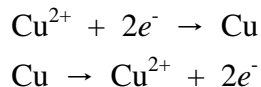


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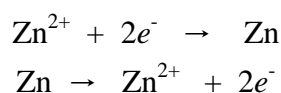
## Electrochemical Cells\*

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If a copper strip is placed in a solution of copper ions, one of the following reactions may occur:

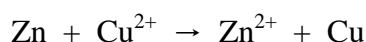


The electrical potential that would be developed by these reactions prevents their continuation. These reactions are called half-reactions or half-cell reactions. There is no direct way to measure the electrical potential (electromotive force, emf) of a half-cell reaction. Similarly, a zinc strip in a solution of zinc ions has the possible reactions:



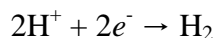
But these are also prevented from occurring by the electrical potential that would build up. If the metal electrodes (copper and zinc) in the two solutions are connected by a wire, and if the solutions are electrically connected by perhaps a porous membrane or a bridge that minimizes mixing of the solutions, a flow of electrons will move from one electrode, where the reaction is  $\text{M}_1 \rightarrow \text{M}_1^{n+} + ne^{-}$ , to the other electrode, where the reaction is  $\text{M}_2^{n+} + ne^{-} \rightarrow \text{M}_2$ .

In this case, the zinc metal goes into solution as zinc ions, and the copper ions plate out. The overall cell reaction is:



The electromotive force for such a cell, which is written as  $\text{Zn}|\text{Zn}^{2+}||\text{Cu}^{2+}|\text{Cu}$ , can be measured.

By convention, all half-cell emf's are compared to the emf of the standard hydrogen electrode. The standard hydrogen electrode is defined as a platinum electrode covered with platinum black that is in contact with hydrogen gas at 1 atmosphere pressure and a 1 molar solution of hydronium ions (actually, it is defined for unit activity). The hydrogen electrode half-cell reaction is



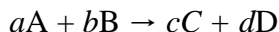
The emf of a half-cell, with respect to the standard hydrogen electrode, is called the *reduction potential*. Standard oxidation potentials,  $E^{\circ}$ , are for 1-molar solutions. Consequently, the difference between the oxidation potentials of two half-cells is the emf

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\* adapted from C. B. Anderson, Basic Experimental Chemistry

they would develop if connected together as a cell. The emf for the Zn-Cu cell described would be  $E = E^{\circ}_{\text{red}}(\text{Zn}) - E^{\circ}_{\text{red}}(\text{Cu}) = 0.77 - (-0.34) = 1.10 \text{ V}$  if the solutions are 1.0 M.

If a cell reaction can be written as



then the emf of the cell can be expressed in the form of the following equation, developed by Nernst:

$$E = E^{\circ} - (RT/nF) \ln ([C]^c [D]^d / [A]^a [B]^b)$$

If all the concentrations are 1 M, then the natural logarithmic term becomes zero and  $E = E^{\circ}$ , which is the reason for choosing 1-molar concentration as the standard condition. If the system is at equilibrium, then

$$\frac{[C]^c [D]^d}{[A]^a [B]^b}$$

and the emf developed by such a cell at equilibrium must be zero. Therefore,

$$0 = E^{\circ} - (RT/nF) \ln K_c \quad \text{-OR-} \quad \ln K_c = nFE^{\circ}/RT$$

In these equations,  $F$  is Faraday's Constant (96,485 C/mol  $e^-$ ),  $n$  is the number of electrons transferred in the oxidation-reduction step, and  $R$  is the gas constant in units of electrical work (8.314 J/K mol).

To measure the emf of a galvanic cell, a sensitive meter is needed, but it is important that the meter not draw a significant amount of current. If the current produced by the cell to be measured is large, the cell will become polarized, and the emf will be decreased. Many solid state voltmeters have sufficiently high impedance that they can be used to measure the emf of a cell accurately.

## Procedure

### Part 1: The Daniell Cell

Place 1.0 M  $\text{ZnSO}_4$  solution in a 25-mL beaker and 1.0 M  $\text{CuSO}_4$  solution in another beaker of the same size. The liquid levels should be the same. In the zinc solution, place a clean strip of zinc, and in the copper solution, a clean strip of copper. The zinc strip may be cleaned by dipping it in a beaker of about 2 M  $\text{HCl}$ . The copper strip can be cleaned by dipping it in a beaker of 2 M  $\text{HNO}_3$ . Rinse the electrodes with deionized water thoroughly before using them.

