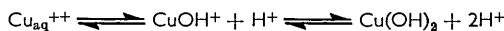


### 641. The Hydrolysis of Copper(II) Ion.

By D. D. PERRIN.

Copper(II) ion is hydrolysed to form polynuclear complexes of the type,  $\text{Cu}_n(\text{OH})_{2n-2}^{++}$ . The acid dissociation constant,  $*\beta_{22}$ , corresponding to the formation of  $\text{Cu}_2(\text{OH})_2^{++}$ , has been obtained as a function of temperature and of ionic strength, and  $*\beta_{34}$  has been calculated for 20°. The assumption that, for all complexes bigger than  $\text{Cu}_2(\text{OH})_2^{++}$ , the formation constant,  $k$ , is the same for the successive addition of each  $\text{Cu}(\text{OH})_2$  "link" provides a quantitative and consistent interpretation of the pH values obtained when dilute solutions of copper(II) ion are titrated with alkali. Mononuclear complexes such as  $\text{CuOH}^+$  are not present in appreciable amounts in these solutions.

A NUMBER of investigators have attempted, by measuring the pH of solutions of pure copper(II) salts, to study the hydrolytic equilibria of copper(II) ion. (Results are tabulated in ref. 1. Except that concentrations in this paper are calculated from hydrogen-ion activities instead of concentrations, symbols are as given in this reference.) In most cases it has been assumed that the principal reactions are:



but this has led to values of the acid dissociation constant,  $*K_1$ , which range, at room temperature, from  $10^{-6.5}$  to  $10^{-7.9}$ . On the other hand, more extensive studies have shown conclusively that polynuclear complex formation is important.<sup>2,3</sup> In particular, the assumption that only the species,  $\text{Cu}_2(\text{OH})_2^{++}$ , is formed, with  $\log *\beta_{22} = -10.95 \pm 0.10$ , reproduces quantitatively most of Pedersen's data<sup>2</sup> at 18° for the partial hydrolysis of copper(II) nitrate solutions ranging from 0.005M to 0.999M.<sup>3</sup> The deviations at lower concentrations (0.001M and 0.002M) were explained by assuming the formation of  $\text{CuOH}^+$ , with  $\log *K_1 = -8$ . Similarly, for 0.010–0.10M-copper perchlorate in 3M-sodium perchlorate, at 18°, Berecki-Biedermann<sup>3</sup> found  $\log *\beta_{22} = -10.6 \pm 0.1$ .

In the present work a potentiometric method has been used to study the partial hydrolysis of dilute solutions of copper(II) perchlorate over a temperature range and also, at 20°, under conditions where hydrolysis was much more extensive.

#### EXPERIMENTAL

A stock copper perchlorate solution (0.0483M; pH 4.0) was prepared by passing barium perchlorate solution into a well-washed column of the cupric salt of a cation-exchange resin (Amberlite IR-120). The copper concentration of the eluate, which was very weakly acid and gave no test for barium ion, was determined by cation exchange (IR-120,  $\text{H}^+$ ), the liberated acid being titrated with standard alkali. The reaction vessel for the hydrolysis experiments consisted of a 200 ml., tall form, lipless, Pyrex beaker closed by a loosely-fitting Perspex stopper through which passed the electrodes, a thermometer, a bubbler, and fine-bore Polythene tubing connected to a micrometer syringe. The rim of the stopper was coated on the underside with a layer of polyurethane "foam." Standard 0.100M-potassium hydroxide, carbonate-free, was added by micrometer syringe. Solutions were stirred by passing scrubbed nitrogen at a constant flow rate as indicated by a manostat. All pH measurements were made by using a Vibron Electrometer Model 33B (Electronic Instruments Ltd.) which was fitted with an internally shielded glass electrode and a saturated calomel electrode and which could be read directly to 0.001 pH unit. The output of the pH meter was also applied directly to a Rectiriter recording milliammeter (Texas Instruments Inc.) to facilitate assessment of pH constancy

<sup>1</sup> Bjerrum, Schwarzenbach, and Sillén, "Stability Constants. Part II. Inorganic Ligands," The Chemical Society, London, Spec. Publ. No. 7, 1958.

<sup>2</sup> Pedersen, *Kgl. Danske Videnskab. Selsk.*, 1943, 20, 7.

<sup>3</sup> Berecki-Biedermann, *Arkiv Kemi*, 1956, 9, 175.

and of attainment of equilibria. The pH of freshly-prepared 0.05M-potassium hydrogen phthalate was taken as  $\text{pH}_t = 4.000 + \frac{1}{2}[(t - 15)/100]^2$ , where  $t$  is in °C; and, as secondary standard, 0.05M-sodium borate  $\text{pH}_t = 9.270 - 0.0085(t - 15)$ . Temperatures were maintained constant to  $\pm 0.05^\circ$ .

