2. Time effects of long duration were encountered in solutions below the critical concentration for micelle formation.

3. Insoluble monolayers of octadecylamine hydrochloride spread on various sub-solutions have been investigated by means of the film balance.

4. An increase in temperature causes octadecylamine hydrochloride films to become more expanded. The heat of spreading at an area of 35 Å.[2] per molecule was estimated to be 320 ergs cm.[-2]. This value was compared with values for other insoluble films possessing different polar groups.

5. An increase in the size of the anion in the case of the hydrohalide films at small areas gives the effect of increased temperature.

6. The behavior of oxygen acid salts of octadecylamine has been studied.

Hydrous Cupric Hydroxide and Basic Cupric Sulfates

BY HARRY B. WEISER, W. O. MILLIGAN AND E. L. COOK

The hydrous blue gel thrown down by the addition of a base to a cupric salt solution is transformed into black cupric oxide at a rate which depends on the conditions of formation and subsequent treatment. A survey of the literature[1] concerned with the composition and stability of the blue gel discloses certain moot questions which are cleared up, at least in part, by the following phase rule and X-ray diffraction study.

I. The System CuO–H₂O

The blue gelatinous mass obtained by the addition of dilute alkali to a cupric salt solution is hydrous cupric hydroxide which gives an X-ray diffraction pattern distinct[2,3] from that of black cupric oxide formed by its decomposition. Earlier investigators claimed to have prepared a number of hydrates of cupric oxide varying in composition from $CuO \cdot 3H_2O$ to $8CuO \cdot H_2O$.[1] Since the samples analyzed were not obtained under equilibrium conditions, the compositions formulated were the accidental result of the conditions of drying. More recently, however, Losana[4] concluded from dehydration isobars that the decomposition of cupric hydroxide under suitable conditions may yield definite lower hydrates corresponding to 3, 4, 6, and 8 moles of cupric oxide per mole of water. This conclusion was questioned by Champetier and Thuau[5] who dehydrated cupric hydroxide at 105° and, at intervals, removed samples which were examined by X-ray diffraction methods. The diffraction data disclosed the existence of only two crystalline phases, the patterns being for cupric hydroxide or cupric oxide or for a mixture of the two. At 105° the decomposition of cupric hydroxide is fairly rapid, and therefore, unfortunately, the sample was probably never in equilibrium during the dehydration; hence the alleged hydrates claimed by Losana may have been passed over because of too rapid decomposition of the hydroxide. Accordingly, the more comprehensive experiments reported in the following paragraphs were carried out.

Experimental

Preparation of Stable Samples of Cupric Hydroxide.—Under otherwise constant conditions, the rate of the transformation at room temperature of cupric hydroxide to cupric oxide is higher the smaller the crystals of the hydroxide. Relatively large crystals, sufficiently stable for accurate phase rule studies, may be obtained in several ways.[1] Two samples were prepared: one by a modification of Böttger's[6] method and a second by the slow decomposition of complex cupric-ammonia hydroxide.

Sample 1.—Following Böttger's general procedure, a green basic salt[7] was precipitated from boiling N cupric sulfate solution by the slow addition of 6 N ammonium hydroxide until the blue color of the cupric ammonia complex just began to appear in the supernatant solution. After the green precipitate had been washed several times to remove excess sulfate ions, it was placed in an evaporating dish and triturated with 5% sodium hydroxide solution to convert it into cupric hydroxide. The preparation was washed by the aid of a centrifuge until the wash water gave no test for sulfate ions with barium chloride, and was then

(1) Weiser, "Inorganic Colloid Chemistry," Vol. II, John Wiley and Sons, New York, N. Y., 1935, p. 149.

(2) Posnjak, unpublished results reported at the 76th meeting of the American Chemical Society, Swampscott, Mass., September, 1928.

(3) Neville and Oswald, J. Phys. Chem., 35, 60 (1931).

(4) Losana, Gazz. chim. ital., 53, 75 (1923).

(5) Champetier and Thuau, Compt. rend., 194, 93 (1932); cf. Levi, Giorn. chim. ind. applicata. 12. 97 (1930).

(6) Böttger, Jahrsberichte, 198 (1858).

