

COMPONENTS: (1) Copper(I) oxide; Cu_2O ; [1317-39-1] (2) Water; H_2O ; [7732-18-5]	EVALUATOR: T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506 U.S.A. October 1984
CRITICAL EVALUATION: <p>The only solubility data reported for unipositive copper are for Cu_2O. There is no substantial evidence for the existence of a solid CuOH. Bevillard examined samples of Cu_2O prepared by various methods and samples of substances that might have been CuOH (1). The examination consisted of chemical analysis and X-ray diffraction measurements. The conclusion reached was that the existence of CuOH is doubtful. The preparations appeared to be Cu_2O with varying amounts of water. Color differences among various samples of Cu_2O were ascribed to differences in particle size.</p> <p>Unlike investigations of the other transition series metals of Groups I and II of the Periodic Table, no attention has been given to the solubility of Cu_2O in water or in solutions of alkalis. No acidic, basic or solubility product constants have been reported on the basis of solubility measurements.</p> <p>Feitknecht (2) calculated a solubility product constant value of 1.26×10^{-15} for CuOH, presumably at 298 K. The calculation was based on thermodynamic and e.m.f. data that were available. However, some of these values were revised in the process of carrying out the calculations. An attempt had been made earlier to determine the solubility product constant experimentally (3). The method involved the measurement of the e.m.f. of a cell containing a $\text{Cu}_2\text{O}/\text{Cu}$ electrode immersed in a solution of NaOH or KOH. The value of the K_{sp} reported was 1.0×10^{-14} at 290 K. This is ten times the value calculated for 298 K (2). It is evident from this that the solubility product constant for CuOH has not been determined, but it probably is of the order of 10^{-15}.</p> <p>The solubility of Cu_2O in aqueous NH_3 has been measured at 298 K (4). The purpose of the work was to gather information about the composition of Cu(I)-NH_3 complexes. Considerable care was taken in making the solubility measurements, and there is no reason to consider these values as doubtful. However, there are some uncertainties in the values and the two samples of Cu_2O that were used show some differences in solubility, Figure 1. These differences may be due to differences in particle size.</p> <p>Two investigations of the solubility of Cu_2O have been made because of the possibility that it may be an intermediate in the corrosion of copper. In one such study (5) the rate of dissolution of Cu_2O was measured in a variety of aqueous salt solutions, but the report contains no solubility data. Concentrations of dissolved Cu_2O were measured after two time intervals, the longer being one day, and there was no assurance that the solutions were saturated. The rate of dissolution was measured as a function of pH. Except in solutions of Na_3PO_4, the "solubility" of Cu_2O passed through a minimum at a pH of 11 to 12. The data are presented only in graphical form and no temperature is specified.</p> <p>In the other solubility investigation related to the corrosion of copper (6) the solubility of Cu_2O was measured in supercritical steam at a temperature of 895 K. The pressure varied from 186×10^5 to 310×10^5 Pa. The pH range was 7.5 to 9.6, but the solubility of Cu_2O was constant in this pH range. The solubility of Cu_2O was more dependent on pressure than on the temperature. The values reported are to be considered tentative until further, similar, work is reported.</p>	

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CRITICAL EVALUATION:

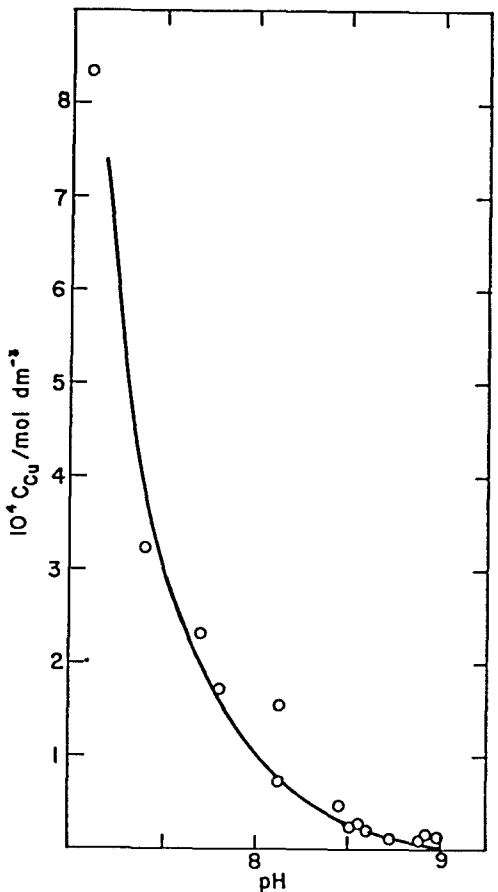


Figure 2. Solubility of Cu_2O in sea water at 298 K. (8).

