# CXIX.—*The Nature of Metal-ammonia Compounds in Aqueous Solution. Part I.*

By H. M. DAWSON and J. McCRAE.

REYCHLER (*Bull. Soc. Chim.*, 1895, [iii], **13**, 387; *Ber.*, 1895, **28**, 555) has shown that the freezing point of a solution of silver nitrate is not appreciably altered by the addition of 2 molecules of ammonia per molecule of salt, but that further addition of ammonia is accompanied by a considerable lowering of the freezing point. In the case of copper sulphate solutions, the freezing point is depressed to some extent by the addition of 4 molecules of ammonia per molecule of salt, whilst in the case of copper nitrate the addition of a similar quantity of ammonia produces very little change in the temperature at which ice separates from the solution. Similar results were obtained by him for the variation of the equivalent conductivity of solutions of silver nitrate, copper sulphate, and copper nitrate on the addition of corresponding quantities of ammonia.

From Reychler's experiments, it is evident that the number of molecules present in the silver nitrate solution is not increased on the addition of 2 mols. of ammonia to 1 mol. of salt. When more ammonia is added, then the total number of molecules in the solution is increased, each molecule of ammonia added increasing the molecular lowering by about 19·5 units (theory 18·6). The addition of 4 molecules of ammonia to a solution containing 1 molecule of copper nitrate increases the number of molecules only to a very slight extent (increase of molecular lowering 2·5), but the similar addition to a solution of copper sulphate causes an appreciable change (7·7 in the molecular lowering).*

Konowaloff (*J. Russ. Phys. Chem. Soc.*, 1899, **31**, 910; Abstr., 1900, ii, 265) determined the partial pressure of ammonia of ammoniacal salt solutions by drawing a current of air through the solutions contained in a thermostat at 60° into a standard acid solution. He finds that the partial pressure of the ammonia of the salt solution is expressed by the formula $P=P_1(n-k.m)$, where $P_1$ = partial pressure of ammonia from pure aqueous ammonia solution, $n$ = number of gram-molecules of ammonia and $m$ = number of gram-mols. of salt per litre, and $k$ a constant. For silver nitrate, he finds $k=2$, and for cadmium nitrate, zinc nitrate, nickel chloride, copper nitrate, copper chloride, copper sulphate, and copper acetate $k$ = approx. 4 (3·4 to

---

* The effect produced by the addition of more ammonia than 4 molecules per molecule of copper salt has not been investigated, and in consequence the deduction of conclusions from Reychler's experiments is made somewhat difficult.

4·04). Some salt solutions which are not at first precipitated by ammonia were also investigated, and it was found that the partial pressure of ammonia in such ammoniacal salt solutions was greater than the partial pressure of pure aqueous ammonia solution, except in the cases of calcium and strontium chlorides. In these two cases, there is probably some specific action between the ammonia and the dissolved electrolyte, but for the others the results are in accordance with those obtained for the influence of dissolved salts on the absorption coefficient of such gases as hydrogen, nitrogen (Steiner, *Ann. Phys. Chem.*, 1894, [ii], **52**, 275; Braun, *Zeit. physikal. Chem.*, 1900, **33**, 721), and nitrous oxide (Gordon, *Zeit. physikal. Chem.*, 1900, **18**, 7; Roth, *Zeit. physikal. Chem.*, 1897, **24**, 114), and also on the solubility of ethyl acetate (Euler, *Zeit. physikal. Chem.*, 1900, **31**, 360) and phenylthiocarbamide (Rothmund, *Zeit. physikal. Chem.*, 1900, **33**, 402).

According to the law of distribution (Nernst) of a substance between two non-miscible media, the condition of equilibrium at a given temperature is determined by a constant ratio of the concentrations, if the molecular weight of the distributed substance is the same in the two media. If we invert this distribution theorem, it follows that deviations from the constant concentration ratio will serve as a measure of any molecular change which the distributing substance undergoes in one or other of the media, as Hantzsch and Sebaldt (*Zeit. physikal. Chem.*, 1899, **30**, 258) have pointed out. Such molecular changes probably occur in ammoniacal salt solutions, and the investigation of the distribution-coefficient of ammonia between such salt solutions and a medium non-miscible with water will indicate the formation of any complex compounds produced by combination of the salt and ammonia. The deviation of the distribution-coefficient for the salt solution from the value found for pure water and a non-miscible medium will measure the complexity of such compounds. The investigation of this deviation forms the subject of the present paper.

Hantzsch and Sebaldt (*loc. cit.*, 266), in an attempt to elucidate the constitution of ammonia and amine solutions, have investigated the distribution of these substances between water and various non-miscible organic liquids. They find that the ratio of the concentration of ammonia in water to that in chloroform is independent of the absolute value of the concentrations, that is, $\frac{c_1}{c_2}$ = constant, where $c_1$ = concentration in water, and $c_2$ = concentration in chloroform. In their calculations, Hantzsch and Sebaldt take account of the electrolytic dissociation of aqueous ammonia solution, but neglecting this—which is extremely small at the concentrations used—the ratio $\frac{c_1}{c_2}$ is practically constant. Without entering into a discussion of the nature of aqueous ammonia solution, we can conclude from the constancy of this ratio that the molecular complexity of the ammonia in both solvents is the same. This being the case, the conditions under which the problem to be solved has been investigated are as simple as possible.

