

# Potentiometric Halide Titration with $\text{Ag}^+$

## Introduction

Mixtures of halides can be titrated with  $\text{AgNO}_3$  solution as described in Section 26-6 in the textbook. In this experiment, you will monitor the activity of  $\text{Ag}^+$  as the titration proceeds. The theory of the potentiometric measurement is described in Section 14-2 of the textbook.

Each pair of students is given a vial containing 0.22–0.44 g of KCl plus 0.50–1.00 g of KI (both weighed accurately). The goal is to determine the percent by mass of each component in the sample.

## Procedure

1. Pour your unknown carefully into a 50- or 100-mL beaker. Dissolve the solid in ~20 mL of water and pour the solution into a 100-mL volumetric flask. Rinse the sample vial and beaker five times with small portions of  $\text{H}_2\text{O}$  and transfer the washings to the flask. Dilute to the mark and mix well.

2. Dry 1.2 g of  $\text{AgNO}_3$  (FM 169.87) at  $105^\circ\text{C}$  for 1 h and cool in a desiccator for 30 min with minimal exposure to light. Some discoloration is normal (and tolerable in this experiment) but should be minimized. Accurately weigh 1.2 g and dissolve it in a 100-mL volumetric flask. After cleaning and acclimating, fill a buret with the standard  $\text{Ag}^+$  solution.

3. Set up the copper reference electrode as shown in the diagram below. Moisten a 5 cm piece of thread with 0.100M  $\text{CuSO}_4$  and place it halfway into the end of a 15 cm glass tube. Moisten a rubber septum and insert it on the tube, as shown in the diagram below. Make sure that a short piece (about  $\frac{1}{2}$  an inch) of the thread is easily exposed on both the inside and outside of the septum wall. Fill the tube about  $\frac{3}{4}$  full with 0.100M  $\text{CuSO}_4$  and insert the Cu wire electrode. Make sure that only copper is in contact with the  $\text{CuSO}_4$  solution. This electrode is connected to the positive terminal (red clip).

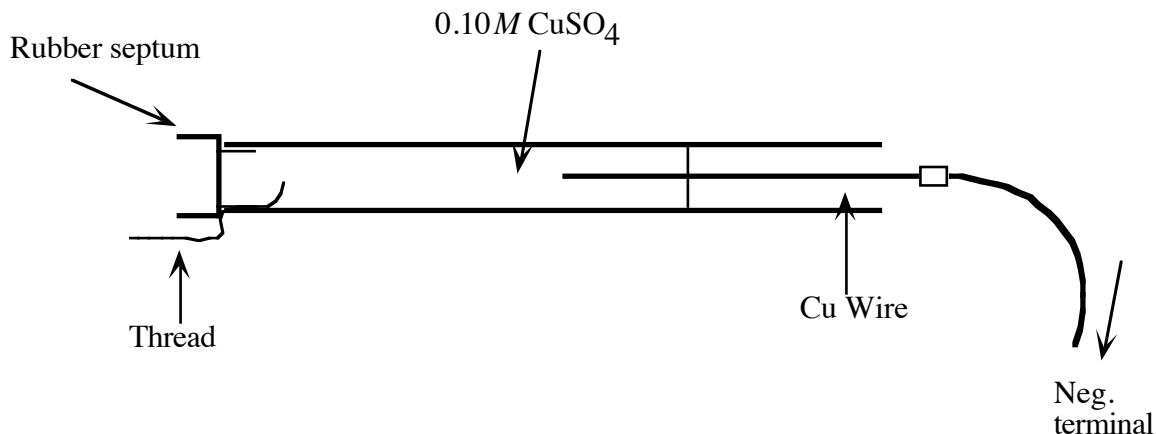


Figure 1. Diagram of the copper reference electrode

4. Pipet 25.00 mL of the unknown halide solution into a 100 mL beaker. Insert the copper reference electrode and a silver wire (electrode connected to the negative (black) terminal) in the solution. With the silver electrode make sure that only the silver metal portion is in contact with the solution and that this is not in contact with the thread from the copper electrode. Add a magnetic stir bar to the solution and begin stirring. Record the initial level of  $\text{AgNO}_3$  in a 50-mL buret and add ~1 mL of titrant to the beaker. Record this volume and then measure the voltage in the cell using the LoggerPro software.

5. Titrate the solution with ~1-mL aliquots until 50 mL of titrant have been added or until you can see two abrupt voltage changes. You need not allow more than 15–30 s for each point. Record the volume and voltage at each point. Make a graph of millivolts versus milliliters to find the approximate positions ( $\pm 1$  mL) of the two end points.

6. Stop the run, remove and rinse the electrodes well with distilled water. Clean the beaker and set up the titration apparatus again with another 25.00 mL of halide solution.

7. Perform an accurate titration using 1-drop aliquots near the end points (and 1-mL aliquots elsewhere). You need not allow more than 30 s per point for equilibration.

8. Prepare a graph of millivolts versus milliliters and locate the end points as in Figure 26-10 of the textbook. The I<sup>-</sup> end point is taken as the intersection of the two dashed lines in the inset of Figure 26-10. The Cl<sup>-</sup> end point is the inflection point (the steepest point) at the second break. Calculate milligrams of KI and milligrams of KCl in your solid unknown.

## Data Analysis

First identify which endpoint indicates the amount KCl and which endpoint indicates the amount of KI. Use the endpoint volumes of each and the concentration of the Ag<sup>+</sup> in each solution to determine the number of moles of KI and KCl in a 25 mL aliquot of the solution. Then determine the mass of KI and KCl present in the unknown sample and the percent by mass of each.