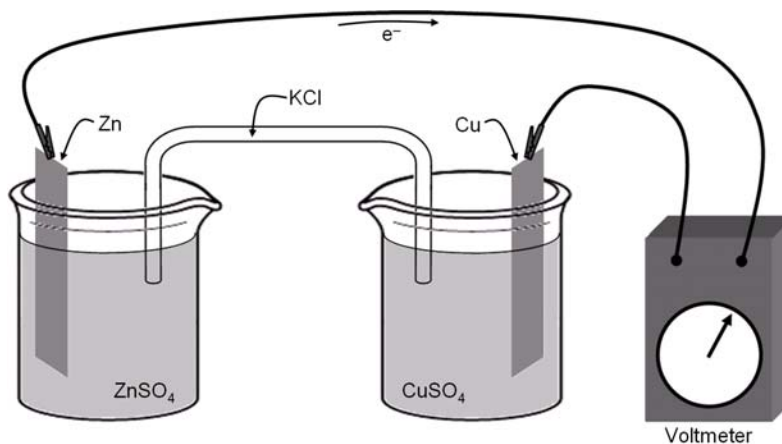
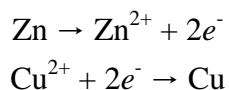
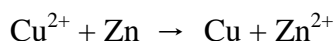


Figure One

Obtain a multimeter along with one red and one black wire. Set up the meter to measure 2V DC Voltage. Attach the red wire to the V port and the black wire to the COM port. Note the sign of the voltage; it must be positive (+) or reverse which electrode the red and black probes are touching. When  $E^{\circ}_{\text{cell}}$  is positive, the black electrode is the anode. The cells are connected with a cotton length soaked in 0.5 M potassium chloride (see Figure One above). Electrons will flow from the zinc electrode to the copper electrode because of the reactions occurring in the half-cells:



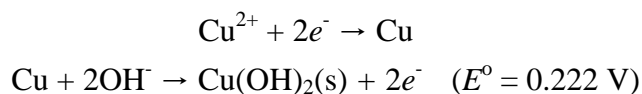
The overall reaction for the cell is:



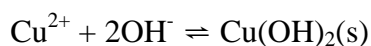
Measure the voltage of this cell. Also, measure the voltage of a Daniell cell with 0.10 M  $\text{ZnSO}_4$  and 1.0 M  $\text{CuSO}_4$ , and with 1.0 M  $\text{ZnSO}_4$  and 0.10 M  $\text{CuSO}_4$ .

### Part 2: Solubility Product of Copper(II) Hydroxide

If an electrochemical cell can be built in which the half-cell reactions are:



the overall cell reaction is the reverse of the solubility product of cupric hydroxide:



From the Nernst equation, we know that:

$$E = E^{\circ} - \frac{RT}{2F} \ln \frac{1}{[\text{Cu}^{2+}] [\text{OH}^{-}]^2}$$

The inverse natural logarithm changes the equation to:

$$E = E^{\circ} + \frac{RT}{2F} \ln [\text{Cu}^{2+}] [\text{OH}^{-}]^2$$

Solving for the standard reduction potential results in:

$$E^{\circ} = E - \frac{RT}{2F} \ln [\text{Cu}^{2+}] [\text{OH}^{-}]^2$$

Consequently, if we can measure the emf,  $E$ , of such a cell, we can calculate  $E^{\circ}$  if we know the concentration of cupric ion in one half-cell and the concentration of hydroxide ion in the other half-cell.

In the introductory discussion, we have shown from the Nernst equation that the following relationship exists:

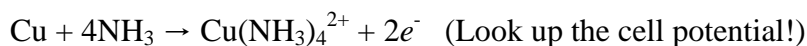
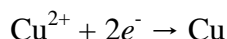
$$\ln K_c = nFE^{\circ}/RT$$

Therefore, if  $E^{\circ}$  is obtained, it can be converted into a value of the solubility product  $K_{sp}$ .

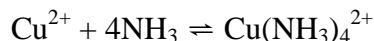
Construct a cell of two beakers. In a 25-mL beaker, place 1.0 M  $\text{CuSO}_4$  solution and a clean copper strip. The copper strip can be cleaned in dilute nitric acid, but it must be washed well with distilled water. Until it is put into the copper sulfate solution, it should be kept in dilute  $\text{HNO}_3$  but rinsed with deionized water before use. In another 25-mL clean beaker, add the same height of 1.0 M potassium hydroxide solution. Add a copper electrode to this KOH solution. Connect wires to the electrodes and the appropriate terminals of the voltmeter or potentiometer. The KOH side is the negative electrode, because copper goes into the oxidized form ( $\text{Cu}^{2+}$ ) because of the low concentration of  $\text{Cu}^{2+}$  in the KOH solution. Now add a new salt bridge made of a cotton length soaked in 0.5 M KCl. Measure the emf of the cell as soon as possible. The cell is polarized very easily. To get around this difficulty, clean the electrodes again, rinse, and return them to the solutions. Re-measure the voltage. Also measure the emf of the cell which uses 0.10 M copper sulfate and 1.0 M potassium hydroxide. Calculate the solubility product,  $K_{sp}$ , using the equations above. Literature values range from  $10^{-14}$  to  $10^{-20}$ , the latter being considered the best value. Taking the standard  $E^{\circ}$  of the Cu-Cu<sup>2+</sup> half-cell to be -0.34 V, evaluate  $E^{\circ}$  for the Cu-Cu(OH)<sub>2</sub>, OH<sup>-</sup> half-cell.

