

THE THREE-COMPONENT SYSTEM—CuO, SO₃, H₂O—
AT 25°¹

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In two previous papers² we have determined the composition of the solutions and of the solids resulting when lime is added in great excess to solutions of copper sulphate, and also when the sum of the bases present is exactly equivalent to the sulphuric acid. In the former paper it was found that at 25° the solid phases containing calcium were lime and gypsum, and that the solid phases containing copper were two modifications of copper hydroxide. The latter paper contained the mutual solubility relations of copper sulphate and calcium sulphate at 25°. When lime is added to a solution of copper sulphate in insufficient quantity to precipitate all the copper, the resulting precipitate at 25° is light green in color, and under the microscope was seen to consist of the well-known crystals of gypsum mixed with a green substance containing copper.

The composition of the green precipitate could not be determined on account of the quantity of calcium sulphate which was mixed with it. Where a base having a more soluble sulphate was employed, such as soda or potash, a precipitate was obtained having physical characteristics the same as that mixed with the gypsum. This precipitate was undoubtedly a basic sulphate of copper.

There have been recorded in the literature a number of basic sulphates of copper stable at ordinary temperatures. According to Sabatier,³ many of the basic sulphates are not definite compounds, but more probably are mixtures. Brief reference will be made here to those which are said to exist under ordinary conditions of temperature and moisture.

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² Jour. Phys. Chem., **11**, 632, 637 (1907).

³ See Moissan: *Traité de Chimie minérale*, 5, 81 (1906).

Sabatier¹ prepared $5\text{CuO}\cdot 2\text{SO}_3\cdot 5\text{H}_2\text{O}$ by contact of another basic sulphate, $4\text{CuO}\cdot \text{SO}_3\cdot 4\text{H}_2\text{O}$ with a saturated solution of copper sulphate. The former is green in color and is decomposed in cold water to the latter compound, copper sulphate passing into solution.

This latter basic sulphate of copper, $4\text{CuO}\cdot \text{SO}_3\cdot 4\text{H}_2\text{O}$, *langite*, was prepared by Sabatier¹ by contact of copper oxide or hydroxide in the cold with solutions of copper sulphate containing less than 63 grains of copper per liter. It was also prepared by Pickering² by treating copper sulphate solution with ammonia, and by Kane³ by treating with water the product formed by heating a compound of copper sulphate and ammonia ($\text{CuSO}_4\cdot 4\text{NH}_3\cdot \text{H}_2\text{O}$). Langite is not changed in the air below 150° nor when treated with cold water.

André⁴ has described the compound $4\text{CuO}\cdot \text{SO}_3\cdot 16\text{H}_2\text{O}$, produced by saturating a hot ammonium sulphate solution with copper oxide and pouring the liquid into cold water.

Smith⁵ has recorded the compound $6\text{CuO}\cdot \text{SO}_3\cdot 6\text{H}_2\text{O}$, obtained by adding a slight excess of potash to a solution of copper sulphate.

Kane⁶ formed the compound $8\text{CuO}\cdot \text{SO}_3\cdot 12\text{H}_2\text{O}$ by precipitating copper from a solution of copper sulphate with alkali, stopping just short of the point where the solution becomes alkaline. The existence of this compound has been questioned by Smith.⁵

The present paper contains the results of experiments by treating various solutions of copper sulphate with copper oxide or copper hydroxide. The same final state was obtained regardless of the form in which the excess of copper oxide was added to the solutions. When ignited copper oxide was employed, a longer period of time was required for the attain-

¹ Comptes rendus, 125, 101 (1897).

² Chem. News, 47, 181 (1883).

³ Ann. Chim. Phys. [2], 72, 269 (1839).

⁴ Comptes rendus, 100, 1138 (1885).

⁵ Phil. Mag., 23, 496 (1843).

⁶ Ann. Chim. Phys. [2], 72, 269 (1839).

ment of equilibrium conditions. The bottles containing the oxide were kept at 25° over two months, while those containing the hydroxide required only a few weeks to come to equilibrium. At the end of this time the solutions were analyzed for copper oxide and sulphuric anhydride; and also the precipitates freed as far as possible from the mother-liquor were analyzed. These compositions were plotted on a triangular diagram and the corresponding points joined by straight lines. In all the solutions copper and sulphuric acid were found in equivalent quantities, the net result being a loss from the solution of copper sulphate and possibly of water. The following table gives the results of the analyses.

