

Crystallization of Anhydrous Copper Sulfate From Sulfuric Acid—Ammonium Sulfate Mixtures

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The growth of CuSO_4 crystals from a nonaqueous solvent, composed of $(\text{NH}_4)_2\text{SO}_4$ and H_2SO_4 is described. Solubility of CuSO_4 in solvents of varying $(\text{NH}_4)_2\text{SO}_4$ to H_2SO_4 ratio, at 200 °C, has been determined, as well as the temperature dependence of the solubility in $0.35(\text{NH}_4)_2\text{SO}_4-0.65\text{H}_2\text{SO}_4$. Single crystal specimens, weighing up to 150 mg have been obtained.

1. Introduction

Anhydrous CuSO_4 , isostructural with orthorhombic ZnSO_4 , is of particular interest because of its antiferromagnetic properties at low temperatures. Fundamental investigations on this compound would be greatly enhanced if single crystal specimens were readily available. Kokkoros and Rentzeperis [1]¹ obtained CuSO_4 single crystals up to 1 mm in length by evaporation of an aqueous solution obtained by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in water and adding H_2SO_4 . Conditions under which the anhydrous salt may be obtained from an aqueous solution have been described in the early literature [2]. Kreines [3], in an effort to prepare crystal specimens of this salt for magnetic susceptibility and anisotropy studies, dissolved CuSO_4 in molten $(\text{NH}_4)_2\text{SO}_4$; then, by controlling the rate of decomposition of the solvent, he was able to obtain single crystals of CuSO_4 weighing up to 2 mg. Like many other sulfates, CuSO_4 undergoes decomposition before the melting point is reached so that growth from the melt under normal laboratory conditions is precluded. The use of a nonaqueous solvent appears to be the most promising approach, and experiments in our laboratory indicate that a sulfuric acid-ammonium sulfate mixture offers some definite advantages over the single components as a solvent for CuSO_4 single crystal growth.

2. Experimental Results and Discussion

Starting reagents used throughout this work were Baker "Analyzed Reagent" grade. The $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was further purified by recrystallization from distilled and demineralized water, then dehydrated by heating in a muffle furnace at 350 °C for 24 hr under a dry nitrogen atmosphere. The anhydrous powdered salt was stored in a desiccator over phosphorous pentoxide.

The sulfuric acid was adjusted to 100 percent composition by adding fuming sulfuric acid to the commercial 96 percent reagent, the freezing point method [4] being used to determine when the 100 percent composition point was reached.

Solvents of various compositions were then prepared by heating a measured quantity of H_2SO_4 to 150 °C and adding a weighed amount of $(\text{NH}_4)_2\text{SO}_4$ to give the desired composition.

The solubility of CuSO_4 in solvents of varying $(\text{NH}_4)_2\text{SO}_4-\text{H}_2\text{SO}_4$ ratios, at 200 °C, is indicated in figure 1. The experimental points were determined by adding powdered CuSO_4 to the solvent, maintaining the temperature at 200 °C ± 2 °C for 24 hr to assure equilibrium, sampling the solution, and determining the copper content and sulfate content iodometrically and gravimetrically, respectively. The sulfate analysis was corrected for the amount of sulfate present as CuSO_4 so that the ordinates of figures 1 and 2 show the ratio of copper to solvent sulfate in the solution.

As figure 1 indicates, the solubility of CuSO_4 in pure H_2SO_4 is relatively low, but increases rapidly as the $(\text{NH}_4)_2\text{SO}_4$ content of the solvent increases. However, increasing the $(\text{NH}_4)_2\text{SO}_4$ ratio also increases the viscosity of the solvent at any given temperature, so that higher temperatures are necessary to maintain the solvent in a fluid state. Practical working temperatures are limited by the fact that $(\text{NH}_4)_2\text{SO}_4$ undergoes considerable decomposition above 300 °C. Since crystal growth is dependent on diffusion through the solution and since higher viscosities affect diffusion adversely, solvents of higher mole ratio than 0.35 $(\text{NH}_4)_2\text{SO}_4$ were not considered.

The temperature dependence of CuSO_4 solubility in $0.35(\text{NH}_4)_2\text{SO}_4-0.65\text{H}_2\text{SO}_4$ is shown in figure 2. In determining the experimental points, the temperature of the solution was controlled at the given value ± 2 °C and maintained for 24 hr with occasional stirrings before sampling. A study of the copper content of the solution as a function of time, at the lowest temperature shown in figure 2, indicated that 24 hr was an adequate period to achieve equilibrium. Analyses for copper and sulfate were made as indicated above.

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¹ Figures in brackets indicate the literature references at the end of this paper.

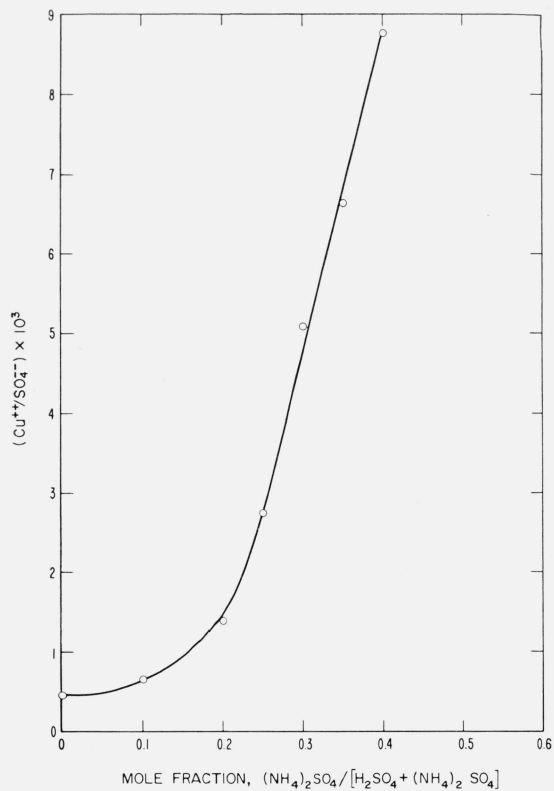


FIGURE 1. Solubility of CuSO_4 in $(\text{NH}_4)_2\text{SO}_4\text{-H}_2\text{SO}_4$ of varying composition at 200°C .

