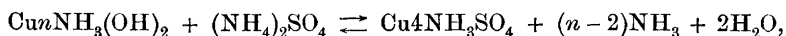
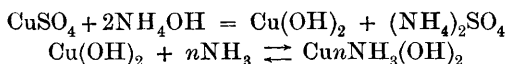


CLXVII.—*The Nature of Ammoniacal Copper Solutions.*

HARRY MEDFORTH DAWSON.

IN two previous papers (Dawson and McCrae, *Trans.*, 1900, **77**, 1239 ; 1901, **79**, 1072) experimental data have been recorded which tend to throw some light on the nature of aqueous solutions of certain metal-ammonia compounds. In the former paper ammoniacal solutions of copper, zinc, cadmium and nickel salts were investigated and the conclusion was drawn that these metals form ammonia compounds of the same type. The method of investigation employed consisted in measuring the total and free ammonia in the ammoniacal solutions. The free ammonia was determined by measuring the amount extracted when the solutions were shaken up with chloroform at a definite temperature. The molecular ratio of combined ammonia to metal was found to vary between 3.15 and 4.0. For a given concentration of the metallic salts the ratio was found to increase with the quantity of ammonia present, and with a fixed proportion of total ammonia to metal, the molecular ratio of combined ammonia was found to increase with the absolute concentration. Dissociation phenomena were thus indicated by the experimental data, and it was suggested that the changes which take place when ammonia is gradually added to a solution of one of these salts (for example, copper sulphate) might be represented by the scheme :



$n$  being less than 4 and probably equal to 2.\*

According to this scheme the ammoniacal solution of copper sulphate represents a complex system, in which the copper is present in the form of three different ions,  $\text{Cu}_4\dot{\text{N}}\text{H}_3$ ,  $\text{Cu}n\dot{\text{N}}\text{H}_3$ , and  $\dot{\text{Cu}}$ , the relative proportions of these depending upon the concentration of the solution and the relative proportions of ammonia and copper salt.

Since the publication of these results, Locke and Forssall (*Amer. Chem., J.*, 1904, **31**, 268) have investigated ammoniacal solutions of copper sulphate, and arrived at the conclusion that the copper in such solutions is almost entirely present in the form of a very stable ion,  $\text{Cu}_4\dot{\text{N}}\text{H}_3$ . The differences in the value of the molecular ratio of

\* The value of  $n$ , previously supposed equal to 2, will not be discussed in this paper.

combined ammonia to copper with varying concentration of the solutions as found by McCrae and myself, are stated to be due to the fact that the method employed by us does not give the correct values for the concentration of free ammonia in the solutions. The experimental method of Locke and Forssall, which consisted in passing a current of electrolytic gas through a column of the solution immersed in a thermostat, and measuring the amount of ammonia removed by a known volume of the gas, does not, however, differ essentially from the mode of examination adopted by us.\* It is precisely on this account that the conclusions deduced from the two series of experimental data might be expected to agree. Locke and Forssall, however, found that the molecular ratio of combined ammonia to copper is constant, and independent of the total ammonia concentration, and this, they point out, is not consistent with the view that more than one complex copper compound is present in the solution. The fact that the experimentally determined values of the ratio  $\text{NH}_3 : \text{Cu}$  are considerably smaller than four, as required by the complex ion  $\text{Cu}\dot{\text{A}}\text{NH}_3$ , is supposed to be entirely due to the smaller solubility of ammonia in ammoniacal copper solutions as compared with pure water. Not only is this assumption made, but from the difference between the required molecular ratio and that actually found in the case of the least concentrated copper solution examined, a measure of the decrease in the solubility is deduced. By means of the empirical formula suggested by Jahn (*Zeit. physikal. Chem.*, 1895, **18**, 8), to express the influence of concentration on the lowering of the solubility of certain gases in water on the addition of electrolytes, values are then deduced as correction factors for the two more concentrated solutions examined. The actual values recorded by these authors for the constant molecular ratio  $\text{NH}_3 : \text{Cu}$  are 4.03, 3.98 and 3.95 for 0.0235, 0.0470 and 0.1175 molecular copper solutions respectively.