(7) The X-ray diffraction pattern of this green material is identical with the pattern designated as $4CuO \cdot SO_3 \cdot 3H_2O$ in diagram 8, Fig. 4.

dried on a porous plate in air. The resulting sample of cupric hydroxide was quite stable. It did not darken when heated for a few hours at 90° in a hot-air oven or under water but blackening was observed after prolonged heating at this temperature.

Sample 2.—Since alkali is known to have a destabilizing action on cupric hydroxide[1] and ammonium hydroxide a stabilizing action,[8] a procedure was worked out for preparing well-crystallized cupric hydroxide by the slow decomposition of the complex cupric-ammonia hydroxide.
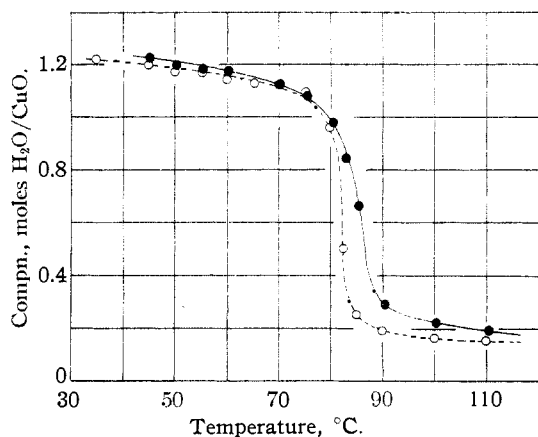

Fig. 1.—Dehydration isobars of cupric hydroxide: O, sample 1; ●, sample 2.

When equivalent amounts of ammonium hydroxide and cupric sulfate were mixed, the resulting precipitate consisted of cupric hydroxide contaminated with some of the green basic salt which did not dissolve readily in excess ammonium hydroxide. When the experiment was repeated with cupric chloride, any basic salt formed was more readily dissolved in ammonium hydroxide, but the cupric hydroxide gel from the chloride was peptized easily on thorough washing. Accordingly, the precipitate was thrown down from N cupric chloride solution containing about 10% of N cupric sulfate which greatly minimized the peptization upon washing. The ammonium hydroxide (6 N) was added slowly with constant stirring until the supernatant solution was a permanent deep-blue because of the formation of some cupric-ammonia complex. The precipitate was washed by the aid of a centrifuge until the wash water contained no more than a trace of chloride. The gel was then dissolved in 6 N ammonium hydroxide and the resulting solution placed in a Pyrex evaporating dish in a vacuum desiccator over sulfuric acid. By reducing the pressure, the excess ammonia was removed rapidly until a green deposit just started to form on the walls of the container. The solution was then transferred to another evaporating dish and allowed to stand over sulfuric acid in a desiccator at atmospheric pressure. The granular cupric hydroxide which precipitated slowly during several hours, was washed thoroughly and subsequently dried in the air on a porous plate. This preparation was stable for a considerable time at 85° and could be heated at 100° in contact with water for many hours without blackening. The X-ray diffraction pattern of the sample consisted of

(8) Allmand, J. Chem. Soc., 95, 2154 (1909).

sharp lines, indicating that the crystals were relatively large.

Isobaric Dehydration,—Triplicate samples of the two cupric hydroxide preparations described above were analyzed for their water content and subjected to isobaric dehydration at 23.6 mm. vapor pressure, corresponding to the vapor pressure of water at 25°. Two of the triplicate samples were weighed, and samples for X-ray diffraction analysis were removed from the third one. At temperatures between 25 and 55°, the samples were placed in a container, at successive constant temperatures, in a thermostatically controlled water-bath. Above 55° the samples were heated in a thermostatically controlled hot-air oven. Air saturated at 25° was passed over the sample at the rate of 3–4 liters per minute. The air was saturated by bubbling it through a large container of water at about 30° and then through a series of two bottles of water and a trap submerged in a thermostat regulated at 25°. Complete details of the procedure have been described previously.[9] The time required for the samples to come to equilibrium varied from five to two weeks, the longer time being required at the lower temperatures, and especially at the decomposition temperature. The isobars for the two preparations are shown in Fig. 1. The points on the curves represent the average values for two separate samples which agree within ±0.02 mole of water per mole of cupric oxide. From these isobars it is evident that only a small loss of weight takes place at each temperature until above 80°. Sample 1 lost most of its water at 82.5° and sample 2 between 82.5 and 90°. The shape of the isobars is typical of that for a hydrous monohydrate or hydroxide. There is no indication of the formation of a hydrate or hydroxide in which the $CuO:H_2O$ ratio is greater than 1.

