

than nitrates. This is in accord with the measurements of Just and the equilibrium measure-

ments of La Mer and Friedman.

ATLANTA, GEORGIA

RECEIVED AUGUST 29, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, GEORGIA SCHOOL OF TECHNOLOGY]

Neutral Salt Action. II. The Effect of Neutral Salts on the Hydrolysis of Copper Sulfate¹

BY HAROLD B. FRIEDMAN AND JEFFERSON A. STOKES, JR.²

1. Introduction

The effect of neutral salts on various types of chemical equilibria has been studied by many investigators. However, little work has been devoted to the salt effect on hydrolysis. In those few cases, the investigations have been limited to esters.³ An electrometric method readily permits the determination of the low concentration of hydrogen ions existing in solutions of copper sulfate.

2. Historical

Denham⁴ using an electrometric method with a hydrogen electrode determined the degree of hydrolysis of a number of different salts and obtained excellent results in many cases. He did not investigate the effect of neutral salts since he thought that they "interfered with the measurement of hydrolysis."

Poma and Albonico⁵ studied the effect of neutral salts on the hydrolysis of methyl acetate and found that neutral salts accelerated the rate and increased the degree of hydrolysis. The increase was in the order of potassium, sodium, lithium, and iodides, nitrates, bromides, and chlorides.

O'Sullivan⁶ determined the hydrolysis of 0.1 *N* copper sulfate by an electrometric method in which he used a quinhydrone electrode. The results which he obtained are not to be relied upon, as his measurements on four solutions of identical concentration vary as much as 3.5 mv. An increase of e. m. f. with time is also noted.

(1) Constructed from a thesis presented to the Department of Chemistry, Georgia School of Technology, in partial fulfillment of the requirements of the degree of Master of Science in Chemistry.

(2) Present address, E. I. du Pont de Nemours & Company, Inc., Richmond, Virginia.

(3) Thomas and Whitehead, *J. Am. Leather Chemists Assn.*, **25**, 127 (1930), have some measurements on SO_4^{2-} and Cl^- on solutions of aluminum salts, but they varied the ratios of their concentrations in a manner that makes direct comparison difficult. However, their results will be discussed in a subsequent paper in which one of us has studied aluminum sulfate as a hydrolyzing salt.

(4) Denham, *J. Chem. Soc.*, **93**, 41-63 (1908).

(5) Poma and Albonico, *Atti Accad. Lincei*, **24**, I, 747 (1915).

(6) O'Sullivan, *Trans. Faraday Soc.*, **21**, 319 (1925).

These erratic results may be due to the possible oxidation of the quinhydrone, since the measurements extend over a period of two days. Also, there is a possibility of diffusion of potassium chloride from the salt bridge into the solution in this prolonged measurement, resulting in an increase of e. m. f. O'Sullivan attributes "it, therefore, to gradual coagulation of the colloidal particles of cupric hydroxide, produced by hydrolysis, whereby adsorbed acid would be set free."

O'Sullivan did not investigate the neutral salt effect on the hydrolysis of copper sulfate.

3. Preparation and Purification of Materials

All salts used in this investigation were of c. p. grade and were purified very carefully by recrystallizations from water. In all operations, freshly distilled water was used. The water was boiled immediately before use to expel the dissolved gases.

The purified salts were dried in an oven at 110° for a period of twelve hours. The dry salts were put into glass-stoppered bottles and kept in a desiccator over concentrated sulfuric acid.

Copper Sulfate.—C. p. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was three times recrystallized. Solutions were prepared from this purified salt, standardized by thiosulfate and checked by electrolysis. The two methods agreed to one part in one thousand.

Potassium Chloride, Potassium Sulfate, Sodium Chloride, and Sodium Sulfate.—These neutral salts were recrystallized twice from water, except the potassium chloride for use in the calomel electrodes which was recrystallized three times. The sodium chloride was precipitated from a saturated solution by means of hydrogen chloride gas. This necessitated longer drying at about 140° to free the salt from hydrogen chloride incorporated in the crystals.

Quinhydrone.—The quinhydrone was the standard Eastman product and was not further purified.