No.	Liquid		Residue	
	Percent CuO	Density	Percent CuO	Percent SO ₃
1	1.165	1.0192	33.96	9.75
2	2.18	1.0443	33.23	9.85
3	3.25	1.0672	33.27	10.43
4	4.30	1.0916	31.80	10.55
5	5.22	1.1103	31.58	11.01
6	6.21	1.1360	26.40	10.42
7	7.14	1.1559	27.23	11.07
8	7.99	1.1745	27.92	11.63
9	8.72	1.2009	26.42	11.88

In the accompanying diagram the lines joining the points on the curve AD to the corresponding points representing the compositions of the residues do not meet within the triangle, although they tend to converge. This indicates that the solid phases consist of a series of solid solutions consisting of copper oxide, sulphur dioxide and possibly water. Thus there is no definite basic compound at this temperature. It will be observed that all the lines pass between the points marked M and N on the diagram, which points represent the compositions of the two basic sulphates which have the best status in the literature, *viz.*, $5\text{CuO} \cdot 2\text{SO}_3 \cdot 5\text{H}_2\text{O}$ and $4\text{CuO} \cdot \text{SO}_3 \cdot 4\text{H}_2\text{O}$. The points representing the formulas $4\text{CuO} \cdot \text{SO}_3 \cdot 16\text{H}_2\text{O}$

and $6\text{CuO}\cdot\text{SO}_3\cdot 6\text{H}_2\text{O}$, cited above, both lie near the area through which the lines pass.

In a paper recently published by Pickering¹ it has been shown that when just enough alkali is added to a solution of copper sulphate, the precipitate contains four equivalents of copper oxide to one equivalent of sulphuric anhydride, or $4\text{CuO}\cdot\text{SO}_3$. This agrees well with the composition of the limiting solid solution in equilibrium with water, which solid solution is represented by a point on the line AP of the diagram. The ratio of copper oxide to sulphuric anhydride at any point on this line is equal to the ratio CP:BP, which is very nearly 4:1.

The range of solutions which exist in equilibrium with the solid solutions is from pure water on the one hand to a solution saturated with copper sulphate on the other. Unfortunately, the bottle containing both the limiting solid solution and solid copper sulphate was broken in the thermostat. It is certain, however, that the composition of the limiting solution would have been found to be the same as the solution saturated with copper sulphate in the absence of any of the solid solution, because copper and sulphuric acid in the solutions were always in equivalent proportions.

It is impossible from the data in hand to give the composition of the solid solutions, which would be represented by a line between points on the limiting straight lines below the points representing the composition of the residues.

The other possible solutions in the three component system—copper oxide, sulphuric anhydride, water—are obtained when the total acid is in excess of the copper oxide. The solubility of copper sulphate in sulphuric acid solutions at 0° has been determined by Engel,² who considers that there is a definite combination of sulphuric acid and water, the rest of the water present dissolving copper sulphate as if no acid were present. In the present experiments copper sulphate was added to different aqueous solutions of sulphuric

¹ Jour. Chem. Soc., 91, 1981 (1907).

² Comptes rendus, 104, 506 (1887).

acid. After two weeks constant agitation in the thermostat at 25°, the solutions were analyzed and also the solid phase with adhering mother-liquor. The results have been plotted in the accompanying figure, and it will be seen that over a certain range the lines joining the corresponding points pass through the point representing the composition $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. At greater concentrations of sulphuric acid there is a range of solutions in which the tri-hydrate ($\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$) is stable, and at still higher concentrations the monohydrate ($\text{CuSO}_4 \cdot \text{H}_2\text{O}$) is stable. Finally, a solution was obtained in which the anhydrous salt was the stable solid phase.