By reason of the considerable solubility of ammonia in chloroform, and, at the same time, of the small reciprocal solubility of water and chloroform, the latter is particularly adapted for our investigation.*

## EXPERIMENTAL.

The method of experimentation was as follows: 50 c.c. of solution containing the salt and ammonia were thoroughly shaken in a separating funnel with a known volume of chloroform. The separating funnel was placed in a thermostat, and after having acquired the temperature of the bath, the chloroform and aqueous solution were repeatedly shaken until it could be assumed that equilibrium had been established. Hantzsch and Sebaldt have shown that this takes place very quickly. After the chloroform had completely settled from the salt solution (about ½ hour), the funnel was removed from the thermostat, the two layers at once separated, and without any loss of time the ammonia in each was estimated. We may assume, from the result of special experiments, that during the course of the experiment practically no ammonia is lost. The amount of ammonia in the chloroform solution was determined by adding a known volume of this (either 40 or 70 c.c.) to about 80 c.c. of water contained in a stoppered bottle. This was then directly titrated with 0·1 normal acid, using methyl-orange as indicator, the end point being taken when a permanent pinkish colour appeared in the aqueous layer after shaking the chloroform through it. We have proved by preliminary experiments that this method of determining the ammonia in chloroform is accurate. In the first experiments with copper sulphate solution, the quantity of ammonia in the aqueous solution was determined by distilling a known volume of the solution, to which an excess of alkali had been added, into a known volume of normal sulphuric acid solution and titrating back, after diluting, with 0·1 normal alkali. It was also proved that the accuracy of this method is satisfactory. Besides, as we always knew the total amount of ammonia present and the volume of both the aqueous solution and the chloroform, we had a check on the analysis. In the case of colourless solutions (aqueous), it was unnecessary to distil off the ammonia, and the quantity was determined by direct titration of a

---

* According to Herz (*Ber.*, 1898, **31**, 2669), 100 volumes of chloroform dissolve 0·152 volume of water, and 100 volumes of water dissolve 0·420 volume of chloroform at the ordinary temperature.

known volume with 0·1 normal acid. It was afterwards found possible to titrate the copper salt solution directly, as the intense blue colour of the copper-ammonia ions disappears before the end point is reached, and the colour due to the copper ions in the very dilute solution which we used in the titration was much too weak to mask the end point in any way. The amount of ammonia found by these methods agreed perfectly. The total amount of ammonia found was usually a trifle less than that added, but the difference was nearly always less than 1 per cent. of the total, and never exceeded 1·5 per cent.

The aqueous solution was obtained by taking a known volume (*a*) of normal salt solution, adding a known volume (*b*) of approximately normal aqueous ammonia solution (sufficient to precipitate the metal hydroxide completely, then wholly redissolve it) and then $(50 - a - b)$ c.c. of water. The amount of chloroform used was either 100 c.c., 70 of which were taken for the titration, or 50 c.c., of which 40 were taken. The amount of 0·1 normal acid used in the titration varied between 4 and 16 c.c. for the chloroform, and between 10 and 40 c.c for the aqueous solution.

### *Distribution-coefficient of Ammonia between Water and Chloroform.*

The results obtained at 20° with varying absolute concentrations of ammonia are given in the following table :

| Total ammonia in original aqueous solution. Gram-mol. per litre. | Concentration of ammonia in $CHCl_3$. $c_2$. Gram per litre. | Concentration of ammonia in aqueous part. $c_1$. Grams per litre. | Coefficient $\frac{c_1}{c_2}$. | Mean. |
|---|---|---|---|---|
| 0·365 | 0·2317 | 6·001 | 26·0 | |
| 0·373 | 0·2281 | 6·138 | 26·9 | |
| 0·444 | 0·2730 | 7·295 | 26·7 | |
| 0·532 | 0·3499 | 8·737 | 26·1 | 26·3 |
| 0·548 | 0·3380 | 9·024 | 26·7 | |
| 0·712 | 0·4342 | 11·290 | 26·0 | |
| 0·892 | 0·5431 | 14·140 | 26·0 | |

The deviations from the mean value shown by the above numbers are quite irregular, and no regular variation of the distribution-coefficient with the concentration is observable. The accuracy of the later determinations in the paper (after some experience had been gained) is probably much greater than that measured by the deviations of the single observations in the above series from the mean.

The coefficient decreases with rise of temperature. Thus, at 25° the following results were obtained :

| Total ammonia in original aqueous solution. Gram-mol. per litre. | Concentration of ammonia in chloroform. $c_2$. Gram per litre. | Concentration of ammonia in aqueous part. $c_1$. Grams per litre. | Coefficient, $\frac{c_1}{c_2}$. | Mean. |
|---|---|---|---|---|
| 0·286 | 0·1870 | 4·695 | 25·1 | 24·9 |
| 0·381 | 0·2511 | 6·247 | 24·9 | |
| 0·567 | 0·3111 | 7·667 | 24·7 | |
| and at 30°: | | | | |
| 0·382 | 0·2687 | 6·245 | 23·2 | 23·2 |
| 0·478 | 0·3375 | 7·815 | 23·2 | |

*Experiments with Copper Sulphate Solution.*

The requisite volume of normal copper sulphate solution was introduced into the separating funnel, and varying volumes of approximately normal ammonia solution added; then a volume of water so as to make the total addition up to 50 c.c. The distribution-coefficient was determined at 20° with the following results:

| Total ammonia in the original solution. Gram-mol. per litre. | Concentration in $CHCl_3$. $c_2$. Gram per litre. | Concentration in the aqueous part. $c_1$. Grams per litre. | Coefficient. $\frac{c_1}{c_2}$. |
|---|---|---|---|
| With 0·1 normal: | | | |
| 0·2403 | 0·0470 | 3·975 | 84·5 |
| 0·2765 | 0·0633 | 4·593 | 72·5 |
| 0·2814 | 0·0662 | 4·739* | 71·5 |
| 0·3497 | 0·1129 | 5·858* | 51·9 |
| 0·3635 | 0·1152 | 5·974 | 51·9 |
| 0·4473 | 0·1618 | 7·474* | 46·2 |
| 0·4564 | 0·1675 | 7·456 | 44·5 |
| 0·5374 | 0·2141 | 8·746 | 40·9 |
| 0·5608 | 0·2314 | 9·340* | 40·4 |
| 0·6286 | 0·2663 | 10·465* | 39·3 |
| 0·6887 | 0·2679 | 10·220 | 38·2 |
| 0·7201 | 0·3228 | 11·680 | 36·2 |
| 0·8047 | 0·3779 | 12·980 | 34·3 |
| With 0·4 normal: | | | |
| 0·9256 | 0·1148 | 15·500 | 135·1 |
| 1·2302 | 0·2961 | 20·420 | 69·0 |
| 1·5396 | 0·4906 | 25·300 | 51·6 |

