

of each component in the conductivity functions is the same as in the potential functions.

AUSTIN, TEXAS.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, STANFORD UNIVERSITY.]

## THE BASIC COPPER SULFATES.

BY S. W. YOUNG AND ALLEN EDWIN STEARN.<sup>1</sup>

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### Introductory.

In connection with some investigations on the genesis of copper ores, the problem of the formation and character of Brochantite or native basic copper sulfate comes under consideration. The analyses of this mineral give widely varying results, so divergent in fact as to indicate the probability that the substance is not of fixed composition. It was decided to attack the whole problem from the purely chemical side and the first results of the investigation are contained in this paper.

In looking over the literature on the basic copper sulfates one is struck at once by the large number of such compounds described. In the Gmelin-Kraut "Handbuch" some thirty-five are described as presumably definite compounds. These supposed compounds vary between the limits,  $10\text{CuO}\cdot\text{SO}_3$  and  $2\text{CuO}\cdot\text{SO}_3$ , with varying amounts of water. In some cases, salts, which differ from one another only in water content and this to only a very small degree, are given as distinct individuals. For example, one finds on record  $4\text{CuO}\cdot\text{SO}_3\cdot 3\text{H}_2\text{O}$  and  $4\text{CuO}\cdot\text{SO}_3\cdot 3\frac{1}{2}\text{H}_2\text{O}$ . Five different formulas are given for salts supposed to be identical with natural Brochantite, namely:  $4\text{CuO}\cdot\text{SO}_3\cdot 3\text{H}_2\text{O}$ ;  $7\text{CuO}\cdot 2\text{SO}_3\cdot 5\text{H}_2\text{O}$ ;  $7\text{CuO}\cdot 2\text{SO}_3\cdot 6\text{H}_2\text{O}$ ;  $3\text{CuO}\cdot\text{SO}_3\cdot 2\text{H}_2\text{O}$ ; and  $3\text{CuO}\cdot\text{SO}_3\cdot 3\text{H}_2\text{O}$ .

It seemed, on the face of it, to be highly improbable that such a large number of definite individuals of this class should exist, and good grounds for doubt are to be found by examination of the methods of preparation which have been used. Without going into detail concerning these methods, they may be fairly satisfactorily summarized under three heads:

1. Heating of copper sulfate solutions.
2. Precipitation from copper sulfate solutions by means of alkaline reagents such as sodium, potassium, calcium,<sup>2</sup> and ammonium hydroxides and carbonates, and in some cases by zinc oxide, as well as by acetates of the alkali metals.
3. Dilution of ammoniacal solutions of copper sulfate with water.

<sup>1</sup> Abstract of a thesis presented by Allen Edwin Stearn to the faculty of Stanford University, in partial fulfilment of the requirements of the degree of Master of Arts, May, 1916.

<sup>2</sup> Many salts are described by Pickering as a result of his studies of the Bordeaux mixture.

Of these methods, the second and third are open to the objections that foreign substances are present, and that the composition of the salt will naturally vary with the amount of precipitant used and presumably with the way in which it is added, whether slowly or rapidly. All three methods are open to the objection that, judging from the written accounts of the investigations, the products obtained do not represent equilibrium conditions. As will be shown in the experimental part of this paper, the reactions resulting in the formation of basic copper sulfates are extremely sluggish, requiring about three months at  $25^{\circ}$  for completion. It was with the purpose of adding something of clearness to the knowledge of these compounds that the following experiments were carried out. The general question which we set ourselves to answer is "are the basic sulfates of copper a set of compounds of definite composition, or are they a series of mixed crystals in variable proportions?"

### Experimental.

The method adopted for the production of the basic sulfates was the very simple one of allowing copper sulfate in solution in water, to combine with finely divided copper oxide. Preliminary experiments showed that this reaction was sufficiently rapid to be made use of. If copper oxide is allowed to stand at rest for three or four days in contact with a moderately strong solution of copper sulfate, it becomes thoroughly set into a hard cake of greenish gray, owing to the formation of basic salt. This cake is very hard and very difficultly soluble even in strong acids and ammonia.

