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# CCCLXXXVI.—An Electrometric and a Phase Rule Study of some Basic Salts of Copper.

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THIS paper deals with experiments made to ascertain which of the many basic sulphates and chlorides of copper are definite compounds. Basic sulphates have been reported ranging in composition from 2CuO,SO<sub>3</sub> to 15CuO,SO<sub>3</sub>, with varying water contents. Pickering (J., 1910, **97**, 1851) regarded the latter as a complex salt of orthosulphuric acid and bivalent and what he supposed to be quadrivalent copper atoms, and Noyes (J. Amer. Chem. Soc., 1916, **38**, 1947) suggested that 3CuO,SO<sub>3</sub>,2H<sub>2</sub>O might be the dihydrated cupric salt of the same acid. The basic chlorides which have been described contain from 1 to 4.5 atoms of copper for each atom of chlorine. Naturally occurring basic sulphates and chlorides are langite, 4CuO,SO<sub>3</sub>,4H<sub>2</sub>O; brochantite, containing from 3 to 4 mols. of CuO for 1 mol. of SO<sub>3</sub>, together with varying amounts of water, and atacamite, 4CuO,2HCl,3H<sub>2</sub>O—the number of molecules of water varying from 2 to 5.

Bell and Taber (J. Physical Chem., 1908, 12, 171) and Young and Stearn (J. Amer. Chem. Soc., 1916, 38, 1947), who studied the basic sulphates of copper from the point of view of the phase rule, obtained very conflicting results and were unable to prove the existence of a definite basic sulphate; doubtless because they used substances which approached equilibrium very slowly.

It has long been known that an amorphous, blue precipitate, agreeing very closely in composition with  $4\text{CuO},\text{SO}_3,4\text{H}_2\text{O}$ , is produced by treating copper sulphate solution with an insufficiency of alkali (Kane, Ann. Chim. Phys., 1839, 72, 270; Smith, Phil. Mag., 1845, 23, 501; Field, *ibid.*, 1862, 24, 124). Williamson (J. Physical Chem., 1923, 27, 790) analysed the precipitates obtained by treating molar solutions of copper sulphate with different quantities of alkali. Pickering showed (Chem. News, 1883, 47, 181) that between 1.4 and 1.5 equivalents of potassium hydroxide completely precipitated the copper and that the amount precipitated at any stage of the reaction was directly proportional to the amount of alkali added. He also found a temporary alkalinity to phenolphthalein when 1.5 equivalents of alkali had been added. Similar observations were made by the author, using the oxygen electrode (this vol., p. 2152).

Apart from the little recorded by Kenrick and Lash Miller (*Trans. Roy. Soc., Canada*, 1901, 7, iii, 35), no systematic work has been done on basic cupric chloride. The precipitate formed

when N/5-copper chloride solution was treated at  $85^{\circ}$  with N/5-potassium hydroxide until all the copper had been precipitated had the formula CuCl<sub>2</sub>, 3CuO, 2H<sub>2</sub>O.

# EXPERIMENTAL.

In order to study the mode of precipitation of copper sulphate by sodium hydroxide, electrometric titrations with a copper electrode were carried out. A copper wire electrode, fused into a glass tube, was completely immersed in 100 c.c. of M/100-copper sulphate solution, which was connected through a saturated solution of potassium chloride to a normal calomel electrode. The



E.M.F.'s between the copper and the calomel electrodes were measured by means of a potentiometer and a capillary electrometer. The electrode was about 2 mm. in diameter and was covered with finely divided copper, deposited electrolytically from N/10copper sulphate solution. That electrodes so prepared worked satisfactorily in copper sulphate solution will be seen from the following measurements. At 20°, the E.M.F. of the cell Cu | 0.01M-CuSO<sub>4</sub> | saturated KCl | N-calomel was -0.006 volt. Therefore  $E_h$  Cu | 0.01M-CuSO<sub>4</sub> = +0.283 - 0.006 = 0.277 volt. 0.01M-Copper sulphate being taken as 54.7% dissociated ( $\Lambda_{\infty} = 114$ , and  $\Lambda_{0.01M} = 62.4$ ),  $0.277 = EP_{Cuh} + 0.029 \log 0.00547$ . Whence  $EP_{Cuh} = 0.343$ , which is in agreement with the recent value of Jellinek and Gordon (Z. physikal. Chem., 1924, **112**, 214).