Isothermal Dehydration.—A 95°-isotherm for sample 2 was obtained in an apparatus employing the McBain–Bakr silica spring balance.[10] The technique has been described in detail elsewhere.[11] The isotherm is reproduced in Fig. 2.
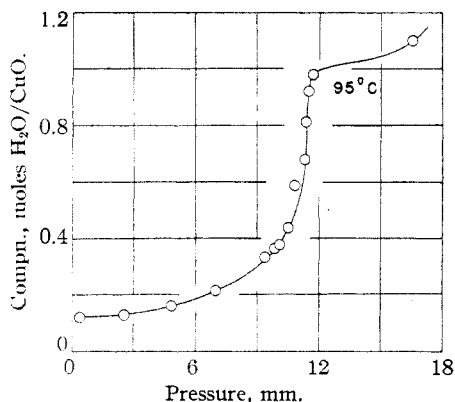

Fig. 2.—Dehydration isotherm of cupric hydroxide (sample 2).

Again, the break in the curve comes at a composition corresponding to $Cu(OH)_2$ and there is no indication of the

(9) Weiser and Milligan, J. Phys. Chem., 38, 513 (1934); THIS JOURNAL, 59, 1670 (1937); Weiser, Milligan and Ekholm, ibid., 58, 1261 (1936).

(10) Bakr and McBain, ibid., 48, 690 (1926).

(11) Weiser, Milligan and Coppoc, J. Phys. Chem., 43, 1109 (1939).

formation of definite lower hydrates during the dehydration process.

X-Ray Analysis.—Small samples were withdrawn from the third bulk sample at intervals during the isobaric dehydration of sample 1, and were examined by standard X-ray diffraction procedure with a Philips-Metalix crystal analysis unit, using Cu Kα X-radiation (nickel foil filter). A few representative patterns are shown in diagram form in Fig. 3. It is apparent from these data that at 23.6 mm. vapor pressure, this sample of cupric hydroxide is stable at all temperatures up to about 80°, the small decrease in weight below this temperature resulting from the loss of adsorbed water. At 82.5°, decomposition of the hydroxide takes place slowly, and even after eighteen days the sample gives the X-ray diffraction pattern of cupric oxide plus a trace of cupric hydroxide. At intermediate time intervals, the diffraction patterns are for mixtures of the two phases in varying proportions. These observations are in agreement with the findings of Champetier and Thuau that there is but one hydrate of cupric oxide [$CuO \cdot H_2O$ or $Cu(OH)_2$] and are in opposition to the conclusion of Losana than four definite lower hydrates of cupric oxide exist.

II.   A Portion of the System CuO-SO_3-H_2O

The system CuO-SO_3-H_2O has been studied in detail in the temperature range 50–200° by Posnjak and Tunell.[12] Contrary to numerous earlier statements in the literature (bibliography in references 12 and 13), Posnjak and Tunell found that only the following eight crystalline phases occur in this system: CuO; $4CuO \cdot SO_3 \cdot 3H_2O$ (mineral Brochantite); $3CuO \cdot SO_3 \cdot 2H_2O$ (mineral Antlerite); $3CuO \cdot 2SO_3 \cdot 5H_2O$; $CuO \cdot SO_3 \cdot 5H_2O$; $CuO \cdot SO_3 \cdot 3H_2O$; $CuO \cdot SO_3 \cdot H_2O$; and $CuO \cdot SO_3$. More recently Binder[13] studied the system at 22° and concluded that $4CuO \cdot SO_3 \cdot 4H_2O$ (X-ray diffraction pattern identical with that of the mineral Brochantite) was the only basic salt stable at this temperature. Binder reported the existence of $4CuO \cdot SO_3 \cdot 4H_2O$, and $3CuO \cdot SO_3 \cdot 2H_2O$ at 100° in substantial agreement with the results of Posnjak and Tunell. Binder also observed that heating cupric sulfate to 650° gives another basic sulfate of composition $2CuO \cdot SO_3$ which reacts with water at 20° to yield $4CuO \cdot SO_3 \cdot 4H_2O$, and at 100° to yield $3CuO \cdot SO_3 \cdot 2H_2O$.

