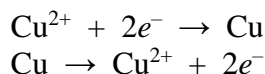
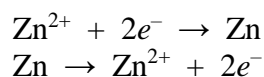

Experiment #13 – Electrochemical Cells*

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

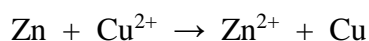


The electrical potential that would be developed by these reactions prevents their continuation. These reactions are called half-reactions or half-cell reactions. There is no direct way to measure the electrical potential (electromotive force, emf) of a half-cell reaction. Similarly, a zinc strip in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



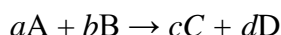
The emf of a half-cell, with respect to the standard hydrogen electrode, is called the *reduction potential*. Standard reduction potentials, E° , are for 1-molar solutions.

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

Consequently, the difference between the oxidation 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:

$$\begin{array}{rccccr} E^{\circ}_{\text{ox}} (\text{Zn} \rightarrow \text{Zn}^{2+}) & + & E^{\circ}_{\text{red}} (\text{Cu}^{2+} \rightarrow \text{Cu}) & = & E^{\circ}_{\text{cell}} \\ -(-0.76 \text{ V}) & + & +0.34 \text{ V} & = & 1.10 \text{ V} \end{array}$$

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

Part 1A: Standard Conditions Place 1.0 M ZnSO₄ solution in a 25-mL beaker and 1.0 M CuSO₄ 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 HCl. The copper strip can be cleaned by dipping it in a beaker of 2 M HNO₃. Rinse the electrodes with deionized water thoroughly before using them.

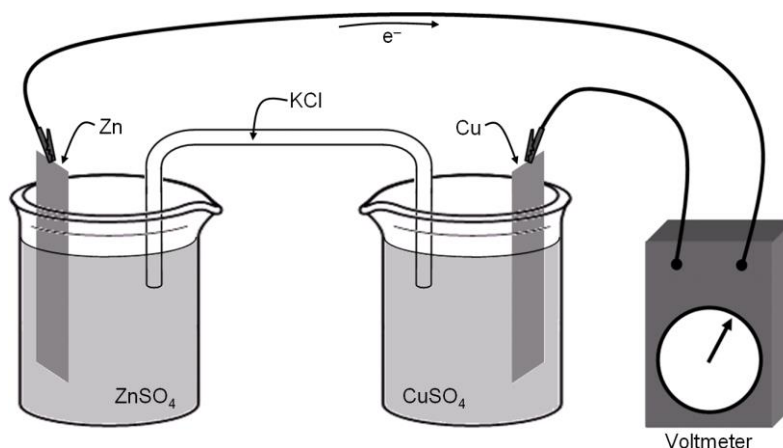
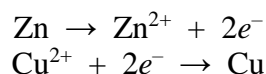
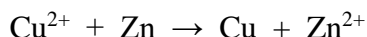


Figure 1

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°_{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 1 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.

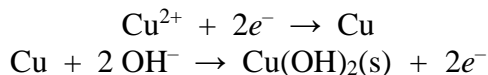
Next measure the voltage of a couple of non-standard Daniell cells following the same procedure:

Part 1B: 0.10 M ZnSO₄ and 1.0 M CuSO₄

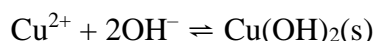
Part 1C: 1.0 M ZnSO₄ and 0.10 M CuSO₄

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° 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° is experimentally obtained, it can be converted into a value of the solubility product K_{sp} . Also, if we use a literature value for K_{sp} , we can calculate the theoretical E° .

