

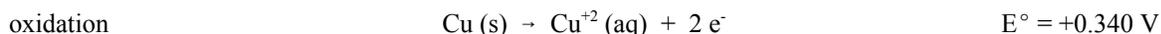
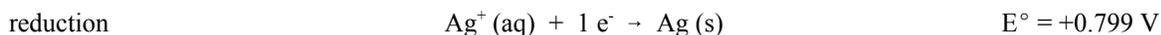
ELECTROCHEMISTRY

Electromotive Force and Reduction Potentials:

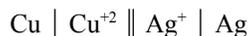
The ΔG of a redox reaction is given by:

$$\Delta G = -nFE \quad (1)$$

where n is the number of electrons in the reaction, F is the Faraday constant, and E is the cell voltage. Equation 1 also applies to half reactions, but in that case E is, **by convention**, the **REDUCTION** potential for the half reaction. Consider the following redox reaction and its component half reactions:



Note that the Cu half reaction is written as an oxidation but the E° for that half reaction is a **REDUCTION** potential. The standard notation for a cell utilizing this reaction is



and the cell voltage is given by

$$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}} = E_{\text{right}} - E_{\text{left}} = E_{\text{Ag}} - E_{\text{Cu}} \quad (2)$$

Remember, E_{red} and E_{ox} are both **REDUCTION** potentials, the subtraction takes care of the fact that one of them is really undergoing oxidation (going in the opposite direction).

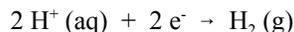
Under non-standard conditions (not 1 M activities or 25°C), the Nernst equation is used

$$E = E^\circ - \frac{RT}{nF} \ln Q \quad (3)$$

where E° is the standard **REDUCTION** potential, R is the ideal gas constant (8.314 J/K•mole), T is the **ABSOLUTE** temperature, and Q is the reaction quotient for the reaction or **reduction half reaction**. At 25°C (298K) Equation 3 becomes

$$E = E^\circ - \frac{0.05916}{n} \log Q \quad (4)$$

Since we can measure only voltage **differences**, we must define a reference point (0 point) for the reduction potential scale. Again **by convention**, the STANDARD hydrogen half reaction



is assigned a reduction potential of **exactly 0 V** (this is a **defined value**). Tables of reduction potentials give voltages with respect to this half reaction.

When measuring cell voltages in the lab, the voltmeter displays the difference between the positive lead and the negative lead, $E = E_+ - E_-$. By convention, red is used to designate positive and black designates negative. Therefore, in the lab, to make sure the voltmeter voltage correctly indicates the line notation for the cell, connect the red lead to the right half cell (cathode - reduction) and the black lead to the left half cell (anode - oxidation).

$$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}} = E_{\text{red}} - E_{\text{black}} \quad (5)$$

PROCEDURE

Part A. Measuring cell voltage.

In this part of the lab you will measure the voltage of these cells.

- $\text{Ag}|0.010\text{ M Ag}^+||0.010\text{ M Cu}^{+2}|\text{Cu}$
- $\text{Pb}|0.010\text{ M Pb}^{+2}||0.010\text{ M Cu}^{+2}|\text{Cu}$
- $\text{Pt}|0.010\text{ M Fe(CN)}_6^{-3}, 0.010\text{ M Fe(CN)}_6^{-4}||0.010\text{ M Cu}^{+2}|\text{Cu}$
- $\text{Pt}|0.010\text{ M I}^{-1}, 0.010\text{ M I}_3^{-1}||0.010\text{ M Cu}^{+2}|\text{Cu}$
- $\text{Cu}|0.0010\text{ M Cu}^{+2}||0.010\text{ M Cu}^{+2}|\text{Cu}$ (solution for the beaker = 5 mL 0.010 M Cu^{+2} + 45 mL deionized water)

Silver (I) compounds, Ag^{+1}

Stains skin dark blue-black. Photoreduction may cause similar staining of clothing.

AVOID CONTACT WITH SKIN AND CLOTHING.

Lead (II) compounds, Pb^{+2}

Poisonous if swallowed

DO NOT INGEST. AVOID CONTACT WITH SKIN AND EYES.

Iodine, I_2 or I_3^{-1}

Solution will stain skin and clothing. Vapor irritates respiratory system and eyes, causes burns, but very little vapor produced for solutions used here.

AVOID CONTACT WITH SKIN EYES, AND CLOTHING.