This section of the present paper is concerned with the conditions of formation of basic cupric sulfates and the role they play in the alleged stabilization of cupric hydroxide gel in the pres-
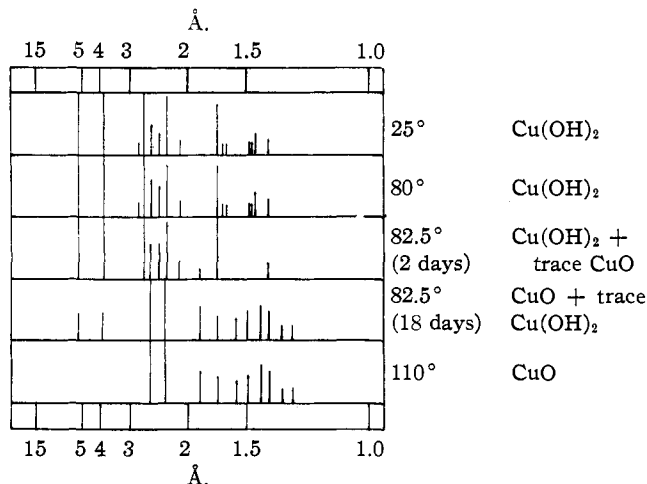

Fig. 3.—X-Ray diffraction patterns.

ence of dilute solutions of heavy metal sulfates.

The instability of blue cupric hydroxide gel is one of its most characteristic properties.[1] Thrown down in the presence of a slight excess of alkali, it decomposes at room temperature into cupric oxide with accompanying changes in color through green, brown, dark brown, and finally to black. Since even a trace of alkali accelerates the decomposition of the blue gel at ordinary temperatures, a clear blue product is best obtained by precipitation at 0° and removing the mother liquor as rapidly as possible by washing with ice water.[14] Such a procedure slows down but does not stop the decomposition of the blue gel.

Tommasi[15] and later Blucher and Farnau[16] noted that the gel remained blue even at 100° when suspended in quite dilute solutions of salts such as manganous sulfate which hydrolyze to give an acid reaction. The phenomenon was attributed by Bancroft[17] and by Blucher and Farnau[16] to stabilization of the blue hydroxide by adsorption on its surface of the hydrous oxides or hydroxides derived from the respective salts. Almost twenty years ago this theory was rendered questionable by the observations of one of us[18] that cupric sulfate is quite as effective as the sulfates of manganese, aluminum, and chromium in preventing darkening of the blue gel; it seemed improbable that blue cupric hydroxide should stabilize blue cupric hydroxide. The absence of darkening at 100° was attributed at that time to

(12) Posnjak and Tunell, *Am. J. Sci.*, **18**, 1 (1929); *J. Phys. Chem.*, **35**, 929 (1931).

(13) Binder, *Compt. rend.*, **198**, 653, 2167 (1934); **201**, 893, 1035 (1935); *Ann. chim.*, [11] **5**, 337 (1936).

(14) Villers, *Compt. rend.*, **120**, 322 (1895).

(15) Tommasi, *Bull. soc. chim.*, [2] **37**, 197 (1882); *Compt. rend.*, **99**, 38 (1884).

(16) Blucher and Fornau, *J. Phys. Chem.*, **18**, 629 (1914).

(17) Bancroft, *ibid.*, **18**, 118 (1914).