The conclusions drawn from numbers so obtained can, obviously, not be accepted. The value of the correction introduced for the diminished solubility of ammonia in the copper solutions is, in the first instance, perfectly arbitrary, and the application of Jahn's formula to solutions of ammonia is not justified by any experimental evidence.†

\* It may be noted that, according to Carveth and Fowler (*J. Physical Chem.*, 1904, **8**, 313), exact measurements of vapour pressure cannot be at all readily obtained by the method of air bubbling. On the other hand, Perman (*ibid.*, 1905, **9**, 36) asserts that the method yields accurate results.

† More recent experiments have led to the setting up of other formulæ to express the influence of electrolytes on the solubility of non-electrolytes in water (compare Rothmund, *Zeit. physikal. Chem.*, 1900, **33**, 401; Euler, *ibid.*, 1904, **49**, 303; Dawson and McCrae, *Trans.*, 1901, **79**, 493).

The purely experimental results obtained by Locke and Forssall appeared, however, to warrant a further inquiry into the matter, and the present investigation has been instituted with this object. In the first paper by McCrae and the author (*loc. cit.*) the primary object was to obtain a general survey of the nature of the ammoniacal solutions and to compare the behaviour of different metals rather than to ascertain with the maximum degree of accuracy the phenomena in the case of any particular metal. The experiments described in this paper, however, represent an attempt to elucidate the nature of ammoniacal solutions of copper sulphate as accurately as is possible by the method of examination employed.

The actual experimental work was carried out in the manner previously described, but in order to obtain greater accuracy, especially in the case of the more dilute solutions, much larger quantities of aqueous solution and of chloroform were employed, and the thermostat, in which the experiments were made, was so arranged that the temperature variations did not exceed  $\pm 0.025^\circ$ .

In reference to the distribution of ammonia between pure water and chloroform, it has already been shown that the concentration ratio  $c_{\text{H}_2\text{O}}/c_{\text{CHCl}_3}$  decreases with increasing ammonia concentration, but the relationship between these two factors could not be determined with a desirable degree of accuracy in the case of dilute solutions containing less than 0.5 mol. of ammonia per litre of aqueous solution. On this account, further measurements have been made according to the improved experimental method. The data are collected in Table I;  $c$  and  $c'$  denote the molar concentration of ammonia in water and chloroform respectively, and  $k$  the distribution ratio  $= c/c'$ . The temperature at which all experiments were made was  $19.5^\circ$ .

TABLE I.

$c$	0.1540	0.1885	0.2011	0.2074	0.3336	0.3958	0.4898
$c'$	0.005919	0.007283	0.007759	0.008028	0.01299	0.01545	0.01923
$k$	26.01	25.87	25.92	25.83	25.67	25.61	25.46
$c$	0.5207	0.6247	0.6674	0.7554	0.8796		
$c'$	0.02043	0.02463	0.02646	0.03005	0.03522		
$k$	25.49	25.36	25.23	25.14	24.98		

If the values of  $k$  are graphically represented as a function of  $c'$ , the points so obtained lie very approximately on the straight line corresponding to the equation :

$$k = 26.16 - 34.14 c' \dots \dots \dots (1)$$

The supposed deviations from this linear relationship, indicated by the earlier experiments at small ammonia-concentrations, are not confirmed by these more accurate measurements.

Before a knowledge of the ratio of distribution of ammonia between water and chloroform can be utilised to determine accurately the quantity of free ammonia in ammoniacal solutions of copper sulphate several points require consideration. Firstly, water and chloroform represent a pair of liquids which at the ordinary temperature are slightly miscible. According to Herz (*Ber.*, 1898, 31, 2669), at 22°, 100 c.c. of water dissolve 0.420 c.c. of chloroform and give 100.39 c.c. of solution, whilst 100 c.c. of chloroform dissolve 0.152 c.c. of water and the volume of the solution is 99.62 c.c. The extent of this mutual solubility is no doubt altered when ammonia is present in the two liquids and copper salt in the water. Secondly, when a copper sulphate solution of definite concentration is shaken up with chloroform, this concentration will undergo a slight change, the amount of which depends at a given temperature on the original concentration and on the relative volumes of the solution and of chloroform which are brought together. In ammoniacal solutions the change of concentration from this cause will also no doubt depend on the ammonia concentration. This change of concentration cannot be directly ascertained from the data which measure the miscibility of pure water and pure chloroform, for the mutual solubility is altered by the presence of the foreign substances (ammonia and copper salt) in the two liquids. Thirdly, the influence which the dissolved copper compound (or compounds) exerts on the distribution of the free ammonia between water and chloroform must be taken into account. This influence is no doubt very considerable and an accurate knowledge of it is necessary for the determination of the true values of the combined ammonia, but its magnitude cannot be determined by direct experiment. On the basis of the numerous data already obtained for salts of the alkali metals (Dawson and McCrae, *Trans.*, 1901, 79, 493), it may be inferred, however, that the direction of this influence is such that the relative solubility of the free ammonia in the water is diminished. In the case of these salts, it is improbable that the effect of the dissolved electrolyte is complicated to any appreciable extent by chemical interaction with the ammonia. The magnitude of the influence is dependent on the nature of the component ions and is additive in character. The carbonates, sulphates, and oxalates are much more active than the iodides, bromides, and nitrates of the same metal.

