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THE ACID DISSOCIATION OF  
THE HYDRATED CUPRIC ION

THE FORMATION OF DIMERIC CUPRIC  
COMPOUNDS

BY

KAI JULIUS PEDERSEN



KØBENHAVN

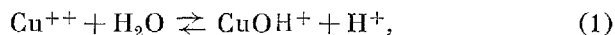
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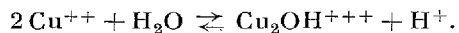
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Our knowledge of the hydrogen ion concentration of solutions of cupric salts, and the equilibria which determine it, is very incomplete. The hydrogen ion concentration of a cupric sulphate solution was first measured by CARRARA and VESPIGNANI<sup>(1)</sup> using the method of inversion of sucrose. KULLGREN<sup>(2)</sup> applied the same method to solutions of cupric chloride and nitrate. The quinhydrone electrode was used by O'SULLIVAN<sup>(3)</sup> and by FRIEDMAN and STOKES<sup>(4)</sup> in cupric sulphate solutions, by QUINTIN<sup>(5)</sup> in cupric nitrate and sulphate solutions, and by ČUPR and ŠIRŮČEK<sup>(6)</sup> in different cupric salt solutions. Finally, the glass electrode was employed for measuring the pH of cupric sulphate solutions by HUGHES<sup>(7)</sup> and by CRANSTON and BROWN<sup>(8)</sup>. A selection of the best measurements is given in Fig. 1.

It is usually assumed that the hydrogen ion concentration is determined by the equilibrium



but the measurements are not sufficiently accurate to test this assumption. If anything, they rather disfavour it. Thus, QUINTIN as well as ČUPR and ŠIRŮČEK state that, when pH is plotted against the logarithm of the concentration of the copper salt, the points fall close to a straight line with the slope one (cf. Fig. 1), or, in other words, the hydrogen ion concentration is roughly proportional to the cupric ion concentration. If this holds, equilibrium 1 alone does not determine the hydrogen ion concentration. The relation found by these investigators rather indicates the equilibrium



JANDER and MÖHR<sup>(9)</sup> recently studied the diffusion of solutions of cupric perchlorate and cupric chloride in the presence of neutral salt or strong acid. For all their solutions, they found the diffusion coefficient to be the same within a few per cent, while pH varied from 5 to 0. However, their pH values were often several units lower than should be expected from measure-

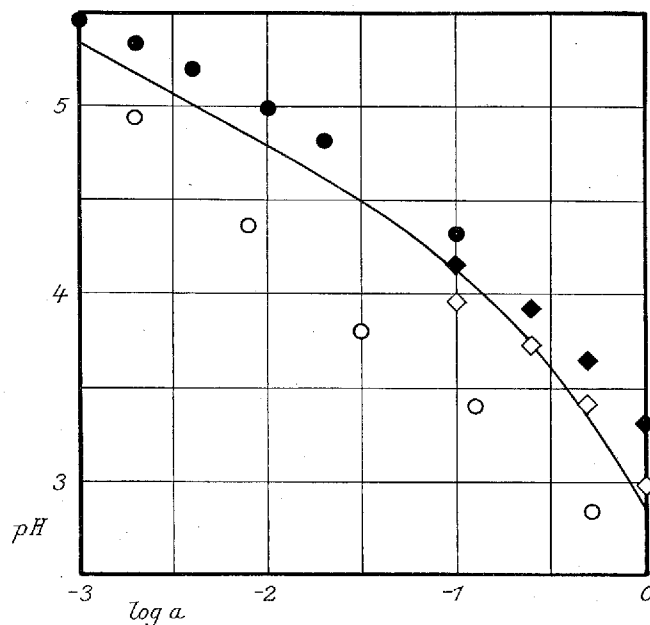


Fig. 1. Measurements of the pH of solutions of cupric nitrate and sulphate ( $a$  molar) by the investigators: QUINTIN (quinhydrone electrode, cupric nitrate, open circles), CRANSTON and BROWN (glass electrode at  $15^{\circ}\text{C}$ ., cupric sulphate, solid circles), and ČUPR and ŠIRŮČEK (quinhydrone electrode at  $20^{\circ}\text{C}$ ., cupric nitrate, open squares, and cupric sulphate, solid squares). The curve represents the measurements of the present author.

ments by other investigators, including the author of the present paper. It appears from their results that the degree of hydrolysis varies from 0 to a very considerable value ( $> 20\%$ ), while the diffusion coefficient is practically constant. Since a dimeric ion would have a smaller diffusion coefficient than the usual cupric ion, they conclude that only monomeric hydrolysis products are present. However, it seems safe to maintain that the degree of hydrolysis of their solutions is always less than  $1\%$ .

Therefore, their measurements cannot give any information concerning the nature of the hydrolysis products.

The object of the present paper is to throw light on the problem of acid-base equilibria in aqueous solutions of cupric ions. For this purpose, the hydrogen ion concentrations of solutions of cupric nitrate, varying in concentration from 1 to 0.001 molar, were measured by means of the glass electrode at 18.0° C. Cupric nitrate was chosen rather than sulphate, because the presence of sulphate ions would make the problem more complicated owing to their power of forming complexes with cupric ions and of combining with hydrogen ions. Furthermore, the greater electric charge of the sulphate ion would cause a greater salt effect. Measurements were carried out both on pure aqueous solutions of cupric nitrate and on solutions containing, in addition, various amounts of nitric acid or sodium hydroxide. It is well known that only very little sodium hydroxide can be added before a precipitate is formed. According to J. BJER-RUM<sup>(10)</sup>, the green crystalline substance which precipitates in weakly alkaline solutions of cupric nitrate has the composition  $\text{Cu}_2(\text{OH})_3\text{NO}_3$ . It was often possible to carry out measurements on solutions containing so much sodium hydroxide that they were supersaturated with respect to the substance forming the precipitate. For such solutions, the e. m. f. remained constant for a period of time, but when they were kept standing sufficiently long, a gradual increase in the hydrogen ion concentration was measured. At the same time, the solutions turned turbid. The greatest concentration of sodium hydroxide which could be maintained without disturbing the measurements was: in 1 molar  $\text{Cu}(\text{NO}_3)_2$  only 0.2 % of the concentration of cupric nitrate, in 0.1 molar  $\text{Cu}(\text{NO}_3)_2$  it was 1.2 %, and in 0.005 molar  $\text{Cu}(\text{NO}_3)_2$  it was more than 10 %. These examples show that the solutions measured were very weakly buffered. There is no sense in carrying out measurements on such systems if the amount of acid or basic impurity present is not known with great accuracy. We shall see later how these impurities may be estimated.