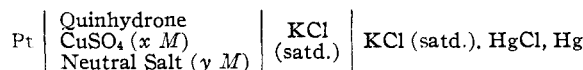
4. Apparatus and Method.—The pH measurements were made with a Leeds and Northrup students' potentiometer, using a quinhydrone electrode and a saturated calomel reference electrode. The cells were immersed in a water thermostat at $25 \pm 0.01^\circ$. The degree of hydrolysis was calculated from pH by the equations

$$-\log C_H = \text{pH}, \quad x = \frac{C_H}{2M}, \quad \text{where } M = \text{molar concn.}$$

The liquid junction potentials were cut down by salt bridges of saturated potassium chloride in agar gel.

Two complete cells were employed so as to obtain duplicate readings and furnish some means of checking the reproducibility of the cells.

The cell arrangement was as follows



The salt solution was placed in the quinhydrone electrode vessel and a sufficient amount of solid quinhydrone added to saturate the solution at 25°. The set-up as indicated was placed in the bath and allowed to reach the temperature of the thermostat before measurements were taken. Measurements were repeated over intervals of two to four minutes for a period of ten to thirty minutes depending upon the constancy of the readings. If the measurements extended over a longer period than thirty minutes (and sometimes less) they were found to vary, usually characterized by a slight increase of potential. The cause of this is probably the diffusion of potassium chloride from the salt bridge, or possibly oxidation of the quinhydrone.

5. Experimental Results

The experimental results are shown graphically in Figs. 1 to 5, discussion of which follows in section 6. In order to show the concordance in the data obtained, the following random samples are given, each measurement tabulated representing an entirely independently prepared cell.

Molality CuSO ₄	Added salt	E. m. f.
0.1000	None	0.2181
		.2183
		.2177
		Av. .2180
.0500	1.0 N NaCl	.2964
		.2964
		.2965
		Av. .2965
.0500	0.75 N KCl	.2777
		.2777
		.2785
		Av. .2780

6. Discussion

In addition to measurements of the effect of sodium and potassium chlorides, and sodium and potassium sulfates on the degree of hydrolysis of copper sulfate, several measurements were made of the effect of sodium and potassium nitrates.

When nitrates were present, it was found that the potentiometer reading increased with time and the amount of quinhydrone present; consequently very little credence could be given these results. However, the initial readings were of sufficient accuracy to show qualitatively that

sodium nitrate increased the degree of hydrolysis more than potassium nitrate, but less than the chlorides of sodium and potassium.

The erratic behavior of the quinhydrone electrode in the presence of nitrates may be due to oxidation of the quinhydrone by the nitrate in the mildly acid solution.

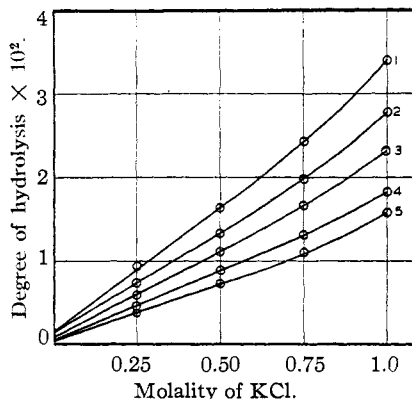


Fig. 1.—1, 0.0125 mole CuSO₄; 2, 0.0188; 3, 0.0250; 4, 0.0375; 5, 0.050.

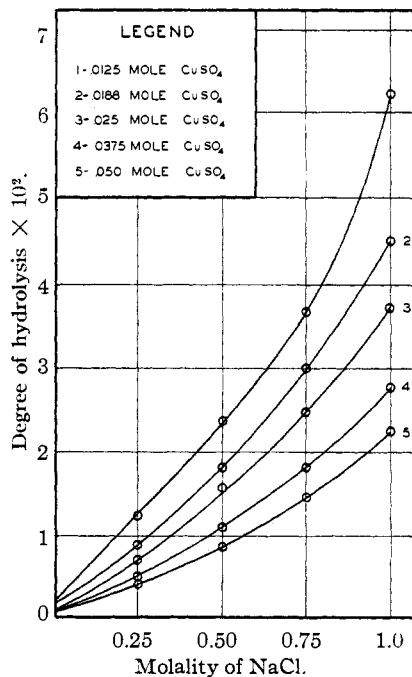


Fig. 2.

In Figs. 1 and 2, the degree of hydrolysis of copper sulfate at five different concentrations ranging from 0.0125 to 0.05 M in the presence of a neutral salt, has been plotted against the molality of the neutral salt present.