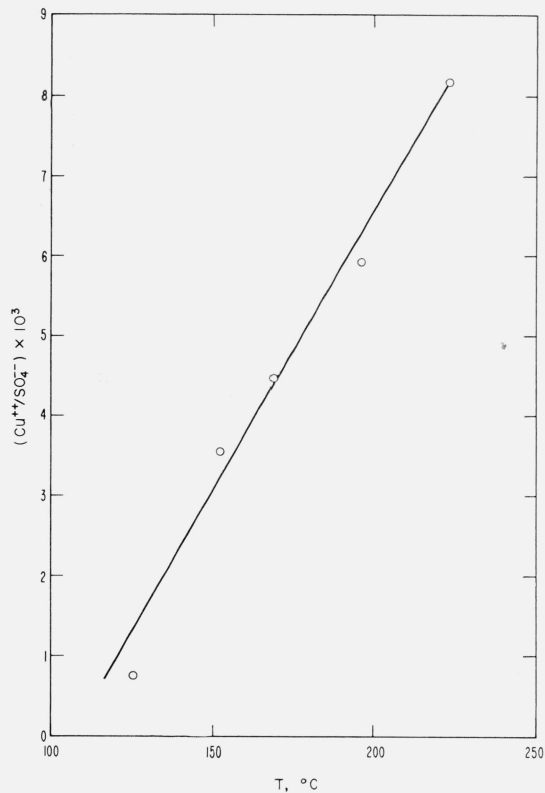


FIGURE 2. Temperature dependence of CuSO_4 solubility in $0.35(\text{NH}_4)_2\text{SO}_4\text{-}0.65\text{H}_2\text{SO}_4$.

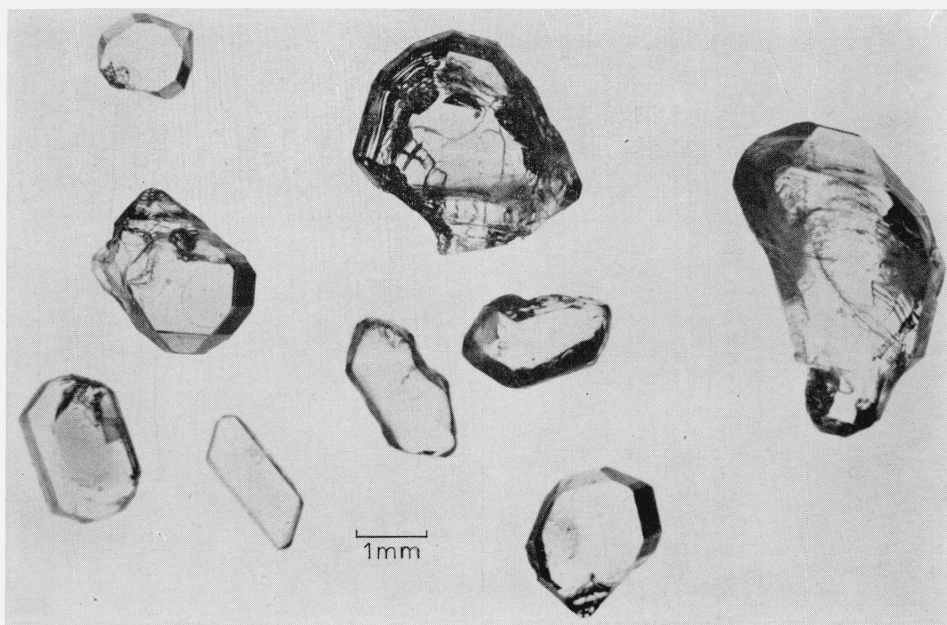


FIGURE 3. CuSO_4 single crystals.

To carry out the crystal growth, approximately 500 ml of solution were placed in a large borosilicate glass test tube, heated by a conventional hot plate. An excess of CuSO_4 powder was added to the solution, and a tantalum sheet, rotating at 10 rpm, was suspended in the solution near the surface. The test tube was loosely covered. The solution temperature was approximately 200 °C with a temperature gradient between the bottom of the container and the tantalum sheet of approximately 5 °C. Single crystals of CuSO_4 grew predominantly at the edges of the tantalum sheet, but occasionally also on the flat surfaces. In three or four days, crystals weighing up to 150 mg have been obtained. Excess solvent was removed from the crystal surfaces by washing in 100 percent H_2SO_4 and heating to 400 °C.

Figure 3 is a photograph of several CuSO_4 crystals. The specimens, which were transparent with a slight greenish tinge, were verified to be single crystals by Laue backscatter x-ray diffraction. Chemical analysis of the crystals indicated a composition of 99.7 percent CuSO_4 .

3. References

- [1] P. A. Kokkoros and P. J. Rentzeperis, *Acta Cryst.* **11**, 361 (1958).
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- [4] L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.* **55**, 1900 (1933).

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