Cupric nitrate hexahydrate was used for the experiments. It was prepared by recrystallization of the best trihydrate available (Schering-Kahlbaum's *Cuprum nitr. puriss.*). 1000 g. of the

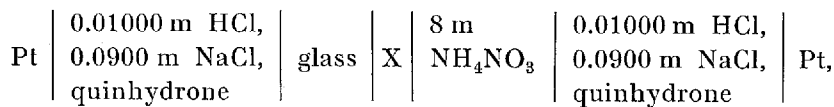
trihydrate were dissolved in 400 ml. of warm water. The solution was cooled down to 0°, seeded with the hexahydrate, and was left for crystallization at 0°. The crystals were separated from the mother liquor and were dried in a desiccator over anhydrous calcium chloride. When the crystals began to effloresce the drying agent was removed. The preparation contained an excess of base, or a deficiency of acid, which increased gradually during storage. At the beginning of the measurements it amounted to  $3 \times 10^{-5}$ , at the end to  $18 \times 10^{-5}$  equivalents per mole of cupric nitrate. This increase is probably due to the fact that the glass basin containing the preparation was inadvertently placed in the desiccator on a perforated iron plate. The nitric acid lost may have distilled from the slightly moist crystals to the iron plate.

Standard solutions of about 1 or 2 molar cupric nitrate were made from the preparation at different times. The solutions, which were kept in a silica flask, were analyzed for copper according to the modified iodometric titration method of HAGEN<sup>(11)</sup>, which gave excellent results (accuracy about 0.1 %). Metallic copper (electrolytically deposited, *pro analysi*) was used as a standard substance.

The barium nitrate used in some of the measurements was a Merck *pro analysi* preparation which was recrystallized and dried at 110° C. It contained no appreciable basic or acid impurities.

The water used for the solutions was redistilled in a still supplying water of a specific conductance of less than  $3 \times 10^{-7}$  ohmcm<sup>-1</sup>. It was stored in bottles covered inside with a layer of paraffin wax.

The cells measured had the composition



where X is the solution under investigation. The glass electrode was of the plane type described by MACINNES and DOLE<sup>(12)</sup>. It was tested before use, and was found to follow practically completely the law holding for the hydrogen electrode through-

out the pH interval in which it was going to be used. As container for the solution under investigation served the vessel shown in Fig. 2. Its total volume was 100 ml., but only 70 ml. of solution were used for the measurement. For the solutions containing more than 0.1 molar cupric nitrate, a similar, but smaller vessel requiring only 10 ml. was applied. The opening D was closed with a rubber stopper carrying the glass electrode which dipped into the solution. The side tube E was completely

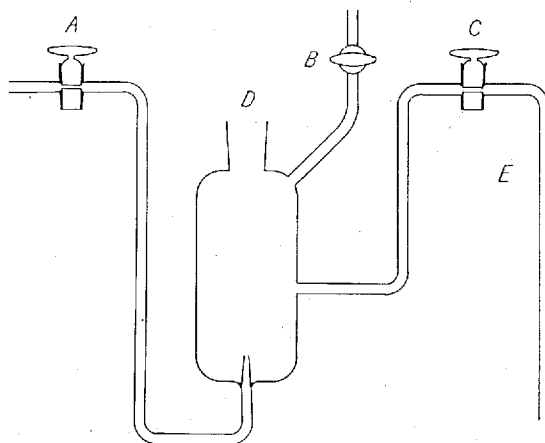


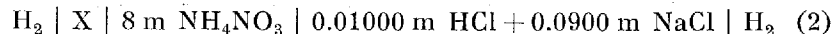
Fig. 2. Electrode vessel.

filled with the solution. Before the measurement, possible traces of carbon dioxide were removed by a vigorous current of pure, carbon dioxide free air which was passed through the solution for 10 minutes. The air entered through the stopcock A and escaped through B.

The ready cell was placed into a liquid paraffin thermostat at  $18.0^{\circ}\text{C}$ . The lower end of E dipped into a test tube containing 8 molar ammonium nitrate which provided connection with the quinhydrone electrode. The levels of the solutions were so arranged that the bridge solution rose a few centimetres into E when the stopcock C was opened. The e. m. f. was measured by means of a valve potentiometer (made by the firm "Radiometer"; Copenhagen). The potential had become constant after a few minutes, and generally it did not change for hours. Only when the solution was supersaturated, a gradual decrease was

observed, as already mentioned, after a longer or a shorter period of constant potential.

At least once every day, a solution of the composition 0.01000 m HCl + 0.0900 m NaCl was measured instead of X. The small potential measured here is the asymmetry potential of the cell. When it is subtracted from the e. m. f. measured for X, the potential  $E$  of a cell of the composition



is obtained.

To a series of measurements at constant cupric nitrate concentration but varying nitric acid or sodium hydroxide concentration, we may apply the equation

$$E = E_a - \frac{RT}{F} \ln(\text{H}^+),$$

where  $(\text{H}^+)$  is the hydrogen ion concentration, and  $E_a$  includes the constant potential of the right half cell, the liquid-liquid potential, and the salt effect of the left half cell. When a sufficiently small amount of acid or base is added,  $E_a$  is constant. For the temperature 18° C. the equation may be written

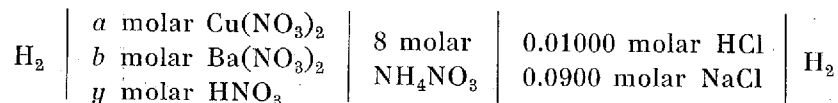
$$-\log(\text{H}^+) = A + 17.32 E, \quad (3)$$

where  $A \equiv -17.32 E_a$ . The value of  $A$  corresponding to an infinitely small concentration of acid or base added will be denoted by  $A_0$ .

$A$  was determined in the following way.  $E$  was measured for solutions of cupric nitrate containing so much nitric acid that the hydrogen ion concentration produced by the cupric ions was either negligible or could be estimated from preliminary values of the equilibrium constants. In no case, this correction exceeded 0.5 % of the concentration of nitric acid added. Also the small acid deficiency of the cupric nitrate, estimated from later measurements, was taken into account.  $(\text{H}^+)$  and  $E$  were introduced into equation 3, and  $A$  was computed.  $A_0$ , the value of  $A$  corresponding to the concentration 0 of nitric acid, was found for each series by extrapolation. The results are given in Table 1. The table includes two series of measurements in



Table 1.

Electromotive force  $E$  volts at 18.0° C. of the cell

measured by means of the glass electrode.  $y = -x - a\delta$ , where  $-x$  is the concentration of nitric acid added, and  $\delta$  is the deficiency of nitric acid in the preparation of cupric nitrate expressed in equivalents per mole.  $A$  has been computed from equation 3.  $A_0$  is the value of  $A$  corresponding to  $y = 0$ .