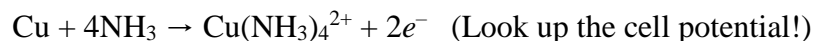
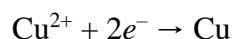
Construct a cell of two beakers. In a 25-mL beaker, place 1.0 M CuSO_4 solution and a clean copper strip. The copper strip can be cleaned in dilute nitric acid, but it must be washed well with distilled water. Until it is put into the copper sulfate solution, it should be kept in dilute HNO_3 but rinsed with deionized water before use. In another 25-mL clean beaker, add the same height of 1.0 M KOH solution plus 10 drops of 1.0 M CuSO_4 solution. Most of the copper ions will form $\text{Cu}(\text{OH})_2$ (s) in equilibrium with the 1.0 M solution of hydroxide ions. 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 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. 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° of the $\text{Cu}-\text{Cu}^{2+}$ half-cell to be -0.34 V, evaluate E° for the $\text{Cu}-\text{Cu}(\text{OH})_2, \text{OH}^-$ half-cell.

Name: _____

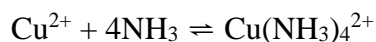
Section: _____

Part 3: Formation Constant of Tetraamminecopper(II) cation

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 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 CuSO_4 solution, and a clean copper strip. In another 25-mL beaker, add the same height of 1.0 M 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 KCl . Determine the voltage of the cell, and then calculate K_f .

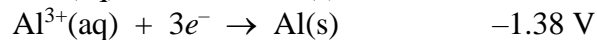
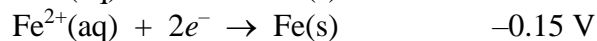
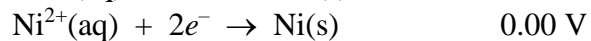
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Section: _____

Pre-Lab 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.

Name: _____

Section: _____

Experiment

Part 1A: E° for: Zn | 1.0 M Zn⁺² || 1.0 M Cu⁺² | Cu

Theoretical: _____ V Experimental: _____ V

Part 1B: E_{cell} for: Zn | 0.10 M Zn⁺² || 1.0 M Cu⁺² | Cu

Theoretical: _____ V Experimental: _____ V

Part 1C: E_{cell} for: Zn | 1.0 M Zn⁺² || 0.10 M Cu⁺² | Cu

Theoretical: _____ V Experimental: _____ V

Name: _____

Section: _____

Part 2: E° and K_{sp} for: $\text{Cu} | \text{Cu}(\text{OH})_2$ in $1.0 \text{ M OH}^- || 1.0 \text{ M Cu}^{2+} | \text{Cu}$

Experimental $E^\circ =$ _____ V

Calculate experimental K_{sp} using experimental E° and the Nernst equation at equilibrium.

Experimental $K_{sp} =$ _____

Calculate the theoretical E° using a literature value for $K_{sp} = 2.2 \times 10^{-20}$.

Theoretical $E^\circ =$ _____ V

Calculate the % error in E° .

% error in $E^\circ =$ _____

Name: _____

Section: _____

Part 3: E° and K_f for: $\text{Cu} | \text{Cu}(\text{NH}_3)_4^{2+}$ in 1.0 M NH_3 || 1.0 M $\text{Cu}^{2+} | \text{Cu}$

Experimental E° = _____ V

Calculate experimental K_f using experimental E° and the Nernst equation at equilibrium.

Experimental K_f = _____

Calculate the theoretical E° using a literature value for $K_f = 1.7 \times 10^{13}$.

Theoretical E° = _____ V

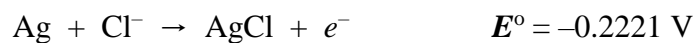
Calculate the % error in E° .

% error in E° = _____

Name: _____

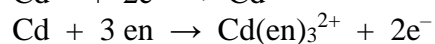
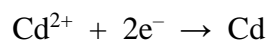
Section: _____

4. Calculate the solubility product of silver chloride, an extremely insoluble salt, from the following oxidation potentials:



5. Construct a standard voltaic cell diagram that will enable you to determine the solubility product of AgCl from the half reactions given in the previous question.

6. A cell that has the following half reactions was constructed.



The measured E° at 25 °C was +0.38 V. Calculate the experimental K_f .