Three typical titration curves are given in Fig. 1. The cupric-

ion concentration scale was calculated from the formula  $E_{obs.} = -0.060 - 0.029 \log$  [Cu<sup>\*\*</sup>]. The dotted line gives the theoretical change in copper-ion concentration calculated on the assumption that 4CuO,SO<sub>3</sub> alone is precipitated. Curves 1 and 2, plotted from results obtained with an electrode having a thin coating of copper (deposited during 5 minutes' electrolysis), and curve 3 (electrode heavily coated during 1 hour's electrolysis) show that the electrodes became untrustworthy as soon as a precipitate appeared. Deduced from the curves, the values for the concentrations during precipitation are much too small and those for the concentrations when precipitation was complete and the solutions had become alkaline are obviously too large. High E.M.F.'s were obtained immediately precipitation was complete, but these fell in the course of 5 minutes to more or less steady values. The effect of the heavy deposit (curve 3) was to render the electrode even more irregular, as may be seen from the second portion of the curve.

The curves show that sudden changes in copper-ion concentration occurred when 1.73 (curve 1), 1.5 (curve 2), and 1.63 equivalents (curve 3) of sodium hydroxide had been added. In titration 2, the alkali was added very slowly, and the mixture was stirred until any green, gelatinous precipitate which might have formed had become pale blue and apparently amorphous. In the other two titrations the alkali was added more rapidly and, although the reactants were thoroughly mixed, stirring was not maintained until the precipitate appeared to have become homogeneous. These experiments show once again that the nature of the precipitate obtained depends on the manner in which the alkali is added. Rapid addition necessitated the use of a larger quantity for complete precipitation and consequently the gelatinous precipitate obtained was more basic than the blue, amorphous \* precipitate produced on careful addition of the alkali. This is the reason why Harned (J. Amer. Chem. Soc., 1917, 39, 252) required in his similar titration of copper sulphate solution sixsevenths of the theoretical quantity of the alkali.

The Anomalous Behaviour of Copper Electrodes in Presence of Copper Hydroxide.—The foregoing observations become of importance in view of the recent measurements of Jellinek and Gordon (loc. cit.) of the solubility product of cupric hydroxide.

<sup>\*</sup> Here and elsewhere in this paper, the term "amorphous precipitate" is used to denote the non-gelatinous, apparently amorphous precipitates obtained when alkali hydroxide is added slowly to dilute solutions of cupric salts. They are sharply distinguished from the gelatinous precipitates produced by rapid mixing.

They precipitated their copper hydroxide from copper sulphate solution with an insufficiency of sodium hydroxide exactly the condition for obtaining basic copper sulphate! The washed precipitate was suspended in alkali solution, and the copper-ion concentration was measured by means of a copper electrode. Their values for  $[Cu^*][OH']^2$  at 20° varied from  $0.7 \times 10^{-13}$  to  $3.0 \times 10^{-13}$ , the mean being  $1.7 \times 10^{-13}$ , but they could not confirm this by measurements with copper oxide. It is interesting to compare these values with those obtained from the curves (Fig. 1), assuming for the moment that the observed E.M.F.'s gave a true measure of the copper-ion concentration and that the basic precipitates had been completely decomposed by the excess of alkali. The hydroxyl-ion concentration when 40 c.c. of 0.0932N-sodium hydroxide had been added, the ionisation of the alkali being assumed to be complete, was  $10^{-1.91}$ , and the cupric-ion concentration was  $10^{-9.55}$  (curve 1; E.M.F. = 0.217 volt),  $10^{-8.62}$  (curve 2; E.M.F. = 0.190 volt), and  $10^{-7.59}$  (curve 3; E.M.F. = 0.160 volt). Therefore  $[Cu^{*}][OH']^2$  is  $4 \times 10^{-14}$  (curve 1),  $3.6 \times 10^{-13}$  (curve 2), and  $3.9 \times 10^{-12}$  (curve 3). Although these values are meaningless, they are of the same order as those of Jellinek and Gordon. The precipitation of basic copper sulphate does not begin until  $p_{\rm H}$  5.6 has been attained, and from the method described by the author (loc. cit.), the presence of the sulphate in the precipitate being assumed not to affect greatly the precipitation  $p_{\rm H}$ , it follows that the solubility product of cupric hydroxide is probably of the order 10-20 \*