* The ammonia was determined by distillation; in the other cases by direct titration. In the cases marked with an asterisk also 50 c.c. of chloroform were used, and 40 taken for the titration, otherwise 100 were used and 70 taken.

| Total ammonia in the original solution. Gram-mol. per litre. | Concentration in $CHCl_3$. $c_2$. Gram per litre. | Concentration in the aqueous part. $c_1$. Grams per litre. | Coefficient. $\frac{c_1}{c_2}$. |
|---|---|---|---|
| With 0·2 normal: | | | |
| 0·4590 | 0·0700 | 7·695 | 109·8 |
| 0·5509 | 0·1168 | 9·170 | 78·5 |
| 0·6403 | 0·1703 | 10·590 | 62·2 |
| 0·7338 | 0·2225 | 12·080 | 54·3 |
| 0·9165 | 0·3316 | 14·980 | 45·2 |
| With 0·05 normal: | | | |
| 0·1741 | 0·0566 | 2·915 | 51·5 |
| 0·2681 | 0·1084 | 4·359 | 40·2 |
| 0·3564 | 0·1587 | 5·780 | 36·4 |
| 0·3575 | 0·1610 | 5·942 | 36·9 |

Ten c.c. of approximately normal ammonia solution were not sufficient to precipitate and completely redissolve the copper salt in 5 c.c. of normal copper sulphate solution, so that we may safely assume that it requires more than 4 molecules of ammonia per molecule of copper sulphate to transform the whole of the copper salt into the complex compound and at the same time leave no undissolved residue.

Conclusions as to the nature of the compound formed are drawn later in the paper—at present we may notice that the above results are included in the curves given on p. 1251.

These results show that the concentration of ammonia in the chloroform depends, not only on the amount of ammonia, but also on the concentration of the salt in the aqueous solution.

The coefficient thus obtained gives the ratio of the concentration of the total ammonia in the aqueous part to that in the chloroform. If we assume that the salt solution would give the same coefficient as pure water provided that no action took place between the salt and ammonia, then from the knowledge of the distribution coefficient between pure water and chloroform, we may calculate from the concentration in the chloroform the concentration of ammonia in the salt solution which is necessary in order that equilibrium may exist between the dissolved ammonia in the two media. This latter we may regard as free ammonia and the difference from the total ammonia will give us the fixed ammonia, and knowing the concentration of the salt solution we may further calculate the molecular ratio between fixed ammonia and salt.

Since a possible experimental error of 0·5 unit may be made in the determination of the distribution-coefficients, we have considered it more exact to plot mean curves with the concentration of ammonia in the chloroform as abscissa and distribution-coefficient as ordinate, and from these curves to calculate the proportion of fixed ammonia at any concentration, rather than from each separate experiment.

Before the results obtained from these curves are given, we proceed to show that the same curves are capable of representing the experimental results arrived at with other salts than copper sulphate.

### *Experiments with Copper Chloride.*

A normal solution of this salt was prepared by precipitating a solution of 12·488 grams of crystallised copper sulphate with hot caustic potash, filtering and washing the copper oxide, and dissolving it in hydrochloric acid. The copper chloride solution was evaporated to dryness, then dissolved in water and evaporated again to dryness, and this was repeated until the residue showed scarcely any acid reaction. It was then dissolved in water and made up to 100 c.c. The solution so obtained was acid, but it was proved that the error introduced on account of ammonia required to neutralise this was negligibly small.

The distribution-coefficient was determined in a tenth normal solution at 20° with varying concentration of ammonia with the following results :

| Total $NH_3$ in original solution. Gram-mol. per litre. | Concentration of $NH_3$ in $CHCl_3$. Gram per litre. | Concentration of $NH_3$ in aqueous part. Grams per litre. | Coefficient. |
|---|---|---|---|
| 0·2808 | 0·0662 | 4·729 | 71·4 |
| 0·4682 | 0·1719 | 7·821 | 45·5 |
| 0·6581 | 0·2884 | 10·947 | 38·0 |

If we compare these coefficients with those obtained in decinormal copper sulphate solution at corresponding concentrations of ammonia, we find that they agree closely and certainly within the experimental error.

### *Experiments with Zinc Sulphate.*

A normal solution of zinc sulphate was prepared by dissolving 14 grams of the crystallised salt $ZnSO_4,7H_2O$ in water and making up the solution to 100 c.c. To the requisite volume of this solution with varying quantities of approximately normal ammonia, water was added so as to make the total addition up to 50 c.c. and the coefficient was determined with this, when the following results were obtained :

| Total $NH_3$ in original solution. Gram-mol. per litre. | Concentration of $NH_3$ in $CHCl_3$. Gram per litre. | Concentration of $NH_3$ in aqueous part. Grams per litre. | Coefficient. |
|---|---|---|---|
| With 0·1 normal: | | | |
| 0·4689 | 0·1727 | 7·832 | 45·2 |
| 0·5449 | 0·2204 | 8·861 | 40·2 |
| 0·5611 | 0·2306 | 9·349 | 40·5 |
| 0·6613 | 0·2876 | 11·001 | 38·2 |
| With 0·05 normal: | | | |
| 0·3740 | 0·1714 | 6·213 | 36·4 |
| 0·4634 | 0·2260 | 7·684 | 34·0 |
| 0·5358 | 0·2679 | 8·610 | 32·2 |
| 0·5650 | 0·2868 | 9·357 | 32·6 |
| 0·6295 | 0·3230 | 10·100 | 31·3 |
| 0·6613 | 0·3455 | 10·883 | 31·5 |
| With 0·025 normal: | | | |
| 0·3752 | 0·2021 | 6·205 | 30·7 |
| 0·4675 | 0·2591 | 7·722 | 29·8 |
| 0·5593 | 0·3165 | 9·232 | 29·2 |

With decinormal and twentieth normal copper sulphate solutions and the same concentration of ammonia, almost the same coefficients were obtained.

### *Experiments with Cadmium Iodide.*

A normal solution was prepared by dissolving 18·3 grams of cadmium iodide in water and making up to 100 c.c.

