CLV.—*The Iodides of Copper.*

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IN the analytical estimation of copper by the cuprous iodide method, it is found expedient to employ a quantity of potassium iodide greater than that represented by the equation commonly given for the reaction, $2\text{CuSO}_4 + 4\text{KI} = 2\text{K}_2\text{SO}_4 + 2\text{CuI} + \text{I}_2$. The operation is by this means performed in a shorter time, since, if sufficient potassium iodide be employed, the liberated iodine remains in solution as KI_3 , and also the increased mass of one of the reacting substances carries the reaction more nearly to completion. When, however, no such excess of potassium iodide is employed, it is generally assumed that iodine is precipitated along with the cuprous iodide and, if the resultant mixture be titrated with sodium thiosulphate, the iodine will be removed more or less rapidly from the precipitate by the regenerated alkaline iodide, so that the accuracy of the analysis will depend only on the velocity with which the reaction $2\text{Cu}'' + 4\text{I}' \rightleftharpoons 2\text{CuI} + \text{I}_2$ approaches its equi-

librium point. The backward reaction in this equation indicates the presence of cupric iodide in solution, and that this does exist was first demonstrated by Moritz Traube (*Ber.*, 1884, 17, 1066). He obtained a green solution containing 0.08 gram of cupric iodide in 100 c.c. by digesting cuprous iodide with a saturated solution of iodine in water. Later, Carnegie (*Chem. News*, 1889, 59, 57) professed to have obtained a solution ten times as strong by digesting iodine with water and an excess of cuprous iodide at 80°. The cupric iodide could not, however, be isolated in the solid form by concentration of its solution, for, although it is stable at a boiling temperature, it loses half of its iodine on evaporation to dryness. With these observations the entire mechanism of this important reaction seemed to be elucidated. During some preliminary observations of the equilibrium point in the reaction between copper sulphate and potassium iodide, however, we made several observations which seemed to indicate that the conclusion stated by Traube (*loc. cit.*), and apparently generally accepted, namely, that when there is no excess of potassium iodide present the precipitate is a mixture of cuprous iodide and iodine, is incorrect. Under these conditions it was found that the deep red supernatant liquid did not contain enough potassium iodide to correspond with the amount of iodine present in it as estimated by sodium thiosulphate. The precipitate also did not have the appearance of a mixture of iodine and cuprous iodide, but contained a very heavy green substance, much of which was soluble in water after filtration, forming a deep brown solution, although it contained only traces of potassium iodide. At the same time evidence was obtained of the extreme instability of the supposed compound in the observation that after a short exposure to the air the olive-green precipitate changed into white cuprous iodide. On this account, the substance could not be dried for analysis, and accordingly an indirect method for its examination had to be adopted. After treatment of the solid with water, an excess of potassium iodide was added to the solution and the whole of the dissolved iodine capable of being titrated by sodium thiosulphate was determined. To a second portion of the solution, sodium hydrogen carbonate* was added to precipitate all the cupric salt, and the remaining iodine was then titrated by thiosulphate. The first operation will titrate the x atoms of iodine of the formula $\text{CuI} \cdot x\text{I}$, and the second only the $x - 1$ atoms of the formula $\text{CuI}_2 \cdot (x - 1)\text{I}$. From the ratio $\frac{x}{x - 1}$, the composition of the substance

can be at once deduced. For example, if it has the composition CuI_3 , only one atom of iodine will be titrated in the presence of bicarbonate

* A dilute solution of sodium bicarbonate saturated with carbon dioxide was employed.

and two without it; if it has the composition CuI_4 , the ratio will be 3 to 2, and so on.