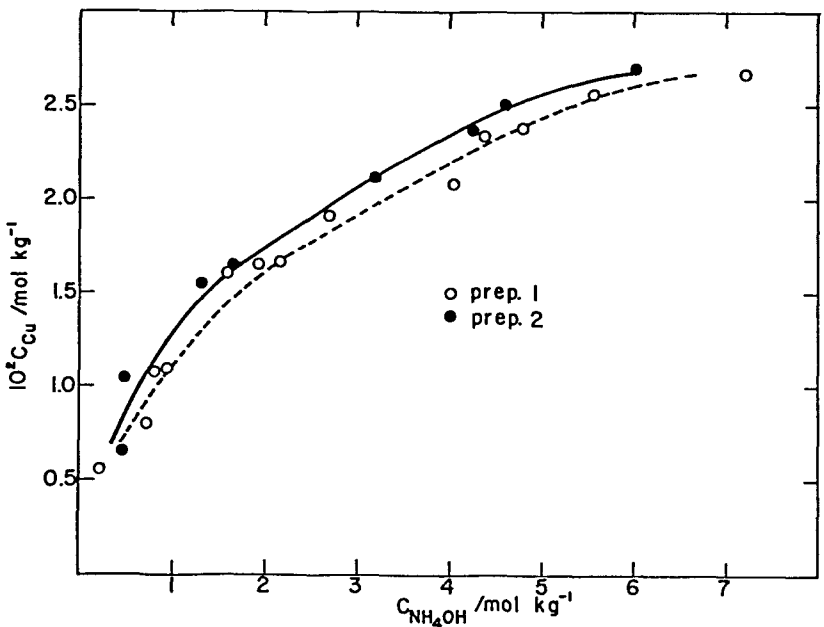


Figure 1. Solubility of Cu_2O in aqueous NH_3 at 298 K. (4). Preparation 2 contains a much larger proportion of very small microcrystalline particles than does Preparation 1.

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<p>CRITICAL EVALUATION:</p> <p>One of the characteristics of Cu₂O is its toxicity. For this reason it can be used as a fungicide and in marine anti-fouling paints. An interest in the possible use of Cu₂O as a fungicide to treat certain seeds prompted an investigation of the effect of hydrolyzed protein material and certain amino acids on the water solubility of Cu₂O (7). The nitrogenous materials increase the water solubility of Cu₂O at 298 K. The results that were reported were qualitative in nature, and the source of the nitrogenous materials was not identified. Therefore, no data sheet was prepared for this report.</p> <p>Two studies were undertaken because Cu₂O is an ingredient of marine anti-fouling paints. This application requires a knowledge of the solubility of Cu₂O in sea water. The rate of dissolution of Cu₂O in sea water was the main interest in one investigation (8), but some solubility data were also included, Figure 2. It is not evident from the report whether a natural or a synthetic sea water was used. At the pH of sea water (8.1) the solubility of Cu₂O at 298 K is given as 8.6×10^{-5} mol dm⁻³. Ragg (9) measured the solubility of Cu₂O in Baltic Sea water (pH = 8.1). The temperature was not specified, but it probably was around 290 K. The solubility value reported was about one-tenth the value reported earlier (8). The paper by Ragg contains practically no experimental detail. The value of Ferry and Carritt (8) is to be preferred, but must be considered tentative.</p> <p>Because of an interest in the processes whereby certain metals may enter the environment, Shlyapnikov and Shtern began a study of the solubility of metal oxides in NaCl solutions exposed to CO₂ at elevated pressures. The first paper (10) contains only a few data and there are inconsistencies between data in the text and in the Tables. Later a more thorough study was made of the solubility of Cu₂O under such conditions (11). The solubility of Cu₂O increases with increasing concentration of NaCl or KCl, and with increasing pressure of CO₂. Under these conditions the copper in Cu₂O is oxidized to Cu²⁺. There is no reason to reject these values, but because they are the only ones available for these systems, they can only be considered as tentative.</p> <p style="text-align: center;">References</p> <ol style="list-style-type: none"> 1. Bevilard, P. <i>Bull. Soc. Chim. Fr.</i> 1950, 561. 2. Feitknecht, W. <i>Helv. Chim. Acta</i> 1944, 27, 771. 3. Allmand, A. J. <i>J. Chem. Soc.</i> 1909, 95, 2151. 4. Donnan, F. G.; Thomas, J. S. <i>J. Chem. Soc.</i> 1912, 99, 1788. 5. Wilson, L. <i>Australia Dept. Supply, Aeron. Res. Lab.</i> 1964, Note 19. 6. Pocock, F. J.; Stewart, J. F. <i>J. Eng. Power</i> 1963, 85, 33. 7. Marten, E. A.; Leach, J. G. <i>Phytopathology</i> 1944, 34, 459. 8. Ferry, J. D.; Carritt, D. E. <i>Ind. Eng. Chem.</i> 1946, 38, 612. 9. Ragg, M. <i>Farbe u. Lack</i> 1950, 56, 435. 10. Shlyapnikov, D. S.; Shtern, E. K. <i>Dokl. Akad. Nauk SSSR</i> 1975, 225, 428; <i>Doklady Acad. Sci. USSR, Earth Sci. Sect. (Eng. transl.)</i> 1975, 225, 185. 11. Shlyapnikov, D. S.; Shtern, E. K. <i>Zhur. Neorg. Khim.</i> 1977, 22, 1100; <i>Russ. J. Inorg. Chem. (Engl. transl.)</i> 1977, 22, 604. 	