Jellinek and Gordon do not refer to the work of Immerwahr (Z. anorg. Chem., 1900, 24, 269) on the potentials of copper electrodes in baryta solutions containing colloidal copper hydroxide or ignited copper oxide. The E.M.F.'s were so irregular that she did not calculate the solubility product of cupric hydroxide. Calculation shows that the solubility product varies from  $3 \times 10^{-12}$  to  $8 \times 10^{-16}$  for the colloidal hydroxide and to  $8 \times 10^{-23}$  for the ignited oxide. Allmand (J., 1909, 95, 2151) traced the erratic behaviour of the copper electrode to the reaction Cu<sup>\*\*</sup> + Cu  $\implies$  2Cu<sup>\*</sup> taking place at the electrode, cuprous hydroxide being formed, and arrived by an indirect method at the value  $10^{-19}$  for the solubility product of cupric hydroxide, which is of the same order as that calculated from the precipitation  $p_{\rm H}$ , viz.,  $10^{-20}$ . Jellinek and Gordon, who stated that to their knowledge no value for the solubility

<sup>\*</sup> For the titration given in this vol., p. 2151, the limiting [Cu<sup>•</sup>] was equivalent to 0.6 c.c. of N/10-sodium hydroxide in 120 c.c. Therefore [Cu<sup>•</sup>] =  $0.3/120M/10 = 10^{-5.6}$ . [OH'] =  $10^{-14+5.6} = 10^{-8.4}$ . Whence [Cu<sup>•</sup>][OH']<sup>2</sup> =  $10^{-20}$ .

product of cupric hydroxide is recorded in the literature, had evidently not seen Allmand's paper.

This reducing action of the copper electrode accounts for its irreversible behaviour in the titrations, and the exceptionally low voltages obtained in No. 3 show that the reduction process was being considerably influenced by the nature of the layer deposited on the electrode.

<sup>•</sup>The System CuO-SO<sub>3</sub>-H<sub>2</sub>O at  $25^{\circ}$ .—The substances used in the investigation were selected for their capacity to enter rapidly into equilibrium, namely, the amorphous basic sulphate, free sulphuric acid, and copper sulphate solution. The stock basic sulphate was kept as reactive as possible by suspending it in water. For certain equilibria, wet hydrated copper oxide had to be used.

The amorphous basic sulphate was prepared by adding N/10sodium hydroxide (about 1.2 mols. for each mol. of copper sulphate) drop by drop and with continuous shaking to 10 litres of M/20copper sulphate, every care being taken to prevent the formation of any gelatinous precipitate. The precipitate was washed by decantation with 20 to 30 litres of water, pressed on a Büchner funnel, and immediately immersed in water (Found in air-dried samples : CuO, 67.2, 67.6; SO<sub>3</sub>, 17.1, 17.2. 4CuO,SO<sub>3</sub>,4H<sub>2</sub>O requires CuO, 67.7; SO<sub>3</sub>, 17.0%). On keeping the precipitate, which was quite insoluble in water, in different quantities of sulphuric acid over-night, in every case 1.33 mols. of copper sulphate passed into solution for each molecule of sulphuric acid employed, thereby showing that the ratio of copper to sulphate in the residual solid remained unaltered, viz., 4:1.

Quantities of the basic sulphate were placed in liquid phases (100 to 200 c.c.) composed of sulphuric acid and copper sulphate in various proportions, the quantities of acid being such that the rests should be small (about 2 g.). The mixtures were placed in a thermostat at 25° and shaken daily. Equilibrium was attained in less than a week, but 2 or 3 months were allowed to elapse before the final check analyses were made. The results shown in the most basic part of the isotherm necessitated the use of hydrated copper oxide. This was prepared by precipitation from a dilute copper sulphate solution at about 50° with a small excess of sodium hydroxide. It was somewhat dehydrated and brownish-black, but it had to be deposited at a moderately high temperature so that it should not be so gelatinous that it could not be washed free from alkali and sodium sulphate. This hydrated oxide was also used with sulphuric acid to confirm some determinations of the equilibria of mixtures prepared from the basic sulphate. The analyses of the various liquid phases and rests are in Table I.

