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Experiment 12

A Solid Electrolyte, Cu_2HgI_4

William R. Robinson

Notes for Instructors

Purpose

To synthesize copper(I) tetraiodomercurate(II), Cu_2HgI_4, and study its changes in color and conductivity as the compound undergoes a phase transition upon heating.

Method

Bright red, thermochromic Cu_2HgI_4 is synthesized from $CuSO_4$, KI, and $Hg(NO_3)_2$; when heated, the compound changes to a dark brown color, but returns to its original red color when it is allowed to cool. The resistance of Cu_2HgI_4 dramatically decreases when it is heated as a result of enhanced ion mobility in the high-temperature structure.

Materials

0.5 M Copper (II) sulfate solution

1.0 M Potassium iodide solution

6 M Acetic acid solution

Sodium sulfite, Na_2SO_3

0.05 M Mercury(II) nitrate solution

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Stirring hot plate
Filter paper, Büchner funnel, suction flask, and water aspirator
Distilled water
Glass capillary tubes, 1.5 × 100 mm (one end sealed), optional
Glass capillary tubes, 1.5 × 100 mm (open both ends)
18-Gauge copper wire
Ohmmeter
Rubber band
Solid-State Model Kit

A Solid Electrolyte, Cu_2HgI_4

Purpose

To synthesize copper(I) tetraiodomercurate(II), Cu_2HgI_4, and study its changes in color and conductivity as the compound undergoes a phase transition upon heating.

Introduction

Cu_2HgI_4 is thermochromic; it reversibly changes color with temperature. At low temperatures this compound is bright red, and at high temperatures it is dark brown. In the low-temperature form, the Cu^+ and Hg^{2+} ions are arranged in separate alternating layers, packed between layers of I^- ions (Figure 1). In the high-temperature form, the I^- ions occupy the same positions as before, but the metal ions now randomly occupy all the tetrahedral holes in the iodide array. The transition from one crystal form to the other takes place fairly sharply at a distinct temperature.

In the high-temperature form, the number of metal ions is smaller than the number of positions among which these ions are distributed. Thus, it is easy for the metal ions to move through the crystal by simply moving into unoccupied positions. In the high temperature form the metal ions diffuse through the crystal much like they would diffuse through an aqueous solution. With suitable equipment we can easily demonstrate that the electrical conductivity of the high-temperature form is much larger than that of the low-temperature form.

Copper(I) tetraiodomercurate(II) is prepared by the reaction of copper(II) sulfate with potassium iodide, followed by the addition of mercury iodide. The copper(II) ion is reduced by the iodide ion, forming solid CuI (*see* the Appendix).

$$2Cu^{2+}(aq) + 4I^-(aq) \rightleftarrows 2CuI(s) + I_2(aq)$$

In the presence of excess iodide ion, the iodine undergoes further reaction to form the triiodide ion.

$$I_2(aq) + I^-(aq) \rightleftarrows I_3^-(aq)$$

The net ionic equation therefore becomes,

$$2Cu^{2+}(aq) + 5I^-(aq) \rightleftarrows 2CuI(s) + I_3^-(aq)$$

NOTE: This experiment was written by William R. Robinson, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

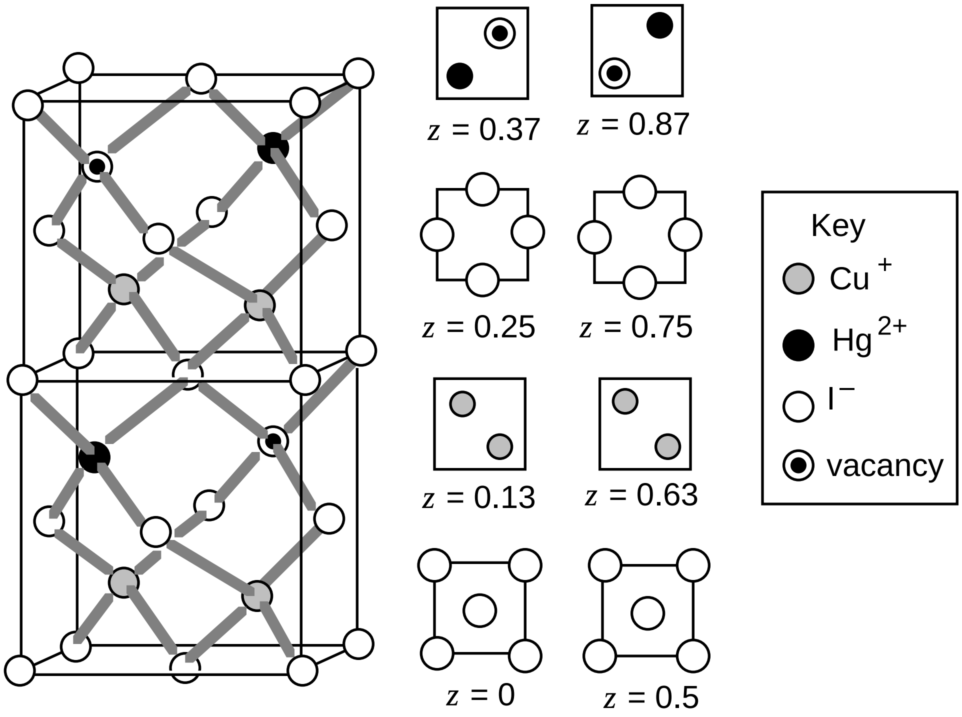

Figure 1. The structure of the low-temperature form of Cu_2HgI_4.