$a$	$b$	$\delta 10^5$	$y$	$E$	$A$	$A_0$
1.000	0	18	0.04975	-0.0578	2.304	2.308
			0.02468	-0.0403	2.305	
			0.01002	-0.0180	2.309	
0.500	0	16	0.04098	-0.0424	2.122	2.123
			0.02008	-0.0247	2.125	
			0.00801	-0.0016	2.123	
0.200	0	8	0.01027	-0.0023	2.028	2.033
			0.004104	0.0205	2.031	
			0.002059	0.0377	2.032	
0.100	0	3	0.01000	-0.0005	2.009	2.018
			0.005015	0.0166	2.012	
			0.002525	0.0335	2.017	
0	0.100		0.01000	-0.0005	2.009	2.018
			0.005017	0.0166	2.012	
			0.002528	0.0335	2.017	
			0.001025	0.0561	2.017	
0.0500	0	8	0.005134	0.0160	2.012	2.021
			0.002055	0.0387	2.017	
			0.001033	0.0558	2.019	
0.0200	0	3	0.005138	0.0154	2.022	2.040
			0.002059	0.0378	2.032	
			0.001033	0.0558	2.033	
0.0100	0	3	0.00504	0.0153	2.033	2.058
			0.002021	0.0373	2.048	
			0.001018	0.0542	2.054	
0.0020	0.0080	3	0.002021	0.0374	2.046	2.058
			0.001018	0.0544	2.050	
			0.000413	0.0767	2.056	

Table 1 (continued).

$a$	$b$	$d \cdot 10^5$	$y$	$E$	$A$	$A_0$
0.0050	0	18	0.005005	0.0154	2.034	2.072
			0.002006	0.0372	2.053	
			0.001011	0.0540	2.060	
			0.000410	0.0762	2.067	
0.0020	0	18	0.005040	0.0152	2.034	2.086
			0.002020	0.0364	2.064	
			0.001018	0.0531	2.072	
			0.000413	0.0753	2.080	
0.0010	0	18	0.005005	0.0145	2.050	2.097
			0.002006	0.0363	2.069	
			0.001011	0.0528	2.081	
			0.000410	0.0749	2.090	

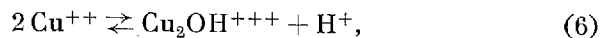
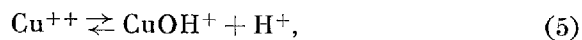
solutions containing barium nitrate. It is seen that, both in 0.1 and 0.01 molar cupric nitrate, the cupric ions may be replaced by barium ions without altering the value of  $A_0$ .

In the following, the hydrogen ion concentration of solutions of cupric nitrate containing small concentrations of sodium hydroxide or nitric acid will be computed from the measurements by means of the formula

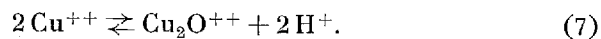
$$-\log(\text{H}^+) = A_0 + 17.32 E, \quad (4)$$

where  $A_0$  has the values given in Table 1. Before analyzing the results given in Table 2, we must consider the theory to be applied.

We may explain the hydrogen ion concentrations of the solutions under the assumption that the following three equilibria take place



and



In these schemes the water of hydration has been omitted. The mass action constants are

$$k_1 = \frac{(\text{CuOH}^+) (\text{H}^+)}{(\text{Cu}^{++})}, \quad (8)$$

$$k_2 = \frac{(\text{Cu}_2\text{OH}^{+++}) (\text{H}^+)}{(\text{Cu}^{++})^2}, \quad (9)$$

and

$$k_3 = \frac{(\text{Cu}_2\text{O}^{++}) (\text{H}^+)^2}{(\text{Cu}^{++})^2}. \quad (10)$$

We consider a series of measurements in  $a$  molar cupric nitrate. The cupric nitrate has an acid deficiency of  $\delta$  equivalents per mole.  $x$  molar sodium hydroxide, or  $-x$  molar nitric acid, has been added. It follows from the theory that

$$\begin{aligned} (\text{H}^+) + x + a\delta &= (\text{CuOH}^+) + (\text{Cu}_2\text{OH}^{+++}) + 2(\text{Cu}_2\text{O}^{++}) \\ &= k_1 \frac{(\text{Cu}^{++})}{(\text{H}^+)} + k_2 \frac{(\text{Cu}^{++})^2}{(\text{H}^+)} + 2k_3 \frac{(\text{Cu}^{++})^2}{(\text{H}^+)^2}, \end{aligned}$$

which may also be written as follows

$$\frac{[(\text{H}^+) + x] (\text{H}^+)}{(\text{Cu}^{++})} + \frac{a\delta (\text{H}^+)}{(\text{Cu}^{++})} = k_1 + k_2 (\text{Cu}^{++}) + 2k_3 \frac{(\text{Cu}^{++})}{(\text{H}^+)}. \quad (11)$$

If the decrease in cupric ion concentration owing to the reactions 5 to 7 is denoted by  $A$ , we get

$$(\text{Cu}^{++}) = a - A \quad (12)$$

and

$$\begin{aligned} A &= (\text{CuOH}^+) + 2(\text{Cu}_2\text{OH}^{+++}) + 2(\text{Cu}_2\text{O}^{++}) \\ &= (\text{H}^+) + x + a\delta + (\text{Cu}_2\text{OH}^{+++}) \\ &= (\text{H}^+) + x + a\delta + k_2 \frac{(\text{Cu}^{++})^2}{(\text{H}^+)}. \end{aligned}$$

An approximation leads to

$$A = (\text{H}^+) + x + k_3 \frac{a^2}{(\text{H}^+)}. \quad (13)$$

From the equations 11 and 12 we obtain

$$k = (k_1 + ak_2) + 2k_3 \frac{(\text{Cu}^{++})}{(\text{H}^+)}, \quad (14)$$

where

$$k \equiv \frac{[(\text{H}^+) + x](\text{H}^+)}{(\text{Cu}^{++})} + \frac{\alpha \delta (\text{H}^+)}{(\text{Cu}^{++})} + k_2 A. \quad (15)$$

In order to test the theory, we first compute  $A$  from equation 13 and a preliminary value of  $k_2$ , and then  $(\text{Cu}^{++})$  from equation 12.  $k$  of equation 15 is a sum of three terms, the first and most important of which may now be calculated. The third term is a very small correction and may be estimated from a preliminary value of  $k_3$ . The relative importance of the second term, which contains the unknown  $\delta$ , decreases when  $x$  increases within a series of measurements at constant  $a$ . If we as a first approximation put  $\delta = 0$ , preliminary values of  $k$  may be calculated and plotted against  $\frac{(\text{Cu}^{++})}{(\text{H}^+)}$  (the solid circles in Fig. 3). According to equation 14, the true value of  $k$  leads to a straight line when  $a$  is constant; actually, the points computed under the assumption that  $\delta = 0$  fall on a curve which approaches a straight line with increasing  $x$ . Generally, the approach is the more rapid the smaller  $a$ . By the method of trial and error, we find the value of  $\delta$  for which a rectilinear plot is obtained (open circles in Fig. 3). From the straight line, the numerical values of the two constants  $(k_1 + ak_2)$  and  $2k_3$  in equation 14 may be determined. The series chosen as an example in Fig. 3 is one in which the deviation from the straight line of the points computed for  $\delta = 0$  is fairly great. Only for two of the 15 series, namely when  $a = 1$  and  $a = 0.5$ , the deviations were greater.