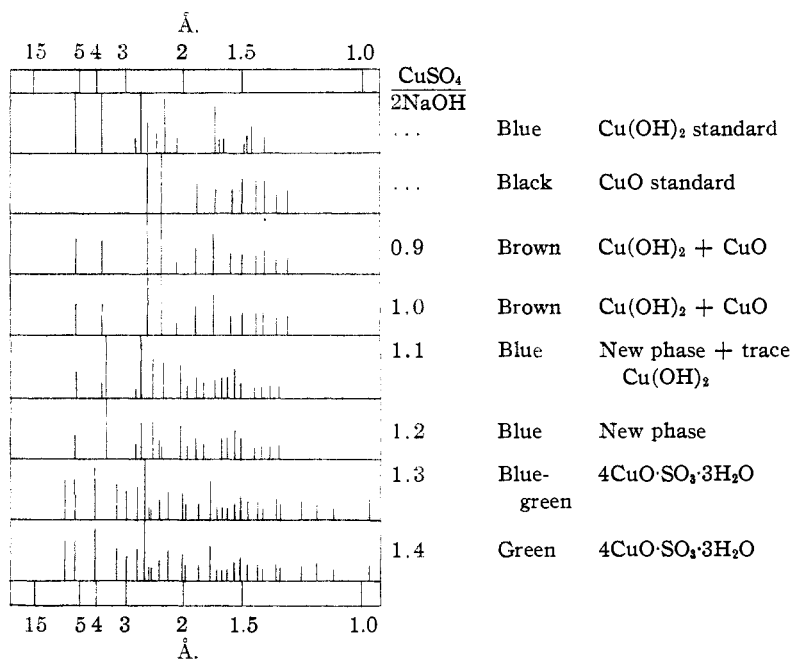(18) Weiser, *J. Phys. Chem.*, **27**, 501 (1923).

Fig. 4.—X-Ray diffraction patterns.

a change from the instable, loose, voluminous gel into the stable, dense, granular powder considered in the first section of this paper, as a result of the solvent action of the acid solutions. Fowles[19] suggested that the stabilizing effect of such salts as the sulfates of copper, manganese, and chromium results from the removal of adsorbed alkali (an accelerator) and the formation of basic cupric salts which are stable. But since adsorption of a stable basic salt would tend to stabilize the blue gel, it is unnecessary to assume that all the gel is converted to basic sulfate.[1] The following quantitative study was made in an attempt to determine the cause of the alleged stabilization of the blue gel.

Experimental

Effect of Salts on Cupric Hydroxide Gel.—The color changes which take place on heating cupric hydroxide gel with solutions of heavy metal sulfates are illustrated by the following experiment. To 10 ml. of 0.1 N sodium hydroxide at 0–5° in a 25-ml. test-tube was added 10 ml. of 0.1 N cupric sulfate at 0–5°, and the mixture was shaken thoroughly. The resulting gel of cupric hydroxide was thrown down in a centrifuge, washed once with 10 ml. of ice water, and thrown down again. To the precipitate was added 10 ml. of cupric sulfate solution of the concentrations shown in the first column of Table I and the mixture shaken until the gel was well dispersed. The mixture was then placed in a water-bath at 100° and any color change was observed after definite time intervals. The observations are recorded in Table I. These experiments show that at

(19) Fowles, *Chem. News*, **128**, 2 (1924).

100°, small amounts of cupric sulfate do not prevent the blue cupric hydroxide from changing to brown, the color of highly dispersed cupric oxide. Larger amounts retard the darkening but the distinctive color of the hydroxide gel changes to bluish-green, suggesting that a chemical change has taken place. Similar results were obtained by heating cupric hydroxide with the same concentrations of solutions of manganous sulfate and cobalt sulfate.

X-Ray Diffraction Analysis.—To determine whether or not any new crystalline phases are formed by digesting cupric hydroxide gel in dilute cupric sulfate solution, the following experiments were carried out. To 10 ml. of 0.1 N sodium hydroxide were added varying amounts of 0.1 N cupric sulfate as given in the second column of Table II. The resulting precipitates were washed several times, allowed to remain moist four to five hours, and finally dried on a porous plate. The color of the resulting products is recorded in the fourth column of the table. The samples were examined by X-ray diffraction methods with the results shown in chart form in Fig. 4 and summarized in the last column of Table II. These data show that the darkened precipitates (samples 1 and 2) were cupric oxide with traces of cupric hydroxide. Sample 3 which was blue contained a hitherto unidentified crystalline phase. Sample 4 gave the pattern of the new phase and samples 5 and 6 were converted into the known basic salt corresponding to the mineral Brochantite.[12]