Sodium sulfite is added to this mixture to reduce the triiodide ion back to iodide,

$$I_3^- (aq) + SO_3^{2-} (aq) + 3H_2O \rightarrow 3I^- (aq) + SO_4^{2-} (aq) + 2H_3O^+$$

The solid copper(I) iodide can be separated from the reaction mixture by carefully pouring off the excess solution of supernatant liquid.

A mercury(II) iodide precipitate is synthesized by the reaction of mercuric nitrate with potassium iodide,

$$Hg^{2+} (aq) + 2I^- (aq) \rightleftarrows HgI_2 (s)$$

Finally, Cu_2HgI_4 is prepared by adding the solid copper(I) iodide to the mixture containing the mercury(II) iodide precipitate.

Procedure

Wear eye protection.

Synthesis of Cu_2HgI_4

CAUTION: The chemicals used in this experiment, particularly mercury-containing compounds, are toxic. Avoid

creating or breathing dust. Avoid eye and skin contact. Wash your hands thoroughly after handling.

Add 5 mL of 0.5 M $CuSO_4$, 6 mL of 1 M KI, and several drops of 6 M acetic acid to 50 mL of deionized water in a 150-mL beaker. A precipitate will form. Weigh out about 0.2 g of Na_2SO_3. Dissolve this Na_2SO_3 in about 10 mL of water and add the solution, stirring continuously, to the beaker containing the CuI precipitate. Allow the precipitate of copper(I) iodide to stand for several minutes. Pour off as much of the supernatant solution as possible without losing more than a few percent of the precipitate.

Add 25 mL of 0.05 M $Hg(NO_3)_2$, 3 mL of 1 M KI, and 100 mL of deionized water to a 250-mL beaker. Add the suspension of copper(I) iodide just prepared, using a stream of deionized water from a wash bottle to wash all of the CuI from the beaker.

Heat the mixed suspension of CuI and HgI_2 almost to the boiling point for about 20 minutes on a hot plate while stirring with a magnetic stirrer. During this digestion period, a single dark-brown solid should form. Suction filter this solution while it is still hot. Wash the precipitate with portions of acetone. **CAUTION: Acetone is quite volatile and flammable. No open flames should be present.**

Let the solid air-dry for 10 minutes.

Determination of the Transition Temperature

The transition temperature of Cu_2HgI_4 lies between 40 and 90 °C, a temperature that can be conveniently studied using a water bath. You should be able to determine the transition temperature by finding the temperature at which a color change takes place as a sample of Cu_2HgI_4 cools. A small amount of Cu_2HgI_4 can be rubbed onto the surface of a piece of filter paper, and the filter paper can then be placed into a beaker of water of known temperature. It is convenient to start with a beaker of hot water and to approach the transition temperature with the stepwise addition of cold water. Record the measured transition temperature. An alternative approach to the determination of the transition temperature involves packing a small amount of dry Cu_2HgI_4 precipitate into a piece of capillary tubing that has one end sealed. The capillary tube is used as a small test tube and immersed in a hot-water bath. The color is observed as the temperature of the water bath is decreased by the addition of cold water.

Comparison of Electrical Conductivities

Insert a straight piece of copper wire (18-gauge) into a glass capillary tube (Figure 2). The fit should be tight. Push the open end of the tube into some Cu_2HgI_4 so that some of the material is stuck in the tube. Flip the tube upside down and tap the copper wire end against a hard surface so that the Cu_2HgI_4 falls to the wire. Repeat this tapping until there is about 1 cm of the material in the tube. Finally, insert another length of copper wire into the open end of the glass capillary, so the Cu_2HgI_4 is packed between the two copper electrodes. In order to ensure a tightly packed tube, carefully bend the copper wire electrodes and place a rubber band around the electrodes:

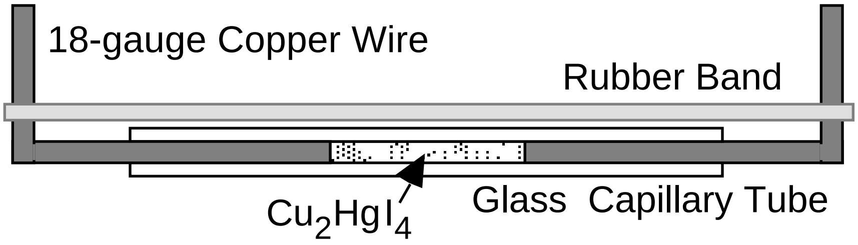

Figure 2. Apparatus for measuring conductivity.

