Sandved,[7] and has a maximum value of 0.09 mv. The two constants 1.45 and 0.1338 were determined by trial, with the aid of Scatchard's[8] results above 0.1 M. The values of c were calculated by means of the equation

$$c_{25^\circ} = M - M\,(0.0029 + 0.0184\,M + 0.0001\,M^2) \qquad (9)$$

which was derived from data in the "International Critical Tables."

The average values for E°_b as calculated by means of the three equations are −0.22247, −0.22235 and −0.22239 volt, respectively, with mean deviations from the average of 0.08, 0.09 and 0.08 millivolt, respectively. The average of the three values, −0.22240 volt, may therefore be used for E°_b (E° of the silver chloride electrodes used). By Equation 2*

$$\mathrm{Pt,H_2,H_2O,OH^-};\ E^\circ = 0.82840 \text{ volt } \pm 0.10 \text{ mv.}$$

Therefore, by Equation 3

$$K_w = (0.988 \pm 0.004) \times 10^{-14}$$

Summary

The ionization constant of water has been determined at 25° from the electromotive force of cells without liquid junction and found to be equal to $(0.988 \pm 0.004) \times 10^{-14}$.

A new method has been outlined for the determination of the ionization constants of weak electrolytes from the electromotive force of cells without liquid junction.

New Haven, Connecticut

[Contribution from the Division of Inorganic Chemistry, Department of Chemistry, University of Wisconsin]

THE AMMONATES OF COPPER SELENITE[1]

By Loren C. Hurd, George I. Kemmerer and V. W. Meloche

Received June 30, 1930 Published October 6, 1930

As a part of the study of selenium and its compounds being made at this Laboratory, it was thought that an investigation of the compounds formed by the action of ammonia on the metallic selenates and selenites might yield results of interest. The present report deals with the compounds formed by the action of ammonia on copper selenite.

During the course of an investigation of a number of ammonates of metallic salts, Boutzaureanu[2] prepared a monammonate monohydrate of

---

[7] Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

[8] Scatchard, This Journal, **47**, 641 (1925).

[1] Abstracted from a portion of a thesis submitted to the Faculty of the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1929. This work was started under the direction of the late Victor Lenher, continued under the supervision of the late George Kemmerer, and completed under the guidance of Professor V. W. Meloche.

[2] Boutzaureanu, *Ann. chim. phys.*, **6**, 18, 346 (1889).

copper selenite. His method of preparation was to dissolve copper selenite in ammonium hydroxide and to allow the resulting dark blue solution to evaporate. The residue was a blue product corresponding in composition to the formula $CuSeO_3 \cdot NH_3 \cdot H_2O$.

Preparation of Copper Selenite Dihydrate.—The direct neutralization of selenious acid with copper carbonate or precipitated copper oxide yielded a flocculent green precipitate, the color and composition of which varied with the preparation. Boutzaureanu[2] converted this basic salt to the normal dihydrate by subjecting it to the action of a 5% solution of selenious acid in a closed bomb at a temperature of 250° for two hours. It was found that although this method yielded the normal dihydrate, it was usually contaminated with small amounts of elementary selenium. Inasmuch as almost all of the preparations to be described were checked on the weight conversion basis, it was necessary to devise a method of preparation which would yield pure copper selenite dihydrate in large quantities.

The most satisfactory method for the preparation of copper selenite was to add to a hot 15% solution of selenious acid a saturated solution of copper acetate. The flocculent green precipitate first formed immediately redissolved and precipitated the slightly soluble copper selenite dihydrate. The product was filtered on a sintered glass plate, washed with a 1% solution of selenious acid and then with distilled water. Analysis of the air-dried product yielded results in harmony with the calculated values for the dihydrate. In some cases the water content was slightly higher than the calculated percentage. In such cases the selenium and copper content was correspondingly low. The methods of analysis used through the work have been described in an earlier paper.[3]