Liquid phases.		Rests.				
				Mol. SO./		
% CuO.	% SO <sub>3</sub> .	% CuO.	% SO <sub>3</sub> .	mol. CuÖ.	Solid phas	es.
0	0	84.45	6.17	0.073	CuO (hydrated 4CuO.SO.,4E	) and I.O.
0	0	80.85	8.79	0.108		
Ó	Ó	77.56	11.77	0.121		••
0	0	73.75	13.82	0.186	,,	••
0	0	69.50	16.90	0.242	••	••
0	0	67.78	17.30	0.255	4CuO.SO.,4H,0	).
0.02	0.02	67.90	17.60			
0.09	0.09	26.36	6.77		.,	
0.12	0.12	9.24	$2 \cdot 43$			
0.58	0.58	7.89	2.46			
3.12	3.19	$31 \cdot 23$	9.85			
5.54	5.56	15.96	7.75			
7.17	7.18	$24 \cdot 10$	10.27	0.314		
9.28	9.33	Eutectic			4CuO,SO <sub>3</sub> ,4H <sub>2</sub> O CuSO <sub>4</sub> ,5H <sub>2</sub> O	) and

The first six sets of data show that the addition of sulphuric acid to the hydrated copper oxide failed to cause any solution until the solid phase had assimilated sufficient sulphuric acid to convert it into the basic sulphate containing 4CuO to  $1SO_3$ . Neither copper nor sulphate could be found in the colourless liquid phases. The analyses given are those of the air-dried solid phases. These changed in colour as their sulphate content increased, passing from the brownish-black of the hydrated oxide through increasingly brighter shades of brown to greenish-brown and finally to the greenish-blue colour of the 4:1 salt. The basic sulphate did not change in colour on boiling, but decomposed on addition of varying quantities of alkali, yielding more basic products having similar colours. The other liquid phases were copper sulphate.

The results given in Table I are plotted in Fig. 2; the section BC has been constructed from the data of Bell and Taber (*loc. cit.*). The solid phase which was in equilibrium with the liquid phases represented by AB was 4CuO,SO<sub>3</sub>,4H<sub>2</sub>O, for the tie-lines joining the points corresponding to each liquid phase and the point corresponding to its respective rest all pass through the point D, which indicates that the solid phase contained 67.7% CuO, 17.0% SO<sub>3</sub>, and 15.3% H<sub>2</sub>O (Schreinemakers). Had the solid phases in equilibrium with water as liquid phase been mixtures of two definite solid phases, it would have been expected that the points representing their compositions would lie on the straight line joining the two points corresponding to the compositions of the two solid phases. If in the present system the rests comprised mixtures of the basic salt 4CuO,SO<sub>3</sub>,4H<sub>2</sub>O and a definitely hydrated copper oxide, this line would have been one joining the point D to the point, corresponding to the particular hydrated oxide, on the HO-CuO axis. Actually the points lie on one of two straight lines, DE and DF, where E represents CuO,0.28H,O and F, CuO,0.05H,O. It appears from the phase rule that as the liquid phases which were in equilibrium with these highly basic rests were of fixed composition as far as could be ascertained, the rests were composed of two solid phases. Bearing in mind the gradual change in the colour of the rests, it seems probable that the two solid phases were the 4:1 sulphate and copper oxide, hydrated to varying extents. The degree of hydration of the copper oxide, although by no means fixed, was of the same order as that found in the ordinary precipitated black copper oxide, i.e., corresponding approximately to CuO,0.25H2O. There appeared, however, a tendency for the hydration to become considerably less as the proportion of the 4:1 salt became predominant, shown by those points which fall on DF.

