now have a saturated copper oxalate solution with a CuC_2O_4 precipitate dispersed in it.
- [14] Rinse the tip of the black lead and of the reference electrode with distilled water and wipe dry. Then record the potential of the saturated copper oxalate solution. The reference electrode and red lead remain as before.
- [15] Clean the black lead and rinse the reference electrode when you are finished measuring the potential. Discard the nickel oxalate solution in the provided waste container and thoroughly rinse the beaker before using it again.
- [16] Repeat steps [11 – 15] four more times using solutions D1 – D4 instead of the full-strength sodium oxalate solution in successive steps. At each step the concentration of the oxalate ion should be diminished by $\sim 1/2$.
- [17] When finished rinse your electrode tube several times with distilled water. Discard all solutions in the container specified by your instructor.

Analysis 4:

- Q1: Determine the molarity of Cu^{2+} in each of the anode cells. It will be half the molarity of the **Cu-R** solution. Refer to this value as $[\text{Cu}^{2+}]_o$.
- Q2: Determine the molarity of the sodium oxalate solutions D0-D4.
- Q3: Under column $[\text{C}_2\text{O}_4^{2-}]_o$ in Table 5 record the initial concentration of oxalate ion that was in each anode cell. These values are half the values obtained for solutions D0-D4.
- Q4: Record the cell potentials for the five copper oxalate solutions in Table 5, subtracting the bias voltage, $\mathcal{E}_{\text{bias}}$, measured in step [12].
- Q5: Use the Nernst relation, relationship. $\mathcal{E} = -29.55 \log \left(\frac{[\text{Cu}^{2+}]_{\text{anode}}}{[\text{Cu}^{2+}]_{\text{cathode}}} \right)$, to determine the concentration of Cu^{2+} in the anode cell, $[\text{Cu}^{2+}]_{\text{anode}}$, and place this value in Table 5.
- Q6: The concentration of $\text{C}_2\text{O}_4^{2-}$ in the anode cell is given by:
- $$[\text{C}_2\text{O}_4^{2-}]_{\text{anode}} = [\text{C}_2\text{O}_4^{2-}]_o - \{[\text{Cu}^{2+}]_o - [\text{Cu}^{2+}]_{\text{anode}}\}$$
- Include these values in Table 5.
- Q7: Determine pK_{sp} from $\text{K}_{\text{sp}} = ([\text{Cu}^{2+}][\text{C}_2\text{O}_4^{2-}])_{\text{anode}}$ and record it in Table 5

Table 5: K_{sp} of CuC_2O_4

Analyte Dilution	$[C_2O_4]_o$ mol/L	Corrected Cell potential $\mathcal{E} - \mathcal{E}_{bias}$ (mV)	$[Cu^{2+}]_{anode}$ Mol/L	$[C_2O_4^{2-}]_{anode}$ mol/L	pK_{sp}
1 D0					
1/3 D1					
1/9 D2					
1/27 D3					
1/81 D4					

Q8: What was your average value of pK_{sp} ? Which data set would you expect to have the least error?