Remember that the right side is reduction, so it is the cathode, and the left side is oxidation, so it is the anode.

- At a pH meter station, gather together two 250 mL beakers, a porous porcelain cup, a set of electrodes (two Cu wires, Ag wire, Pb strip, Pt electrode), and a small piece of sandpaper.
- Meter set-up and operation. Refer to the figures and table below to identify the appropriate buttons to use.
 - Connect the BNC to alligator cable to the pH meter, if it's not already attached.
 - Clip the red and black leads together and turn on the meter.
 - Set the meter to display millivolts (mV).
 - If the meter does not read 0.0 mV with the leads shorted, record the value displayed (offset) and **subtract** it from all cell measurements.

Orion 420



Orion 520



IQ Scientific



Power button in bottom row. Turns off automatically if idle for several minutes.

Mode button toggles between pH, mV, and Rel mV. Arrow on display points to selected mode on case.

Always on. Measure/Standby button in bottom row toggles between these to states.

Mode button toggles between pH, mV, and Rel mV. Label on display indicates selected mode.

Power button is top center.

pH/mV button in second row toggles between pH 1 dec pl, pH 2 dec pl, and mV. Mode selected (Label) appears on left side of display.

CAUTION: ELECTROLYTE SOLUTIONS SPILLED ON ELECTRICALLY POWERED EQUIPMENT PRESENT A SHOCK HAZARD AND MAY ALSO DAMAGE THE EQUIPMENT. HANDLE SOLUTIONS CAREFULLY AND WIPE UP ANY SPILLS IMMEDIATELY.

3. Use the sandpaper to clean off the Cu and Pb electrodes. Rinse them off with deionized water.
4. Assemble the Cu half cell (cathode for all the cells): Pour about 20 mL of 0.010 M Cu^{+2} solution into the porcelain cup, and set it in an empty beaker (to prevent tipping) until you are ready to use it.
5. Set up the first cell as shown in Figure 4:
 - a. Pour about 50 mL of 0.010 M Ag^{+1} (anode solution) into a 250 mL beaker and drop in a stirring bar.
 - b. Set the porcelain cup with Cu^{+2} solution into the beaker and position the cup near the edge of the beaker.
 - c. Place the beaker and contents on a magnetic stirrer and position things so the stirring bar spins freely without hitting the porcelain cup. Set the stirrer to spin at a moderate rate - good mixing without splashing.
 - d. Clip the red lead from the meter to a Cu electrode (cathode, reduction) and insert it into the cup. Make sure the electrode contacts the solution.
 - e. Clip the black lead to a Ag (anode, oxidation) electrode and insert it into the beaker. Make sure the electrode contacts the solution and does not interfere with the stir bar.



Figure 4 Cell Set-up

- f. Arrange the clips and leads so you do not have to hold them. Your body acts as an antenna and produces noisy readings when you are holding the leads or electrodes.
 - g. Record the voltage for the cell. If the voltage is a little unstable, estimate the middle of the range.
 - h. Remove the anode, rinse, and dry.
 - i. Set the porcelain cup assembly into an empty beaker to keep it from tipping over. You will use this cup and solution for several other measurements.
 - j. Pour the solution in the beaker into the appropriate recovery bottle, being careful to retain the stir bar. Rinse out the beaker with deionized water.
6. Measure the voltage of the other cells using step 5.

Part B. Exploring Electrodeposition.

1. Move to an electrodeposition station and gather together a 100 mL beaker, 2 Cu electrodes (one with a strip of insulation and one bare - not the same electrodes as for Part A), and a small piece of sandpaper.
2. Use the sandpaper to clean the portion of the Cu electrodes that will contact solution, rinse and dry. Record the mass of each electrode (analytical balance - 4 decimal places).
3. Assemble the electrodeposition cell as shown in Figure 5.
 - a. Pour about 50 mL of 0.10 M CuSO_4 into a 100 mL beaker. Drop in a stirring bar and set it on the stirrer.
 - b. Hang the two Cu electrodes over the edge of the beaker so that the cleaned ends dip into the CuSO_4 solution.
 - c. Plug a black banana lead into the black port on the power supply (black box). Attach an alligator clip to the other end and connect it to the Cu electrode with the insulation.
 - d. Plug a red banana lead into the red port on the power supply. Attach a spade connector to the other end and fasten it to the positive (+) post of the ammeter.
 - e. Attach a spade connector to the end of a second red banana lead and fasten it to the negative (-) post of the ammeter. Attach an alligator clip to the other end but **don't connect it yet. Make sure the red and black leads are never shorted together!**
4. Set the ammeter to the 100 mA range.
5. Make sure the power supply on the end of the bench is turned on and the voltage set to about +5 V.
6. Run an electrolysis for 600 seconds (10 min). Time starts when you clip the red lead to the bare Cu electrode. Read the ammeter - look at the 0-100 scale and estimate between the smallest divisions.
7. After about 4½ minutes, read the ammeter again. At 600 seconds disconnect the bare Cu electrode. Record the actual elapsed time (nearest second).
8. Remove the electrodes, rinse, and dry. Mass each electrode again (analytical balance - 4 decimal places). Carefully observe the portion of each electrode that was under the solution. Note especially any differences.
9. Repeat the electrolysis two more times (total of three runs with three sets of data).