The Hydrated Ammonates of Copper Selenite

Copper Selenite Diammonate Monohydrate.—Fifty grams of copper selenite dihydrate was dissolved in 50 cc. of concentrated ammonium hydroxide and the solution transferred to an eight-inch pyrex tube. The tube was placed in a thermostat at 60° and a rapid stream of ammonia gas passed into the solution. Following the evaporation of the bulk of the liquid there remained a mass of blue crystals. The product was removed from the tube, transferred to a sintered glass filter and pressed dry by means of a piece of rubber dental dam tied over the top of the funnel. Following the removal of most of the liquid, the product was placed over freshly ignited lime for one hour. Analysis of the material yielded results in accord with the calculated values for $CuSeO_3 \cdot 2NH_3 \cdot H_2O$.

Anal. Calcd. for $CuSeO_3 \cdot 2NH_3 \cdot H_2O$: CuO, 32.76; Se, 32.61; NH_3, 14.02. Found: CuO, 32.42; Se, 32.20; NH_3, 14.45 (all av. of 3 detns.).

Copper selenite diammonate monohydrate was a blue crystalline salt, the color of which was slightly lighter than the B shade of the normal tone of Mulliken's color standards.[4] It was very unstable. Traces of moisture caused a liberation of ammonia with

---

[3] Hurd and Lenher, This Journal, **52**, 3857 (1930).

[4] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, **1904**, Color Charts, Vol. I.

the formation of lower ammonates and basic salts. The ammonate was not completely soluble in water but dissolved readily in acids and ammonia solution. It was insoluble in liquid ammonia.

Copper selenite diammonate monohydrate was also prepared by the action of anhydrous ammonia gas on copper selenite dihydrate at 25°. The product was usually slightly moist in spite of prolonged exposure over desiccating agents in an atmosphere of ammonia. The compound when prepared in this manner usually contained slightly more water and ammonia than the calculated amounts.

Passage of ammonia into an ammoniacal solution of copper selenite did not yield a precipitate until the solution was cooled below 10°. Below this temperature a mass of crystals was obtained which when warmed melted to a blue viscous liquid. Analysis of numerous samples did not yield results in harmony with values calculated from any simple formula. Analysis of acid solutions of the product indicated the copper selenite–ammonia ratio to be as 1:3.

Copper Selenite Monammonate Monohydrate.—Solutions of copper selenite containing an excess of ammonia were allowed to evaporate slowly at room temperatures. After a short time a green deposit was formed on the sides and bottoms of the crystallizing dishes. Analysis of the product indicated that it consisted essentially of a basic copper carbonate. A few small crystals were deposited over the bulk of the green scale. Analysis of these products yielded results in approximate agreement with values calculated from the formula $CuSeO_3 \cdot NH_3 \cdot H_2O$. However, when solutions of copper selenite in carbon dioxide-free ammonium hydroxide were allowed to evaporate out of contact with air, a large mass of green crystals was obtained. Analysis of this product substantiated the formula assigned by Boutzaureanu.[2]

Anal. Calcd. for $CuSeO_3 \cdot NH_3 \cdot H_2O$: CuO, 35.25; Se, 35.07; NH_3, 7.54. Found: CuO, 35.13; Se, 34.95; NH_3, 7.67 (all av. of 3 detns.).

Copper selenite monammonate monohydrate so prepared was a dark greenish-blue crystalline mass. It was not readily soluble in water but dissolved easily in dilute mineral acids and ammonia solution. It was not altered by prolonged exposure to air and remained unchanged over phosphorus pentoxide. The compound was also prepared by exposing $CuSeO_3 \cdot 2NH_3 \cdot H_2O$ to the air. Ammonia was evolved and analysis of the light green powder remaining indicated that its composition was the same as that of the salt prepared in the manner of Boutzaureanu.[2]

Anal. Calcd. for $CuSeO_3 \cdot NH_3 \cdot H_2O$: CuO, 35.25; Se, 35.07; NH_3, 7.54. Found: CuO, 34.94; Se, 35.05; NH_3, 7.67 (all av. of 3 detns.).