The precipitate was first rapidly drained from the supernatant liquid at the pump and then treated repeatedly with insufficient water for complete solution. These several fractions were then examined by the method described above, and in some instances a portion was evaporated to dryness and the potassium iodide present determined by solution in water and titration with $N/10$ silver nitrate. In the following table, the results of the first experiment are given. The precipitate was obtained by mixing 20 c.c. of a solution containing one mol. of copper sulphate per litre, 60 c.c. of water and 20 c.c. of a solution containing two mols. of potassium iodide per litre. The mixture was well agitated in a stoppered bottle for half an hour at the room temperature, then filtered and some of the precipitate shaken with three successive quantities of 100 c.c. of water, which were finally titrated with $N/10$ thiosulphate solution.

	Filtrate.	Solution I.	Solution II.	Solution III.
20 c.c. without NaHCO_3 required	26.2 c.c.	16.45	3.9	—
20 c.c. with NaHCO_3 required	16.5	10.3	1.4	0.3
Ratio	1.59 to 1	1.6 to 1	2.8 to 1	—

Twenty c.c. of the filtrate required, after evaporation to dryness, only 7.52 c.c. of $N/10$ silver nitrate solution. The filtrate evidently still contains potassium iodide, but in less amount than that required for the formation of KI_3 with the iodine present. That the soluble matter in the precipitate is not KI_3 was shown by lixiviating the remainder with 500 c.c. of water, evaporating the brown solution to dryness, and titrating the soluble portion of the residue with $N/10$ silver nitrate, when only 1.75 c.c. were required, whereas about 60 c.c. of $N/10$ thiosulphate were necessary to titrate the iodine even after the addition of sodium bicarbonate. The difference in the ratios of solutions I and II is, of course, due to the fact that there is a large amount of cuprous iodide in the precipitate, and that solution II is therefore relatively much richer in cupric iodide than in $\text{CuI}_2 \cdot (x-1)\text{I}$. The value of x in the latter is already indicated by the ratio found in solution I. The ratio is approximately 3 to 2 and, inasmuch as the solution certainly contains some cupric iodide since it has been shaken with cuprous iodide, this may be taken as a strong indication that the olive-green compound has the composition $\text{CuI}_2 \cdot \text{I}_2$, in which three of the iodine atoms would be titrated without, and only two after, addition of bicarbonate. Assuming this to be the case, the simplest way to obtain it in a state of purity would evidently be to precipitate copper sulphate by a solution of iodine in potassium

iodide which contains two atoms of iodine and two molecules of potassium iodide for every atom of copper. This was accordingly done by adding 20 c.c. of the solution containing 1 mol. of copper sulphate per litre to 20 c.c. of the solution containing 2 mols. of potassium iodide per litre, after first dissolving 5.08 grams of iodine in the potassium iodide. In order to ensure equilibrium, the mixture was well shaken for half an hour at the ordinary temperature before filtration. The precipitate was a very dense olive-green powder which settled rapidly, unlike cuprous iodide. It was well agitated with water in four successive quantities of 100 c.c. each, and the four solutions thus obtained were titrated with thiosulphate as above, with the following results :

	Solutions			
	I.	II.	III.	IV.
20 c.c. without NaHCO_3 required	17.0 c.c.	14.0 c.c.	13.4 c.c.	12.4 c.c.
20 c.c. with NaHCO_3 required ...	11.2 "	9.0 "	8.6 "	8.2 "
Ratio	1.52 to 1	1.55 to 1	1.55 to 1	1.51 to 1

The remainder of the precipitate was entirely soluble to a deep brown solution in 500 c.c. of water, and 10 c.c. of this required 5.1 c.c. without, and 3.4 c.c. with, bicarbonate, showing a ratio of 3 to 2. In a second preparation, a solution of the precipitate required 6.65 c.c. of $N/10$ thiosulphate without, and 4.32 c.c. with, bicarbonate for 10 c.c., showing a ratio of 1.54:1. The value 6.65 indicates that 100 c.c. of the solution ought to yield on evaporation to dryness 0.4325 gram of CuI . It actually yielded 0.4320 gram, showing that the method adopted is sufficiently accurate. When an attempt was made to concentrate this solution by removing some of the water as ice, the same olive-green solid separated along with the ice.