The experimental procedure was as follows: 100 ml. of a copper perchlorate solution of known concentration, ranging from 0.000242M to 0.00483M and containing a known (low) concentration of perchloric acid and various amounts of potassium nitrate to alter the ionic strength, were titrated against potassium hydroxide solution, adequate time being allowed after each addition to ensure that equilibrium was attained. Hydrolysis constants were calculated from the initial concentration of cupric ion, the concentration of potassium hydroxide added, and the hydrogen-ion activity as measured by the glass electrode. At the start of each experiment it was necessary to determine accurately the concentration of free acid present in the solution. This was given directly by the initial hydrogen-ion concentration which was high enough to ensure that at this point hydrolysis of cupric ion was negligible. At very low ionic strengths,  $[\text{H}^+]$  was calculated directly from  $a_{\text{H}^+}$  as given by pH, by assuming  $-\log f = \frac{1}{2}I^{\frac{1}{2}}$ . At higher ionic strengths this estimate was used in plotting  $[\text{H}^+] + [\text{KOH}]$  against  $[\text{KOH}]$ , and the accurate value was taken as the intercept of the two linear portions of the plot.

The assumption that hydrolysis proceeded through the formation only of mononuclear copper-hydroxyl complexes failed to give consistent hydrolysis constants. However, good agreement was found at low values of  $Z$  (the average number of hydroxyl groups bound per copper atom) =  $([\text{H}^+] + [\text{KOH}] - [\text{HClO}_4])/[\text{Cu}^{++}]_{\text{T}}$  by assuming the only complex present to be  $\text{Cu}_2(\text{OH})_2^{++}$ , so that  $*\beta_{22}$  was given by

$$*\beta_{22} = \frac{[\text{Cu}_2(\text{OH})_2^{++}](a_{\text{H}^+})^2}{[\text{Cu}^{++}]^2} = \frac{([\text{H}^+] + [\text{KOH}] - \text{HClO}_4)(a_{\text{H}^+})^2}{2([\text{Cu}^{++}]_{\text{T}} + [\text{HClO}_4] - [\text{H}^+] - [\text{KOH}])^2} \quad (1)$$

Data from a typical experiment are presented in Table 1.

TABLE 1. Evaluation of  $*\beta_{22}$  from potentiometric titration.

$[\text{Cu}(\text{ClO}_4)_2] = 0.000966\text{M}$ .  $[\text{HClO}_4] = 0.000033\text{M}$ . Temp.  $15^\circ$ . Titrated with 0.100M-KOH.  $[\text{Cu}_2(\text{OH})_2^{++}]$  assumed =  $\frac{1}{2}([\text{H}^+] + [\text{KOH}] - [\text{HClO}_4])$ .

$[\text{KOH}]$ ( $\mu\text{M}$ )	pH	$[\text{H}^+] + [\text{KOH}] - [\text{HClO}_4]$ ( $\mu\text{M}$ )	$[\text{Cu}^{++}]$ ( $\mu\text{M}$ )	$Z$	$-\log *\beta_{22}$
0	4.515				
20	4.890				
40	5.696				
60	6.010	28.0	938	0.03	(10.82)
80	6.163	47.7	918	0.05	(10.87)
100	6.276	67.5	898	0.07	10.93
120	6.348	87.4	879	0.09	10.93
140	6.402	107	859	0.11	10.93
160	6.447	127	839	0.13	10.93
180	6.508	147	819	0.15	10.97
200	6.543	167	799	0.17	10.96
220	6.571	187	779	0.19	10.95
240	6.599	207	759	0.22	10.94
260	6.626	227	739	0.24	10.93
Average					10.94

It has been suggested<sup>2,3</sup> that at low concentrations of copper appreciable amounts of both  $\text{CuOH}^+$  and  $\text{Cu}_2(\text{OH})_2^{++}$  are formed. The plot of  $([\text{H}^+] + [\text{KOH}] - [\text{HClO}_4])(a_{\text{H}^+})/[\text{Cu}^{++}]$  against  $[\text{Cu}^{++}]/(a_{\text{H}^+})$ , where  $(\text{Cu}^{++}) = [\text{Cu}^{++}]_{\text{T}} - ([\text{H}^+] + [\text{KOH}] - [\text{HClO}_4])$ , should then (see Appendix) give a straight line of slope  $2*\beta_{22}$  and an intercept equal to  $*K_1$ . The estimate of  $*K_1$  obtained in this way is very sensitive to experimental error because, at the low values of  $[\text{Cu}^{++}]_{\text{T}}$  and  $Z$  that must be used, the system is very poorly buffered. Pedersen's measurements in the range,  $[\text{Cu}^{++}]_{\text{T}} = 0.001 - 0.005\text{M}$ , lead to  $*K_1 = 1 \times 10^{-8}$  but this estimate may be in error, because the initial solutions were not sufficiently acid to ensure that hydrolysis of  $\text{Cu}^{++}$  was negligible or to enable, either directly or by extrapolation, corrections to be applied for any adventitious traces of acidic or basic materials. The importance of the latter is readily seen from the fact that, for  $[\text{Cu}^{++}]_{\text{T}} = 0.001\text{M}$ , an error of  $4 \mu\text{M}$  in the hydrogen-ion concentrations used by Pedersen would alter the value obtained for  $*K_1$  from  $1 \times 10^{-8}$  to 0. Results obtained in the present work, with  $[\text{Cu}^{++}]_{\text{T}} = 0.000242\text{M}$  and  $0.000966\text{M}$  are presented in

Fig. 1. They suggest that  $*K_1$  is much less than  $10^{-8}$  but the measurements are not sufficiently accurate for a new value to be assigned. It is also concluded that for copper concentrations down to at least 0.00025M,  $\text{CuOH}^+$  is not a major product of the hydrolysis of cupric ion.