TABLE I

Normality of CuSO$_4$	Color or precipitate after			
	1 min.	3 min.	5 min.	30 min.
0.002	blue	brown	brown	brown
.006	blue	olive-brown	olive-brown	brown
.008	blue	blue-green	blue-green	brown
.012	blue	blue-green	blue-green	greenish-brown
.014	blue	light blue	blue-green	blue-green

TABLE II

Sample	Ml. of solns. mixed 0.1 N CuSO$_4$	0.1 N NaOH	Color of ppt.	Composition of ppt. from X-ray analysis
1	9	10	Dark brown	Cu(OH)$_2$ + CuO
2	10	10	Lighter brown	Cu(OH)$_2$ + CuO
3	11	10	Blue	New phase + trace Cu(OH)$_2$
4	12	10	Blue	New phase
5	13	10	Blue-green	4CuO·SO$_3$·3H$_2$O
6	14	10	Green	4CuO·SO$_3$·3H$_2$O

These results show conclusively that cupric hydroxide gel is not stabilized in the presence of small amounts of cupric sulfate, but is transformed into a new crystalline phase that proved to be a new basic salt. In the presence of larger amounts of cupric sulfate, the basic sulfate corresponding to Brochantite is formed.

Å.

15	5 4 3	2	1.5	1.0		
					$\dfrac{CuSO_4}{2NaOH}$	
					1.00	$Cu(OH)_2$
					1.10	$5CuO \cdot SO_3 \cdot xH_2O$ + some $Cu(OH)_2$
					1.20	$5CuO \cdot SO_3 \cdot xH_2O$
					1.25	$5CuO \cdot SO_3 \cdot xH_2O$
					1.28	$5CuO \cdot SO_3 \cdot xH_2O$ + some $4CuO \cdot SO_3 \cdot 3H_2O$
					1.35	$4CuO \cdot SO_3 \cdot 3H_2O$

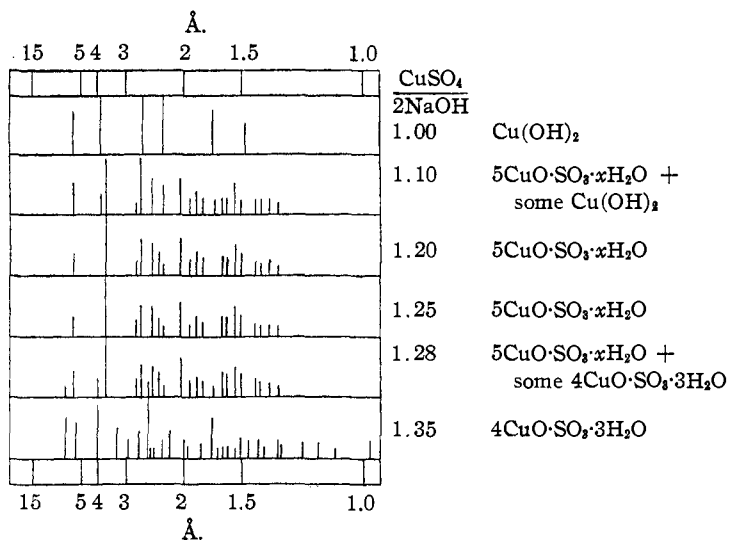| 15	5 4 3	2	1.5	1.0

Å.

Fig. 5.—X-Ray diffraction patterns.

The X-radiogram of the compound formed by digesting cupric hydroxide in 0.005 N manganous sulfate is the same as the X-ray diffraction pattern for the new basic salt (sample 4, Table II). There is no indication of a shift of lines, which might possibly result from substituting manganous ions for some of the cupric ions. The effect of larger amounts of manganous ions has not been studied.