The following table gives the results of the analytical data:

Solution			Residue		Solid phases
Density	Percent CuO	Percent SO_3	Percent CuO	Percent SO_3	
1.2142	9.17	9.26	30.24	30.35	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
1.2248	5.91	15.90	30.62	31.30	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
1.2593	3.39	23.09	29.11	31.08	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
1.2934	1.82	28.75	31.15	31.70	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
1.4061	1.32	39.74	30.34	32.08	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
1.4256	—	41.29	29.81	35.26	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$
1.4249	—	41.04	27.4	38.47	$\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$
1.4516	1.38	43.63	32.65	38.29	$\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$
1.4915	1.02	47.82	32.77	38.70	$\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$
1.5124	—	49.07	20.16	47.54	$\text{CuSO}_4 \cdot \text{H}_2\text{O}$
1.5408	0.38	51.46	30.42	46.89	$\text{CuSO}_4 \cdot \text{H}_2\text{O}$
1.5643	0.368	53.51	26.34	48.73	$\text{CuSO}_4 \cdot \text{H}_2\text{O}$
1.6824	0.109	62.14	26.46	51.76	$\text{CuSO}_4 \cdot \text{H}_2\text{O}$
1.7752	0.105	68.34	31.82	51.82	$\text{CuSO}_4 \cdot \text{H}_2\text{O}$
1.8118	0.15	72.41	30.50	54.12	$\text{CuSO}_4 \cdot \text{H}_2\text{O}$
1.8266	0.07	74.26	30.50	59.70	CuSO_4

Besides the above hydrates, Graham¹ has recorded the compound $\text{CuSO}_4 \cdot 2\text{H}_2\text{O}$, obtained by confining the pentahydrate in a dry space for a week at 20°. From his study of the vapor tensions of the hydrates of copper sulphate,

¹ Phil. Mag., 6, 419 (1835).

Lescoeur¹ concludes that a compound of this composition does not exist, and from the solubility determinations of the present paper no evidence was obtained for the existence of this compound. Two other hydrates, $\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$, have been recorded by Lecoq de Boisbaudran.² These were obtained by adding a small crystal of nickel sulphate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) or of ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) to a supersaturated solution of copper sulphate. Crystals isomorphous with those salts separated but were metastable; copper sulphate pentahydrate, the stable solid phase, soon separated from the solutions and the higher hydrates disappeared.

From his work on the relative vapor pressures of copper sulphate crystals in various stages of dehydration, Andreae³ concludes that there exist only the pentahydrate, trihydrate and monohydrate.

The figure shows that the solubility of copper sulphate is depressed upon the addition of sulphuric acid, for from D to E the curve approaches the side AC of the triangle. Between the points D and E the lines joining the corresponding points for solution and residue all meet in the point 5, which represents the composition $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; from E to F the corresponding lines meet in the point 3, which represents the composition $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$; from F to G the corresponding lines meet in the point 1, which represents the composition $\text{CuSO}_4 \cdot \text{H}_2\text{O}$. Beyond the point G, only one line was determined and this line passes through the point O, representing the composition CuSO_4 . Undoubtedly the solid phase is anhydrous copper sulphate, although this can not be affirmed from the data at hand, for by this method of representation, it is necessary to have at least three lines meeting at a point before the existence of a compound is definitely established.

The quantity of copper oxide in solution is very small for

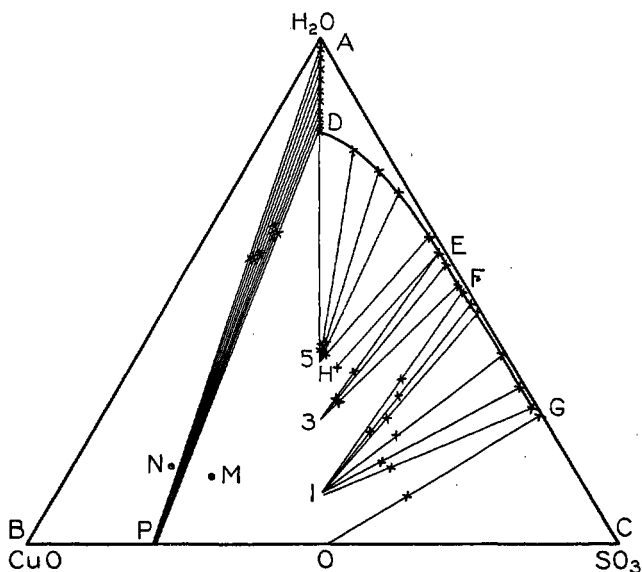
¹ Bull. Soc. chim. Paris, [2], 46, 285 (1886); Comptes rendus, 102, 1466 (1886); Ann. Chim. Phys. [6], 21, 544 (1890).