The results of the measurements and computations are presented in Tables 2 and 3. The numbers of the series, given in the first column of Table 2, indicate the chronological order. It is seen that  $\delta$ , which is given in the same column, increases with time. When the same standard solution of cupric nitrate was used for preparing the solutions in several series, the same  $\delta$  was found.  $x$ , the concentration of sodium hydroxide added, is given in the second column. Nitric acid is reckoned as sodium hydroxide with negative sign. An asterisk denotes the addition of so much base that a precipitate was formed during the

measurement. In these cases, the potential decreased gradually after having been constant for a time.  $E$ , given in the next column, is the electromotive force in volts after subtraction of the asymmetry potential. Therefore,  $E$  may be considered the e. m. f. of the combination stated in scheme 2.  $-\log(\text{H}^+)$ , presented in the fourth column, has been computed by means of

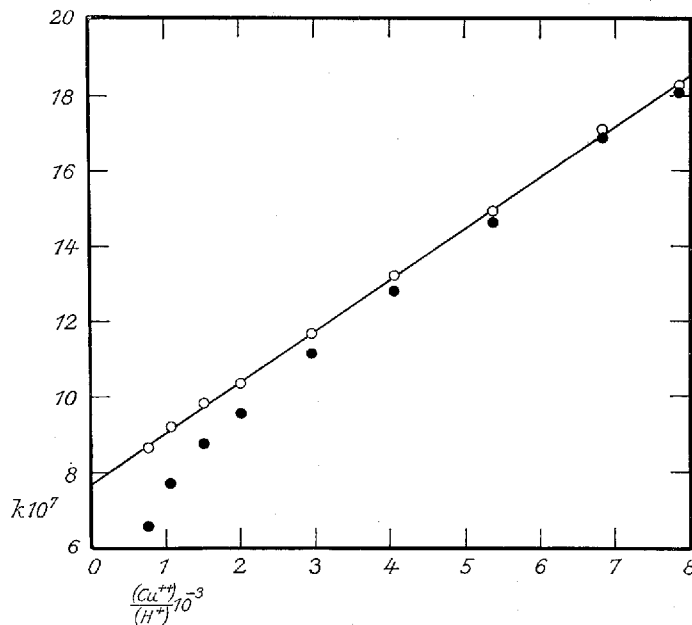


Fig. 3. Series 9: 0.200 m  $\text{Cu}(\text{NO}_3)_2$ . Solid circles:  $\delta = 0$ . Open circles:  $\delta = 8 \times 10^{-5}$ .

equation 4 and the values of  $A_0$  in Table 1. The computations of  $\frac{(\text{Cu}^{++})}{(\text{H}^+)^2}$  and  $k$ , given in the next two columns, were carried out as previously explained.

When  $k$  is plotted against  $\frac{(\text{Cu}^{++})}{(\text{H}^+)^2}$ , the points for each series fall close to a straight line, in agreement with equation 14. The constants  $(k_1 + ak_2)$  and  $k_3$  determined from the plot are shown in the fourth and sixth column of Table 3. By means of these values and equation 14, the values of  $k$  given in the last column of Table 2 were calculated. The agreement between  $k$  found from the measurement and  $k$  calculated from formula 14 is satisfactory. Only in the least acid solutions of some of the

Table 2.

	$x \cdot 10^4$	$E$	$-\log(H^+)$	$\frac{(Cu^{++})}{(H^+)} \cdot 10^{-3}$	$k \cdot 10^7$ found	$k \cdot 10^7$ formula
Series 12 0.9994 m $Cu(NO_3)_2$ $d = 18 \times 10^{-5}$	-10.23	0.0342	2.900	0.793	5.25	5.25
	- 5.09	0.0424	3.042	1.100	5.27	5.28
	0.00	0.0509	3.190	1.546	5.35	5.32
	3.39	0.0567	3.290	1.945	5.31	5.36
	7.43	0.0626	3.392	2.459	5.42	5.41
	12.56	0.0693	3.508	3.208	5.46	5.48
	18.57	0.0754	3.614	4.093	5.59	5.57
	*25.50	0.0793	3.681	4.771	(6.18)	5.64
Series 11 0.5031 m $Cu(NO_3)_2$ $d = 16 \times 10^{-5}$	-10.19	0.0494	2.979	0.479	2.32	2.35
	- 4.085	0.0658	3.263	0.921	2.36	2.40
	- 2.034	0.0725	3.379	1.203	2.46	2.43
	0.000	0.0795	3.500	1.589	2.50	2.47
	1.390	0.0842	3.581	1.914	2.52	2.51
	3.768	0.0913	3.704	2.539	2.58	2.58
	7.038	0.0990	3.838	3.454	2.70	2.69
	11.70	0.1072	3.980	4.783	2.84	2.84
*18.66	0.1155	4.123	6.636	3.06	3.06	
Series 9 0.2000 m $Cu(NO_3)_2$ $d = 8 \times 10^{-5}$	- 2.081	0.0897	3.587	0.772	0.864	0.872
	- 1.036	0.0980	3.730	1.073	0.920	0.913
	0.000	0.1066	3.879	1.512	0.981	0.973
	0.932	0.1138	4.004	2.015	1.034	1.041
	2.624	0.1235	4.172	2.963	1.169	1.170
	4.688	0.1314	4.309	4.057	1.320	1.319
	7.465	0.1385	4.432	5.376	1.491	1.498
	11.19	0.1446	4.537	6.829	1.710	1.696
13.87	0.1481	4.598	7.848	1.826	1.834	
*16.32						
Series 5 0.1000 m $Cu(NO_3)_2$ $d = 3 \times 10^{-5}$	- 2.058	0.0944	3.653	0.450	0.434	0.433
	- 1.033	0.1069	3.870	0.741	0.468	0.477
	- 0.520	0.1145	4.001	1.001	0.507	0.516
	0.000	0.1218	4.128	1.341	0.578	0.567
	0.704	0.1307	4.282	1.911	0.659	0.652
	1.641	0.1388	4.422	2.635	0.778	0.760
	2.797	0.1460	4.547	3.508	0.889	0.891
	4.243	0.1519	4.649	4.430	1.018	1.029
5.854	0.1564	4.727	5.291	1.151	1.158	
9.305	0.1630	4.841	6.852	1.387	1.391	
*12.54	0.1672	4.914	8.077	1.578	1.574	

Table 2 (continued).