To establish more sharply the conditions of formation of the basic salt in which the ratio of $CuO:SO_3$ is greater than 4, samples were prepared in which the graduations of excess cupric sulfate added were smaller than those shown in Table II; and X-radiograms of the resulting samples were obtained. The X-ray diffraction data given in chart form in Fig. 5 show the range of complete transformation into the new basic salt and indicate the probable ratio of $CuO:SO_3$ to be 5. The X-radiogram of this new crystalline phase is distinct from the patterns of cupric hydroxide and the various basic sulfates described by Posnjak and Tunell, and by Binder. The interplanar spacings and relative intensities for samples 5 and 6 (Table II) agree closely with the values reported by Posnjak and Tunell[12] for their synthetic $4CuO \cdot SO_3 \cdot 3H_2O$ and the mineral Brochantite. The strongest lines found by us, and by Posnjak and Tunell, agree with the values of Binder[13]; but the latter reported some additional lines of relatively weak intensity. It appears from the observations of Binder that there is some question as to whether this basic salt has the composition $4CuO \cdot SO_3 \cdot 4H_2O$ or $4CuO \cdot SO_3 \cdot 3H_2O$. Indeed Binder found that a well-washed, air-dried basic salt obtained by the action of cupric sulfate on cupric hydroxide at 22° had the composition $4.02CuO \cdot SO_3 \cdot 3.83H_2O$. This sample after being heated in air at 150° for fifty hours had the composition $3.99CuO \cdot SO_3 \cdot 3.01H_2O$. The X-radiograms of both the air-dried and heated material were identical with each other and with the mineral Brochantite. Binder makes special mention that precautions were taken against rehydration of the heated sample. It seems reasonable to the present authors that the basic salt actually has the composition $4CuO \cdot SO_3 \cdot 3H_2O$, and that the air-dried product contains approximately one mole of adsorbed water at

room temperature and at ordinary humidity. This question probably can be settled by obtaining a complete dehydration isobar or isotherm for this substance.

Electrometric Titration of Cupric Sulfate with Sodium Hydroxide.—In a rapid mixing apparatus,[20] constant amounts of cupric sulfate solution (0.951 N) were mixed with varying amounts of sodium hydroxide solution (0.975 N) in a total volume of 25 ml. The pH value of the several mixtures was determined with a glass electrode and the data are plotted in Fig. 6. The resulting curve shows two breaks: one at the equivalent point and the second at a composition corresponding to a ratio of $CuOSO_3$ of 5. The definitely crystalline material gives the distinctive X-ray diffraction pattern labeled "new phase" and "$5CuO \cdot SO_3 \cdot xH_2O$" in Figs. 4 and 5, respectively. Chemical analysis of the air-dried material gives the composition $5CuO \cdot 1.02SO_3 \cdot 6.2H_2O$. Since complete dehydration isobars or isotherms will be required to determine the exact amount of combined water in this new basic sulfate, the compound is represented in this paper by the formula $5CuO \cdot SO_3 \cdot xH_2O$.

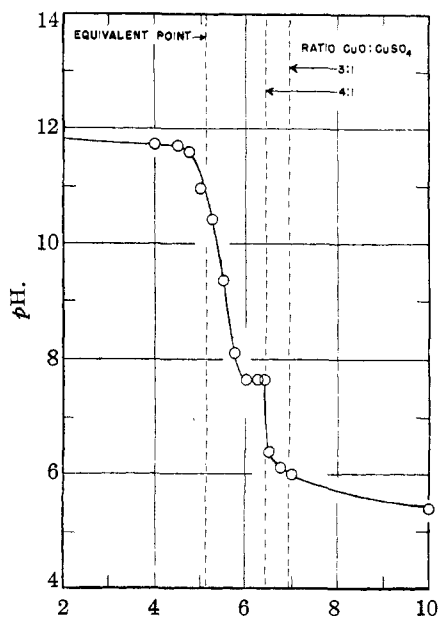Ml. of 0.951 N CuSO₄ added to 5.0 ml. 0.975 N NaOH.

Fig. 6.—Electrometric titration curve.

Summary

1. By the application of the techniques of X-ray diffraction and of isothermal and isobaric dehydration, it has been shown that cupric hydroxide, $Cu(OH)_2$, is the only compound formed in the system $CuO-H_2O$. This result is in agreement with the findings of Champetier and Thuau,

(20) Weiser and Milligan, J. Phys. Chem., **40**, 1075 (1936).

and is in opposition to the conclusions of Losana that four definite lower hydrates of cupric oxide may exist.