These analyses show that both solution and solid contain copper and iodine in the ratio of four atoms of the latter to one of the former. This fact taken along with the evident homogeneity of the precipitate seemed to point to the existence in both of a compound of the same type as KI_3 , namely, $\text{I}\cdot\text{CuI}_3$. It will be evident from the sequel that this conclusion is not justified with regard to the solution, although all the evidence obtainable points to this constitution for the solid. The existence of such a compound seemed to indicate the possibility of the production of a still higher polyiodide, namely, CuI_6 , and accordingly an attempt was made to prepare this by a similar method.

Solutions of copper sulphate and of potassium iodide containing dissolved iodine in the molecular ratio CuSO_4 to 2KI_3 were mixed and well shaken. The precipitate, which was much darker in colour as if it contained free iodine, was shaken up with water and this solution titrated as before. It showed still the same iodine ratio (3 : 2) by the

two methods, and in agreement with this solid iodine remained when it was treated with much water. Also it was observed that when several more dilute solutions in which the iodine ratio was greater than 3:2 were shaken with iodine at the ordinary temperature all gave as final value the ratio 3:2. These results seemed to indicate that no higher compound than CuI_4 is capable of existence at least at the ordinary temperature. When the solution of the tetriodide was heated on the water-bath, however, with an excess of iodine and the liquid titrated, it was found that much more iodine was dissolved. At a temperature of 80° , the values approximate to those required by the formula CuI_6 . On cooling, this solution deposited iodine, a result which was taken to indicate that CuI_4 is the highest iodide which can exist at the ordinary temperature, at least in the presence of water, although the results obtained by Jørgensen (*J. pr. Chem.*, 1870, [ii], 2, 347) seem to indicate that a much higher polyiodide can exist in alcoholic solution.

When the deep red solution obtained by treating the tetriodide with water is sufficiently diluted and shaken with cuprous iodide, it becomes bluish-green and contains no iodine which is capable of reacting with starch. This is the solution of pure cupric iodide first described by Traube. A solution which contains 0.104 per cent. of CuI_2 gives a colour reaction with starch, which is discharged, however, by adding 0.05 c.c. of $N/50$ thiosulphate to 100 c.c. The limit of existence of pure cupric iodide solution at a temperature of 24° is therefore very nearly 0.1 per cent. The 0.8 per cent. solution obtained by Carnegie contained much polyiodide. As mentioned by Traube, the solution of cupric iodide is stable at 100° , but when evaporated at that or a lower temperature it loses iodine and deposits cuprous iodide. Similarly, when we attempted to concentrate it by removal of the water as ice, cuprous iodide was deposited and the solution became orange-coloured, indicating the presence of polyiodide.

The insolubility of cuprous iodide and the existence of a polyiodide, CuI_x , explain the apparent instability of the cupric salt, since, from the equation $(x-2)\text{CuI} + \text{CuI}_x \rightleftharpoons (x-1)\text{CuI}_2$, the mass law requires that $C_2^{x-1}/C_1 = \text{const.}$, where C_1 and C_2 are the concentrations of polyiodide and of cupric iodide respectively. Any variation of the volume of water must therefore displace the equilibrium point, diminution of volume causing C_1 to increase relatively to C_2 . In order to determine the value of x in the above equation, cuprous iodide was added to the strongest solution of the tetriodide with different quantities of water and well shaken until equilibrium was established. Thereafter the iodine was titrated with $N/50$ thiosulphate with and without bicarbonate. The results are contained in the following table:

Original solution.	Water.	With NaHCO_3 .	Without NaHCO_3 .
1000 c.c.	0	2030	3200
800	200	1580	2560
600	400	1115	1920
400	600	612.5	1280
200	800	176	640
100	900	15	320