Figure 5 Electrodeposition Cell Set-up

10. Pour the CuSO_4 solution into the appropriate recovery bottle. Return the electrodes.

CALCULATIONS

Part A. Measuring cell voltage.

1. Write and balance each net ionic cell reaction.
2. Using the concentrations given and the E° 's from the Standard Reduction Potentials table, calculate each expected E_{cell} .
3. Calculate the percent error for each measured E_{cell} (don't forget to subtract any offset) using the expected E_{cell} as the accepted value.

$$\% \text{ error} = \frac{|\text{your value} - \text{accepted value}|}{\text{accepted value}} \times 100$$

Part B. Exploring Electrodeposition.

1. Using the *average* current and the elapsed time, calculate the mass of Cu that **should** have reacted at each electrode for each electrolysis. This calculation will be the same for both electrodes, one electrode loses that mass and the other electrode gains that mass.
2. For each electrolysis calculate a value for Avogadro's Number based on the number of electrons and the moles of electrons involved in this process:
 - a. Use the mass lost from the anode to calculate the **moles** of electrons involved in the process.
 - b. Use the average current, elapsed time, and the charge on an electron (1.602×10^{-19} coul) to calculate the **number** of electrons involved in the process.
 - c. Divide number of electrons by moles of electrons to get Avogadro's number.
3. Average the values from the three electrolyses and then calculate the percent error for Avogadro's Number (particles/mole).

CONCLUSION CONSIDERATIONS

Part A. Measuring cell voltage.

Make a table listing measured E_{cell} , expected E_{cell} , and % error. Give possible reasons for the observed percent errors.

Part B. Exploring Electrodeposition.

Does the mass lost from the anode match the mass gained by the cathode, as expected?

Does the mass lost/gained match the mass calculated from the current and time?

Are results from the three electrolyses consistent?

If not, give possible reasons for the discrepancies. (These are also possible reasons for the error in your value for Avogadro's number).

Cite your calculated value for Avogadro's Number and the percent error. Give reasons for that percent error.

Prelab (to be completed before you come to lab).

Name _____ Partner's name _____ Date performed _____

Purpose:

Brief Procedure

Reactions:

Safety precautions (be specific):

Reagent	Hazards	Handling	Disposal
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Data Sheet for **ELECTROCHEMISTRY**

Name _____ Partner's name _____ Date performed _____

Part A. Measuring cell voltage.

Meter offset	
cell	Meter Reading
Ag 0.010 M Ag ⁺¹ 0.010 M Cu ⁺² Cu	_____
Pb 0.010 M Pb ⁺² 0.010 M Cu ⁺² Cu	_____
Pt 0.010 M Fe(CN) ₆ ⁻³ , 0.010 M Fe(CN) ₆ ⁻⁴ 0.010 M Cu ⁺² Cu	_____
Pt 0.010M I ⁻¹ , 0.010 M I ₃ ⁻¹ 0.010 M Cu ⁺² Cu	_____
Cu 0.0010 M Cu ⁺² 0.010 M Cu ⁺² Cu	_____

Observations and comments

Part B. Exploring Electrodeposition.

	Initial	Final	Initial	Final	Initial	Final
Mass Cu electrode with insulation	_____	_____	_____	_____	_____	_____
Mass of bare Cu electrode	_____	_____	_____	_____	_____	_____
Current	_____	_____	_____	_____	_____	_____
Elapsed time	_____	_____	_____	_____	_____	_____

Observations and comments