

4. The new solvent solutions are being used to study certain single phase reactions of cellulose.

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### NOTE

**Copper Selenate Tetrammonate Dihydrate.**—In a recent communication the isolation of copper selenate tetrammonate dihydrate,  $\text{CuSeO}_4 \cdot 4\text{NH}_3 \cdot 2\text{H}_2\text{O}$ , was reported,<sup>1</sup> and as Hurd and Lenher<sup>2</sup> did not succeed in preparing this compound, the detailed description of the preparation of this salt will be given.

Alcohol is added to a strong ammoniacal solution of copper selenate, the resulting blue precipitate filtered on a sintered glass plate, washed several times with alcohol and acetone and rapidly dried on a porous plate in the open air. Ten grams of this product, finely powdered, is dissolved by warming in 7.5 cc. of 25% ammonia solution and after filtering through a sintered glass plate is cooled to 15–20° in a closed Erlenmeyer flask. If needle-like crystals appear, two drops of concentrated ammonia should be added and the solution warmed until the crystals have dissolved. The solution is again cooled and if needles appear the process of adding ammonia and warming should be repeated. Eventually, after six to twenty-four hours, large six-sided tables will crystallize out. In most cases only one crystal forms, the edges having a length of about 1 cm.

These crystals are the copper selenate tetrammonate dihydrate. They are of a pure blue color and are easily soluble. After being dried with filter paper, the crystals tarnish in a short time as a result of incipient decomposition. The yield best obtained was 2 g.

Even if the crystals appear perfectly pure and faultless, they always include solvent. For analysis they should be broken up, pressed between filter paper and the pieces pulverized on a porous plate until the powder is perfectly dry. This drying requires practice and must be carried out rapidly, for even the unbroken crystals begin to decompose as soon as the surfaces are dry. The powder is pure blue in color, differing from the monohydrate, which is blue-violet.

The compound analyzes correctly for copper selenate tetrammonate dihydrate, as indicated by the analytical data for the last products which each of us has made and analyzed.

*Anal.* Calcd. for  $\text{CuSeO}_4 \cdot 4\text{NH}_3 \cdot 2\text{H}_2\text{O}$ : Cu, 20.45;  $\text{NH}_3$ , 21.91;  $\text{H}_2\text{O}$ , 11.59. Found (W. L.): Cu, 20.68;  $\text{NH}_3$ , 21.97;  $\text{H}_2\text{O}$ , 11.52; (G. v. K.) Cu, 20.34;  $\text{NH}_3$ , 21.81;  $\text{H}_2\text{O}$ , 11.70.

In view of these results we consider the existence of copper selenate tetrammonate dihydrate as proved. It is improbable that in every experi-

<sup>1</sup> Willy Lange, *Ber.*, **59**, 2113 (1926).

<sup>2</sup> L. C. Hurd and V. Lenher, *THIS JOURNAL*, **52**, 3861 (1930).

ment exactly one molecule of water is included by a monohydrate,  $\text{CuSeO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ , and that a dihydrate is in this way simulated, as suggested by Hurd and Lenher; if inclusion took place, it would be of mother liquor and not pure water, and as a result the analyses would not show such good agreement.

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## THE TEMPERATURE AT WHICH UNBOUND WATER IS COMPLETELY FROZEN IN A BIOCOLLOID<sup>1,2,3</sup>

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In a paper on the "Relation of Hydrophilic Colloids to Winter Hardiness of Insects" presented at the Colloid Symposium at the University of Michigan in June, 1927, Robinson stated,<sup>4</sup> in effect, that all of the free water in a hydrophilic colloid is frozen at a temperature of  $-20^\circ$ , while none of the bound water is frozen. Foote and Saxton<sup>5</sup> using a dilatometer method on inorganic hydrogels found that all of the free and capillary water was not frozen at  $-20^\circ$ . They found in some instances that a temperature of  $-28$  to  $-33^\circ$  was required. They also found that repeated freezing appears to convert most of the capillary water into free water, while it has little effect on the bound water.

In studying one phase of a problem it was desirable to determine the amount of bound water in egg white. Preliminary to this it was necessary to determine the temperature which should be used for the measurement of bound water in such a material.

A variety of methods has been used for the determination of the nature of water in organic material. Of these the method described by Thoenes<sup>6</sup> and earlier by Rubner<sup>7</sup> was used.

<sup>1</sup> Published as Scientific Paper No. 189, College of Agriculture and Experiment Station, State College of Washington.

<sup>2</sup> Presented at the meeting of the Pacific Division of the American Association for the Advancement of Science on June 20, 1930, at Eugene, Oregon.

<sup>3</sup> The Assistance of Mr. Leo Clapsaddle in the preliminary part of this work is gratefully acknowledged. Valuable suggestions made by Prof. C. A. Isaacs regarding the development of the formula are also appreciated.

<sup>4</sup> Robinson, "Colloid Symposium Monograph," 5, 199 (1928).

<sup>5</sup> Foote and Saxton, *THIS JOURNAL*, 38, 588 (1916).

<sup>6</sup> Thoenes, *Biochem. Z.*, 157, 174 (1925).

<sup>7</sup> Rubner, "Abhandlungen der Preussischen Akademie der Wissenschaften," *Physikalisch-Mathematische Klasse*, No. 1, 1-70.