The first column contains the volume of the original solution taken, water being added in each case to make a total volume of 1000 c.c. Assuming that the substances in solution are CuI_4 and CuI_2 , their relative molecular concentrations are readily obtained from the numbers in columns 3 and 4. If C_1 and C_2 be their respective molecular concentrations, the numbers in column 3 will give the values of $2C_1$, while those in column 4 will give the values of $3C_1 + C_2$, from which C_1 and C_2 have been calculated :

C_1 .	C_2 .	C_2/C_1 .
1015	155	$0.37 \cdot 10^4$
790	190	$0.87 \cdot 10^4$
557.5	247.5	$0.27 \cdot 10^5$
306.3	361.2	$0.15 \cdot 10^6$
88	376	$0.60 \cdot 10^6$
7.5	297.5	$0.35 \cdot 10^7$

It is evident that the values of C_2/C_1 are by no means constant as required by the chemical equation $\text{CuI}_4 + 2\text{CuI} \rightleftharpoons 3\text{CuI}_2$. The assumption made above that $x = 4$ is therefore not true for the solution. A possible explanation is that the solid tetriodide does not dissolve as such, but as an equimolecular mixture of CuI_2 and CuI_6 . If so, the equation representing the production of CuI_2 will be $\text{CuI}_6 + 4\text{CuI} \rightleftharpoons 5\text{CuI}_2$, for which the mass law requires that C_4/C_3 should have a constant value, C_4 and C_3 representing the relative molecular concentrations of CuI_2 and of CuI_6 respectively. The values of C_3 and C_4 are readily obtained from the above table of experimental results, the numbers in column 3 giving the values of $4C_3$ and those in column 4 the values of $5C_3 + C_4$.

C_3 .	C_4 .	$C_4/C_3 = K$.
507.5	662.5	$0.25 \cdot 10^{12}$
395	585	$0.17 \cdot 10^{12}$
278.75	525.25	$0.26 \cdot 10^{12}$
153.15	514.3	$0.24 \cdot 10^{12}$
44	420	$0.30 \cdot 10^{12}$
3.75	301.25	$0.66 \cdot 10^{12}$

In this instance the values obtained for K are all of the same order of magnitude at least, and the first five approach as closely to a constant as the method permits, since an error of 1 per cent. in the titrations would account for all the discrepancy. It seems therefore highly probable that the solution contains a hexioidide of copper. It will also most probably contain some tetriodide as represented by the

equilibrium equation $2\text{CuI}_4 \rightleftharpoons \text{CuI}_2 + \text{CuI}_6$, but there is no evident method of determining its amount. The assumption of the presence of a still higher polyiodide gives less satisfactory results. This is evident from the following table, which has been calculated on the assumption that the solution contains CuI_8 .

C_5 .	C_6 .	C_6^7/C_5 .
338.3	416	$0.64 \cdot 10^{16}$
263.3	358.5	$0.29 \cdot 10^{16}$
185.8	309.7	$0.15 \cdot 10^{16}$
102.1	282.7	$0.14 \cdot 10^{16}$
29.3	217.5	$0.79 \cdot 10^{15}$
2.5	151.3	$0.73 \cdot 10^{15}$

The evidence that the solid is CuI_4 may, from the method of the preparation of this product, be considered unsatisfactory. Some of the various equations which might represent the formation of an equimolecular solution of CuI_2 and CuI_6 from a precipitate thus produced are the following :

Solid.		Solution.
1. $2\text{CuI} + 3\text{I}_2$	=	$\text{CuI}_2 + \text{CuI}_6$
2. $2\text{CuI}_2 + 2\text{I}_2$	=	$\text{CuI}_2 + \text{CuI}_6$
3. $\text{CuI} + \text{CuI}_7$	=	$\text{CuI}_2 + \text{CuI}_6$
4. $\text{CuI}_2 + \text{CuI}_6$	=	$\text{CuI}_2 + \text{CuI}_6$
5. 2CuI_4	=	$\text{CuI}_2 + \text{CuI}_6$