It follows from this work that at  $25^{\circ}$  there is only one basic sulphate of copper, viz., 4CuO,  $\text{SO}_3$ ,  $4\text{H}_2\text{O}$ . Sabatier (Compt. rend., 1897, **125**, 101) prepared it from copper oxide and copper sulphate solutions (not exceeding 1*M*). He stated that the salt was converted by saturated copper sulphate solution into a green salt, 5CuO,  $2\text{SO}_3$ ,  $5\text{H}_2\text{O}$ , treatment of which with water regenerated the 4:1 salt. This green salt was probably the ordinary 4:1 salt with copper sulphate adhering. In support of this view is the fact that the rest belonging to the liquid phase which contained  $7\cdot17\%$  CuO (Table I) had, after filtration on a Büchner funnel, a composition corresponding approximately to the formula 3CuO,  $\text{SO}_3$ , although, as its tie-line shows, the actual solid phase was the 4:1salt.

Precipitation of Basic Cupric Chloride.—When N/10-sodium hydroxide or ammonia was added slowly with shaking to M/100cupric chloride solutions, pale blue, amorphous precipitates were obtained, and the mother-liquors became alkaline to phenolphthalein, precipitation being complete, after the addition of 1.5 equivalents of alkali. If the additions were made quickly, precipitates did not separate until about 1 equivalent of alkali had been added, but the solutions became more and more colloidal and alkalinity occurred after the addition of 1.53 equivalents. When, however, more concentrated solutions were rapidly mixed, dark blue, gelatinous precipitates were obtained which, if the amount of alkali added did not exceed 1.5 equivalents, could be transformed by vigorous shaking with the mother-liquor into paler blue, amorphous forms. Provided that not more than 1.5 equivalents of alkali had been added during their formation, the amorphous precipitates did not

blacken on boiling; if a precipitate happened to be gelatinous, it darkened temporarily, but became pale blue and amorphous on continued boiling.

The System CuO-HCl-H<sub>2</sub>O at 25°.—This system was investigated in exactly the same manner as the previous one. The substances used were moist hydrated copper oxide, moist basic cupric chloride, hydrochloric acid, and cupric chloride solution. On being washed by decantation, much of the basic chloride passed into pale blue, colloidal solution, and did not settle out after standing for a week. The colloidal solution was siphoned off and replaced by water, and the process was repeated, during a month, until the remaining precipitate was free from impurities. Samples which had been either air-dried or dried over fused calcium chloride agreed closely in composition with the formula 4CuO,2HCl,3H<sub>2</sub>O (Found : CuO, 72·0; HCl, 16·5. Calc., CuO, 71·5; HCl, 16·4%). The salt was amorphous and insoluble in water; but after it had been boiled with water, the latter gave a faint opalescence with silver nitrate.

Equilibrium was attained in about a week, but the final analyses were not made until 3 months had elapsed.

The first four sets of data in Table II refer to solid phases which had been air-dried. The liquid phases were water. No copper chloride dissolved until each molecule of hydrated copper oxide had reacted with 0.5 equivalent of hydrochloric acid. Thereafter the solid phase was  $4CuO, 2HCl, 3H_2O$ , as shown by the point of intersection of the tie-lines in Fig. 3, and the liquid phases contained cupric chloride only.

Liquid phases.		Rests.			
				Mol. HCI/	
% CuO.	% HĊl.	% CuO.	% HCl.	mol. CuO.	Solid phases.
0	0	90.28	0.03	0.001	CuO (hydrated) and 4CuO,2HCl,3H.O.
0	0	79.30	11.49	0.312	
0	0	74.07	14.90	0.438	
0	0	$72 \cdot 47$	16.57	0.499	4CuO,2HCl,3H.O.
0.16	0.12	$52 \cdot 80$	12.56	0.517	
3.90	3.57	55-37	13.49		
8.35	7.66	<b>56·4</b> 5	14.60		
$15 \cdot 22$	13.96	56.04	16.35		
18.52	17.03	55.72	16.90		
21.24	19.49	51.67	18.14		
25.59	23.51				4CuO,2HCl,3H <sub>2</sub> O and CuCl <sub>2</sub> ,2H <sub>2</sub> O.

TABLE II.