Provision was made for three sets of duplicate samples, one to be run at  $25^{\circ}$ , one at  $37.5^{\circ}$  and one at  $50^{\circ}$ . In each set were six samples. These were placed in six magnesium citrate bottles, and the samples were made up as follows: In each bottle was placed 150 cc. of a solution of copper sulfate containing 0.04394 g. of copper in 1 cc. To the bottles were added amounts of copper oxide corresponding, respectively, to  $1/4$ ,  $1/2$ , 1, 2, 4 and 8 molecules for each molecule of copper sulfate. In addition to the six bottles in each set, a seventh was prepared containing one molecule of copper oxide to one of sulfate. These three extra bottles were designed to serve as check bottles from which samples might be taken from time to time in order to determine the progress and completion of the reaction. The three sets were then placed in thermostats which could be maintained to within 0.1° of the above mentioned temperatures, and were rotated continuously until equilibrium was established, as shown by samples taken from the check bottles. When the copper content of the samples of filtrate taken from the check bottles failed to show any further decrease during one week, it was considered that equilibrium had been attained. The time required for reaching equilibrium at the different temperatures is approximately shown in the following table:

Temperature.	Days required for equilibrium.
25.0°	88
37.5°	22
50.0°	15

These figures show how unreliable must be the conclusions of previous investigators, who have allowed only a few minutes, or at most a few hours (often at room temperature) for the preparation of their salts.

The treatment of the products obtained in the above manner was as follows: The bottles were taken from the thermostat one by one and the contents thrown on a rapid suction filter. As soon as filtration was complete, the solids were placed in specially prepared containers and centrifuged at high speed for an hour, after which they were air dried between watch glasses. Both filtrate and solids were preserved for analysis.

The filtrates were analyzed for copper by the electrolytic method. Through an inadvertence, they were not analyzed for sulfuric acid, as should have been done, in order to check certain conclusions based on the results of analysis of the solids. Table I gives the results of the copper determinations for all the filtrates.

TABLE I.

Amount of copper remaining in 5 cc. of the solutions. In column headed CuO are given the number of molecules of copper oxide added for each molecule of copper sulfate in the original mixtures.

CuO.	25°.	37.5°.	50°.
1/4	0.1916	0.1956	0.1937
1/2	0.1606	0.1661	0.1657
1	0.1099 (0.1153)	0.1094	0.1094
2	0.0028 (0.0369)	0.0022	0.0018
4	0.0008	0.0008	0.0006
8	0.0006	0.0007	0.0002

The initial concentration was 0.2197 g. copper in 5 cc. From the table it is clear that in cases where two molecules of oxide to one of sulfate had been used the removal of copper from the solution was very nearly complete and in cases where more than this quantity of the oxide was used, the removal was always virtually complete. It is also evident that the amount of copper left in the solution is practically independent of the temperature.

In the 25° column there will be noticed two values in parentheses. These were the results obtained in the regular run of the samples. As they were markedly higher than was to be expected from the neighboring results, it was suspected that there might possibly have been formed in these cases a metastable form of higher solubility. Two new bottles were, therefore, prepared in exactly the same way as the others, except that they were seeded with a small amount of salt from some of the bottles that showed normal conduct. These were rotated for ninety days and gave the results used in the 25° column, which are in good agreement with neighboring results.

An examination of the solids obtained in the above experiments showed them to be of two sorts. Those prepared by using the smaller amounts of oxide, up to two molecules to one of sulfate, were clear light grayish green. Those containing larger amounts of oxide were darker in color and showed a tendency toward stratified settlement. This was taken as an indication of an excess of uncombined copper oxide, a conclusion which received confirmation upon a microscopic examination which showed the light green crystals of basic salt and black particles of oxide side by side. The examinations failed to yield any evidence of crystals of basic salt of more than one sort. The crystals were very minute and the evidence of the microscopic examination is of itself perhaps of but little importance, but offers some support to conclusions to be drawn later from the results of analysis.

All samples of the salts obtained, except those which showed free copper oxide, were analyzed for copper, sulfur trioxide and water. It was found that by heating to  $700^{\circ}$  for 15 hours in an electric furnace, all water and  $\text{SO}_3$  were driven off, leaving pure copper oxide showing no traces of  $\text{SO}_3$ .  $\text{SO}_3$  was determined from another sample, by dissolving in hydrochloric acid and precipitating with barium chloride. Water was determined by the difference between this result and that obtained by ignition. Copper was also determined in several samples by electrolysis and gave good checks with the values obtained by ignition. It was found to be impracticable to drive off water without also driving off some  $\text{SO}_3$ , so that direct determinations of water were not made.

In Table II there is given a summary of the analyses, averages only being given. They are the averages of at least two (and often more) determinations in every case.

TABLE II.  
Composition of the Salts.

