Experiment 9*

Thermochromism in the Ionic Conductor, Cu_2HgI_4

*This lab taken from "Teaching General Chemistry; A Materials Science Companion," Eds. Ellis, A.B.; Geselbracht, M.J.; Johnson, B.J.; Lisensky, G.C.; Robinson, W.R.R.; American Chemical Society, **1993**

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 tetragonal form, the Cu^+ and Hg^+ ions are arranged in separate alternating layers, packed between close-packed layers of I^- ions (Fig. 9.20C). In the high-temperature cubic form (Fig. 9.20D), 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. Despite having a solid state (not molecular) structure, Cu_2HgI_4 is readily prepared through a solution synthesis, and its phase change is observable both by through conductivity and a color changes.

Unlike most electrical conductors where electrons move in response to an applied voltage, *ionic* conductors such as Cu_2HgI_4 (and the related solid, Ag_2HgI_4) can transport a current due to the ability of their constituent ions to move in response to an applied voltage. Ionic conductors are the solid analogues of electrolyte solutions, which also conduct electricity via the motion of ions. Ionic conductors are generally broken into two classes – those which conduct cations, and those which conduct anions. The latter class is of crucial importance to fuel cell applications, which demand a material capable of conducting oxygen in the form of O^{2-} ions through a solid barrier.

Structure and Phase Change

The low temperature ordered structure of Cu_2HgI_4 is shown in Figure 9.20C. Although the overall unit cell is tetragonal, with square bases and rectangular sides, it can be viewed as two face-centered cubic (fcc) cells of iodide ions, stacked one atop the other. The structure of Cu_2HgI_4 is closely related to that of the archetypical minerals, ZnS and CaF_2, with the metals occupying tetrahedral voids within a close-packed lattice of the *p*-block element. *[The structure files for ZnS and CaF_2 are in Diamond's directory of sample minerals]*. However, the Cu^+ and Hg^{2+} cations have a special room-temperature ordering not present in the two simpler compounds, giving rise to a larger tetragonal unit cell with about twice the volume of the FCC cubic cell of ZnS (Figure 9.20). In this low-temperature phase, the solid is brick red.

At a temperature of about 67°C, disorder sets in, and the cations are randomly distributed about all of the tetrahedral holes in the structure. The different tetrahedral sites become indistinguishable to x-rays (because X-ray diffraction measures the average occupation of the tetrahedral sites, and on average, every tetrahedral site contains one-fourth of a copper ion and one-eighth of a mercury ion), giving the high temperature phase the same high symmetry cubic unit cell as ZnS and CuF_2. The phase change is accompanied by a color change to red-brown and a marked increase in electrical conductivity. The color change is due to a small decrease in the band gap (2.1 to 1.9 eV) with the change in structure.

Conductivity Mechanism

Above the transition temperature, Cu_2HgI_4 exhibits ionic conductivity (with some electronic conductivity also). Five-eighths of the tetrahedral holes and all of the octahedral holes formed by the iodide ions are vacant, and these open sites provide a possible mechanism for the small copper cations to move through the crystal, carrying charge. It is easiest for a copper cation to jump between tetrahedral holes by moving to an octahedral hole and then to the new tetrahedral hole, rather than jumping directly between tetrahedral holes.