Using an ohmmeter (adjust the meter to read in the 1–10-MΩ range), measure the electrical resistance between the electrodes of the Cu_2HgI_4 sample. Heat the tube with a heat gun (you may use a match instead, but try not to blacken the tube) and measure the electrical resistance between the electrodes. How does the conductivity change as the color changes?

Dispose of the Cu_2HgI_4 in the waste container provided.

The Crystal Structures of Cu_2HgI_4

At room temperature, Cu_2HgI_4 crystallizes in a tetragonal unit cell with unit cell lengths $a = b = 6.09$ Å and $c = 12.24$ Å. All of the angles in a tetragonal cell are 90°. Note that the c-axis length is almost double the a and b axis lengths (the unit cell is almost made from two cubes) as shown in Figure 1.

Study Figure 1 or build a model of the structure of the low-temperature form of Cu_2HgI_4. (For the SSMK, use template D, and modify the directions for expanded face-centered cubic zinc blende.) What is the coordination number and the geometry about the Cu(I) and Hg(II) ions? Even if the iodide ions did form a perfect face-centered cubic array, the cell would not be cubic. Why not?

When Cu_2HgI_4 is heated above the transition temperature, the iodide ions move into the exact positions of a face-centered cubic array, and the Cu^+ and Hg^{2+} ions diffuse through the solid by hopping from tetrahedral site to tetrahedral site. On average throughout the crystal, each tetrahedral site contains one-fourth of a Cu^+ ion and one-eighth of a Hg^{2+} ion. An X-ray measurement of a crystal measures the average of a great many unit cells, so the crystal appears cubic with $a = b = c = 6.10$ Å. Why is the height of the unit cell only half as large as for the low-temperature form?

Build a model of the high-temperature form of Cu_2HgI_4. Use one color of spheres to represent the position of the iodide ions and second color spheres to indicate the location of the tetrahedral sites, which are either empty, occupied by a Cu^+ ion or occupied by a Hg^{2+} ion. (For the SSMK, use template D, and modify the directions for expanded face-centered cubic zinc blende.)

As copper or mercury ions diffuse through the crystal, they can move to an adjacent, empty tetrahedral hole by one of two paths. A direct jump to an adjacent tetrahedral hole is possible, or a jump to an octahedral hole followed by a jump to the second tetrahedral hole is possible. Consider the position of an ion when it is halfway between two tetrahedral holes and when it is halfway between a tetrahedral hole and an octahedral hole. Which of these two paths would require the smallest distortion of the iodide lattice? Remember that the iodide ions are touching.

Appendix. The Stability of Cu(I) Compounds

The synthesis of Cu_2HgI_4 contains some interesting chemistry. Beginning with an aqueous copper(II) sulfate solution that is treated with potassium iodide, a precipitate is formed, but not the one that might first be expected. Rather than obtaining a precipitate of copper(II) iodide, CuI_2, the precipitate analyzes as copper(I) iodide, CuI. Copper(II) is reduced to Cu(I), and some of the iodide (I^-) is oxidized to I_2.

When an element can exist in more than one oxidation state in aqueous solution, each oxidation state will have a different thermodynamic stability. The relative stability of two oxidation states in aqueous solution is most conveniently expressed in terms of the electrochemical potential for the reaction.

$$M^{a+} + (a - b)\,e^- \rightleftarrows M^{b+} \quad \text{where } b < a$$

The potential for a solution containing the ions M^{a+} and M^{b+} is given by the Nernst equation,

$$E = E° - \frac{RT}{nF} \ln \frac{[M^{b+}]}{[M^{a+}]}$$

where n is the number of electrons per ion transferred at the electrode; F is the Faraday constant, 96,480 C/mol; E is the potential of the solution; $E°$ is the standard potential; $[M^{a+}]$ is the concentration of M^{a+} ions in the solution; $[M^{b+}]$ is the concentration of M^{b+} ions in the solution; R is the gas constant; and T is the absolute temperature.

Therefore, any species added to the solution that decreases the concentration of either M^{a+} or M^{b+} and so alters the ratio $[M^{b+}]/[M^{a+}]$ will cause an observable change in the potential and in the relative stability of M^{a+} and M^{b+}. If $[M^{a+}]$ is decreased, then the observable potential will become less positive, that is, the higher oxidation state will become more stable. Alternatively, if $[M^{b+}]$ is decreased, the observed potential will become more positive and the lower oxidation state will become more stable.

Copper(I) iodide is a very insoluble salt ($K_{sp} = 5.1 \times 10^{-12}$). Thus, the addition of iodide ion to a solution of copper(I) will decrease the Cu^+ concentration and increase the ease of reduction of Cu^{2+} to Cu^+. The concentration of Cu^+ in a solution containing iodide ions is so low that even the weakly reducing iodide ion is strong enough to reduce Cu^{2+} to Cu^+.