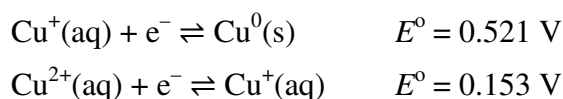


## Microscale Preparation of Copper(I) Chloride

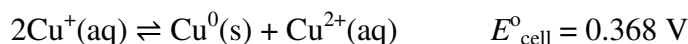
### Introduction

In most of its ionic compounds copper assumes a +2 oxidation state, having the valence configuration  $3d^9$ . In aqueous solution the  $\text{Cu}^{2+}(\text{aq})$  ion typically shows a light blue color, although the presence of coordinating ligands species alternative to  $\text{H}_2\text{O}$  can result in complex ions with varying colors. In all cases the visible absorption is a result of the incompletely filled  $3d$  subshell. If, by contrast, copper assumes a +1 oxidation state, it has the completely filled subshell configuration  $3d^{10}$ . This pseudo-noble gas configuration precludes the observation of photoinduced  $d-d$  (*aka* ligand-field) electronic transitions that give rise to the characteristic colors of most transition metal ions, such as  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ni}^{2+}$ , etc. Thus,  $\text{Cu}^+(\text{aq})$  is colorless in solution, as is  $\text{Zn}^{2+}(\text{aq})$  for example which has an identical valence electron configuration.

Like its coinage metal relative  $\text{Ag}^+$ ,  $\text{Cu}^+$  forms an insoluble chloride, for which  $K_{\text{sp}} = 1.72 \times 10^{-7}$ . Unlike  $\text{Ag}^+(\text{aq})$ , however,  $\text{Cu}^+(\text{aq})$  is unstable with respect to  $\text{Cu}^{2+}(\text{aq})$ . The relevant standard reduction potentials are



Taken together, these show that in aqueous solution  $\text{Cu}^+$  ions will spontaneously *disproportionate* to give metallic  $\text{Cu}^0$  and  $\text{Cu}^{2+}$  ions:



Under nonstandard conditions, the reaction potential,  $E_{\text{cell}}$ , is given by the Nernst equation and the Gibbs free energy of the system can subsequently be determined in a straightforward manner where  $n$  is the electron stoichiometry and  $F$  is Faraday's constant.

$$E_{\text{cell}} = E^\circ_{\text{cell}} - (RT/nF)\ln\{[\text{Cu}^{2+}]/[\text{Cu}^+]^2\}$$

$$\Delta G = -nFE_{\text{cell}}$$

(note: if  $[\text{Cu}^{2+}]/[\text{Cu}^+]^2 = 1$ ,  $\Delta G^\circ = -nFE^\circ_{\text{cell}}$ )

The Nernst equation suggests that any process that removes  $\text{Cu}^+(\text{aq})$  from solution will diminish the overall  $E_{\text{cell}}$ , thereby mitigating the disproportionation reaction. One way of achieving this is to produce the  $\text{Cu}^+$  in the presence of excess chloride ion, resulting in production of a chloride complex of copper(I), followed by precipitation of  $\text{CuCl}(\text{s})$ . Both complex formation and precipitation result in removal of the  $\text{Cu}^+(\text{aq})$  from solution. The precipitate sequesters the  $\text{Cu}^+$  ions in a form that is less susceptible to disproportionation. In the solid state, the  $\text{CuCl}(\text{s})$  lattice energy stabilizes the +1 state, and disproportionation becomes nonspontaneous:



This is the synthetic strategy we will use to obtain copper in the +1 state.

Although  $\text{CuCl}$  stabilizes  $\text{Cu}^+$  relative to disproportionation, this does not mean that the species is impervious to decomposition to the more stable  $\text{Cu}^{2+}(\text{aq})$  ion. In contact with the preparative medium, where  $\text{Cu}^{2+}(\text{aq})$  is being reduced to  $\text{Cu}^+(\text{aq})$ ,  $\text{CuCl}$  will resist reconversion back to  $\text{Cu}^{2+}$  and  $\text{Cl}^-$  ions so long as the reducing agent (metallic copper) is present in excess. However, during collection of the product by filtration,  $\text{CuCl}(\text{s})$  becomes vulnerable to oxidation from  $\text{O}_2$ , either from contact with the air or from significant amounts of  $\text{O}_2$  dissolved in wash liquids – especially in the presence of moisture. Evidence of oxidation is the development of a pale green color due to formation of basic copper(II) chloride,  $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ . *To prevent this oxidative decomposition from occurring it is critically important to avoid allowing any of the several wash liquids to run through the filter completely, thereby avoiding to suck air through the moist product.* As one wash liquid is nearly gone, add the next. The final washings with ether are meant to dry the product. Several ether washes (always avoiding air contact) are likely to be more effective than a single treatment. Any residual moisture should be driven off by immediate oven drying.