Temp.	2 mols CuO to 1 CuSO <sub>4</sub> .		1 mol CuO to 1 CuSO <sub>4</sub> .		1/2 mol CuO. to 1 CuSO <sub>4</sub> .		1/4 mol CuO to 1 CuSO <sub>4</sub> .	
	CuO	%	CuO	%	CuO	%	CuO	%
50°.....	CuO	66.31	CuO	63.33	CuO	59.69	CuO	59.43
	SO <sub>3</sub>	23.50	SO <sub>3</sub>	24.90	SO <sub>3</sub>	25.90	SO <sub>3</sub>	26.10
	H <sub>2</sub> O	10.15	H <sub>2</sub> O	11.80	H <sub>2</sub> O	13.80	H <sub>2</sub> O	14.00
	Total	99.96		100.03		99.39		99.53
37.5°...	CuO	66.20	CuO	63.09	CuO	59.20	CuO	58.57
	SO <sub>3</sub>	23.55	SO <sub>3</sub>	24.75	SO <sub>3</sub>	26.20	SO <sub>3</sub>	26.40
	H <sub>2</sub> O	10.15	H <sub>2</sub> O	12.30	H <sub>2</sub> O	14.55	H <sub>2</sub> O	15.10
	Total	99.90		100.14		99.95		100.17
25°.....	CuO	66.31	CuO	63.21	CuO	61.15	CuO	60.82
	SO <sub>3</sub>	23.46	SO <sub>3</sub>	24.85	SO <sub>3</sub>	25.90	SO <sub>3</sub>	25.85
	H <sub>2</sub> O	10.20	H <sub>2</sub> O	12.10	H <sub>2</sub> O	13.10	H <sub>2</sub> O	13.35
	Total	99.97		100.16		100.15		100.02
25°.....	CuO	66.31	CuO	64.31 <sup>1</sup>	<sup>1</sup> These analyses are from the samples whose solutions gave higher copper values than normal.			
	SO <sub>3</sub>	21.80	SO <sub>3</sub>	23.35				
	H <sub>2</sub> O	11.83	H <sub>2</sub> O	12.50				
	Total	99.94		100.16				

In Table III the results given in Table II have been recalculated so as to express the number of molecules of copper oxide and water in combination with one molecule of copper sulfate. For convenience, the amounts of copper remaining in 5 cc. of the solutions, from which the salts were formed, are also given.

TABLE III.  
Molecular Composition of Basic Sulfates.

Mols CuO to 1 CuSO <sub>4</sub> (originally).	50°.			37.5°.			25°.		
	Mols CuO to 1 CuSO <sub>4</sub> .	Mols H <sub>2</sub> O to 1 CuSO <sub>4</sub> .	G. Cu in 1 cc. sol.	Mols CuO to 1 CuSO <sub>4</sub> .	Mols H <sub>2</sub> O to 1 CuSO <sub>4</sub> .	G. Cu in 1 cc. sol.	Mols CuO to 1 CuSO <sub>4</sub> .	Mols H <sub>2</sub> O to 1 CuSO <sub>4</sub> .	G. Cu in 1 cc. sol.
2.....	1.83	1.92	0.0004	1.83	1.92	0.0004	1.84	1.93	0.0006
1.....	1.55	2.12	0.0219	1.55	2.21	0.0219	1.55	2.16	0.0220
1/2.....	1.31	2.37	0.0331	1.27	2.42	0.0332	1.38	2.26	0.0321
1/4.....	1.28	2.38	0.0387	1.23	2.54	0.0391	1.35	2.29	0.0383

### Discussion of the Results.

The first fact of importance to be noted is the negligible effect of temperature on the composition of the salts formed under otherwise like conditions. So closely do the analyses of the salts produced at the three temperatures check with one another, that it is safe to conclude that within the limits investigated the composition of the salts is independent of the temperature.

In the second place, it is to be noted that the amount of copper oxide in the salt increases with the amount added, as is to be expected. The amount of copper oxide which can be assimilated by one molecule of copper sulfate seems to be limited to about two molecules. The evidence furnished by the experiments is not sufficient to fix this limit beyond doubt, since the next higher amount of copper oxide used was four molecules to one of copper sulfate. Since, however, the salts produced in these cases contained large admixtures of unattacked copper oxide, and since the copper sulfate in the solutions was practically reduced to zero in all cases where two molecules of copper oxide to one of copper sulfate were used, and not where less than this amount was used, the presumption is very strong that this amount represents very closely the limit assimilable under the conditions of these experiments.

Another conspicuous fact shown by the results in Table III is that in all cases as the amount of copper oxide increases the amount of water decreases, and that as a limit the molecules of oxide and water to one of sulfate approach equality in the most basic salt, at the approximate value of two. In so far as is deducible from the evidence obtained in this investigation, the most basic salt which could be prepared by the method used would have approximately the formula  $\text{CuSO}_4 \cdot 2\text{CuO} \cdot 2\text{H}_2\text{O}$ . Whether there is a lower limit to the amount of copper oxide which may

be contained in a basic salt is not determinable from the evidence in hand, and remains a subject for further investigation.