As the cadmium hydroxide precipitated by the ammonia is not so easily redissolved, only a single experiment was made in decinormal solution, using 5 c.c. of the above solution, 40 c.c. of normal ammonia and 5 c.c. of water. The result obtained agrees closely with that found with decinormal copper sulphate solution, and similar absolute concentration of ammonia.

With twentieth normal cadmium iodide solution, the smallest amount of ammonia which would completely precipitate and redissolve 5 c.c. of semi-normal cadmium iodide solution was between 25 and 30 c c. of normal ammonia solution. An experiment was made with 25 c.c. of normal ammonia, but a decided precipitate remained in the aqueous part; with 30 c.c., however, the cadmium hydroxide was completely dissolved. We give the result of the experiment with 25 c.c. of ammonia, but do not place any reliance on the figures:

| Total $NH_3$ in original solution. Gram-mol. per litre. | Concentration of $NH_3$ in $CHCl_3$. Gram per litre. | Concentration of $NH_3$ in aqueous part. Grams per litre. | Coefficient. |
|---|---|---|---|
| With 0·1 normal: | | | |
| 0·7642 | 0·3572 | 12·688 | 35·5 |
| With 0·05 normal: | | | |
| 0·4789 | 0·2402 | 7·935 | 33·0 |
| 0·5712 | 0·2906 | 9·458 | 32·5 |
| 0·6636 | 0·3490 | 10·979 | 31·5 |
| 0·7633 | 0·4167 | 12·642 | 30·3 |

Experiments have also been made with tenth, twentieth, and fortieth normal nickel sulphate solutions, but the separated hydroxide requires the addition of considerable quantities of ammonia before a clear solution is obtained. Without giving the actual results, we may say that they are substantially the same as those obtained with similar concentrations of copper and zinc sulphates.

In order to ascertain whether an increase in the concentration of the $SO_4$ ions in the copper sulphate solution had any influence on the distribution-coefficient, experiments were made with solutions containing a fixed quantity of copper sulphate and (1) varying quantities of sodium sulphate and a fixed amount of ammonia, and (2) varying quantities of ammonia and a fixed amount of sodium sulphate. In the first place, however, the influence of sodium sulphate alone on the distribution-coefficient was determined and it was found that even with fairly large quantities of sodium sulphate the coefficient was but slightly altered, as the following results show. The same quantity of ammonia was added in each case and for comparison the mean value obtained for pure water is appended :

| Concentration of $Na_2SO_4$ in aqueous part. Gram equivalent per litre. | Concentration of $NH_3$ in $CHCl_3$. Gram per litre. | Concentration of $NH_3$ in aqueous part. Grams per litre. | Coefficient. |
|---|---|---|---|
| 0·4 | 0·2979 | 7·233 | 24·3 |
| 0·2 | 0·2885 | 7·199 | 25·0 |
| 0·1 | 0·2836 | 7·240 | 25·5 |
| 0·0 | — | — | 26·3 |

The distribution-coefficient obviously decreases gradually as the concentration of the sodium salt increases, which would indicate a decrease of the solubility of ammonia in the aqueous solution with increasing concentration of sodium sulphate.

From the experimental material relating to the influence of dissolved electrolytes on the absorption-coefficient of water for nitrous oxide and hydrogen, Jahn (*Zeit. physikal. Chem.*, 1895, **18**, 8) has deduced an empirical relationship which may be expressed by the equation

$$\frac{a - a'}{m^{\frac{2}{3}}} = \text{const.},$$

where $a$ is the absorption coefficient of pure water, $a'$ that of the solution, and $m$ the concentration of the dissolved salt in gram-mol. per litre. Although the above values for the distribution-coefficient do not differ much from one another, yet in consideration of the quantities of decinormal acid used in the titrations (12 c.c. for the chloroform, 22 c.c. for the aqueous solution), the numbers are probably accurate to 0·5 per cent. It seemed desirable, therefore, to test whether this empirical equation is capable of representing the dependence of the distribution-coefficient of ammonia on the concentration of the sodium sulphate in the solution.

For the three solutions, the following values are obtained:

| Conc. of $Na_2SO_4$. | $m = 0·05$. | $m = 0·1$. | $m = 0·2$. |
|---|---|---|---|
| $\frac{a - a'}{m^{\frac{2}{3}}}$ | $= 5·8$ | 6·0 | 5·9 |

The expression given by Jahn therefore appears to be capable of representing in this case the influence of the dissolved electrolyte on the distribution-coefficient of ammonia.*

The following table contains the results of experiments made with decinormal copper sulphate solutions, the concentration of the sodium sulphate in the solution varying from 0·1 to 0·4 normal, whilst the amount of ammonia added was the same throughout:

| Concentration of $Na_2SO_4$ in aqueous part. Gram equivalent per litre. | Concentration of $NH_3$ in $CHCl_3$. Gram per litre. | Concentration of $NH_3$ in aqueous part. Grams per litre. | Coefficient. |
|---|---|---|---|
| 0 | 0·1675 | 7·456 | 44·5 |
| 0·1 | 0·1718 | 7·437 | 43·3 |
| 0·2 | 0·1766 | 7·440 | 42·1 |
| 0·3 | 0·1792 | 7·444 | 41·5 |
| 0·4 | 0·1815 | 7·447 | 41·0 |

---

* We are at present engaged in carrying out further experiments with a view of ascertaining the influence of dissolved substances on the distribution-coefficient of ammonia between solutions and chloroform.