	$x 10^4$	$E$	$-\log(\text{H}^+)$	$\frac{(\text{Cu}^{++})}{(\text{H}^+)} 10^{-3}$	$k 10^7$ found	$k 10^7$ formula
Series 6 0.05000 m $\text{Cu}(\text{NO}_3)_2$ + 0.05000 m $\text{Ba}(\text{NO}_3)_2$ $d = 3 \times 10^{-5}$	- 1.028	0.1113	3.946	0.442	0.270	0.268
	- 0.518	0.1228	4.145	0.698	0.306	0.306
	0.000	0.1356	4.367	1.163	0.383	0.376
	0.479	0.1454	4.536	1.714	0.459	0.458
	1.180	0.1544	4.692	2.452	0.571	0.569
	2.122	0.1621	4.826	3.330	0.688	0.700
	3.293	0.1678	4.924	4.164	0.825	0.825
	4.663	0.1726	5.007	5.024	0.953	0.954
7.014	0.1782	5.104	6.250	1.140	1.137	
Series 7 0.02000 m $\text{Cu}(\text{NO}_3)_2$ + 0.08000 m $\text{Ba}(\text{NO}_3)_2$ $d = 3 \times 10^{-5}$	- 0.518	0.1286	4.245	0.351	0.162	0.165
	- 0.210	0.1423	4.483	0.608	0.206	0.203
	0.000	0.1522	4.654	0.900	0.253	0.247
	0.421	0.1667	4.905	1.602	0.345	0.352
	0.935	0.1756	5.059	2.277	0.452	0.453
	1.403	0.1807	5.148	2.788	0.531	0.529
	2.336	0.1876	5.267	3.650	0.658	0.658
	4.144	0.1954	5.402	4.933	0.851	0.850
Series 10 0.05000 m $\text{Cu}(\text{NO}_3)_2$ $d = 8 \times 10^{-5}$	- 1.036	0.1115	3.952	0.447	0.271	0.280
	- 0.518	0.1231	4.153	0.711	0.316	0.323
	- 0.262	0.1292	4.259	0.907	0.363	0.355
	0.000	0.1353	4.364	1.155	0.409	0.395
	0.476	0.1448	4.529	1.687	0.482	0.481
	1.178	0.1537	4.683	2.401	0.595	0.596
	2.339	0.1623	4.832	3.376	0.749	0.754
	3.970	0.1694	4.955	4.465	0.925	0.930
	6.262	0.1756	5.062	5.684	1.126	1.127
	9.367	0.1811	5.158	7.043	1.349	1.346
*11.67	0.184	5.208	7.868	(1.500)	1.479	
Series 8 0.02000 m $\text{Cu}(\text{NO}_3)_2$ $d = 3 \times 10^{-5}$	- 0.520	0.1270	4.240	0.347	0.176	0.178
	- 0.262	0.1377	4.425	0.532	0.225	0.215
	0.000	0.1499	4.636	0.864	0.274	0.271
	0.377	0.1623	4.851	1.415	0.370	0.371
	0.836	0.1710	5.002	1.998	0.471	0.476
	1.401	0.1775	5.114	2.580	0.575	0.581
	2.102	0.1828	5.206	3.177	0.684	0.689
	3.040	0.1877	5.291	3.844	0.807	0.809
	4.204	0.1920	5.365	4.531	0.939	0.933
	5.599	0.1960	5.435	5.282	1.070	1.069
	8.178	0.2010	5.521	6.352	(1.296)	1.262
*9.799	0.2036	5.566	6.985	(1.411)	1.376	

Table 2 (continued).

	$x \cdot 10^4$	$E$	$-\log(\text{H}^+)$	$\frac{(\text{Cu}^{++})}{(\text{H}^+)} \cdot 10^{-8}$	$k \cdot 10^7$ found	$k \cdot 10^7$ formula
Series 1 0.00991 m $\text{Cu}(\text{NO}_3)_2$ $\delta = 3 \times 10^{-5}$	-0.414	0.1324	4.351	0.222	0.157	0.152
	-0.209	0.1450	4.569	0.367	0.174	0.181
	0.000	0.1593	4.817	0.649	0.240	0.236
	0.237	0.1716	5.030	1.058	0.315	0.316
	0.582	0.1815	5.202	1.565	0.414	0.414
	1.161	0.1906	5.359	2.236	0.540	0.545
	1.753	0.1959	5.451	2.747	0.653	0.645
	2.322	0.2000	5.522	3.216	0.733	0.737
Series 2 0.004985 m $\text{Cu}(\text{NO}_3)_2$ + 0.00493 m $\text{Ba}(\text{NO}_3)_2$ $\delta = 3 \times 10^{-5}$	-0.139	0.1553	4.748	0.279	0.147	0.139
	-0.0564	0.1649	4.914	0.408	0.164	0.164
	0.000	0.1710	5.020	0.521	0.186	0.186
	0.158	0.1839	5.243	0.868	0.250	0.253
	0.393	0.1940	5.418	1.294	0.334	0.336
	0.781	0.2034	5.581	1.868	0.433	0.447
	1.171	0.2085	5.669	2.269	0.526	0.525
	1.550	0.2123	5.735	2.621	0.600	0.593
Series 3 0.001980 m $\text{Cu}(\text{NO}_3)_2$ + 0.00793 m $\text{Ba}(\text{NO}_3)_2$ $\delta = 3 \times 10^{-5}$	-0.0423	0.1765	5.115	0.258	0.136	0.129
	0.0000	0.1850	5.262	0.361	0.153	0.150
	0.1331	0.2028	5.570	0.730	0.220	0.222
	0.2918	0.2128	5.744	1.080	0.287	0.290
	0.5278	0.2211	5.887	1.484	0.364	0.367
	0.8178	0.2273	5.995	1.874	0.442	0.446
	1.162	0.2322	6.080	2.238	0.523	0.517
	1.779	0.2389	6.196	2.826	0.632	0.632
	2.330	0.2430	6.267	3.226	(0.725)	0.710
3.497	0.2498	6.385	3.951	(0.887)	0.852	
Series 4 0.001001 m $\text{Cu}(\text{NO}_3)_2$ + 0.00891 m $\text{Ba}(\text{NO}_3)_2$ $\delta = 3 \times 10^{-5}$	-0.0521	0.1799	5.174	0.149	0.102	0.104
	-0.0211	0.1891	5.333	0.215	0.119	0.117
	0.0000	0.1954	5.442	0.276	0.132	0.129
	0.0884	0.2138	5.761	0.571	0.186	0.187
	0.1802	0.2231	5.922	0.820	0.235	0.235
	0.2918	0.2298	6.038	1.060	0.284	0.282
	0.5231	0.2384	6.187	1.458	0.363	0.360
	0.8161	0.2456	6.312	1.883	0.436	0.443
	1.392	0.2530	6.440	2.371	(0.589)	0.539
	2.334	0.2624	6.603	3.074	(0.761)	0.676
*3.488	0.264	6.63	2.782	(1.256)	0.619	
*4.617	0.268	6.70	2.695	(1.715)	0.602	



Table 2 (continued).