The rests which had attained equilibrium with water, after being allowed to settle for a month, presented a striated appearance, pale green layers underlying layers of varying shades of dark

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brown. The layers were roughly separated from one another by spraying with a very fine jet of water. The uppermost contained the least chloride, about 0.1 equivalent for each molecule of copper oxide, and the bottom pale green layers contained the most, about 0.3 equivalent. It was not possible to isolate the bottom layers quite free from the more basic, brown particles; probably the amount of chloride actually present in them was greater than 0.3 equivalent.

These observations seem to indicate that each of the highly basic rests was composed of a mixture of two solid phases as required



by the phase rule, and from Fig. 3 there appears to be no doubt that these were the definite basic chloride (greenish-blue) and dark brown copper oxide of varying hydration.

The basic chloride  $4\text{CuO},2\text{HCl},3\text{H}_2\text{O}$  and the rests which contained more than 0.315 equivalent of chloride tended to pass into colloidal solution. Attempts were made to get some idea of the composition of the colloidal suspensions, and it was found that the basic chloride aggregates contained from 0.27 to 0.33 equivalent of chloride for each molecule of copper oxide.

The curve in Fig. 3 corresponding to those liquid phases which

exist in equilibrium with dihydrated cupric chloride was drawn from Foote's data (J. Amer. Chem. Soc., 1923, 45, 663).

Basic Cupric Nitrate.—Several basic nitrates have been described containing from 1.7 to 3 atoms of copper for each molecule of nitrate. The pale bluish-green precipitate formed when alkali, insufficient for complete reaction, is added to a dilute cupric nitrate solution has been shown by many workers to correspond to the formula  $4CuO,2HNO_3,2H_2O$ . The mineral gerhardtite has the same composition; in some specimens, however, the water content appears to be  $1H_2O$ .

When N/10-sodium hydroxide was carefully added to cupric nitrate solution, precipitation was complete and the solution became alkaline to phenolphthalein after the addition of 1.5 equivalents. The composition of the precipitate agreed with the above formula (Found : CuO, 66.8; HNO<sub>3</sub>, 26.4. Calc., CuO, 66.3; HNO<sub>3</sub>, 26.2%). The basic nitrate was insoluble in water, but on boiling with water it soon blackened and some passed into colloidal suspension. The salt was also much more readily decomposed by alkali than was either the sulphate or the chloride, so much so that when alkali was added rapidly to a cupric nitrate solution alkalinity was not produced until 1.9 equivalents had been added.

Basic Cupric Bromide.-The basic bromide produced by the oxidation of cuprous bromide and by the prolonged digestion of a solution of cupric bromide with copper oxide (Richards, Chem. News, 1891, 63, 75; Sabatier, Compt. rend., 1897, 125, 103) has the formula 4CuO,2HBr,2H<sub>2</sub>O. The substance produced on gradual addition of alkali to cupric bromide solution has apparently not been examined. N/10-Sodium hydroxide gave a pale blue, amorphous precipitate and the mother-liquor became alkaline to phenolphthalein after approximately 1.5 equivalents had been added. This result suggests that the precipitate contained CuO and HBr in the molar ratio of 2:1. The (air-dried) precipitates formed by varying amounts of alkali, however, were slightly more basic [Found : (a) CuO, 60.55; HBr, 29.4. (b) CuO, 61.0; HBr, 30.3, corresponding respectively to 4CuO, 1.91HBr, 2.93H, O and 4CuO, 1.95HBr, 2.52H, O]. It is fairly certain that they were essentially the 4:2 bromide, although the data are insufficient to state what was the exact water content. The basic bromide was insoluble in water and did not blacken when boiled with it. In common with the basic nitrate and the basic chloride, it had a marked tendency to pass into colloidal suspension when treated with water.

### Discussion.

It has been shown that of the many basic sulphates and chlorides of copper which have been reported, only one definite sulphate and one definite chloride exist at 25°, viz, 4CuO,H<sub>2</sub>SO<sub>4</sub>,3H<sub>2</sub>O and 4CuO,2HCl,3H<sub>2</sub>O. Similar nitrate and bromide compounds have been shown to be produced by precipitation with alkali under similar conditions, viz, 4CuO,2HNO<sub>3</sub>,2H<sub>2</sub>O and 4CuO,2HBr,2(?)H<sub>2</sub>O. They are similar not only in composition, but also in form, colour, and insolubility. All these salts are precipitated from solution at hydrion concentrations of about 10<sup>-56</sup>. The similarity in their composition seems to be due to an intrinsic property of either the copper atom or the copper oxide molecule.