As we are dealing with a solid of very unstable character, the experimental means of deciding between these five possible cases are very limited. Any known method of attempting to remove the iodine would leave the same end-product in each, namely, cuprous iodide, so that superficial examination of the solid seemed about the only evidence available. Its apparently homogeneous appearance even when examined under a fairly high magnifying power would seem to exclude the probability of the olive-green precipitate being represented as in 1, 2, or 3, but not 4, because both CuI_2 and CuI_6 may be heavy green solids. Further, we have always observed that the precipitate settles very rapidly when compared with one which does contain cuprous salt—a fact which may be taken as an additional argument against 1 and 3. If equation 4 is the correct one, a somewhat curious coincidence must exist, namely, that the di-iodide and the hexiodide must have the same solubility, and this not only at the ordinary but also at higher and lower temperatures. As this is extremely improbable, the most likely assumption with regard to the nature of the precipitate is that it is a homogeneous solid having the formula CuI_4 .

Traube states that among its reactions cupric iodide yields no precipitate with silver nitrate solution. This is, however, the case only with the less concentrated solutions, corresponding, in fact, to the

dilutions at which cupric chloride and potassium chloride also give only an opalescence. And even here the addition of acids or neutral salts such as sulphates induces precipitation. A solution of cupric iodide containing 0.095 per cent. gives a precipitate at once with silver nitrate, and can be accurately titrated with it, whilst one of 0.063 per cent. gives no precipitate until potassium chromate is added as indicator.

Although pure cupric iodide is unstable in that its solution cannot be concentrated by evaporation or otherwise, it is much more stable than the polyiodides, for when shaken with ether or carbon tetrachloride they yield up iodine to these solvents and cuprous iodide is precipitated. The strongest solution of pure cupric iodide, however, does not colour them in the slightest. It seemed possible, therefore, that in the dry state the solid tetriodide, when treated with ether, might leave a residue of solid cupric iodide. An attempt was made to remove the water from the precipitated tetriodide by washing with a little alcohol in order to treat the solid subsequently in this way. The alcohol, however, formed a very dark brown, viscid solution, and on filtration cuprous iodide remained in quantity on the filter. This solution was allowed to evaporate spontaneously and two crops of black crystals were obtained from it. The first of these showed on analysis the ratio of 1 atom of copper to 7.25 atoms of iodine, while the second gave numbers which agreed accurately with the formula CuI_9 . The calculated percentage of CuI in this formula is 15.75, whilst the value found by heating the well-dried crystals in a porcelain crucible was 15.77 per cent. As was to be anticipated, when treated with water, copper and iodine dissolved out of it in the ratio required by the formula CuI_4 . By treating cuprous iodide with an alcoholic solution of iodine at a temperature of 30° , Jørgensen (*loc. cit.*) obtained a solution which contained approximately nine atoms of iodine to one molecule of CuI . It seemed possible that the crystalline substance just described might represent the compound actually existing in solution. In order to prepare a larger quantity of it, an excess of CuI was treated with an alcoholic solution of iodine at the ordinary temperature. This solution was found to contain 0.0785 gram of CuI to 0.527 gram of iodine. This might represent a compound containing 12.96 per cent. CuI , whilst the formula CuI_{11} requires 13.01. Glistening, black crystals were also obtained from this solution on evaporation, but none of the various fractions gave numbers agreeing with the above formulæ, the first having a lower, the later fractions a higher, iodine content than either CuI_9 or CuI_{11} . In no case, however, did the solid appear to be a mixture of an iodide with free iodine, inasmuch as individual crystals—and they were often 0.5 mm. in

length—when heated or exposed to the air for some time always left a residue of cuprous iodide. A possible explanation is that there are numerous polyiodides of copper, some containing a high percentage of iodine, and that the different fractions were a mixture of these in varying proportions.

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