	$x \cdot 10^4$	$E$	$-\log(\text{H}^+)$	$\frac{(\text{Cu}^{++})}{(\text{H}^+)} \cdot 10^{-3}$	$k \cdot 10^7$ found	$k \cdot 10^7$ formula
Series 15 0.005007 m $\text{Cu}(\text{NO}_3)_2$ $d = 18 \times 10^{-5}$	-0.1027	0.1600	4.843	0.349	0.143	0.153
	0.0000	0.1711	5.035	0.542	0.187	0.192
	0.1451	0.1823	5.229	0.845	0.253	0.254
	0.3855	0.1924	5.404	1.258	0.345	0.337
	0.7067	0.2001	5.538	1.702	0.437	0.428
	1.172	0.2071	5.659	2.227	0.540	0.534
	1.890	0.2139	5.777	2.880	0.666	0.667
	2.930	0.2203	5.888	3.638	0.812	0.821
	4.675	0.2272	6.007	4.605	1.020	1.017
	7.026	0.2335	6.116	5.609	(1.258)	1.221
	9.364	0.2383	6.199	6.417	(1.464)	1.385
	*11.71	0.2403	6.234	6.553	(1.793)	1.412
Series 14 0.002005 m $\text{Cu}(\text{NO}_3)_2$ $d = 18 \times 10^{-5}$	-0.1034	0.1635	4.918	0.166	0.127	0.136
	-0.0515	0.1721	5.067	0.233	0.162	0.150
	0.0000	0.1817	5.233	0.342	0.182	0.174
	0.1197	0.1977	5.510	0.644	0.240	0.238
	0.2936	0.2093	5.711	1.014	0.313	0.318
	0.5458	0.2180	5.862	1.418	0.398	0.405
	0.8330	0.2238	5.962	1.760	0.481	0.478
	1.167	0.2290	6.052	2.126	0.555	0.557
	1.708	0.2346	6.149	2.580	0.667	0.665
	2.335	0.2394	6.232	3.019	(0.777)	0.749
	3.507	0.2464	6.354	3.727	(0.944)	0.901
	4.679	0.2510	6.433	4.154	(1.129)	0.993
	7.017	0.2527	6.463	3.776	(1.862)	0.912
	9.335	0.2544	6.492	3.320	(2.817)	0.814
*13.62	0.2537	6.480	1.931	(7.059)	0.515	
Series 13 0.001007 m $\text{Cu}(\text{NO}_3)_2$ $d = 18 \times 10^{-5}$	-0.0515	0.1769	5.161	0.146	0.132	0.134
	-0.0211	0.1851	5.303	0.202	0.151	0.148
	0.0000	0.1907	5.400	0.252	0.163	0.159
	0.1056	0.2106	5.745	0.553	0.227	0.231
	0.2327	0.2213	5.930	0.836	0.294	0.297
	0.4369	0.2304	6.088	1.177	0.380	0.378
	0.7384	0.2387	6.231	1.585	0.471	0.474
	1.167	0.2459	6.356	2.016	0.582	0.576
	1.759	0.2529	6.477	2.492	(0.709)	0.688
	2.334	0.2578	6.562	2.818	(0.831)	0.765
	3.258	0.2604	6.586	2.625	(1.244)	0.720
	4.672	0.2633	6.657	2.445	(1.914)	0.677
	5.850	0.2650	6.687	2.039	(2.873)	0.581
	7.001	0.2658	6.701	1.532	(4.574)	0.462
8.248	0.2653	6.692				
10.07	0.2657	6.699				
*15.12	0.2725	6.817				

series, values of  $k$  considerably greater than those corresponding to formula 14 are found. Such values are placed in parentheses. Especially in the most dilute solutions, which have the smallest hydrogen ion concentrations, the discrepancy may be due to an acid dissociation of the cupric ion which exceeds that expressed in the schemes 5 to 7. Thus, an ion of the composition  $\text{Cu}_2\text{O}(\text{OH})^+$  may possibly be formed. The discrepancy may also be due to a beginning precipitation. This question has not been examined more closely.

We now consider Table 3 where  $(k_1 + ak_2)$  and  $k_3$  found from the measurements are enumerated. With changing  $a$ , we may expect a variation of  $k_1$ ,  $k_2$ , and  $k_3$  owing to the change of the ionic strength  $\mu$ .  $(k_1 + ak_2)$  varies also as a direct consequence of the change of  $a$ . Within each of the two groups comprising series 5—7 and series 1—4,  $a$  varies, while  $\mu$  is kept constant by replacing the cupric nitrate by barium nitrate. As may be seen from the table,  $k_3$  is constant within each group, while  $(k_1 + ak_2)$  varies linearly with  $a$ . From the latter relation we find

$$k_1 = 4.8 \times 10^{-9} \text{ and } k_2 = 3.16 \times 10^{-7}, \text{ when } \mu = 0.300,$$

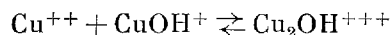
$$k_1 = 7.6 \times 10^{-9} \text{ and } k_2 = 2.1 \times 10^{-7}, \text{ when } \mu = 0.030.$$

Table 3.

Comparison between the mass action constants found from the measurements and those calculated from formulae 16—18.