Part 3 (Optional): Formation Constant of Tetraamminecopper(II) cation

If directed by your instructor, perform the last portion of this experiment. If we construct a cell having the half-reactions:



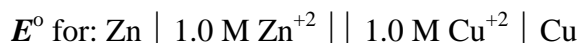
the overall cell reaction is the formation constant of the tetraamminecopper(II) cation:



Just like before, the copper strip can be cleaned in dilute nitric acid, but it must be washed well with distilled water. Until it is put into the copper sulfate solution, it should be kept in dilute  $\text{HNO}_3$  but rinsed with deionized water before use. In a 25-mL beaker, place 1.0 M aqueous ammonia, 10 drops of 1.0 M  $\text{CuSO}_4$  solution, and a clean copper strip. In another 25-mL beaker, add the same height of 1.0 M  $\text{CuSO}_4$  solution and another rinsed copper electrode. Connect the electrodes to the voltmeter. Make the electrical connection by adding a new salt bridge made of a cotton length soaked in 0.5 M  $\text{KCl}$ . Determine the voltage of the cell, and then calculate  $K_f$ .

**Experiment**

Part 1: Provide a summary of results pertaining to each of the following. How closely do your experimental results compare with theoretical calculated results? Briefly comment.

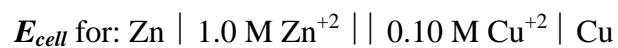


Theoretical: \_\_\_\_\_ V      Experimental: \_\_\_\_\_ V

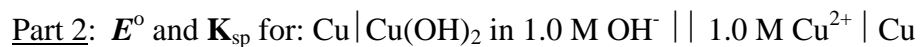
Electrochemical Cells Experiment Thirteen



Theoretical: \_\_\_\_\_ V      Experimental: \_\_\_\_\_ V



Theoretical: \_\_\_\_\_ V      Experimental: \_\_\_\_\_ V



Theoretical: \_\_\_\_\_ V      Experimental: \_\_\_\_\_ V

$K_{sp}$ : \_\_\_\_\_       $K_{sp}$ : \_\_\_\_\_

## Electrochemical Cells Experiment Thirteen

$E_{cell}$  and  $K_{sp}$  for:  $\text{Cu} | \text{Cu}(\text{OH})_2$  in  $1.0 \text{ M OH}^- || 0.10 \text{ M Cu}^{2+} | \text{Cu}$

Theoretical: \_\_\_\_\_ V      Experimental: \_\_\_\_\_ V

$K_{sp}$ : \_\_\_\_\_       $K_{sp}$ : \_\_\_\_\_

Part 3:  $E^\circ$  and  $K_f$  for:  $\text{Cu} | \text{Cu}(\text{NH}_3)_4^{2+}$  in  $1.0 \text{ M NH}_3 || 1.0 \text{ M Cu}^{2+} | \text{Cu}$

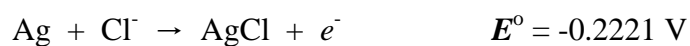
Theoretical: \_\_\_\_\_ V      Experimental: \_\_\_\_\_ V

$K_f$ : \_\_\_\_\_       $K_f$ : \_\_\_\_\_

### Discussion Questions:

1. Describe and sketch the reactions taking place at the electrodes as well as any other processes occurring in the Daniell cell (from Part 1) while it is operating. Note that the electrode reactions produce and consume ions at the electrodes.

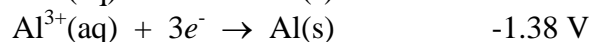
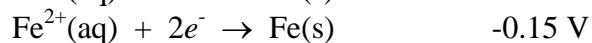
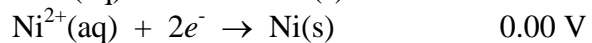
2. How should the voltage change in the Daniell cell if the zinc solution is made more dilute (and the concentration of the copper solution is kept the same)?
3. Design a cell whose voltage, when measured, can be used to calculate the solubility product of silver chloride, AgCl.
4. Calculate the solubility product of silver chloride, an extremely insoluble salt, from the following oxidation potentials:



**Advance Study Assignment:** Electrochemical Cells Experiment

Answer each of the following questions and place the responses on the lines provided.

1. The following data were measured using a nickel electrode as the standard:



- A. Which ion is most easily reduced?

\_\_\_\_\_

- B. Which metal is most easily oxidized?

\_\_\_\_\_

- C. The copper and aluminum electrodes are connected in a battery.

- 1) Which is the anode? cathode?

Anode: \_\_\_\_\_ Cathode: \_\_\_\_\_

- 2) Which is oxidized? reduced?

Oxidized: \_\_\_\_\_ Reduced: \_\_\_\_\_

- 3) What will the battery voltage be?

\_\_\_\_\_

- 4) Write a balanced net ionic equation for the reaction that takes place.

\_\_\_\_\_