TABLE 2. *Effect of ionic strength on  $*\beta_{22}$  at 20°.*

$\text{Cu}(\text{ClO}_4)_2$  solutions, containing low concentrations of  $\text{HClO}_4$  and varied concentrations of  $\text{KNO}_3$ , titrated with 0.100M-KOH.

pH Range	$[\text{Cu}^{++}]_T$ (M)	$I$	$Z$	$-\log * \beta_{22} \pm$ Range (no. of obsns.)
6.226—6.506	0.000242	0.0007	0.041—0.124	$10.53 \pm 0.05$ (3)
5.840—6.196	0.000966	0.0031	0.023—0.081	$10.63 \pm 0.05$ (5)
5.420—5.742	0.00483	0.0147	0.012—0.046	$10.75 \pm 0.03$ (9)
6.064—6.486	0.000966	0.0330	0.042—0.187	$10.80 \pm 0.05$ (8)
5.348—5.745	0.00483	0.0346	0.007—0.037	$10.86 \pm 0.04$ (8)
5.418—5.796	0.00483	0.0946	0.007—0.037	$10.94 \pm 0.04$ (8)
5.417—5.803	0.00483	0.1746	0.008—0.037	$10.97 \pm 0.04$ (8)
6.218—6.521	0.000966	0.2029	0.041—0.145	$11.04 \pm 0.02$ (6)
5.469—5.798	0.00483	0.3146	0.009—0.037	$10.96 \pm 0.02$ (8)
5.376—5.797	0.00483	0.615	0.006—0.044	$10.90 \pm 0.02$ (10)
5.490—5.741	0.00483	1.015	0.016—0.041	$10.79 \pm 0.04$ (7)
5.188—5.764	0.00483	1.515	0.003—0.053	$10.75 \pm 0.02$ (13)

*Effect of Ionic Strength and Temperature on  $*\beta_{22}$ .*—The values of  $*\beta_{22}$  listed in Table 2 were calculated by using eqn. (1). They are in substantial agreement with the values obtained by Pedersen<sup>2</sup> and Berecki-Biedermann<sup>3</sup> and indicate that moderate-to-high ionic strengths produce little change in  $\log * \beta_{22}$  (the variation is less than 0.3 logarithm unit as  $I$  varies from 0.015 to 1.51). The estimates of  $\log * \beta_{22}$  obtained from the results for  $[\text{Cu}^{++}]_T = 0.00097\text{M}$

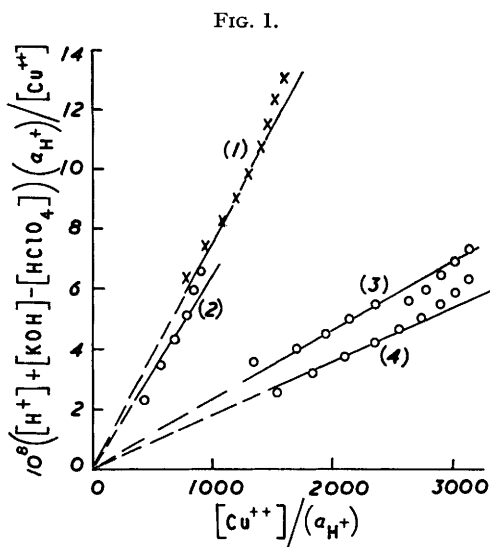


FIG. 1. *Attempted evaluation of  $*K_1$  as intercept.*  
 (1)  $[\text{Cu}(\text{ClO}_4)_2] = 0.000966\text{M}$ ;  $I = 0.00294$ ;  $Z = 0.050 - 0.216$ ; 25°.  
 (2)  $[\text{Cu}(\text{ClO}_4)_2] = 0.000242\text{M}$ ;  $I = 0.0007$ ;  $Z = 0.040 - 0.245$ ; 20°.  
 (3)  $[\text{Cu}(\text{ClO}_4)_2] = 0.000966\text{M}$ ;  $I = 0.00294$ ;  $Z = 0.049 - 0.236$ ; 15°.  
 (4)  $[\text{Cu}(\text{ClO}_4)_2] = 0.000966\text{M}$ ;  $I = 0.203$ ;  $Z = 0.040 - 0.207$ ; 20°.