The experimental method, having regard to the first two disturbing factors, may now be considered. If the relative volumes of water and chloroform are suitably chosen, the volume of the aqueous solution will not be altered after shaking with chloroform. Utilising Herz's data, it can be easily shown that the volume of chloroform which must be shaken up with 100 c.c. of water, in order that this condition

may be satisfied, is given by the equation:  $x = \frac{100}{0.152} \left( 100 - \frac{(100)^2}{100.39} \right)$ , from which  $x = 256$  c.c. If we assume that the ammonia and copper salt do not appreciably affect the mutual solubility of the two liquids, it follows that, by employing ammoniacal copper solutions and chloroform in the volume ratio 1:2.56, the concentration of the dissolved copper will be unchanged. This conclusion and the somewhat arbitrary assumption involved were submitted to the test of experiment. Sixty c.c. of an ammoniacal copper sulphate solution ( $\text{NH}_3 = 1.00$  Cu = 0.0501 mol. per litre) were shaken up with 150 c.c. of chloroform and the resulting aqueous solution was found to contain 0.0502 mol. Cu per litre. The concentration of the dissolved copper is evidently unaltered in these circumstances, and in the experiments to be described the relative volumes were chosen in accordance with this condition.

In respect of the third disturbing factor, it has already been found that the influence of alkali salts on the ammonia distribution is proportional to their concentration. This proportionality has been confirmed by a new series of more accurate experiments with sodium sulphate. In these experiments, the ammonia concentration in the chloroform was very nearly constant and equal to 0.015 mol. per litre, for which concentration the distribution ratio in the case of pure water  $k$  is equal to 25.64. In the table, the sodium sulphate ( $m$ ) and ammonia ( $c$  and  $c'$ ) concentrations in mol. per litre are given in the first, second, and third columns; the fourth contains the values of the distribution ratio  $k'$ , the fifth the values of  $(k - k')/m$ . For the purpose of comparison, the values of  $k - k'/m^{\frac{2}{3}}$  are also given.

TABLE II.

$m$ .	$c$ ( $\text{H}_2\text{O}$ ).	$c'$ ( $\text{CHCl}_3$ ).	$k'$ .	$k - k'/m$ .	$k - k'/m^{\frac{2}{3}}$ .
0.156	0.3694	0.01534	24.07	10.05	5.41
0.313	0.3411	0.01512	22.56	9.84	6.68
0.469	0.3196	0.01512	21.13	9.62	7.47

The values of  $k - k'/m$  are very nearly constant and indicate that the "salting-out" effect is very approximately proportional to the concentration of the dissolved salt, and not to the (concentration) <sup>$\frac{2}{3}$</sup>  as was gratuitously assumed by Locke and Forssall in the case of the vapour pressure.

In a second series of experiments the concentration of the sodium sulphate was in every case 0.313 mol. per litre, whilst the ammonia concentration was varied.

TABLE III.

$c$ ( $\text{H}_2\text{O}$ ).	$c'$ ( $\text{CHCl}_3$ ).	$k$ (from equation 1).	$k'$ .	$k - k'/m$ .
0.1755	0.007668	25.90	22.88	9.65
0.3411	0.01512	25.64	22.56	9.84
0.6543	0.02956	25.15	22.14	9.62

The numbers indicate that the "salting-out" action of the sodium sulphate is independent of the ammonia concentration within the limits of concentration employed.