In the literature, reference is made to several supposed salts which contain higher percentages of copper oxide than any that we have succeeded in obtaining. These salts were, however, invariably obtained by precipitations with alkaline reagents and the presumption is very strong that they were mixtures containing excess of hydroxide.

It is a well-known fact that ordinary solutions of copper sulfate are in general supersaturated with respect to basic sulfate, even though unsaturated with the normal sulfate. This is evidenced by the fact that prolonged standing or short boiling of such solutions results in the deposition of certain amounts of basic sulfates. It has been maintained that such basic sulfates show a definite composition, irrespective of the strength of the solutions from which they are prepared.<sup>1</sup> This point of view is maintained by Pickering in spite of serious lack of agreement in the results of his analyses. In order to convince ourselves upon this point the following experiments were carried out: Three bottles containing copper sulfate solutions of different strengths were prepared. The first contained a solution saturated at 80° diluted with five volumes of water; the second contained a solution which was saturated at 80° plus a considerable additional quantity of small crystals of copper sulfate, while the third contained solution saturated at 80° without any addition whatever. These bottles were placed in an electric oven and kept at 100° for a week, during which time they were frequently shaken. They were then removed, the contents quickly filtered and the basic sulfates (they are extremely insoluble) washed with water to remove excess of copper sulfate. These salts were dried and analyzed for copper. The results are given in Table IV.

TABLE IV.

Solution.	% CuO.
Sat. at 80° and diluted with 5 vols. water.....	66.34
Sat. at 80°.....	67.00
Sat. at 80° with <i>xs</i> CuSO <sub>4</sub> crystals.....	68.21

As is readily seen the composition of the basic sulfates prepared in this way is highly influenced by the concentration of the solutions from which they are prepared.

### Summary.

1. A considerable number of basic sulfates of copper were prepared by the direct action of copper oxide on solutions of copper sulfate, at three different temperatures.

2. The time required for such systems to attain equilibrium is about three months at 25° and about two weeks at 50°.

<sup>1</sup> Cf. Pickering, *Chem. News*, 47, 181.

3. Other conditions being constant, the composition of these basic sulfates is independent of the temperature of preparation within the range investigated.

4. The evidence obtained by a study of these salts makes it seem highly probable that they are not definite compounds, but rather are to be regarded as a three-component system in which all three components,  $\text{CuSO}_4$ ,  $\text{CuO}$  and  $\text{H}_2\text{O}$  (or if one prefers  $\text{CuO}$ ,  $\text{SO}_3$ ,  $\text{H}_2\text{O}$ ) are continuously variable within certain limits.

5. The evidence indicates that the maximum number of molecules of copper oxide that are capable of being taken up by one of copper sulfate is two, and that the formula for the most basic salt is probably quite close to  $\text{CuSO}_4 \cdot 2\text{CuO} \cdot 2\text{H}_2\text{O}$ .<sup>1</sup>

6. In salts of lower basicity the water content of the salt increases as the copper oxide content decreases, but there is as yet no evidence to show whether these changes continue throughout the whole range to normal  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

7. Basic copper sulfates prepared by heating copper sulfate and water together in varying relative amounts does not lead to the formation of definite compounds as has been maintained.

8. There is some evidence indicating the formation, under undetermined conditions, of a metastable series of basic sulfates.

9. In view of the above facts, it is only natural that the mineral Brochantite, should show a variable composition, depending on the conditions of its formation.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS.]

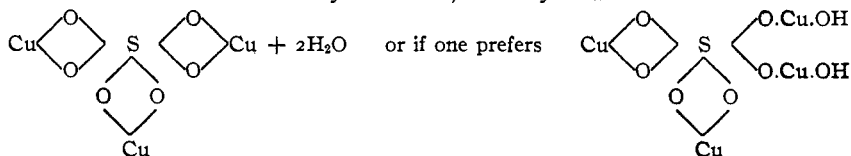
## CHLORIDES IN PRESENCE OF THIOCYANATES.

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Rosanoff and Hill<sup>2</sup> have shown that chlorides can be determined in the presence of thiocyanates by means of Volhard's method after the latter have been decomposed by concentrated nitric acid. This paper intends to show that chlorides can also be titrated with silver nitrate and chromate

<sup>1</sup> Professor W. A. Noyes has kindly called the authors' attention to the fact that this formula corresponds to that of the normal copper salt of orthosulfuric acid,  $\text{S}(\text{OH})_6$ , with two molecules of water of crystallization, and may be written



<sup>2</sup> THIS JOURNAL, 29, 1467 (1907).