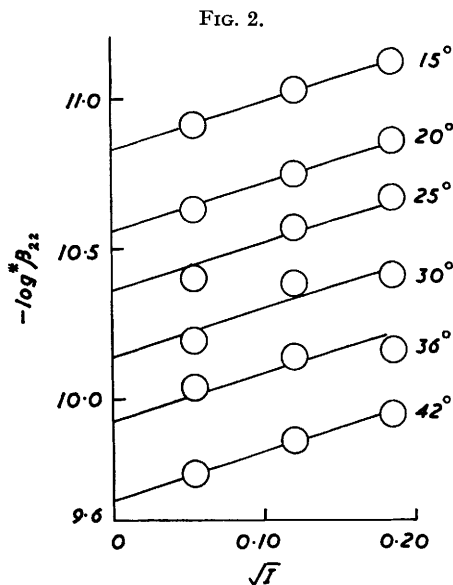


FIG. 2. *Dependence of  $-\log * \beta_{22}$  at low ionic strengths, on temperature.*  
 In all cases  $[\text{Cu}(\text{ClO}_4)_2] = 0.000966\text{M}$  for the lowest point and  $= 0.00483\text{M}$  for the other two.  
 Circles represent uncertainty of  $\pm 0.05$  in  $-\log * \beta_{22}$ .

at  $I \approx 0.03$  and  $I \approx 0.2$  agree, within experimental error, with the corresponding estimates from the results where  $[\text{Cu}^{++}]_T = 0.00483\text{M}$ , and support the conclusion that the formation of mononuclear complexes is not important at these concentrations.

At low ionic strengths, the Debye-Huckel theory predicts that  $-\log * \beta_{22}$  increases directly with  $I^{\frac{1}{2}}$  and, if  $\text{Cu}_2(\text{OH})_2^{++}$  can be considered as a simple bivalent ion, the slope of the line should be close to 2. By assuming that the observed slope (which is about 1.6) remains constant over the temperature range studied, 15–42°, it has been possible to make short extrapolations from the data in Fig. 2 to obtain the values of  $-\log * \beta_{22}$  at zero ionic strength for this temperature range. The equation

$$-\log * \beta_{22} = 3833/T - 2.497 \quad . . . . . (2)$$

where  $T$  is in °K, reproduces these values to within 0.03 logarithm unit.

*More Extensive Hydrolysis of  $\text{Cu}^{++}$ .*—Eqn. (1) is true only at low values of  $Z$ . At higher values of  $Z$ ,  $\log * \beta_{22}$  increases continuously (becomes less negative), indicating that more extensive polynuclear complex formation is occurring. From the preference of cupric ion for a co-ordination number of 4, and the (approximate) 1 : 2 ratio of  $\text{Cu} : \text{OH}$  in copper hydroxide, it seems reasonable to postulate that  $\text{Cu}_2(\text{OH})_2^{++}$  and subsequent complexes are built up by the co-ordination of neighbouring copper atoms through pairs of hydroxyl groups. Such a series of linear, hydroxylated complexes can, on a "core-and-links" hypothesis,<sup>4</sup> result from the stepwise addition of "links" of  $\text{Cu}(\text{OH})_2$  to the "core,"  $\text{Cu}^{++}$ , to give complexes of the general formula,  $\text{Cu}_n(\text{OH})_{2n-2}^{++}$ , where  $n$  is any positive integer.

At suitable values of  $Z$ , the main copper species present in solution would be  $\text{Cu}^{++}$ ,  $\text{Cu}_2(\text{OH})_2^{++}$ , and  $\text{Cu}_3(\text{OH})_4^{++}$  (corresponding to the cases where  $n = 1, 2, 3$ , respectively). Under these conditions, and because  $* \beta_{22}$  is already known, it is possible to evaluate  $* \beta_{34} = [\text{Cu}_3(\text{OH})_4^{++}](a_{\text{H}^+})^4/[\text{Cu}^{++}]^3$  from the experimental results (see Appendix). However, neglect of higher complex formation and restriction to low concentrations of  $\text{Cu}_3(\text{OH})_4^{++}$  limit the accuracy of such estimates. Better estimates of  $* \beta_{34}$  are obtained if correction is made for the amounts of higher complexes also present, by using the theoretical relation given in the Appendix. Within the rather large experimental uncertainty, consistent values of  $* \beta_{34}$  have been obtained from the data given in Table 3. As with  $* \beta_{22}$ ,  $* \beta_{34}$  becomes greater with decreasing ionic strength when  $I$  is small. The greater dependence on  $I^{\frac{1}{2}}$  is also to be expected. A short extrapolation gives  $-\log * \beta_{34} \simeq 21.1$  at  $I = 0$ .

TABLE 3. Evaluation of  $* \beta_{34}$  at 20°.