On the basis of these experimental results the distribution ratio  $k'$  of ammonia between an aqueous solution of an electrolyte and chloroform may be expressed by the equation :

$$k' = k - \delta m = 26.16 - 34.14 \ c' - \delta m \dots \dots \dots (2)$$

in which  $c'$  is the ammonia concentration in the chloroform,  $m$  the concentration of the electrolyte in the aqueous solution, and  $\delta$  the "salting-out" effect produced by the electrolyte at a concentration of 1 mol. per litre.

By means of this equation the concentration of the free ammonia in an aqueous solution of the electrolyte can be determined, and if the total ammonia concentration is known, the combined ammonia is given by the difference. For the molecular proportion of combined ammonia in an ammoniacal copper solution, we have then

$$\text{Mol. ratio } \frac{\text{Combined NH}_3}{\text{Cu}} = \frac{c - k'c'}{m} = \frac{c - kc'}{m} + \delta c' \dots \dots (3)$$

The value of  $\delta$ , which measures the "salting-out" or ammonia displacing effect of the dissolved cupriammonia compound, is, of course, unknown, but the calculation of the combined ammonia may be carried out with two limiting values of  $\delta$ , such that the true value is in all probability intermediate. As a lower limit  $\delta=0$  has been taken, and as a higher limit  $\delta=10$ , which is the value found in the case of sodium sulphate, and represents an ammonia displacing power of considerable magnitude.

Before the experimental numbers are communicated, it may be noted that, according to equation (3), the measurement of the combined ammonia depends on the difference between two quantities, both of which increase with increasing total ammonia concentration. For this reason the accurate determination of combined ammonia in the case of solutions containing considerable excess of ammonia is impracticable. On the other hand, the concentration of ammonia in the chloroform is so small in the case of aqueous solutions containing little free ammonia

that a limit to the accurate experimental determination of combined ammonia is also fixed in this direction. These considerations have determined the limits of the investigation which on general grounds has been confined to dilute solutions.

Four series of experiments have been carried out in which the concentration of the copper salt was respectively 0.0125, 0.025, 0.05, and 0.10 mol. per litre. In each of these series the ammonia concentration was varied, the extreme values for the molecular ratio  $\text{NH}_3:\text{Cu}$  being 5.5 and 24. In most cases, the experiments were made in duplicate. In the table the successive columns contain (1) the ammonia concentration of the aqueous solution in mols. per litre, (2) the molecular ratio of total ammonia to copper, (3) the ammonia concentration of the chloroform solution, (4) the distribution ratio  $k$  calculated from equation (1), and (5) the molecular ratio of combined ammonia to copper calculated for  $\delta=0$  and  $\delta=10$  according to equation (3).

TABLE IV.

*Concentration of Copper, 0.0125 mol. per litre.*

$\text{NH}_3(\text{H}_2\text{O})$ .	Mol. ratio, total $\text{NH}_3/\text{Cu}$ .	$\text{NH}_3(\text{CHCl}_3)$ .	$k$ .	Mol. ratio, Combined $\text{NH}_3/\text{Cu}$ .	
				$\delta=0$ .	$\delta=10$ .
0.1042	8.34	0.002438	26.08	3.25	3.27
0.1055	8.44	0.002479	26.08	3.27	3.29
0.1975	15.80	0.005940	25.96	3.46	3.52
0.2001	16.01	0.006040	25.96	3.46	3.52
0.2981	23.84	0.009860	25.82	3.46	3.56

*Concentration of Copper, 0.025 mol. per litre.*

0.1754	7.02	0.00347	26.04	3.40	3.43
0.1776	7.10	0.00358	26.04	3.37	3.41
0.2169	8.68	0.00500	25.99	3.48	3.53
0.2177	8.71	0.00502	25.99	3.49	3.54
0.3799	15.20	0.01121	25.78	3.64	3.75
0.3800	15.20	0.01123	25.78	3.62	3.73

*Concentration of Copper, 0.05 mol. per litre.*

0.3042	6.08	0.00492	25.99	3.53	3.58
0.3367	6.73	0.00613	25.95	3.55	3.61
0.3370	6.74	0.00616	25.95	3.54	3.60
0.5572	11.14	0.01466	25.66	3.62	3.77
0.5590	11.18	0.01463	25.66	3.67	3.82
0.5964	11.93	0.01605	25.61	3.70	3.86
0.8521	17.04	0.02658	25.25	3.61	3.98

*Concentration of Copper, 0.10 mol. per litre.*

0.5476	5.48	0.00711	25.92	3.64	3.71
0.5486	5.49	0.00710	25.92	3.65	3.72
0.9488	9.49	0.02275	25.38	3.71	3.94
0.9605	9.60	0.02315	25.37	3.73	3.96