Anhydrous Ammonates of Copper Selenite

Copper Selenite Diammonate.—$CuSeO_3 \cdot 2NH_3$ was prepared from $CuSeO_3 \cdot 2NH_3 \cdot H_2O$ in the same manner in which Dennis and Koller[5] prepared $CuSeO_4 \cdot 4NH_3$ from $CuSeO_4 \cdot 4NH_3 \cdot H_2O$. Samples of $CuSeO_3 \cdot 2NH_3 \cdot H_2O$ were placed in a soda lime desiccator and the system held at a pressure of about 15 mm. for six days. Analysis of the residue established the composition of the compound.

Anal. Calcd. for $CuSeO_3 \cdot 2NH_3$: CuO, 35.39; Se, 35.23; NH_3, 15.15. Found: CuO, 35.29; Se, 35.21; NH_3, 15.15 (all av. of 3 detns.).

Copper selenite diammonate is a light blue compound, the color of which matches closely the color GB, tint 1 of Mulliken's charts.[4] The compound is quite stable, samples losing little weight after prolonged desiccation over soda lime or phosphorus pentoxide. When treated with water a basic precipitate was formed and only a small portion of the sample dissolved. It was insoluble in liquid ammonia but reacted with ammonia gas to form higher ammonates.

---

[5] Dennis and Koller, This Journal, **41**, 949 (1919).

Copper Selenite Triammonate.—It was found that either $CuSeO_3{\cdot}2NH_3$ or $CuSeO_3{\cdot}NH_3{\cdot}H_2O$ would react with ammonia gas at 0° to form an ammonate of higher ammonia content. In the case of $CuSeO_3{\cdot}NH_3{\cdot}H_2O$ water was liberated. From the volume of ammonia absorbed by a given weight of the diammonate it was found that the stable phase at 0° was $CuSeO_3{\cdot}3NH_3$.

Twenty grams of $CuSeO_3{\cdot}NH_3{\cdot}H_2O$ were treated with a rapid stream of anhydrous ammonia gas at 25° to remove the water and form the anhydrous diammonate. Following the removal of the water the reaction tube was immersed in an ice-bath and treatment with ammonia gas continued. Analysis of the product indicated that the formula of the addition compound was $CuSeO_3{\cdot}3NH_3$.

Anal. Calcd. for $CuSeO_3{\cdot}3NH_3$: CuO, 32.90; Se, 32.75; NH_3, 21.12. Found: CuO, 32.96; Se, 32.69; NH_3, 20.93 (all av. of 2 detns.).

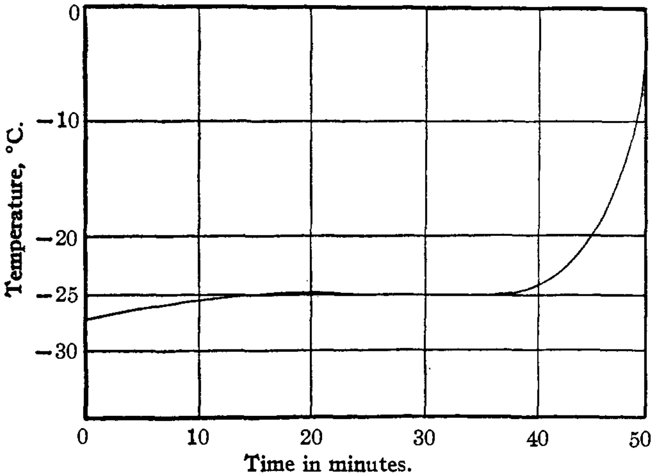

Fig. 1.—$CuSeO_3{\cdot}4NH_3$ to $CuSeO_3{\cdot}3NH_3$.