	[H <sup>+</sup> ] + [KOH] - [HClO <sub>4</sub> ]		$Z$	[Cu <sup>++</sup> ] ( $\mu\text{M}$ )	2[Cu <sub>2</sub> (OH) <sub>2</sub> <sup>++</sup> ] ( $\mu\text{M}$ )	3[Cu <sub>3</sub> (OH) <sub>4</sub> <sup>++</sup> ] ( $\mu\text{M}$ )	-log * $\beta_{34}$	
	( $\mu\text{M}$ )	pH					(approx.)	(corr.)
(1)	39.3	6.580	0.163	203.2	35.2	3.1	21.22	21.27
	49.2	6.635	0.204	194.3	41.5	5.7	21.13	21.19
	59.2	6.694	0.245	184.9	49.3	7.3	21.19	21.26
	69.2	6.730	0.287	176.3	52.9	12.3	21.04	21.13
	79.2	6.774	0.328	167.8	58.5	15.2	21.06	21.17
	99.2	6.818	0.410	152.3	59.2	30.0	20.82	20.97
							Average	21.08
(2)	273.3	6.584	0.283	703.1	230.8	32.1	21.85	21.91
	292.3	6.603	0.304	685.8	239.5	40.7	21.79	21.86
	313.2	6.620	0.324	669.4	246.8	49.8	21.74	21.83
	333.2	6.636	0.345	653.0	252.8	60.2	21.69	21.79
	353.2	6.651	0.365	636.5	257.4	72.1	21.63	21.75
	373.2	6.665	0.386	620.5	261.0	84.5	21.59	21.72
							Average	21.72
(3)	220.2	6.633	0.228	753.0	190.8	22.2	22.29	22.33
	240.2	6.652	0.248	735.5	198.7	31.8	22.18	22.24
	260.2	6.670	0.269	719.1	206.4	40.5	22.12	22.20
	280.2	6.686	0.290	702.5	211.9	51.6	22.05	22.15
	300.2	6.698	0.311	686.8	214.1	65.1	21.97	22.09
	320.2	6.710	0.331	671.6	216.4	78.0	21.91	22.05
							Average	22.09

<sup>4</sup> Sillén, *Acta Chem. Scand.*, 1954, 8, 299.

At still higher values of  $Z$ , a large number of complexes, each with a different formation constant, would be expected to be present simultaneously. If the system is to be mathematically tractable, some simplifying assumption must be made. In the present instance it has been assumed that the formation constant,  $k$ , for the addition of a further  $\text{Cu}(\text{OH})_2$  link to any complex is the same for all complexes. This approximation might be expected to be better for the larger complexes. The relevant equations are (see Appendix):

$$\frac{[\text{Cu}^{++}]_T}{(a_{\text{H}^+})^2} = \frac{x}{k} + \frac{* \beta_{22}}{k^2} \cdot \frac{x^2(2-x)}{(1-x)^2} \quad \dots \quad (3)$$

$$\frac{[\text{H}^+] + [\text{KOH}] - [\text{HClO}_4]}{(a_{\text{H}^+})^2} = \frac{2 * \beta_{22}}{k^2} \cdot \frac{x^2}{(1-x)^2} \quad \dots \quad (4)$$

where  $x = k[\text{Cu}^{++}]/(a_{\text{H}^+})^2$ . Elimination of  $x$  between eqns. (3) and (4) enables  $k$  to be obtained from suitable experimental data. In this way, the arbitrarily selected results for  $Z = 0.741$  in Table 4 give  $k = 10^{-10.20}$ . Knowing  $k$ , it is then possible to calculate  $x$  and hence  $[\text{Cu}^{++}]$  for all points in a titration by using either eqn. (3) or eqn. (4). At low values of  $Z$  (0.082—0.410) the estimates of  $[\text{Cu}^{++}]$  in cols. 4 and 5 of Table 4 are not in good agreement. This is because

TABLE 4. *Test of equations (3) and (4).*

$[\text{Cu}(\text{ClO}_4)_2] = 0.0002415\text{M}$ . Titrated with 0.1M-KOH. Initial  $I = 0.0007$ , final  $I = 0.0005$   
 $-\log * \beta_{22} = 10.53$ .  $-\log k$ , at  $Z = 0.741$ , is 10.20.

[KOH] ( $\mu\text{M}$ )	$Z$	pH	$[\text{Cu}^{++}]$ * ( $\mu\text{M}$ )	$[\text{Cu}^{++}]$ † ( $\mu\text{M}$ )	[KOH] ( $\mu\text{M}$ )	$Z$	pH	$[\text{Cu}^{++}]$ * ( $\mu\text{M}$ )	$[\text{Cu}^{++}]$ † ( $\mu\text{M}$ )
0	0	6.009			240	0.990	6.994	88.0	90.6
10	0.041	6.226	231.8	229.9	260	1.073	7.020	81.3	83.9
20	0.082	6.406	220.3	206.2	280	1.155	7.048	74.3	76.9
30	0.122	6.506	208.4	192.3	300	1.237	7.074	68.3	70.7
40	0.163	6.580	196.8	179.5	320	1.320	7.105	61.5	63.7
50	0.204	6.635	186.0	169.4	340	1.403	7.136	55.2	57.1
60	0.245	6.694	172.5	154.4	360	1.486	7.173	48.4	49.9
70	0.287	6.730	163.3	147.5	380	1.569	7.216	41.2	42.5
80	0.328	6.774	151.2	135.9	400	1.652	7.264	34.4	35.3
100	0.410	6.818	138.6	128.2	420	1.735	7.326	27.0	27.6
120	0.494	6.849	129.5	123.1	440	1.818	7.408	19.4	19.7
140	0.576	6.875	121.7	118.7	460	1.901	7.500	13.3	13.4
160	0.658	6.904	113.2	111.9	480	1.984	7.683	6.08	6.12
180	0.741	6.928	(106.4)	(106.4)	500 ‡	2.066	8.084	1.03	1.03
200	0.824	6.950	100.0	101.4					
220	0.908	6.972	93.9	96.0					

\* Calc. from eqn. (3). † Calc. from eqn. (4). ‡ A faint precipitate was observed at this point.