Series no.	Cu(NO <sub>3</sub> ) <sub>2</sub> molarity	Ba(NO <sub>3</sub> ) <sub>2</sub> molarity	$(k_1 + ak_2) 10^7$ found	$(k_1 + ak_2) 10^7$ formulae	$k_3 10^{12}$ found	$k_3 10^{12}$ formula
12	0.9994	...	5.17	5.17	4.9	5.9
11	0.5031	...	2.29	2.29	5.8	6.3
9	0.2000	...	0.767	0.774	6.8	6.9
5	0.1000	...	0.366	0.364	7.48	7.45
6	0.05000	0.05000	0.202	0.206	7.48	7.45
7	0.02000	0.08000	0.112	0.111	7.48	7.45
10	0.05000	...	0.208	0.193	8.08	8.09
8	0.02000	...	0.115	0.114	9.03	9.02
1	0.00991	...	0.109	0.097	9.76	9.73
2	0.004985	0.00493	0.085	0.086	9.70	9.73
3	0.001980	0.00793	0.079	0.080	9.78	9.73
4	0.001001	0.00891	0.075	0.078	9.78	9.73
15	0.005007	...	0.082	0.093	10.2	10.4
14	0.002005	...	0.100	0.095	10.8	11.1
13	0.001007	...	0.100	0.098	11.8	11.5

In the other cases, where  $\mu$  changes from series to series, it is more difficult to estimate the separate values of  $k_1$  and  $k_2$ . However, it follows from the equilibrium



that an increase in the concentration of cupric salt will favour the ion  $\text{Cu}_2\text{OH}^{+++}$  at the expense of  $\text{CuOH}^+$ . In more concentrated solutions (when  $a > 0.1$ ), the concentration of the ion  $\text{CuOH}^+$  is so small that  $k_2$  may be calculated with sufficient accuracy from  $(k_1 + ak_2)$ , if  $k_1$  can be estimated roughly. On the other hand, in the more dilute solutions (when  $a < 0.01$ ), the ion  $\text{Cu}_2\text{OH}^{+++}$  is of so little importance that  $k_1$  may be calculated from  $(k_1 + ak_2)$  and a very rough value of  $k_2$ .

We have now found  $k_1$ , when  $0.1 \geq a \geq 0.001$ ;  $k_2$ , when  $1 \geq a \geq 0.01$ ; and  $k_3$  in the entire interval  $1 \geq a \geq 0.001$ . The values found for the three equilibrium constants may be expressed by means of the following formulae which, for very dilute solution, agree with the requirements of the DEBYE-HÜCKEL law:

$$-\log k_1 = 7.97 + \frac{0.996 \sqrt{\mu}}{1 + 1.0 \sqrt{\mu}} \quad (16)$$

$$-\log k_2 = 6.819 - \frac{0.996 \sqrt{\mu}}{1 + 1.3 \sqrt{\mu}} \quad (17)$$

$$-\log k_3 = 10.890 + \frac{0.996 \sqrt{\mu}}{1 + 2.36 \sqrt{\mu}} \quad (18)$$

The formulae contain two empirical constants each, while the third constant 0.996 is deduced from the Debye-Hückel theory. The values of  $(k_1 + ak_2)$  calculated by means of formulae 16—17 are given in the fifth column of Table 3, while  $k_3$  calculated from formula 18 is to be found in the last column of the table. A comparison of the calculated values with those obtained from the measurements shows good agreement. Only the values of  $k_3$  for the two most concentrated solutions deviate appreciably from those calculated on the basis of formula 18.

If we extrapolate to the ionic strength 0 by means of the formulae 16—18, we obtain

$$k_1^0 = 1.07 \times 10^{-8},$$

$$k_2^0 = 1.52 \times 10^{-7},$$

and

$$k_3^0 = 1.29 \times 10^{-11}.$$

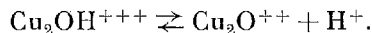
We have seen that the assumption of the three equilibria 5—7 offers a satisfactory explanation for the hydrogen ion concentration of the cupric nitrate solutions. The existence of the three equilibria may be proved more directly in the following way: It has already been shown that the experimental values of  $k$ , defined by equation 15, satisfy equation 14, when the hydrogen and the cupric ion concentrations vary, if only the ionic strength is kept constant.  $k_1$ ,  $k_2$ , and  $k_3$  are constants, but they are not assumed to be equilibrium constants; it follows from this result that

$$(\text{H}^+) + x + a\delta = k_1 \frac{(\text{Cu}^{++})}{(\text{H}^+)} + k_2 \frac{(\text{Cu}^{++})^2}{(\text{H}^+)} + 2k_3 \frac{(\text{Cu}^{++})^2}{(\text{H}^+)^2},$$

when  $(\text{H}^+)$  and  $(\text{Cu}^{++})$  vary, while  $\mu$  is constant. The only possible explanation of this result is that hydrogen ions are produced by the three equilibria 5—7. The empirical constants  $k_1$ ,  $k_2$ , and  $k_3$  are the mass action constants of the equilibria.

The equilibrium constant  $k_1$  is the acid strength of the hydrated cupric ion. At infinite dilution, it is  $1.07 \times 10^{-8}$ . According to J. BJERRUM<sup>(16)</sup>, the cupric ion in aqueous solution is a planar tetraquo ion which, through a more or less stable intermediate form, is in equilibrium with an octahedral hex-aquo ion.

From the equilibria 6 and 7 we derive

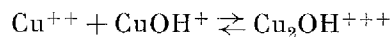


The mass action constant  $\frac{k_3}{k_2}$  of this equilibrium is the acid strength of the ion  $\text{Cu}_2\text{OH}^{+++}$ . At infinite dilution, it is  $8.5 \times 10^{-5}$ . In the ion  $\text{Cu}_2\text{OH}^{+++}$ , the two copper atoms are bound together by the oxygen atom of the hydroxyl group. To the copper atoms are furthermore bound a certain number of water molecules which, as usual, have not been written. It is impossible to say whether the ion  $\text{Cu}_2\text{OH}^{+++}$  splits off the hydrogen ion

from the hydroxyl group or from one of the water molecules. The question whether the ion  $\text{Cu}_2\text{O}^{++}$  contains a naked oxygen bridge, or a hydroxyl bridge and a hydroxyl group directly bound to one of the copper atoms, is therefore left open. The acid strength of the trivalent ion  $\text{Cu}_2\text{OH}^{+++}$  is about 8000 times that of the divalent ion  $\text{Cu}^{++}$ . A change in this direction might be expected on account of the electrostatic effect of the positive charges.

Owing to the fact that the maximum co-ordination number of oxygen is 3, the ion  $\text{Cu}_2\text{OH}^{+++}$  cannot take up another hydrogen ion. A dimeric cupric ion  $\text{Cu}_2^{++++}$  (omitting the water of hydration), therefore, does not exist.

From the equilibria 5 and 6 we derive



with the equilibrium constant

$$\frac{k_2}{k_1} = \frac{(\text{Cu}_2\text{OH}^{+++})}{(\text{Cu}^{++})(\text{CuOH}^+)}$$

which becomes equal to 14.2 at infinite dilution.

Table 4 contains the equilibrium constants  $k_1$ ,  $k_2$ , and  $k_3$  for cupric nitrate solutions, calculated from the formulae 16—18, at round values of the concentration  $a$  molar. The fifth

Table 4.

The equilibrium constants, hydrogen ion concentrations, and degrees of "hydrolysis"  $\alpha$  for pure aqueous solutions of cupric nitrate ( $a$  molar), calculated by means of the formulae 16—18.