The presence of considerable quantities of sodium sulphate has, therefore, very little effect on the ratio of distribution of ammonia between the copper sulphate solution and chloroform. The variation is of the same order of magnitude as was obtained in the case of solutions containing no copper sulphate, as is evident from the following comparison:

| | $\frac{c_1}{c_2}$ | Diminution of $\frac{c_1}{c_2}$. |
|---|---|---|
| Water | 26·3 | 7·6 per cent. |
| 0·4 normal $Na_2SO_4$ solution | 24·3 | |
| 0·1 normal $CuSO_4$ solution | 44·5 | 7·8 " |
| 0·1 normal $CuSO_4$ + 0·4 normal $Na_2SO_4$ sol. | 41·0 | |

A similar small influence of the sodium sulphate is observable if the concentration of the ammonia is varied as the following table indicates, the corresponding values for the same concentrations of ammonia without sodium sulphate being added for comparison:

With 0·1 normal $CuSO_4$ and 0·4 normal $Na_2SO_4$:

| Concentration of $NH_3$ in original solution. Gram-mol. per litre. | Concentration of $NH_3$ in $CHCl_3$. Gram per litre. | Concentration of $NH_3$ in aqueous part. Grams per litre. | Coefficient. | Coefficient without $Na_2SO_4$. |
|---|---|---|---|---|
| 0·2774 | 0·0675 | 4·582 | 67·9 | 69·8 |
| 0·3678 | 0·1243 | 6·003 | 48·2 | 50·2 |
| 0·4594 | 0·1815 | 7·447 | 41·0 | 42·5 |

From these data, it is evident that the only influence exerted by the sodium sulphate on the distribution of ammonia between copper sulphate solution and chloroform is of the same nature and magnitude as the influence exerted on the distribution equilibrium between water and chloroform. The sodium sulphate exerts apparently no specific action on the copper salt as regards the formation of the complex ammonia compound, although in the above solutions of the mixed sulphates the degree of dissociation of the copper sulphate is diminished to a very considerable extent. The action of sodium sulphate on the ratio of the free and combined ammonia in the copper salt solution will be referred to later.

Two or three determinations were also carried out at 20° with calcium chloride solutions. Whereas the presence of sodium sulphate produces an effect such that for a given concentration of ammonia in the chloroform the concentration in the aqueous solution as compared with that in pure water is diminished, the calcium chloride acts in the opposite direction, and must be classed with the salts of copper, cadmium, zinc, and nickel. This corresponds with the results arrived at by Konowaloff for the partial pressure of ammonia over solutions of calcium chloride.

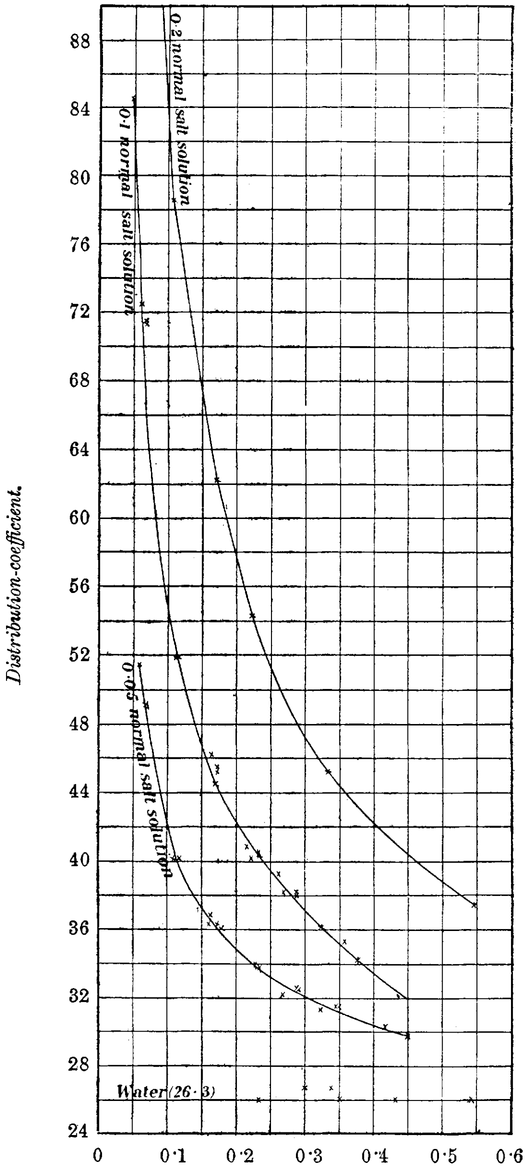
The following numbers were obtained:

| Concentration of $NH_3$ in original solution. Gram-mol. per litre. | Concentration of $NH_3$ in $CHCl_3$. Gram per litre. | Concentration of $NH_3$ in aqueous part. Grams per litre. | Coefficient. |
|---|---|---|---|
| With 0·2 normal calcium chloride solution: | | | |
| 0·3640 | 0·2125 | 6·002 | 28·2 |
| With 0·1 normal calcium chloride solution: | | | |
| 0·2652 | 0·1585 | 4·369 | 27·6 |
| 0·4384 | 0·2645 | 7·220 | 27·3 |

If the value of the distribution-coefficient obtained in the first experiment be compared with that found with a copper sulphate solution of the same strength and with the same concentration of ammonia in the chloroform layer, an enormous difference is observable, the two numbers being 56 and 28·2. The amount of ammonia fixed by the calcium chloride is, therefore, very small, and if it be assumed that an ammonia complex of the same type as that yielded by copper, zinc, and cadmium is formed, the calcium-ammonia compound must be dissociated to a relatively far greater extent than the other compounds.

With the results obtained above, mean curves have been drawn, showing the dependence of the distribution-coefficient on the concentration of the ammonia in the chloroform layer. It has been found that one curve will represent the 0·1 normal solutions of copper sulphate, zinc sulphate, copper chloride, and cadmium iodide, and that another curve will represent exactly the results for 0·05 normal solutions of copper sulphate, zinc sulphate, and cadmium iodide. These curves are shown in the figure on p. 1251. The curve is a mean one, and in the calculation of the amount of fixed ammonia, none of the experimental results were used directly. For the purpose of calculation, we have selected points on the curve representing ammonia concentrations corresponding with a certain integral number of molecules of ammonia per molecule of salt in the aqueous solution after the distribution had taken place. Thus, in a decinormal solution of any of the salts used, the concentration of the salt was 0·05 molecule per litre, and the concentrations of the ammonia chosen were respectively 0·25, 0·30, 0·35, 0·40, 0·45, and 0·50 molecule, or 4·267, 5·121, 5·975, 6·828, 7·681, 8·535 grams, per litre, that is, the