$\log * \beta_{34}$  ( $= -21.17$  from Table 3) is appreciably less than the assumed value of  $\log * \beta_{22} + \log k = -20.73$ . However, over the range,  $Z = 0.494$ — $2.066$ , the experimental data given in Table 4 yield values of  $[\text{Cu}^{++}]$  which agree, in pairs, within 5%. As the two equations provide independent estimates of  $[\text{Cu}^{++}]$  the agreement supports the postulated "core-and-links" mechanism. The low solubility of copper hydroxide prevents the testing of these equations at significantly higher copper concentrations.

## DISCUSSION

Pedersen's data on the hydrolysis of dilute (0.001—0.010M) copper nitrate solutions<sup>2</sup> have been re-examined on the assumption that the only complex present was  $\text{Cu}_2(\text{OH})_2^{++}$ . Values of  $* \beta_{22}$  obtained in this way are listed in Table 5. They agree well with results obtained in the present study and support the conclusion that, at these concentrations and  $Z$  values, the species  $\text{CuOH}^+$  is not present in appreciable amounts. The constant,  $*K_1$ , must be much smaller than previously published estimates have suggested. The stability of  $\text{Cu}_2(\text{OH})_2^{++}$  relative to  $\text{CuOH}^+$  may be due to the chelate effect<sup>5</sup> arising from ring formation. The suggestion that  $\text{Cu}_2(\text{OH})_2^{++}$  is as shown in (I) is consistent with

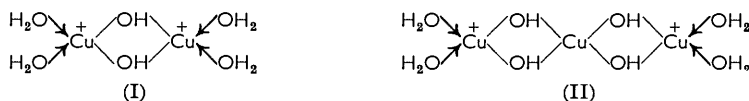
<sup>5</sup> Schwarzenbach, *Helv. Chim. Acta*, 1952, **35**, 2344.

TABLE 5. Recalculation of Pedersen's data for dilute solutions, on the assumption that only  $\text{Cu}_2(\text{OH})_2^{++}$  is formed.

$10^5[\text{Cu}(\text{NO}_3)_2]$ (M)	$10^5[\text{Ba}(\text{NO}_3)_2]$ (M)	$I^{\ddagger}$	$Z$	$-\log * \beta_{22} \pm \text{Range}$		
				(a)	(b)	(c)
100.7	0	0.055	0.024—0.232	$10.82 \pm 0.03$	$10.67 \pm 0.03$	10.76
200.5	0	0.078	0.028—0.234	$10.88 \pm 0.02$	$10.75 \pm 0.02$	10.80
500.7	0	0.122	0.015—0.187	$10.94 \pm 0.03$	$10.84 \pm 0.03$	10.87
100.1	891	0.172	0.030—0.234	$10.91 \pm 0.04$	$10.84 \pm 0.04$	10.94
198.0	793	0.172	0.016—0.177	$10.93 \pm 0.02$	$10.86 \pm 0.02$	10.94
498.5	493	0.172	0.009—0.032	$10.93 \pm 0.02$	$10.86 \pm 0.02$	10.94
991	0	0.172	0.002—0.023	$10.92 \pm 0.03$	$10.85 \pm 0.03$	10.94

(a)  $[\text{H}^+]$  being instead of  $a_{\text{H}^+}$ . (b) From Pedersen's estimated pH values. (c) From eqn. (2) and Fig. 2 of present paper which give, at  $18^\circ$ ,  $-\log * \beta_{22} = 10.674 + 1.58I^{\ddagger}$ .

Werner's interpretation of the structures of basic copper salts.<sup>6</sup> Similarly,  $\text{Cu}_3(\text{OH})_4^{++}$  would have the structure (II).



The structures of higher complexes would depend on whether, in this series, copper is always 4-co-ordinate or whether it may also be 6-co-ordinate. Thus Werner considered  $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ , *i.e.*,  $\text{Cu}_4(\text{OH})_6\text{Cl}_2$ , to consist of a copper ion at the centre of an octahedron, co-ordinated, through the corresponding pairs of OH groups, to three  $\text{Cu}(\text{OH})_2$  molecules which lie along three edges of the octahedron.<sup>6</sup> On the other hand, X-ray and other evidence shows that in copper complexes there are usually four groups in a plane close to the copper ion with two groups perpendicular to this plane and lying further away.<sup>7</sup> This is a consequence of the Jahn-Teller effect<sup>8</sup> which operates because  $\text{Cu}^{++}$  has only nine  $3d$ -electrons and which greatly reduces the ability of  $\text{Cu}^{++}$  to form stable 6-co-ordinate complexes. This would suggest that the hydroxyl complexes are more likely to consist of two-dimensional chains rather than three-dimensional aggregates. All copper ions except the terminal ones would be co-ordinated to four hydroxyl groups and, more weakly, to two water molecules perpendicular to the plane of the hydroxyl groups. In either case the complexes formed would belong to a series,  $\text{Cu}_n(\text{OH})_{2n-2}^{++}$ .

TABLE 6. Thermodynamic data for copper-hydroxyl complexes in solution.

