

EXPERIMENT 7A

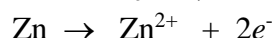
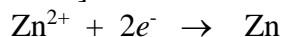
Electrochemical Cells

INTRODUCTION:

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



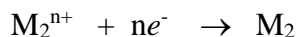
The electrical potential that would be developed by these reactions prevents their continuation. These reactions are called half-reactions or half-cell reactions. There is no direct way to measure the electrical potential (electromotive force, emf) of a half-cell reaction. Similarly, a zinc strip in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



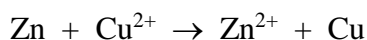
But these also are prevented from occurring by the electrical potential that would build up. If the metal electrodes (copper and zinc) in the two solutions are connected by a wire, and if the solutions are electrically connected by perhaps a porous membrane or a bridge that minimizes mixing of the solutions, a flow of electrons will move from one electrode, where the reaction is



To the other electrode, where the reaction is



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



The electromotive force for such a cell, which is written as below, 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

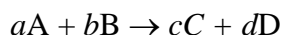


By definition, the standard reduction potential of the hydrogen half-cell is 0.00 V at standard state. The emf of a half-cell, with respect to the standard hydrogen electrode, is called the **reduction potential**. Standard reduction potentials, E° , are for 1 molar solution. Consequently, the difference between the reduction potentials of two half-cells is the emf they would develop if connected together as a cell. The emf for the Zn-Cu cell described would be

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} (\text{Cu}) - E_{\text{anode}}^{\circ} (\text{Zn}) = 0.34\text{V} - (-0.77\text{V}) = 1.10 \text{ V}$$

if the solutions are 1.0 molar.

If a cell reaction can be written



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

$$E = E^{\circ} - (2.3RT / nF) \log ([\text{C}]^c [\text{D}]^d / [\text{A}]^a [\text{B}]^b)$$

If all the concentrations are 1M, then the logarithmic term becomes zero and

$$E = E^{\circ}$$

which is the reason for choosing 1 M 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,

$$0 = E^{\circ} - (2.3RT/nF)\log K_{\text{eq}}$$

or

$$\log K_{\text{eq}} = (nF E^{\circ}) / (2.3 RT)$$

In these equations, F is the Faraday, n is the number of electrons transferred in the oxidation-reduction step, and R is the gas constant in units of electrical work.

MEASURING EMF

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 0.1 M ZnSO_4 solution in a 100-mL beaker, and 0.1M 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 placing it in a beaker of about 2M HCl (made by diluting one volume of 6M HCl with two volumes of water). The copper strip can be cleaned by placing it in a beaker of 2M HNO_3 (made by diluting one volume of 6M HNO_3 with two volumes of water). Rinse the electrodes with deionized water thoroughly before using them.

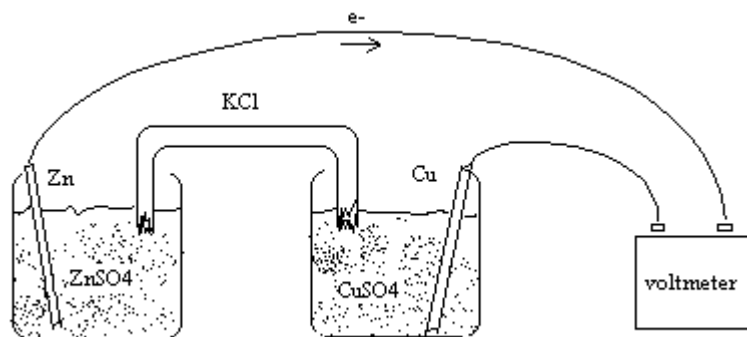
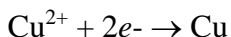
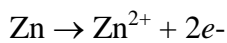


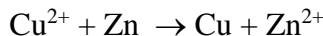
Fig. 1

Attach the wires to the electrodes, connecting them to the voltmeter or potentiometer. (On the potentiometer the black terminal is negative, and the red terminal is positive. Connect the wire from the zinc electrode to the black terminal on the potentiometer, and the copper electrode to the red terminal.) The cells are connected with a U-tube filled with 0.5 M potassium chloride and closed with cotton stuffed into the ends. See Fig. 1. Short lengths of plastic or Tygon tubing may be used instead of glass U-tubes. No large air bubbles should be in the U-tube, or the electrical resistance will be high.

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



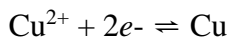
The cell may be represented as



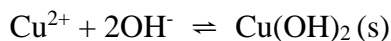
Measure the voltage of this cell. Also, measure the voltage of a Daniell cell with 0.01 M ZnSO₄ and 0.1 M CuSO₄, and with 0.1 M ZnSO₄ and 0.01 M CuSO₄.