In Figs. 3 and 4, these data have been plotted

differently, to show the variation of the degree of hydrolysis of the copper sulfate as functions of the molality of the copper sulfate in the presence of the neutral salts.

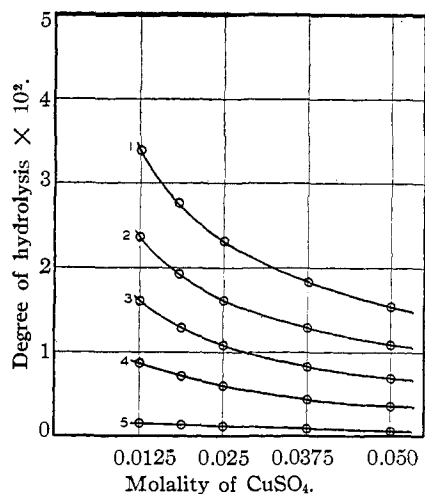


Fig. 3.—1, 1.0 mole of KCl; 2, 0.075; 3, 0.050; 4, 0.025; 5, 0.00.

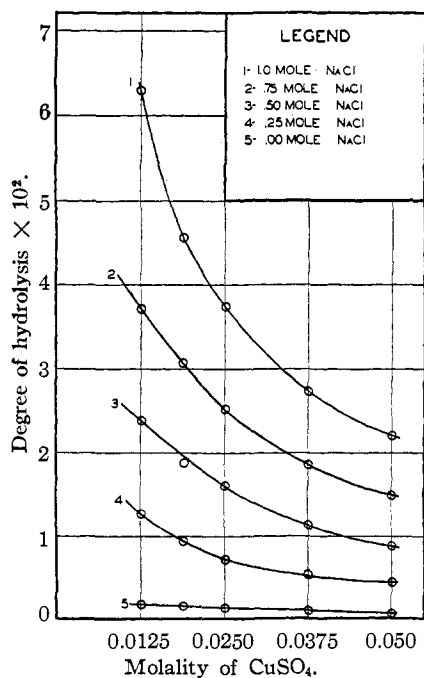


Fig. 4.

An inspection of these four figures shows an increase in the degree of hydrolysis, (1) with dilution of copper sulfate, (2) with an increase in the concentration of neutral salt.

In Fig. 5, the degree of hydrolysis of copper sulfate, alone and in the presence of the sulfates of sodium and potassium, has been plotted against

the molality of copper sulfate. While the hydrolysis without neutral salt increases with dilution, and also increases with addition of nitrates and chlorides of sodium and potassium, there is a marked *decrease* upon addition of the sodium and potassium sulfates. Potassium sulfate causes a larger decrease than sodium sulfate.

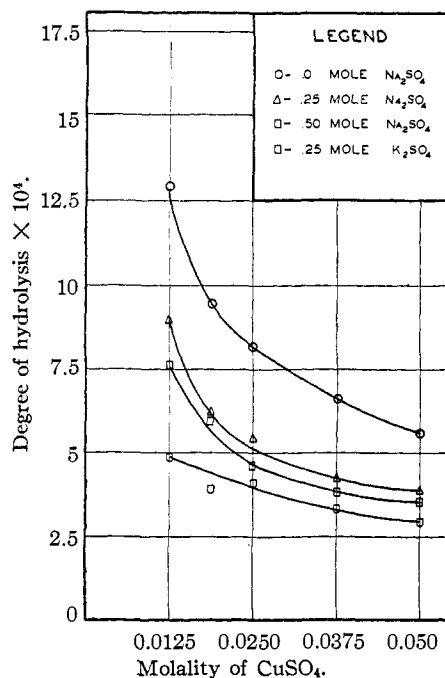
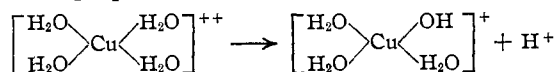


Fig. 5.