*Variation of distribution-coefficient with varying concentration of the Ammonia.*



*Concentration of Ammonia in the Chloroform. Gram per litre.*

ratio of salt molecules to ammonia molecules was 1 : 5, 1 : 6, 1 : 7, 1 : 8, 1 : 9, 1 : 10. Now, the concentration of ammonia in the aqueous solution is not given by the curve; we had, therefore, to ascertain by trial the points on the curve corresponding to the special concentrations required, the coefficient multiplied by the concentration in chloroform giving the concentration of ammonia in the aqueous solution. It is obvious that only a part of the curve is of use for calculating accurately the fixed ammonia. If the coefficient is too small and near the coefficient for pure water (26·3), then, since the difference of these two numbers is a factor in the calculation, the error becomes considerable; on the other hand, when the coefficient is too high, this means that the concentration of ammonia in the chloroform is too small to permit of its being determined with any great degree of accuracy. In our calculations of the fixed ammonia, we have remained within such limits that the experimental errors do not vitiate our conclusions.

In the following tables, the last column contains the ratio of the number of molecules of 'fixed' ammonia per molecule of salt, the second column the ratio of the total number of molecules of ammonia per salt molecule.

| Strength of $NH_3$ in aqueous part. | Mol. ratio salt : total $NH_3$ in aqueous part. | Concentration of $NH_3$ in $CHCl_3$. Gram per litre. | Coefficient. | Free $NH_3$. Grams per litre. | Fixed $NH_3$. Grams per litre. | Fixed $NH_3$. Gram-mol. per litre. | Mol. ratio. Salt : $NH_3$. |
|---|---|---|---|---|---|---|---|
| With 0·1 normal solutions: | | | | | | | |
| 0·25 *N* | 1 : 5 | 0·06 | 71 | 4·260 | 2·682 | 0·157 | 1 : 3·14 |
| 0·30 | 1 : 6 | 0·09 | 57 | 5·130 | 2·763 | 0·162 | 1 : 3·24 |
| 0·35 | 1 : 7 | 0·1175 | 51·2 | 6·015 | 2·926 | 0·171 | 1 : 3·43 |
| 0·40 | 1 : 8 | 0·145 | 47 | 6·815 | 3·002 | 0·176 | 1 : 3·52 |
| 0·45 | 1 : 9 | 0·175 | 44 | 7·700 | 3·098 | 0·181 | 1 : 3·63 |
| 0·50 | 1 : 10 | 0·205 | 42 | 8·610 | 3·208 | 0·188 | 1 : 3·76 |
| With 0·05 normal solutions: | | | | | | | |
| 0·15 *N* | 1 : 6 | 0·0475 | 54·6 | 2·593 | 1·344 | 0·079 | 1 : 3·16 |
| 0·175 | 1 : 7 | 0·0575 | 51·7 | 2·973 | 1·460 | 0·086 | 1 : 3·44 |
| 0·20 | 1 : 8 | 0·0725 | 47·7 | 3·458 | 1·551 | 0·091 | 1 : 3·64 |
| 0·225 | 1 : 9 | 0·085 | 45·0 | 3·825 | 1·589 | 0·093 | 1 : 3·72 |
| 0·25 | 1 : 10 | 0·1025 | 41·7 | 4·274 | 1·578 | 0·092 | 1 : 3·68 |
| 0·30 | 1 : 12 | 0·1850 | 38·1 | 5·143 | 1·593 | 0·093 | 1 : 3·72 |
| 0·35 | 1 : 14 | 0·1650 | 36·4 | 6·006 | 1·665 | 0·097 | 1 : 3·88 |
| 0·40 | 1 : 16 | 0·1925 | 35·1 | 6·757 | 1·694 | 0·099 | 1 : 3·96 |
| 0·45 | 1 : 18 | 0·225 | 34·0 | 7·650 | 1·732 | 0·101 | 1 : 4·04 |

For completeness, the same tabulation is given for the stronger solutions of copper sulphate, which have been used, the proportions of fixed ammonia per molecule of salt being calculated in this case directly from the concentrations of ammonia actually employed in the experiments—the number of observations not being sufficient for tracing a curve.

| Mol. ratio of salt to total $NH_3$. | Free $NH_3$. Grams per litre. | Fixed $NH_3$. Grams per litre. | Fixed $NH_3$. Gram-mol. per litre. | Mol. ratio. Salt : fixed $NH_3$. |
|---|---|---|---|---|
| With 0·2 normal copper sulphate : | | | | |
| 1 : 4·51 | 1·842 | 5·853 | 0·343 | 1 : 3·43 |
| 1 : 5·37 | 3·072 | 6·098 | 0·357 | 1 : 3·57 |
| 1 : 6·20 | 4·479 | 6·111 | 0·358 | 1 : 3·58 |
| 1 : 7·08 | 5·852 | 6·228 | 0·365 | 1 : 3·65 |
| With 0·4 normal copper sulphate : | | | | |
| 1 : 4·54 | 3·019 | 12·48 | 0·731 | 1 : 3·65 |
| 1 : 5·98 | 7·787 | 12·63 | 0·740 | 1 : 3·70 |
| 1 : 7·41 | 12·900 | 12·40 | 0·727 | 1 : 3·64 |

At all concentrations investigated, the amount of ammonia combined with 1 molecule of salt slowly increases as the total concentration of the ammonia becomes larger. This increase in the amount of fixed ammonia is, however, relatively small, for example, in the case of decinormal copper sulphate solution, the further addition of a quantity of ammonia equal to that sufficient to conveniently dissolve the originally precipitated hydroxide (100 per cent. increase in total ammonia) only produces an increase of about 11 per cent. in the former. Furthermore, it appears that with increasing concentration of the copper sulphate solution the effect of doubling the total amount of ammonia under the same conditions is less, that is, the relative increase of the fixed ammonia becomes smaller.