	$2\text{Cu}_{\text{aq}}^{++} \rightleftharpoons \text{Cu}_2(\text{OH})_2^{++} + 2\text{H}_{\text{aq}}^+$
$\Delta G^\circ$ (kcal.) .....	14.2 (15°), 14.1 (25°), 14.0 (36°), 13.9 (42°)
$\Delta H^\circ$ (kcal.) .....	17.5
$\Delta S^\circ$ (cal./degree) .....	11.4
	$\text{Cu}_{\text{aq}}^{++} + \text{Cu}_2(\text{OH})_2^{++} \rightleftharpoons \text{Cu}_3(\text{OH})_4^{++} + 2\text{H}_{\text{aq}}^+$
$\Delta G^\circ$ (kcal.) .....	14.0 (20°)
	$\text{Cu}_{\text{aq}}^{++} + \text{Cu}_n(\text{OH})_{2n-2}^{++} \rightleftharpoons \text{Cu}_{n+1}(\text{OH})_{2n}^{++} + 2\text{H}_{\text{aq}}^+ (n > 2)$
$\Delta G^\circ$ (kcal.) .....	$\approx 13.7$ (20°)

Estimates based on  $*\beta_{34}$  and  $k$  indicate that higher complexes than  $\text{Cu}_2(\text{OH})_2^{++}$  are not present in significant amounts under the experimental conditions summarised in Tables 1 and 2. Eqn. (2) can therefore be used to calculate the thermodynamic functions governing the formation of  $\text{Cu}_2(\text{OH})_2^{++}$  in solution. The values given in Table 6 have been obtained

<sup>6</sup> Werner, "Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie," Zurich, 1st edn., 1905; 2nd edn., 1908.

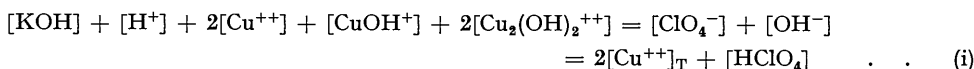
<sup>7</sup> Orgel, Proc. Tenth Solvay Conference, Brussels, 1956, 296.

<sup>8</sup> Jahn and Teller, Proc. Roy. Soc., 1937, A, 161, 220.

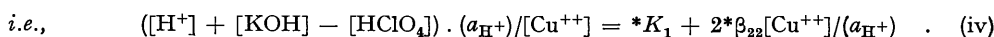
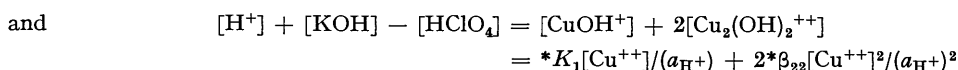
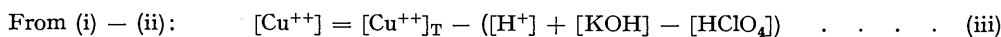
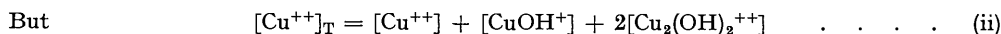
from eqn. (2) by using the identities,  $-\Delta G^\circ = 2.3026RT \log \beta_{22}^*$ ;  $d(-\Delta G^\circ)/dT = \Delta S^\circ$ ; and  $\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$ . The observed entropy is consistent with the effects of difference in the degree of hydration of the complex relative to its components. It has been suggested<sup>9</sup> that co-ordination of a water molecule to an ion requires an entropy change equal to the entropy of crystallization of water, namely,  $-5.3$  e.u. Although this is an oversimplification, particularly because it neglects differences in the extent of the region of disordered solvent molecules around the reacting species,<sup>10</sup> the value of  $\Delta S^\circ = +10.6$  which it predicts for the formation of  $\text{Cu}_2(\text{OH})_2^{++}$  is in good agreement with experiment. The same entropy change would also be predicted for each successive step in the building up of larger complexes.

## APPENDIX

To find  $\beta_{22}^*$  and  $\beta_{34}^*$  when both  $\text{CuOH}^+$  and  $\text{Cu}_2(\text{OH})_2^{++}$  are present. When potassium hydroxide is added to a copper perchlorate solution containing perchloric acid, we have, from electroneutrality:

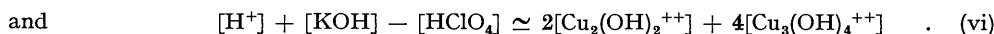
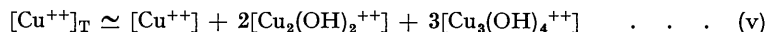


when  $[\text{OH}^-]$  is negligible.



Both constants can then be obtained by plotting the quantity on the left of eqn. (iv) (which is known from the experimental data) against  $[\text{Cu}^{++}]/(a_{\text{H}^+})$ .