As yet, we are not prepared to postulate a mechanism for these effects. In the cases of the nitrates and chlorides, it is probable that we are measuring the simple primary salt effect, which approximates linearity. In all cases, but especially in the presence of sulfates, it is possible that adequate explanation is to be found in the formation of the Werner-like complexes suggested to account for a similar process by Thomas and Whitehead.³ By analogy with their case, we would propose



Here, the copper ion, with its coordination number of four, has about it four aquo groups, and the first stage of the hydrolysis is indicated by the right-hand member of the equation, which accounts for the increase in acidity upon addition of the chloride or nitrate. However, in the case of added sulfate, the sulfate may remove hydrogen ion in the form of HSO_4^- , thereby re-

ducing the acidity instead of increasing it. This effect is consistent with the results of Thomas and Whitehead for aluminum salts, and of Wilson and Kern,⁷ and of Thomas and Baldwin⁸ for chromium salts, in which these investigators found that chloride ion always increased the hydrogen ion activity of the solutions to which it was added but that sulfate ion decreased it, particularly when in low concentrations. They point out that the presence of sulfate ions produces a much more complicated system. According to Thomas and Baldwin, there is the tendency of the sulfate to replace the hydroxo groups in the Werner complex which would, of course, tend to make the solution less acid, and it would do so more effectively than the chloride ion of the same equivalent concentration if the stability of the sulfato-complexes follows the same order of stability that holds for other Werner complexes, namely, oxalate > acetate > formate > sulfate > chloride > nitrate. These are in order of decreasing stability, and would account for the greater effectiveness of sulfate over that of chloride ion, at low concentrations.

In this work no attempt has been made to cor-

(7) Wilson and Kern, *J. Am. Leather Chem. Assoc.*, **12**, 445 (1917).

(8) Thomas and Baldwin, *This Journal*, **41**, 1981 (1919).

rect for the salt error of the quinhydrone electrode in the strong salt solutions. Not only are we out of the range for which such corrections are available, but it is in a sense just that quantity that we are measuring, in comparing the differences in e. m. f. with and without the added salts. Furthermore, irrespective of any salt error, our data are directly available for comparative studies in specific interaction of ions at corresponding concentrations.

Summary

A study has been made by an electrometric method of the effect of various neutral salts on the hydrolysis of copper sulfate in aqueous solutions.

It has been found that the several neutral salts increased the degree of hydrolysis of copper sulfate in the following order: potassium nitrate, sodium nitrate, potassium chloride and sodium chloride. Those which showed a decrease are, in order: sodium sulfate and potassium sulfate.

Also, it has been found that the extent of hydrolysis showed an increase with dilution of copper sulfate. Factors involved in the mechanism of the hydrolysis have been discussed.

ATLANTA, GEORGIA

RECEIVED AUGUST 29, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Reactions of Zirconium Tetrabromide in Liquid Ammonia¹

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I. Zirconium Tetrabromide and Liquid Ammonia

Several investigators³ have examined the action of gaseous ammonia on zirconium tetrahalides both in the solid form at various temperatures and in solution in ether. A number of ammonates have been reported as well as the products of their thermal decomposition. Formulas for ammonates deduced solely from the composition of a solid obtained by treating a

halide with ammonia are open to question because the solid so formed may be a mixture of amide (imide or nitride) or ammonobasic salt and ammonium halide. For example, Stahler and Denk^{3c} succeeded in removing a large amount of ammonium iodide from the "ammonate" of zirconium iodide, $ZrI_4 \cdot 8NH_3$, by extraction with liquid ammonia. Whereas the zirconium content of the ammonate was 12%, that of the washed residue was 45%. Young⁴ reports that zirconium tetrabromide is soluble at least to the extent of 2 g. per 10 ml. of liquid ammonia at -33° . On the other hand, experiments in this Laboratory⁵ indicated that zirconium tetrabromide is ammonolyzed by liquid ammonia at 0° or higher.

The present study has shown that an ammonolytic equilibrium

(1) This paper is based upon a dissertation submitted by Ernest W. Bowerman to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1937.

(2) Present address: Humble Oil and Refining Company, Baytown, Texas.

(3) (a) S. R. Paykull, *Ber.*, **6**, 1467 (1873); (b) T. M. Matthews, *This Journal*, **20**, 821-3, 840 (1898); (c) A. Stahler and B. Denk, *Ber.*, **33**, 2611-2617 (1905); (d) L. Wolther, *Chem. Z.*, **32**, 606-607 (1908); (e) P. Bruère and E. Chauvenet, *Compt. rend.*, **167**, 201-203 (1918).

(4) R. C. Young, *This Journal*, **57**, 1195-1196 (1935).

(5) H. J. Wolthorn, Thesis, The Ohio State University, 1933.