Copper selenite triammonate so prepared had a bright blue color midway between the GB and B normal tone colors of Mulliken's charts.[4] The ammonate was partially soluble in water. It was relatively unstable and decomposed into the diammonate and ammonia when stored at room temperature. The transition point was found to be in the neighborhood of 19.8°.

Copper Selenite Tetrammonate.—Fifty grams of copper selenite dihydrate was placed in an eight-inch pyrex test-tube and treated with ammonia gas at a temperature of 60°. After eight hours' passage of the gas, the product was removed, crushed and the ammonia treatment continued until the last traces of water had been removed. The tube was then cooled and immersed in a Dewar flask containing liquid ammonia. Passage of gas through the mass was continued until there seemed to be no further absorption. Anhydrous liquid ammonia was then condensed in the tube and the suspension thoroughly stirred. Following removal of the liquid, large samples were quickly removed and sealed into tubes. The tubes were weighed, broken under dilute acid and analysis of the solution made in the usual manner.

Anal. Calcd. for $CuSeO_3{\cdot}4NH_3$: CuO, 30.74; Se, 30.59; NH_3, 26.31. Found CuO, 30.39, 30.12; Se, 30.25, 30.01; NH_3, 25.50, 25.86.

Inasmuch as analytical results on preparations of the tetrammonate were seldom in good agreement, it was thought advisable to investigate the warming curve of the system $CuSeO_3.4NH_3$–$CuSeO_3.3NH_3$ between the temperature of boiling liquid ammonia and 0°. Accordingly approximately 50 g. of the ammonate was prepared in the manner described. When the excess of ammonia had been removed, the material was quickly mixed with 15 g. of $CuSeO_3{\cdot}3NH_3$ and the system allowed to warm slowly. Temperature was indicated by a toluene thermometer and recordings were taken every thirty seconds. Figure 1 shows a plot of the results obtained in a typical run. The transition point for the system fell at −25 ± 1°. It is interesting to note that the product may be warmed to 0° in the absence of decomposition products. Figure 2 is illustrative of the type of curve obtained when the triammonate inoculation was not made.

Copper Selenite Monammonate.—All anhydrous ammonates of copper selenite were found to decompose at or below 120° to yield $CuSeO_3{\cdot}NH_3$. The compound was most conveniently prepared by heating $CuSeO_3{\cdot}2H_2O$ in an atmosphere of ammonia at a temperature of 60°. When the water had been removed, the temperature was raised to 120° and the passage of gas continued for several hours. Analysis of the residue established the identity of the salt.

Anal. Calcd. for $CuSeO_3{\cdot}NH_3$: CuO, 38.29; Se, 38.11; NH_3, 8.19. Found: CuO, 38.20; Se, 37.99; NH_3, 8.17 (all av. of 3 detns.).

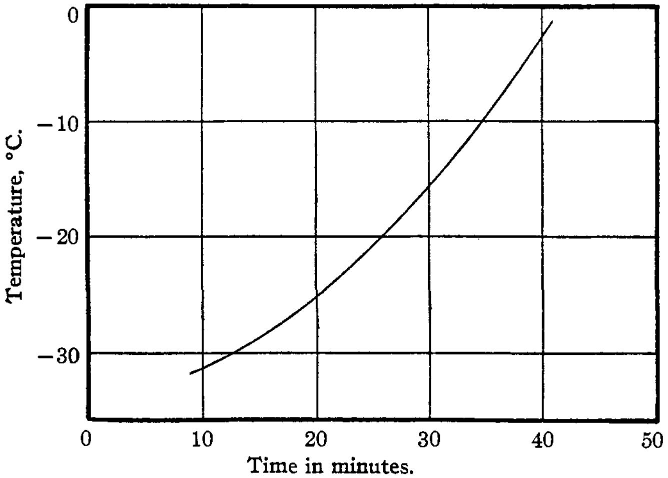

Fig. 2.—Warming curve for $CuSeO_3{\cdot}4NH_3$ in the absence of decomposition products.