Another comparison which enables us to get a fuller insight into the nature of the equilibrium in the ammoniacal salt solution is that of the amount of combined ammonia for the same molecular ratio between the salt and the total ammonia at different dilutions. The proportion 6 molecules of total ammonia per molecule of salt lies within the range of the experiments at all the concentrations of copper sulphate investigated, and for this reason has been chosen for the comparison :

| Mol. ratio of $CuSO_4$ to total $NH_3$. | Concentration of $CuSO_4$. | Mol. ratio of $CuSO_4$ to fixed $NH_3$. |
|---|---|---|
| 1 : 6 | 0·05 *N* | 1 : 3·16 |
| 1 : 6 | 0·1 | 1 : 3·24 |
| 1 : 6 | 0·2 | 1 : 3·58 |
| 1 : 6 | 0·4 | 1 : 3·70 |

Dilution of the solution is obviously accompanied by an increase in the dissociation of the copper ammonia compound, its influence being opposite to that due to an increase in the proportion of ammonia relatively to the copper salt. Further dilution is attended by precipitation, indicating that as the above dissociation increases the solution becomes saturated with regard to one of the dissociation products. It is furthur of interest to calculate in the same way the amount of fixed ammonia per molecule of salt for the same molecular ratio between the total ammonia and copper salt in presence of varying quantities of sodium sulphate. In the calculation of the free ammonia in the aqueous solution, it is obviously incorrect to use the value of the distribution coefficient for pure water and chloroform, and the value of the coefficient obtained on p. 1247 for the corresponding pure sodium sulphate solution has been employed.

With 0·1 normal copper sulphate solution:

| Concentration of $Na_2SO_4$. | Coefficient. | Free $NH_3$. Grams per litre. | Fixed $NH_3$. Grams per litre. | Fixed $NH_3$. Gram-mol. per litre. | Mol. ratio of $CuSO_4$ to fixed $NH_3$. |
|---|---|---|---|---|---|
| 0 *N* | 26·3 | 4·405 | 3·051 | 0·1787 | 1 : 3·57 |
| 0·1 | 25·5 | 4·381 | 3·056 | 0·1790 | 1 : 3·58 |
| 0·2 | 25·0 | 4·415 | 3·025 | 0·1772 | 1 : 3·54 |
| 0·3 | 24·6 | 4·408 | 3·036 | 0·1779 | 1 : 3·56 |
| 0·4 | 24·3 | 4·410 | 3·037 | 0·1779 | 1 : 3·56 |

At all concentrations of sodium sulphate, the proportion of fixed ammonia is exactly the same within the limits of experimental error, the deviation from the mean being but 0·5 per cent.

The results thus far obtained would indicate that in all the solutions investigated, in presence of a considerable excess of ammonia, 1 molecule of the salt takes up 4 molecules of ammonia in some way or another, so that the latter can no longer act as free ammonia and participate directly in the equilibrium which is established between this and the ammonia in the chloroform. As the amount of ammonia decreases with reference to the amount of salt, or if the ratio of these remains constant and the dilution increases, the compound formed in solution gradually undergoes dissociation so that the combined ammonia per molecule of salt is considerably diminished, the lowest ratio obtained in our experiments being 3·16 molecules of ammonia per molecule of salt. The assumption of a dissociating compound, $CuSO_4,4NH_3$, would agree with this, and with the fact that on addition of alcohol to an ammoniacal copper sulphate solution a compound of the formula $CuSO_4,4NH_3,H_2O$ is precipitated, although the latter observation does not prove that this compound is present in considerable quantity, for the addition of alcohol may result in a disturbance of the conditions of equilibrium, and in the resulting alcoholic solution the solubility product of the above compound may be small. If we assume, however (as is generally done), that the above compound dissociates electrolytically with the formation of $Cu4NH_3$ and $SO_4$ ions, then whether the ammonia in solution is a dissociation product of the undissociated salt or of the positive ion, we should expect to find that the addition of sodium sulphate would have some influence on the equilibrium between the copper salt and the ammonia, for application of the law of mass action shows that the concentration of the positive ion as well as that of the undissociated complex will be altered as a result of the increase in concentration of the $SO_4$ ions. Experiment shows, however, that the addition of sodium sulphate has no influence on the equilibrium in question, the proportion of combined ammonia at the same concentration being the same.

Results which we have obtained with ammoniacal solutions of copper oxide seem to indicate that such a complex can not be exclusively formed in the salt solutions. The blue colour of the solution of copper oxide in ammonia is apparently the same as that of a solution obtained by precipitating a cold solution of a copper salt with ammonia and redissolving in excess, and we should consequently expect that the same complex would be present.

Although in the case of the oxide more ammonia is required to obtain a clear solution containing a given quantity of copper than in the case of the salts, the amount of combined ammonia referred to one atom of copper is, however, very much smaller in the former case, as will be seen from the succeeding details.

### *Experiments with Copper Oxide.*

Some copper sulphate was precipitated with alkali and well washed by decantation. The copper oxide was then shaken with ammonia solution (approximately normal). The amount of copper oxide in the solution was determined by evaporating a known volume to dryness, igniting, and weighing the residual copper oxide. 140 c.c. gave 0·2236 gram CuO, that is, the solution was 0·0401 normal.

Fifty c.c. of this solution were shaken with 100 c.c. of chloroform, and the distribution-coefficient determined, result A being obtained:

| Total $NH_3$ in original solution. Gram-mol. per litre. | Concentration of $NH_3$ in $CHCl_3$. Gram per litre. | Concentration of $NH_3$ in aqueous part. Grams per litre. | Coefficient. |
|---|---|---|---|
| A. 0·7278 | 0·4477 | 12·200 | 27·25 |
| B. 0·1734 | 0·03979 | 1·440 | 36·2 |

Calculating from the concentration of ammonia in the chloroform that the concentration of free ammonia in the aqueous part is $0·4477 \times 26·3 = 11·774$ grams per litre, this leaves $12·2 - 11·774 = 0·426$ gram per litre of ammonia in combination with the copper oxide. That is, 0·0201 gram-mol. of copper oxide is combined with 0·0249 gram-mol. of ammonia; the complexity is represented by $CuO,1·24NH_3$.