In regard to the two series of numbers in column (5), it is to be noted that the true values of the combined ammonia are in all probability intermediate to the two values given. Although the true values are not determinable by the experimental method employed in this investigation, yet the numbers indicate with certainty that, for a given copper concentration, the molecular ratio of combined ammonia to copper increases with increase in the total ammonia concentration. The variation of the proportion of combined ammonia for a given alteration in the ammonia concentration is evidently greater when the ammonia displacing influence of the dissolved complex compound is taken into account in the calculation.

The following numbers, which are interpolated from the data in the previous table, show the variation of the proportion of combined ammonia with the concentration of the solution when the ratio of total ammonia to copper is kept constant.

TABLE V.

Concentration of copper salt, mol. per litre.	Mol. ratio, total $\text{NH}_3/\text{Cu}$ .	Mol. ratio, combined $\text{NH}_3/\text{Cu}$ .	
		$\delta=0$ .	$\delta=10$ .
0.0125	8.0	3.25	3.27
0.025	8.0	3.43	3.49
0.05	8.0	3.58	3.67
0.10	8.0	3.69	3.86

It is clear that with increasing dilution the proportion of combined ammonia decreases to a considerable extent, and the variation is greater when it is assumed that  $\delta=10$  than when  $\delta=0$ .

Some experiments carried out with solutions of the crystalline salt,  $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ , may now be described. The cupriammonia sulphate was prepared according to the method described by André (*Compt. rend.*, 1885, 100, 1138) by passing ammonia into a concentrated and well-cooled solution of copper sulphate, washing the separated crystals with aqueous ammonia and drying over lime. Analysis of the crystals gave  $\text{Cu}=25.85$ ,  $\text{NH}_3=27.86$ , the formula requiring  $\text{Cu}=25.85$  and  $\text{NH}_3=27.76$  per cent.

Concentrated solutions of this salt appear to be quite stable, but on dilution precipitation takes place. A freshly-prepared solution containing approximately 0.1 mol. per litre appears to be optically clear, but care must be taken in the preparation of the solution if the formation of a precipitate is to be avoided. On standing for some days, a portion of the copper is precipitated from such a solution. It was of some interest to determine the proportion of combined ammonia in these solutions, and two freshly-prepared approximately 0.1 molar



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solutions were examined, the data obtained being given in the following table. In the case of the second solution, the copper concentration was determined both before and after shaking with chloroform. The difference in the two values indicates that a small proportion of the copper was removed from the aqueous solution by the process of extracting with chloroform, and it is possible that this represents copper already present in the form of colloidal or suspended copper hydroxide. In the interpretation of the experimental data, this possibility must be kept in mind.

TABLE VI.

Copper concentration.	$\text{NH}_3 (\text{H}_2\text{O}).$	$\text{NH}_3 (\text{CHCl}_3).$	Mol. ratio, combined $\text{NH}_3/\text{Cu}.$	
			$\delta=0.$	$\delta=10.$
0.1021	0.4044	0.001995	3.45	3.47
{ 0.0990 (before expt.)	0.3918	0.00210	3.40	3.42 }
{ 0.0985 (after ,, )	0.3918	0.00210	3.42	3.44 }

The values of the ratio of combined ammonia to copper indicate that an aqueous solution of the substance  $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$  contains a considerable quantity of free ammonia resulting from the dissociation of the complex compound, and the data agree satisfactorily with those obtained in the examination of solutions containing larger quantities of ammonia.

The observations recorded in this paper lead the author to conclude that the view of Locke and Forssall, according to which ammoniacal solutions of copper sulphate contain copper exclusively in the form of a stable complex ion,  $\text{Cu} \cdot 4\ddot{\text{N}}\text{H}_3$ , is untenable.

In concentrated solutions or solutions containing considerable excess of ammonia, the copper appears to be present very largely in the form of this ion, but on dilution of the solution or decrease in the relative proportion of the ammonia, this complex ion undergoes dissociation with the separation of ammonia, the process leading ultimately to the precipitation of copper hydroxide from solution. Although the exact nature of the changes is not yet known, yet the experimental facts are in agreement with the equations on p. 1666. It is hoped that experiments which are in progress will throw further light on the nature of this complex system.

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