Previous workers have attempted to account for the sulphate and the nitrate as complex salts of ortho-acids, but such an explanation cannot be applied to the basic chloride or the basic bromide. The usual way of representing these basic salts as if they were double salts, e.g., CuSO<sub>4</sub>, 3Cu(OH)<sub>2</sub>, H<sub>2</sub>O, is unsatisfactory, for they have none of the properties of double salts inasmuch as they are Werner (Ber., 1907, 40, 4444), on the basis of his coinsoluble. ordination theory, regards them as the normal salts of a hypothetical hexolcupric base, e.g.,  $\left[\operatorname{Cu}\begin{pmatrix}\operatorname{HO}\\\operatorname{HO}\\\operatorname{Cu}\end{pmatrix}_{3}\right]$ SO<sub>4</sub>, H<sub>2</sub>O. This representation seems to be equally open to objection. Such a constitution would suggest that, contrary to the facts, the salt has to some extent the capacity of dissolving, which by comparison with difficultly soluble salts of metals, e.g., lead and silver, is in some way connected with the nature of the acid radical, and would ionise in solution into "hexolcupric" and sulphate ions. The comparative inertness of these basic compounds to reaction and their similarity in properties to copper hydroxide seem to show that they are essentially compounds of this base of some unknown kind. Until something is known about their constitution it is perhaps better to represent them thus,  $Cu_4(OH)_6SO_4$ ,  $H_2O$ . Were it known that the co-ordination number of bivalent copper is 6, the Werner theory might be considered to supply a tentative explanation why these basic salts contain copper and the acid in the equivalent ratio of 4:1. The ammine compounds of cupric salts have such widely varying compositions that no definite co-ordination number can be assigned. If the constitution of the cupric complexes in ammoniacal solutions be considered, the co-ordination number is probably 4.

Chatterji and Dhar state (Discussion on Colloids, Faraday and Phys. Soc., 1920, 124) that the blackening on boiling of copper hydr-

oxide can be prevented by the addition of a little normal salt, which is adsorbed and thus renders the copper hydroxide stable. They do not appear to have considered what may be the effect of the formation of basic salts. The retention of the colour on boiling is a property of such salts—less marked, it is true, in the case of the nitrate (see pp. 2801, 2803, 2805).

Since the foregoing pages were written, Krüger has published some work on the basic sulphates of copper (J. pr. Chem., 1924, **108**, 278). He obtained a product having the formula  $4\text{CuO},\text{SO}_3,4\text{H}_2\text{O}$ , and also basic sulphates whose analyses, although irregular, indicated the formulæ  $4\text{CuO},\text{SO}_3,3\cdot5\text{H}_2\text{O}$ ,  $4\text{CuO},\text{SO}_3,5\text{H}_2\text{O}$ , and  $3\text{CuO},\text{SO}_3,2\cdot5\text{H}_2\text{O}$ . The water contents of the first two of these three substances are probably due to imperfect purification, and the last is undoubtedly a mixture of the definite basic salt and copper sulphate.

### Summary.

(1) According to the manner of mixing and the quantity of alkali used, either apparently amorphous or gelatinous precipitates may be obtained by adding alkalis to solutions of the sulphate, chloride, bromide, or nitrate of copper.

(2) The individualities of the basic salts  $Cu_4(OH)_6SO_4$ ,  $H_2O$  and  $Cu_4(OH)_6Cl_2$ ,  $H_2O$  have been established.

(3) The behaviour of the  $Cu|Cu(OH)_2$ , NaOH electrode has been shown to be erratic, and the value of Jellinek and Gordon for  $[Cu''][OH']^2$  untrustworthy.

(4) Observations have been made on the darkening of suspensions of basic copper salts on boiling.

(5) The constitutions of the basic salts have been discussed with special reference to Werner's co-ordination theory.

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