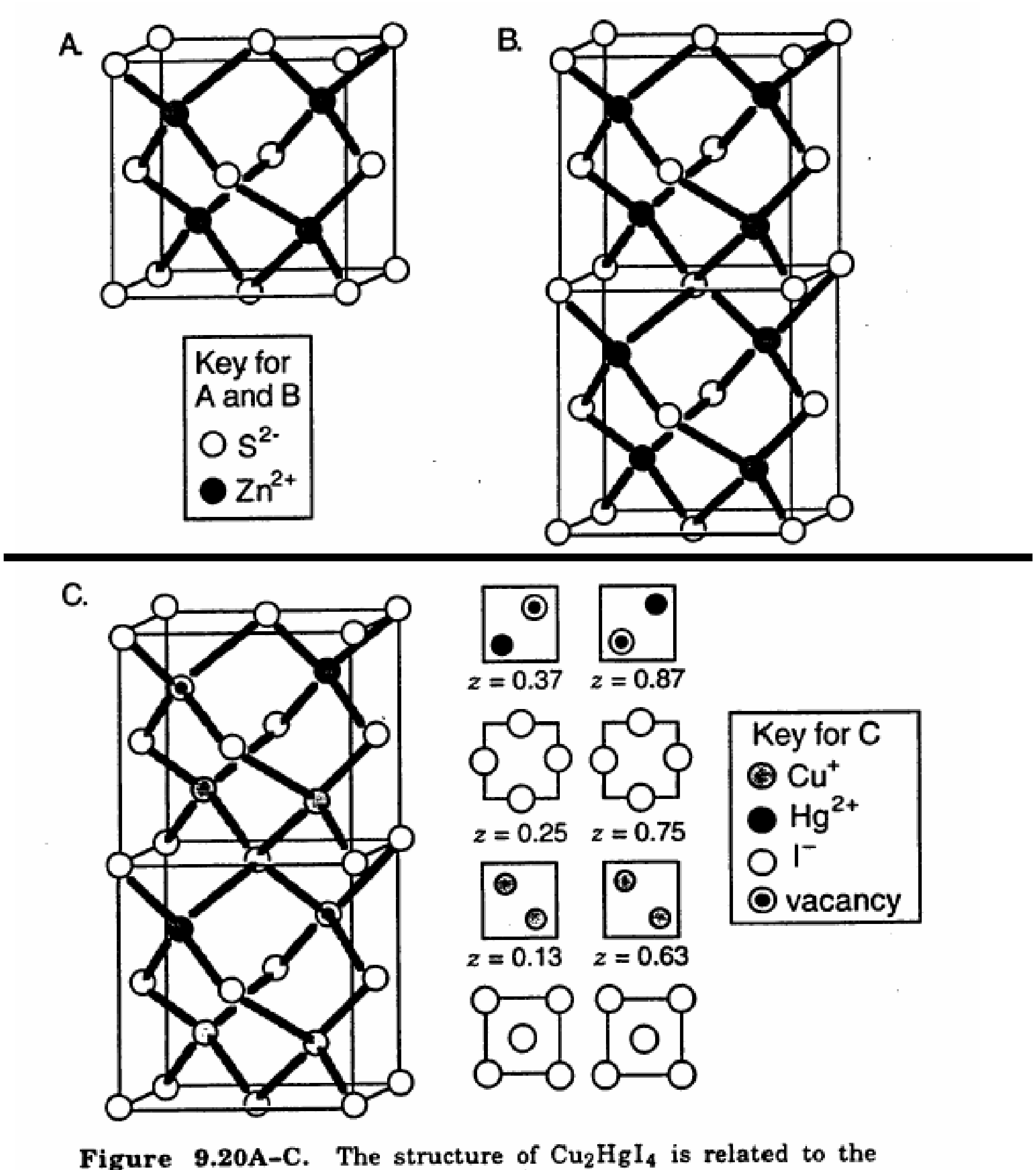

Figure 9.20A–C. The structure of Cu_2HgI_4 is related to the structures of ZnS (sphalerite) and of CaF_2 (fluorite). A: A sphalerite unit cell. B: Two stacked sphalerite unit cells. C: The ordered (low-temperature) structure of Cu_2HgI_4, with the z layer sequence. Three-eighths of the tetrahedral holes are occupied (2 of the 10 vacancies are shown; *see* the fluorite-like structure in D).

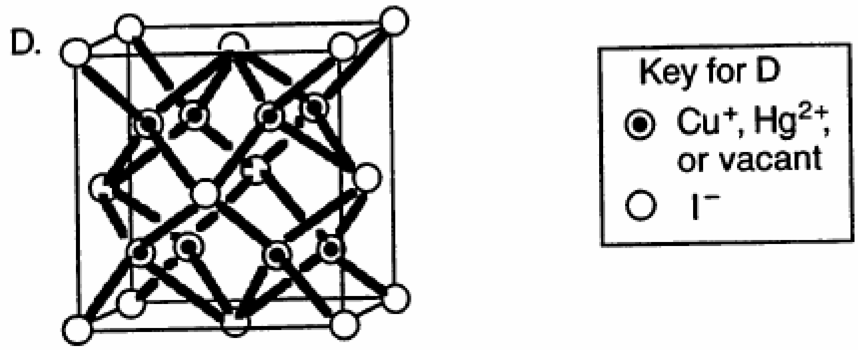

Figure 9.20D. The disordered (high-temperature) structure of Cu_2HgI_4. The cations are randomly distributed throughout all of the tetrahedral holes.

Chemical reactivity

Copper(I) tetraiodomercurate(II), Cu_2HgI_4, is prepared by combining copper(I) iodide with mercury iodide. Copper(I) iodide is formed by reacting copper(II) sulfate with potassium iodide, in which the iodide ion reduces Cu(II) to Cu(I), thereby forming solid CuI (see Appendix).

$$2Cu^{2+}(aq) + 4I^-(aq) \leftrightarrows 2CuI(s) + I_2(aq) \tag{1}$$

In the presence of excess iodide ion, the iodine undergoes further reaction, forming triiodide ions

$$I_2(aq) + I^- \leftrightarrows I_3^-(aq) \tag{2}$$

The net ionic equation for the formation of copper(I) iodide is shown below (eq. 3).

$$2Cu^{2+}(aq) + 5I^-(aq) \leftrightarrows 2CuI(s) + I_3^-(aq) \tag{3}$$

Triiodide can act as an oxidizing agent, by the reversal of equations 2 and 1, so it must be removed from solution. Sodium sulfite is used to reduce the triiodide ion back to iodide, eq. 4.

$$I_3^-(aq) + SO_3^{2-}(aq) + 3H_2O \leftrightarrows 3I^-(aq) + SO_4^{2-}(aq) + 2H_3O^+(aq) \tag{4}$$

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 an anion metathesis reaction, in which mercuric nitrate is combined with potassium iodide. The insolubility of HgI_2 helps to pull the equilibrium toward the right of eq. 5.

$$Hg^{2+}(aq) + 2I^-(aq) \leftrightarrows HgI_2(s) \tag{5}$$

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

$$2\,CuI(s) + HgI_2(s) \rightarrow Cu_2HgI_4(s) \tag{6}$$