Part 2: Solubility product of cupric hydroxide

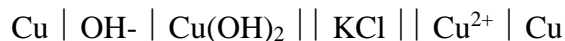
If an electrochemical cell can be built in which the half-cell reactions are



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



Such a cell can be written as



From the Nernst equation,

$$E = E^{\circ} - \frac{2.3RT}{2F} \log \frac{1}{[\text{Cu}^{2+}] [\text{OH}^{-}]^2}$$

$$E = E^{\circ} + \frac{2.3RT}{2F} \log [\text{Cu}^{2+}] [\text{OH}^{-}]^2$$

$$E^{\circ} = E - \frac{2.3RT}{2F} \log [\text{Cu}^{2+}] [\text{OH}^{-}]^2$$

Consequently, if we can measure the emf, E , of such a cell, we can calculate E° , 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

$$\log K_{\text{eq}} = (nF E^{\circ}) / (2.3 RT)$$

So if E° is obtained, it can be converted into a value of the solubility product. The factor $2.3RT/F$ is equal to 0.0592 V at 25°C.

Construct a cell of two beakers. In a 100 or 150 mL beaker, place 0.10 M CuSO₄ solution and a clean copper strip. The copper strip can be cleaned in dilute nitric acid, but it must be washed well

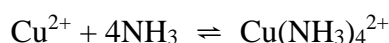
with distilled water. Until it is put into the copper sulfate solution, it should be kept in dilute HCl, but rinsed with deionized water before use. In a clean beaker, add the same height of 0.10 M potassium hydroxide solution. Add a copper electrode to this KOH solution. Connect wires to the electrodes and the appropriate terminals of the voltmeter or potentiometer. The KOH side is the negative electrode, because copper goes into the oxidized form (Cu^{2+}) because of the low concentration of Cu^{2+} in the KOH solution. Now add the salt bridge, which is a U-tube filled with KCl and closed off by wads of cotton in each end. The cotton wads must be soaked. 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 reduction potential E° of the $\text{Cu}-\text{Cu}^{2+}$ electrode to be 0.34 V, evaluate E° for the $\text{Cu}-\text{Cu}(\text{OH})_2, \text{OH}^-$ electrode.

Part 3: Formation constant of tetraamminecopper(II) cation

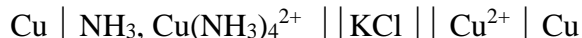
Similarly, if we can construct a cell having the half-reactions



the overall cell reaction is the formation equilibrium for tetraamminecopper(II) cation



Such a cell can be written



The Nernst equation can be written

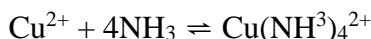
$$E = E^\circ - \frac{2.3RT}{2F} \log \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}] [\text{NH}_3]^4}$$

$$E^\circ = E + \frac{2.3RT}{2F} \log \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}] [\text{NH}_3]^4}$$

and the formation constant, K_f , is related by

$$\log K_f = (2F E^\circ) / (2.3 RT)$$

Clean the copper strips in 6M nitric acid. To a 100-ml beaker labeled #1, add 50 mL of 1.0M aqueous ammonia and 0.25 mL (this small volume may be measured using a calibrated medicine dropper, probably about 5 drops) of 0.1M cupric sulfate solution. Mix well and add a rinsed copper electrode. To another 100-mL beaker labeled #2, add 50 mL of 0.1M cupric sulfate and another rinsed copper electrode. Connect the electrodes to the voltmeter. Which electrode is negative? Make the electrical connection by adding the salt bridge. Determine the cell potential. Using the calibrated medicine dropper, add 2.25 ml (probably about 45 drops) more of 0.1M cupric sulfate to the beaker containing cupric ammine complex, mix well, and determine the voltage of the cell. Assuming that the reaction of the 0.25 mL of 0.1M cupric sulfate solution and 1 M aqueous ammonia goes to completion



Calculate the concentration of cupric ammine complex in the first cell. Using this value for $[\text{Cu}(\text{NH}_3)_4^{2+}]$, $[\text{Cu}^{2+}] = 0.10 \text{ M}$, and $[\text{NH}_3] = 1.0 \text{ M}$, calculate E° from the preceding equation, and then calculate K_f . Do the same for the second cell containing 2.25 mL 0.1M cupric sulfate.

Chemicals & Equipment:

- Voltmeter (high impedance, reads $\pm 1.999\text{VDC}$, input impedance $1000\text{M}\Omega$)
- Two alligator clips
- Two 100-mL beakers
- Zinc electrode
- Two copper electrodes (3.5 x 1 x 1/16 inch)
- Glass or plastic U-tube (6-8 mm ID)
- 10-mL graduated cylinder
- 100-mL graduated cylinder
- transfer pipette
- 100 mL 0.10 M zinc sulfate
- 200 mL 0.10 M copper sulfate
- 10 mL 0.5 M potassium chloride
- 20 mL 6 M Hydrochloric acid
- 20 mL 6 M nitric acid
- 100 mL 1.0 M potassium hydroxide
- 100 mL 1.0 M ammonia
- cotton