² Comptes rendus, 65, 1249 (1867); 66, 497 (1868).

³ Zeit. phys. Chem., 7, 260 (1891).

the greater quantities of sulphuric acid, and at the point E there is less than 2 percent copper oxide to 41.29 percent of sulphuric trioxide in solution; at the point F still less copper is in solution, and at G only a very small amount.

The straight line EH which passes through E does not pass through the point 5 or the point 3, but passes between them. This is due to the fact that at E two solid phases are present, the dark blue copper sulphate pentahydrate and lighter copper sulphate trihydrate, both of which could be



easily seen in the residue. The exact position of the point F has not been definitely determined, although it may be stated from the data the percentage of sulphuric acid lies between 47.8 and 49.1; also the exact determination of the point marked G was not made, the solution at this point being very concentrated with respect to sulphuric acid.

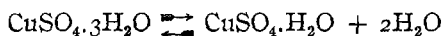
The transformation represented by the equation



takes place under certain well-defined conditions; and conversely the coexistence of the two hydrates is possible only

under certain well-defined conditions. Lescoeur¹ has determined the vapor pressure at different temperatures at which the two hydrates coexist; at 25° this vapor pressure was 8.5 mm. Frowein,² also, has made similar determinations and, by extrapolation, the value 7.2 mm was found as the vapor pressure at 25°. The present data show that this transformation takes place in a solution containing 41.29 percent SO₃ and 1.42 percent CuO. Neglecting the small influence of the small quantity of copper oxide upon the vapor pressure, the vapor pressure of a solution containing 41.29 percent SO₃ was computed as 8.60 mm at 25° from the results of Sorel;³ as 8.48 mm from the data of Regnault;⁴ and as 8.45 mm from the data of Richards.⁵ These values agree well with the values for the vapor pressure at which this transformation takes place as found directly by Lescoeur. Thus the vapor pressure data and the solubility data agree in a satisfactory manner.

Again, the transformation represented by the scheme



takes place at a definite vapor pressure for each temperature. Extrapolating from the results of Lescoeur at slightly higher temperature, the value 3.2 mm was found. Again neglecting the small influence of the copper oxide present at the point F, and computing from the available measurements, the vapor pressure of a solution containing 48.5 percent SO₃, which is very close to the composition of the solution at F, the value 4.5 mm was obtained. The lack of agreement may be ascribed to the fact that Lescoeur's determinations are recorded in whole numbers of millimeters and in halves of millimeters and are therefore correct only to half a millimeter. Further, the value 3.2 mm is an extrapolated value, the lowest measurements made being 5 mm at 30°, and 7.5 mm at 35°. Conse-

¹ Loc. cit.

² Zeit. phys. Chem., **1**, 1 (1887).

³ Zeit. angew. Chem., **1**, 272 (1889).

⁴ Ann. Chim. Phys. [3], **15**, 179 (1845)

⁵ Proc. Am. Acad., **33**, 23 (1897-98).

quently the error in the value taken, 3.2 mm, is probably very great.

From what has been presented above it follows that:

(1) There is at 25° no definite basic sulphate of copper, all the basic sulphates being solid solutions, as is shown by the fact that the lines in the accompanying diagram do not meet within the triangle. The solutions in contact with these basic sulphates contain sulphuric anhydride and copper oxide in equivalent quantities, and are all slightly acid in reaction.

(2) At 25° the following hydrates of copper sulphate are stable: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ between the vapor pressure of water at this temperature and 8.5 mm; $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ between vapor pressures of 8.5 mm and 4.5 mm approximately; $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ between the latter value and a very low vapor pressure, probably about 0.1 mm. The anhydrous salt CuSO_4 is stable below this last vapor pressure.

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