2. The spontaneous decomposition of cupric hydroxide gel gives brown to black cupric oxide. The decomposition of the gel is accelerated in contact with solution of dilute alkali. The rate of decomposition of relatively large crystals of cupric hydroxide is very much slower under all conditions than that of the minute crystals constituting the gel.

3. If the ratio of equivalents of cupric sulfate (0.1–1.0 N) to alkali (0.1–1.0 N) in a mixture is equal to or less than one, the resulting blue precipitate is pure cupric hydroxide; if this ratio is equal to or greater than 1.33, the precipitate is the basic salt, $4CuO \cdot SO_3 \cdot 3H_2O$, identical with the mineral Brochantite; if the ratio is 1.25, a previously unidentified basic salt of the formula

$5CuO \cdot SO_3 \cdot xH_2O$, is obtained; with ratios between 1 and 1.25, the precipitate is a mixture of cupric hydroxide or oxide and the new basic salt in varying proportions; and with ratios between 1.25 and 1.33, the resulting precipitates are mixtures of the $5CuO \cdot SO_3 \cdot xH_2O$ and $4CuO \cdot SO_3 \cdot 3H_2O$ in varying proportions.

4. The identity of the new basic salt has been established as $5CuO \cdot SO_3 \cdot xH_2O$ by (a) its characteristic X-ray diffraction pattern; (b) the existence of a break in an electrometric titration curve at a ratio of $CuSO_4 : 2NaOH = 1.25$; and (c) the results of chemical analysis of relatively large crystals.

5. The alleged stabilization of blue cupric hydroxide in the presence of low concentrations of heavy metal sulfates is not a stabilization phenomenon but consists in the formation of the blue basic salt, $5CuO \cdot SO_3 \cdot xH_2O$.

The Crystal Structure of Diphenylselenium Dichloride[1]

BY JAMES D. McCULLOUGH AND GABRIELE HAMBURGER

Introduction

During the recent investigation of the crystal structure of diphenylselenium dibromide[2] carried out in this Laboratory, X-ray diffraction photographs of diphenylselenium dichloride were prepared in view of a possible isomorphism. Although crystals of the dibromide and dichloride were both reported by Gilta[3] to be orthorhombic bipyramidal with similar axial ratios, the space group of the dibromide was found to be D_{2h}^{14}—Pbcn with a four molecule unit while that of the dichloride was found to be D_{2h}^{15}—Pbca with an eight molecule unit. Because of the above contrast and the general interest in molecules involving central atoms with unshared electron pairs, further work on the dichloride was considered worth while.

Experimental

Diphenylselenium dichloride was prepared by mixing equivalent quantities of Eastman Kodak Co. diphenylselenium and pure chlorine, both being previously dissolved in carbon tetrachloride.

The solid thus formed was recrystallized from carbon bisulfide and crystals to be used in the structure determination were prepared by the slow evaporation of a carbon bisulfide solution. Most of the crystals formed were of the type described by Gilta, but a few were in the form of small needles with the elongation in the direction of the a axis (Gilta) which is the b axis of the X-ray unit employed later.

Complete sets of oscillation photographs about the a and b axes of the X-ray unit were prepared using Cu K_α radiation. The crystals chosen were very small and approximately cylindrical so as to minimize differential absorption effects. Measurements on these photographs lead to a unit cell with $a_0 = 7.59$ Å., $b_0 = 17.97$ Å. and $c_0 = 17.77$ Å., all values ± 0.03 Å. The axial ratios of this cell, $a:b:c = 0.4224:1:0.9888$, when properly transformed to correspond to the axes used by Gilta, give the values $0.5056:1:0.8542$. These are in fair agreement with his ratios, $0.4986:1:0.8531$. In view of the slight difference between the lengths of the b and c axes of the X-ray unit, one might suspect that an error had been made in performing the transformation, interchanging these two axes. A careful examination of the X-ray photographs

(1) Presented in part at the meetings of the American Association for the Advancement of Science, Pasadena, June, 1941.
(2) McCullough and Hamburger, THIS JOURNAL, 63, 803 (1941).
(3) G. Gilta, Bull. soc. chim. Belg., 46, 275 (1937).