$a$	$k_1 10^9$	$k_2 10^7$	$k_3 10^{12}$	$-\log(\text{H}^+)$	pH	$\alpha 10^3$
1.000	2.51	5.15	5.90	3.137	2.85	1.43
0.500	3.02	4.49	6.25	3.456	3.36	1.34
0.200	3.98	3.67	6.87	3.856	3.85	1.22
0.100	4.79	3.16	7.45	4.125	4.13	1.17
0.0500	5.62	2.74	8.09	4.362	4.36	1.18
0.0200	6.76	2.32	9.02	4.634	4.62	1.36
0.0100	7.59	2.10	9.73	4.823	4.79	1.64
0.00500	8.32	1.93	10.35	5.004	4.95	2.08
0.00200	9.12	1.78	11.1	5.234	5.17	2.98
0.00100	9.55	1.71	11.5	5.405	5.33	3.99
0	10.7	1.52	12.9			

column shows  $-\log(\text{H}^+)$  for a pure  $a$  molar cupric nitrate solution, calculated from the constants given in the table.

In their papers, most of the earlier investigators give the SØRENSEN pH of the cupric salt solution. Generally, the liquid-liquid potential is partly eliminated by means of a bridge solution, such as concentrated potassium chloride or ammonium nitrate, and the remaining liquid-liquid potential is neglected. The results of the present measurements may be expressed in the same way if, instead of formula 4, the following formula is used

$$\text{pH} = 2.022 + 17.32 E, \quad (19)$$

2.022 being the pH of the reference solution: 0.01000 m HCl + 0.0900 m NaCl. If  $E$  is eliminated from the equations 4 and 19, we obtain

$$\text{pH} = -\log(\text{H}^+) + 2.022 - A_0.$$

The pH values given in the sixth column of Table 4 have been calculated from  $-\log(\text{H}^+)$  by means of this formula. When these values are plotted against  $\log a$ , the curve of Fig. 1 is obtained.

The degrees of reaction ("hydrolysis") of the cupric ions according to each of the three equilibria 5—7 are

$$\alpha_1 = \frac{(\text{CuOH}^+)}{a} = \frac{k_1(\text{Cu}^{++})}{a(\text{H}^+)},$$

$$\alpha_2 = \frac{2(\text{Cu}_2\text{OH}^{+++})}{a} = \frac{2k_2(\text{Cu}^{++})^2}{a(\text{H}^+)},$$

and

$$\alpha_3 = \frac{2(\text{Cu}_2\text{O}^{++})}{a} = \frac{2k_3(\text{Cu}^{++})^2}{a(\text{H}^+)^2},$$

respectively. The total degree of reaction is  $\alpha = \alpha_1 + \alpha_2 + \alpha_3$ . The degrees of reaction have been calculated for pure cupric nitrate solutions by means of the equilibrium constants and the hydrogen ion concentrations given in Table 4.  $\alpha$  is to be found in the last column of Table 4. When  $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_3$ , and  $\alpha$  are plotted against  $\log a$ , the four curves of Fig. 4 are obtained. The figure shows how the relative importance of the three equilibria varies with the concentration of the cupric nitrate. Roughly speaking, the concentrations of the three ions are of

the same order of magnitude, when  $0.1 > a > 0.01$ . In more concentrated solutions, the ion  $\text{Cu}_2\text{OH}^{+++}$  gains more and more predominance, while the ion  $\text{Cu}_2\text{O}^{++}$  and, first and foremost, the ion  $\text{CuOH}^+$  gradually disappear. In solutions more dilute

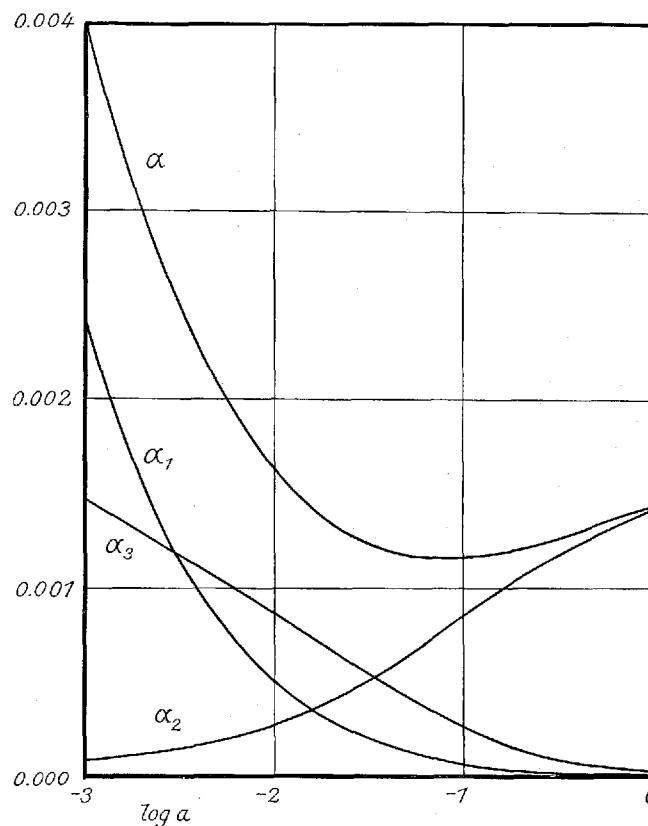


Fig. 4. The degrees of reaction ("hydrolysis") of the cupric ion in an  $a$  molar solution of cupric nitrate.

$$\alpha_1 = (\text{CuOH}^+)/a \quad \alpha_2 = 2(\text{Cu}_2\text{OH}^{+++})/a \quad \alpha_3 = 2(\text{Cu}_2\text{O}^{++})/a$$

$$\alpha = \alpha_1 + \alpha_2 + \alpha_3.$$

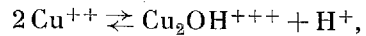
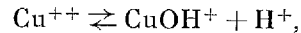
than 0.01 molar, the form  $\text{Cu}_2\text{OH}^{+++}$  gradually disappears. At sufficiently high dilution, only the monomeric ion  $\text{CuOH}^+$  will remain.

I wish to express my thanks to the head of the laboratory, Professor NIELS BJERRUM, for advice and kind interest in my work.

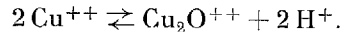
### Summary.

The hydrogen ion concentration of aqueous solutions of cupric nitrate was measured at 18.0° C. by means of the glass electrode. The range of concentrations examined extended from 0.001 to 1 molar cupric nitrate. The examination included both aqueous solutions and solutions to which small concentrations of nitric acid or sodium hydroxide had been added.

The measurements show that the following equilibria take place



and



The mass action constants of the equilibria have been computed.

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