NAME _____

SECTION _____

Electrochemical Cells**REPORT SHEET****EXPERIMENT 7A****Part 1. Experimental values** (Show all work in notebook.)Cell Voltage for: Zn | 0.1M ZnSO₄ | 0.5M KCl | 0.1M CuSO₄ | Cu _____Cell Voltage for: Zn | 0.01M ZnSO₄ | 0.5M KCl | 0.1M CuSO₄ | Cu _____Cell Voltage for: Zn | 0.1M ZnSO₄ | 0.5M KCl | 0.01M CuSO₄ | Cu _____Calculate the standard potential, E° , for each cell using

$$E^\circ = E + (2.3RT / nF) \log ([Zn^{2+}] [Cu (s)] / [Cu^{2+}] [Zn (s)])$$

Sample calculation:

Experimental values E° for: Zn | 0.1M ZnSO₄ | 0.5M KCl | 0.1M CuSO₄ | Cu _____ E° for: Zn | 0.01M ZnSO₄ | 0.5M KCl | 0.1M CuSO₄ | Cu _____ E° for: Zn | 0.1M ZnSO₄ | 0.5M KCl | 0.01M CuSO₄ | Cu _____percent error for E° _____%**Part 2. Experimental values**Cell Voltage for: Cu | 0.1M OH⁻ | Cu(OH)₂ | KCl | 0.1M Cu²⁺ | Cu _____Cell Voltage for: Cu | 0.1M OH⁻ | Cu(OH)₂ | KCl | 0.1M Cu²⁺ | Cu _____Cell Voltage for: Cu | 1.0 M OH⁻ | Cu(OH)₂ | KCl | 0.1M Cu²⁺ | Cu _____

Calculate:

 E° for: Cu | 0.1M OH⁻ | Cu(OH)₂ | KCl | 0.1M Cu²⁺ | Cu _____ E° for: Cu | 0.1M OH⁻ | Cu(OH)₂ | KCl | 0.1M Cu²⁺ | Cu _____ E° for: Cu | 1.0 M OH⁻ | Cu(OH)₂ | KCl | 0.1M Cu²⁺ | Cu _____

Sample Calculation:

Calculate K_{sp} if $K_{sp} = 1/K_f$:

K_{sp} for: Cu | 0.1M OH⁻ | Cu(OH)₂ | KCl | 0.1M Cu²⁺ | Cu _____

K_{sp} for: Cu | 0.1M OH⁻ | Cu(OH)₂ | KCl | 0.1M Cu²⁺ | Cu _____

K_{sp} for: Cu | 1.0 M OH⁻ | Cu(OH)₂ | KCl | 0.1M Cu²⁺ | Cu _____

Sample Calculation:

percent error for K_{sp}

_____ %

Part 3. Experimental values

Cell Voltage for: Cu | NH₃, (0.25mL) Cu(NH₃)₄²⁺ | KCl | 0.1M Cu²⁺ | Cu _____

Cell Voltage for: Cu | NH₃, (2.50 mL) Cu(NH₃)₄²⁺ | KCl | 0.1M Cu²⁺ | Cu _____

[Cu(NH₃)₄²⁺] from cell 1 = _____

E^o for: Cu | NH₃, (0.25mL) Cu(NH₃)₄²⁺ | KCl | 0.1M Cu²⁺ | Cu _____

E^o for: Cu | NH₃, (2.50 mL) Cu(NH₃)₄²⁺ | KCl | 0.1M Cu²⁺ | Cu _____

Sample calculation:

K_f for: Cu | NH₃, (0.25mL) Cu(NH₃)₄²⁺ | KCl | 0.1M Cu²⁺ | Cu _____

K_f for: Cu | NH₃, (2.50 mL) Cu(NH₃)₄²⁺ | KCl | 0.1M Cu²⁺ | Cu _____

Sample calculation:

*Keep the average K_f value from this experiment for comparison to the K_f obtained from experiment 7b, Formation of a complex ion. You will be asked which method was more accurate. In the space below, write down some notes about this experiment to help refresh your memory.

NAME _____

SECTION _____

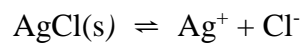
EXPERIMENT 7A

Electrochemical Cells

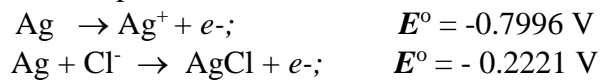
POST-LABORATORY QUESTIONS

1. Describe & sketch here & in your notebook, the reactions taking place at the electrodes, and any other processes necessarily occurring in the Daniell cell 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. How will a large air bubble in the salt bridge affect the operation of the cell? Can you suggest a reason? What purpose does the salt bridge serve in the electrochemical cell? Discuss alternative possibilities.

4. (a) Design a cell whose voltage, when measured, can be used to calculate the solubility product of silver chloride



- (b) Calculate the solubility product of silver chloride, an extremely insoluble salt, from the following standard oxidation potentials:



5. Design a cell whose voltage, when measured, can be used to calculate the formation constant of the diamminesilver cation

