of the totally different experimental conditions, no direct comparisons can be drawn between his work and that now reported.

Salt Effect.—Another similarity between change in intensity of fluorescence and the color change of indicators is found in the influence of added neutral salts. In order to determine and demonstrate this effect, solutions of equal quinine content ($3\ M \times 10^{-6}$) and equal Sörensen values ($P_H = 1.31$, as determined by the hydrogen electrode) containing various proportions of sulfuric acid and sodium sulfate were compared, with the following results: normality in total sulfate, 0.2, 0.4, 1.4; intensity of fluorescence, 100, 94.5, 82.0.

The authors are indebted to a grant from the Warren Fund of the American Academy of Arts and Sciences for the purchase of apparatus for the work here reported and further work along these lines now under way.

Summary

1. A study has been made of the effect of varying the hydrogen-ion concentration upon the intensity of the fluorescence of certain sulfonic acids and of quinine.

2. For each substance studied there is a characteristic range of 0.2 Sörensen (P_H) units within which about 75% of the total change in intensity occurs.

3. The curves obtained show such close agreement with the theoretical dissociation curves of weak electrolytes as to suggest strongly a causal relationship between dissociation and fluorescence.

4. The intensity of fluorescence is affected by the total salt content of the solutions even at equal hydrogen-ion concentrations.

5. Chloride ions inhibit the fluorescence of the sulfonic acids studied as well as that of quinine.

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[CONTRIBUTION FROM THE VENABLE HALL OF CHEMISTRY OF THE UNIVERSITY OF NORTH CAROLINA]

BASIC COPPER SULFATE AT 100°[1]

BY JAMES M. BELL AND GEORGE M. MURPHY[2]

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Introduction.—Several investigations have been made to determine the formulas of the basic sulfates of copper. It seems probable that in

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[1] Since this paper was prepared the December number of the Journal of the Chemical Society has come to our notice. In that JOURNAL, Britton [*J. Chem. Soc.*, **127**, 2796 (1925)] who has made a phase rule study of the basic sulfates of copper at 25°, has also found only one basic sulfate, the formula of which agrees with that obtained by us at 100°.

[2] This paper is constructed from a thesis presented by G. M. Murphy to the Graduate School of the University of North Carolina in partial fulfilment of the requirements for the Degree of Master of Science in Chemistry, June, 1925.

some cases equilibrium conditions have not been obtained and hence analyses of solid phases are of little value. Thus Young and Stearn[3] found that the time for equilibrium between copper sulfate in solution and finely divided copper oxide was 88 days at 25°, 22 days at 37.5° and 15 days at 50°. In the present investigation we have determined the minimum time for equilibrium at 100° and also have investigated the ternary system, $CuO-SO_3-H_2O$ at 100°.

Analytical Methods.—Copper was determined volumetrically by adding potassium iodide solution in excess and titrating the free iodine with thiosulfate solution. Sulfur trioxide was found gravimetrically as barium sulfate, and the water content by difference.

Minimum Time for Equilibrium at 100°.—In order to find the minimum time necessary to reach equilibrium at 100°, the following procedure was followed. Several test-tubes, each containing 3 g. of pure finely divided cupric oxide (from the J. T. Baker Chemical Company) and 20 cc. of a solution containing 11.40% of cupric sulfate by weight, were put into boiling water and at different times a test-tube was cooled quickly and 10 cc. of the clear solution contained in it was analyzed for its copper content. The results follow.

TABLE I

RESULTS

Time, hours	0	0.5	1.0	1.25	1.5	2.75	3.75		
$CuSO_4$, g. in 10 cc.	1.274	0.937	0.671	0.642	0.544	0.469	0.432		
Time, hours	4.25	4.75	5.25	5.75	6.25	6.75	7.25	7.75	8.25
$CuSO_4$, g. in 10 cc.	0.410	0.391	0.383	0.375	0.371	0.370	0.375	0.370	0.370

From these results it is evident that at least six hours are required for the copper content of the solution to reach a constant value.

The Three-Component System at 100°.—To solutions of different concentration in copper sulfate, the same amount of cupric oxide was added and the mixtures were held at 100° for at least eight hours. The resulting solutions were analyzed for copper, and the sulfate content was taken as the chemical equivalent, since the solution was neutral. The residues

TABLE II

RESULTS AT 100°

	Solutions		Residues	
	CuO, %	SO_3, %	CuO, %	SO_3, %
1	2.07	2.08	64.36	14.96
2	3.03	3.05	65.14	15.02
3	4.51	4.54	66.32	15.10
4	5.50	5.53	67.00	15.62
5	7.00	7.04	67.53	15.97
6	8.22	8.27	67.75	16.84
7	9.68	9.75	67.89	17.73

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[3] Young and Stearn, THIS JOURNAL, **38,** 1947 (1916).

with solutions removed as much as possible by suction were analyzed for both copper and sulfate. The results are shown in Table II.

When these results are plotted on a triangular diagram the lines joining solution and residue form a very narrow pencil and the existence and position of a point of convergence cannot be proved satisfactorily by the usual method. Fortunately, the effect of water on the solids of the residues was negligible, for when the solids were washed with small portions of water, the third washing gave negative tests both with barium chloride and ammonium hydroxide. The solid which dried on standing at room temperature could, therefore, be safely analyzed and the result accords with the formula $4CuO.SO_3.4H_2O$.

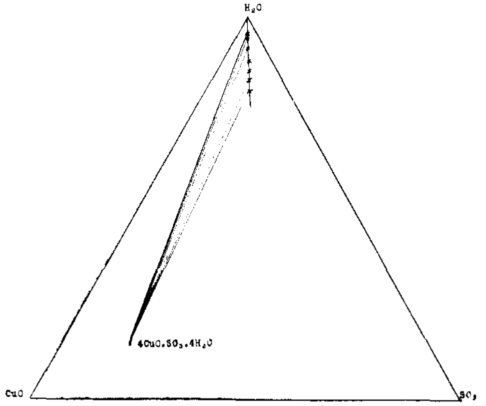

Fig. 1.—Equilibrium in the ternary system $CuO-SO_3-H_2O$ at 100°.

Anal. Calcd. for $4CuO.SO_3.4H_2O$: CuO, 67.7; SO_3, 17.0. Found: CuO, 67.8; SO_3, 17.7.

The tie lines in the diagram, therefore, converge on the point representing the above formula, which has probably the best status of all the formulas for the basic sulfates of copper.

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DETERMINATION OF IODINE IN NATURAL WATERS

BY H. W. BRUBAKER, H. S. VAN BLARCOM AND N. H. WALKER

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About two years ago we began to make a survey of the principal water supplies of Kansas to determine the iodine content for the various communities of the state. Before doing this it seemed advisable to try out some of the most acceptable methods of making this determination in order to select one for both accuracy and ease of manipulation. We finally decided to try to adapt a method, used by Dr. Andrew Hunter,[1] for the determination of small amounts of iodine in thyroid tissue, to the determination of iodine in water. This method consists in oxidizing the iodine to iodate by boiling with a solution of sodium hypochlorite acidified with phosphoric acid. The boiling is continued until all of the free chlorine

[1] Hunter, *J. Biol. Chem.*, **7,** 336 (1909).