*Evaluation of  $\beta_{34}^*$  when  $\beta_{22}^*$  is known.* If experimental conditions are chosen such that  $\text{Cu}^{++}$ ,  $\text{Cu}_2(\text{OH})_2^{++}$ , and  $\text{Cu}_3(\text{OH})_4^{++}$  are the main copper species present, we have:



Hence,



Making the substitution,  $[\text{Cu}_2(\text{OH})_2^{++}] = \beta_{22}^*[\text{Cu}^{++}]^2/(a_{\text{H}^+})^2$  in (vii) and solving the resulting quadratic equation, we have

$$\beta_{22}^*[\text{Cu}^{++}]/(a_{\text{H}^+})^2 \simeq \{1 + \beta_{22}^*(4[\text{Cu}^{++}]_T + 3[\text{HClO}_4] - 3[\text{H}^+] - 3[\text{KOH}])/2(a_{\text{H}^+})^2\}^{\frac{1}{2}} - 1$$

Once  $[\text{Cu}^{++}]$  is known,  $[\text{Cu}_2(\text{OH})_2^{++}]$  and hence, from eqn. (v),  $[\text{Cu}_3(\text{OH})_4^{++}]$  can be obtained. Finally, an approximate estimate of  $\beta_{34}^*$  can be calculated by inserting these values in the identity,

$$\beta_{34}^* = [\text{Cu}_3(\text{OH})_4^{++}](a_{\text{H}^+})^4/[\text{Cu}^{++}]^3$$

To refine this estimate, eqn. (vii) must be expanded to allow for the presence of higher complexes, the exact form of (vii) being

$$4[\text{Cu}^{++}]_T + 3[\text{HClO}_4] - 3[\text{H}^+] - 3[\text{KOH}] = \sum_{n=1}^{\infty} (6 - 2n)[\text{Cu}_n(\text{OH})_{2n-2}^{++}]$$

<sup>9</sup> Ulich, *Z. Elektrochem.*, 1930, **36**, 497.

<sup>10</sup> Frank and Evans, *J. Chem. Phys.*, 1945, **13**, 507.

The necessary correction is made by assuming that  $k$  is a constant, given by  $*\beta_{34}/*\beta_{22}$ , and using the relations developed in the next paragraph. From the initial estimates of  $[\text{Cu}^{++}]$  and  $*\beta_{34}$  a more accurate value of  $*\beta_{34}$  is found. The process is repeated until constancy is obtained. [Results for 0.000242M-copper perchlorate, at higher  $Z$  values, suggest that this estimate of  $k$  is too low. However, at higher copper concentrations, solubility limitations prevent the direct experimental determination of  $k$  by using eqns. (3) and (4).]

*Derivation of equations (3) and (4).* It is assumed that hydrolysis of cupric ion proceeds by stepwise polynuclear complex formation, commencing with the ion,  $\text{Cu}_2(\text{OH})_2^{++}$ , and adding "links" of  $\text{Cu}(\text{OH})_2$ . If the formation constant,  $k$ , for the addition of any link is independent of the size of the complex, we have, for  $n \geq 2$ :

$$[\text{Cu}_n(\text{OH})_{2n-2}^{++}] = *\beta_{22}k^{n-2}[\text{Cu}^{++}]^n/(\alpha_{\text{H}^+})^{2n-2}$$

But the total copper concentration,

$$[\text{Cu}^{++}]_{\text{T}} = \sum_{n=1}^{n=\infty} n[\text{Cu}_n(\text{OH})_{2n-2}^{++}]$$

Hence 
$$[\text{Cu}^{++}]_{\text{T}} = [\text{Cu}^{++}] + *\beta_{22} \sum_{n=2}^{n=\infty} \{nk^{n-2}[\text{Cu}^{++}]^n/(\alpha_{\text{H}^+})^{2n-2}\}$$

That is,

$$\frac{[\text{Cu}^{++}]_{\text{T}}}{(\alpha_{\text{H}^+})^2} = \frac{x}{k} + \frac{* \beta_{22}}{k^2} \sum_{n=2}^{n=\infty} nx^n$$

where  $x = k[\text{Cu}^{++}]/(\alpha_{\text{H}^+})^2$ . Summation of this binomial series gives

$$\frac{[\text{Cu}^{++}]_{\text{T}}}{(\alpha_{\text{H}^+})^2} = \frac{x}{k} + \frac{* \beta_{22}}{k^2} \cdot \frac{x^2(2-x)}{(1-x)^2}, \text{ which is eqn. (3).}$$

Similarly, if a solution of copper perchlorate, acidified with perchloric acid, is titrated with potassium hydroxide:

$$[\text{H}^+] + [\text{KOH}] - [\text{HClO}_4] = \sum_{n=2}^{n=\infty} (2n-2)[\text{Cu}_n(\text{OH})_{2n-2}^{++}]$$

Hence,

$$\begin{aligned} \frac{[\text{H}^+] + [\text{KOH}] - [\text{HClO}_4]}{(\alpha_{\text{H}^+})^2} &= \frac{2*\beta_{22}}{k^2} \sum_{n=2}^{n=\infty} (n-1)x^n \\ &= \frac{2*\beta_{22}}{k^2} \cdot \frac{x^2}{(1-x)^2}, \text{ which is eqn. (4).} \end{aligned}$$

DEPARTMENT OF MEDICAL CHEMISTRY,  
THE AUSTRALIAN NATIONAL UNIVERSITY,  
CANBERRA, AUSTRALIA.

[Received, January 29th, 1960.]