### Procedure

In a 125-mL flask, bring 100 mL of distilled water to a vigorous boil. Turn off the heat, place a cork stopper loosely on the flask mouth, allow cool and tighten the stopper when cool enough to touch. This will remove much of the dissolved  $\text{O}_2$  from the water. Add 60 mL of this water to another clean 125-mL flask, add 2 mL of ether, stopper tightly, shake and quickly release the pressure of gaseous ether. This will help to remove residual  $\text{O}_2$ . Keep the flask of deaerated water tightly stoppered until it is needed in the following procedure.

Dissolve 2 g of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in 5 mL of deionized water in a 50-mL Erlenmeyer flask, and then add 5 mL of concentrated hydrochloric acid and 1.5 g of fine copper turnings. In a well ventilated fume-hood, heat this reaction mixture on a hot plate, keeping  $\text{O}_2$  out of the mixture by inverting a small beaker over the mouth of the flask. *Avoid vigorous boiling (check the boiling point of hydrogen chloride) and make note of any observations.* When no further change occurs, carefully decant the warm solution into the 125-mL flask containing the 60 mL of deaerated water. Take care to prevent unreacted copper metal from being transferred with the solution.  $\text{CuCl}(\text{s})$  will precipitate in the 125-mL flask as a fine white powder. *In the following filtration procedure take care in controlling the strength of vacuum while maintaining the volume of solvent in the Hirsch funnel.* Collect the solid by suction filtration on Hirsch funnel and filter paper, taking care to keep the cake of precipitated  $\text{CuCl}(\text{s})$  covered with liquid at all times to avoid oxidation with atmospheric  $\text{O}_2$ . As the level of liquid approaches the precipitate, add more reaction solution. After adding the last portion of solution and before all the liquid has been sucked through the filter, successively wash with two 4-mL portions of ethyl alcohol, and then four 4-mL portions of diethyl ether. With each wash liquid, *gently* stir up the precipitate, let the level fall to just above the cake, and then add the next wash liquid. After the final ether wash, allow the precipitate to be sucked to dryness, but no more than one minute beyond the point at which all liquid has passed through the filter. Immediately transfer the product (still in the filter funnel) to a warm oven ( $110^\circ\text{C}$ ) or vacuum oven ( $70 - 80^\circ\text{C}$ ), and allow to dry for approximately one hour. Transfer the dried product to a preweighed and labeled sample bottle. Seal tightly to prevent contact with moist air. Weigh the bottle and sample to determine the actual yield of  $\text{CuCl}(\text{s})$ .

## Reactions of CuCl

Prepare an aqueous solution of potassium chloride by adding approximately 0.1 g of KCl to 10 mL of water. To this solution, add a small amount of CuCl(s) - about the amount that covers the tip of a micro-spatula). Now add a few drops of 10% aqueous ethylenediamine, make note of any observations.

*At each stage note what happens and interpret your results.*

*It is recommended to consult the inorganic chemistry literature or texts to interpret these results.*

## Laboratory Report

1. Submit your sample, ensuring that the solid is dry and the vial securely closed. Points will be awarded if your sample retains its color for 1 week.
2. Your written report should include
  - a) balanced equations for the reactions by which CuCl(s) is produced
  - b) a statement of grams of product and percent yield
  - c) a brief explanation of any unexpected results or departures from the procedure.
3. Describe your observations and interpretations, including balanced chemical equations, for the reactions you carried out with CuCl and both aqueous KCl and ethylenediamine.
4. In this synthetic procedure CuCl(s) does not precipitate until the reaction mixture is diluted with water. Explain this observation.
5. In this experiment copper metal functions as a reducing agent. Suggest an alternative procedure for preparing CuCl(s) using an alternative reducing agent. *Keep in mind that the reducing agent must be proposed based upon a calculated free energy of reaction and the capability of cleanly separating the product without exposing CuCl(s) to air oxidation.* Give full citations for the source(s) of your procedure or pertinent data used in developing it.