$CuSeO_3{\cdot}NH_3$ was a green powder when prepared in the manner described. The color was close to the BG, normal tone of Mulliken's charts.[4] It was insoluble in water and soluble in dilute mineral acids and ammonia solution. $CuSeO_3{\cdot}NH_3$ absorbed ammonia below 120° to form higher ammonates. The compound was stable at ordinary temperatures and could be exposed to the air with little alteration. Above 150° $CuSeO_3{\cdot}NH_3$ was decomposed with the liberation of ammonia and the production of reduction products of copper selenite.

Summary

1. A new hydrated ammonate of copper selenite, $CuSeO_3{\cdot}2NH_3{\cdot}H_2O$, has been prepared and identified.
2. Four new anhydrous ammonates of copper selenite, $CuSeO_3{\cdot}NH_3$,

$CuSeO_3 \cdot 2NH_3$, $CuSeO_3 \cdot 3NH_3$ and $CuSeO_3 \cdot 4NH_3$ have been prepared, identified, and their ranges of stability determined.

3. Evidence has been given for the existence of a new hydrated ammonate having the general formula $CuSeO_3 \cdot 3NH_3 \cdot xH_2O$.

4. The work of Boutzaureanu has been checked and the existence of $CuSeO_3 \cdot NH_3 \cdot H_2O$ substantiated.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

THE ACTIVITY COEFFICIENTS OF CESIUM CHLORIDE AND HYDROXIDE IN AQUEOUS SOLUTION[1]

BY HERBERT S. HARNED AND ORION E. SCHUPP, JR.

RECEIVED JUNE 30, 1930 PUBLISHED OCTOBER 6, 1930

The present investigation comprises the evaluation of the activity coefficients at 25° of cesium chloride and hydroxide from measurements of the cells

$$Ag \mid AgCl \mid CsCl(m) \mid Cs_xHg \mid CsCl(0.1) \mid AgCl \mid Ag \qquad \text{(Type I)}$$

and

$$H_2 \mid CsOH(m) \mid Cs_xHg \mid CsOH(0.05) \mid H_2 \qquad \text{(Type II)}$$

Experimental

Cells.—Cells of the type developed by MacInnes and Beattie,[2] Harned,[3] Knoble[4] and Åkerlöf[5] were used. A vacuum technique was always employed and all solutions were boiled *in vacuo* before introduction into the cells. Each cell had a capacity of 100 cc. They were carefully dried before each measurement so as to avoid the waste of solution accompanying the usual method of rinsing.

Electrodes.—Silver–silver chloride electrodes of the kind referred to as Type II in a recent investigation by Harned[6] were used. The hydrogen electrodes were of platinized platinum foil 0.7 by 3 cm. in size. The cesium amalgams were made either by electrolysis of the chloride in a vessel containing a porous cup which served to separate the anode and cathode solutions, or by the electrolysis of cesium hydroxide. Some of the measurements of the cells containing cesium chloride were made with a 0.01% amalgam, while others were obtained by employing a 0.1% amalgam. Both strengths yielded good consistent results, although the potentiometer readings were somewhat difficult to obtain with the 0.01% amalgam. On the other hand, it is important to note that although the 0.1% amalgam gave satisfactory results in the hydroxide solutions, the more dilute amalgam did not.

Cesium Chloride.—This was obtained from the mineral pollucite, $H_2O \cdot 2Cs_2O \cdot 2Al_2$-

---

[1] Constructed from part of the thesis presented by O. E. Schupp, Jr., to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy, 1930.

[2] MacInnes and Beattie, THIS JOURNAL, **42**, 1117 (1920).

[3] Harned, *ibid.*, **47**, 676 (1925).

[4] Knoble, *ibid.*, **45**, 70 (1923).

[5] Åkerlöf, *ibid.*, **48**, 1160 (1926).

[6] Harned, *ibid.*, **51**, 417 (1929).