A current of air, free from carbon dioxide, was aspirated through 100 c.c. of the ammoniacal copper oxide solution; the ammonia was absorbed by a measured volume of sulphuric acid as a gauge of the amount of ammonia lost. After sufficient ammonia had been removed, so that a higher coefficient would be obtained, the solution was made up to 100 c.c., the concentration of copper thus remaining the same. A very slight turbidity was produced on addition of the small quantity of water. The distribution coefficient was determined with this solution, and the result B (above) obtained. Calculating as before, we have

Free ammonia in aq. part, $0·03979 \times 26·3 = 1·046$;
Fixed ammonia, $1·440 - 1·046 = 0·394$ gram per litre,
or 0·0231 gram-mol. per litre.
Therefore, $0·02CuO : 0·0231NH_3$,

that is, the complexity is represented by $CuO,1·15NH_3$.

Two portions of the original ammoniacal solution were again treated as above, but instead of making up to 100 c.c. with water, dilute ammonia was added, and thus any slight formation of a precipitate was avoided.

With these solutions and two others prepared in the same way, which were respectively 0·0225 and 0·08 normal with respect to the dissolved copper oxide, the distribution coefficients were determined as before. All the results are contained in the following table, with the exception of the first experiment, which is omitted in consequence of the use of a large excess of ammonia. With regard to the most concentrated copper oxide solution (0·08 normal), it should be mentioned that this was obtained as the result of an attempt to prepare as strong a solution as possible. For this purpose, ordinary copper oxide, which appears to dissolve somewhat more readily than the precipitated oxide, was shaken with fairly strong ammonia (4 normal) for a considerable time, and after filtering through asbestos exposed to a current of air as before until a precipitate began to be formed. The solution was again filtered, the amount of dissolved copper oxide estimated, and a portion used at once for the determination of the distribution-coefficient. A further precipitation was observed to have taken place from the solution after standing 24 hours, although the number of molecules of ammonia per molecule of copper oxide in the solution was about 7. A solution containing the same amount of copper present as sulphate, on the other hand, has no tendency to precipitate if 5 molecules (or even less) of ammonia are present.

| Mols. total $NH_3$ per mol. of CuO in original solution. | Concentration of $NH_3$ in $CHCl_3$. Gram per litre. | Concentration of $NH_3$ in aqueous part. Grams per litre. | Coefficient. | Fixed $NH_3$. Gram per litre. | Fixed $NH_3$. Gram-mol. per litre. | Mol. fixed $NH_3$ per mol. of CuO. |
|---|---|---|---|---|---|---|
| With 0·04 normal copper oxide : | | | | | | |
| 9·17 | 0·0996 | 3·131 | 31·4 | 0·512 | 0·030 | 1·50 |
| 6·07 | 0·0612 | 2·073 | 33·9 | 0·464 | 0·0272 | 1·36 |
| 4·22 | 0·03979 | 1·440 | 36·2 | 0·394 | 0·0231 | 1·15 |
| With 0·0225 normal copper oxide : | | | | | | |
| 24·2 | 0·1627 | 4·642 | 28·55 | 0·363 | 0·0212 | 1·89 |
| With 0·08 normal copper oxide : | | | | | | |
| 6·90 | 0·1439 | 4·717 | 32·8 | 0·933 | 0·0547 | 1·37 |

Although the experimental errors in these determinations are greater than in the case of the salts, it is evident that we have to deal here, as before, with a dissociation phenomenon. The series of experiments with 0·04 normal copper oxide solutions shows that, by increasing the concentration of the ammonia, the concentration of the complex copper-ammonia compound is also increased, and the experiment with 0·0225 normal copper oxide shows that in presence of a large excess of ammonia the number of molecules of ammonia combined per molecule of copper oxide approximates to two. The effect of dilution on the proportion of fixed ammonia (the ratio of total ammonia to copper oxide remaining constant) cannot be deduced from the above numbers, very probably on account of the unavoidable errors of experiment. This would, however, appear to be the same as in the case of the salt solutions, for dilution leads eventually to precipitation in each instance.

We may say that the experimental data point to the formation of a dissociating compound of the formula $CuO2NH_3$ or $Cu2NH_3.(OH)_2$, which compound is a di-acid base dissociating electrolytically with formation of $Cu2NH_3$ and OH ions. Whether the ammonia is a dissociation product of the positive ion or of the undissociated compound cannot as yet be definitely answered.

If we now turn again to the consideration of the equilibrium in ammoniacal solutions of copper salts, some light may be thrown on the nature of this from the results obtained with copper oxide solutions. The deep blue colour of the solutions appears to be the same, dilution of each solution leads apparently to the precipitation of copper hydroxide, and in each case we have a dissociation phenomenon in which ammonia is one of the dissociation products, the only difference being that whereas in presence of a large excess of ammonia 2 molecules of ammonia become fixed per molecule of copper oxide, in the case of the salts for 1 molecule of the latter we have 4 molecules of ammonia combined, and further, that in the former case, for the same quantity of copper more ammonia is required for the complete solution than in the latter.

When ammonia is gradually added to a solution of a copper salt the following changes probably occur:

In the first stage, copper hydroxide is precipitated.

$$CuSO_4 + 2NH_3 + 2H_2O = (NH_4)_2SO_4 + Cu(OH)_2 \qquad (1).$$

The copper hydroxide then dissolves in excess of ammonia with the formation of the soluble base $Cu2NH_3.(OH)_2$.

$$Cu(OH)_2 + 2NH_3 \rightleftarrows Cu2NH_3.(OH)_2 \qquad (2).$$

The complex base probably reacts further with the ammonium sulphate thus:

$$Cu2NH_3.(OH)_2 + (NH_4)_2SO_4 \rightleftarrows Cu4NH_3.SO_4 + 2H_2O \qquad (3).$$

The complex salt $Cu4NH_3.SO_4$ and the base $Cu2NH_3.(OH)_2$ probably both exist in the ammoniacal copper salt solution. According to equation (3), the effect of dilution would be a progress of the reaction from right to left, which would, however, result in an increase of the complex base; if equation (2) represents, however, a dissociation equilibrium, it is obvious that increasing dilution of the salt solution will lead eventually to precipitation of the copper hydroxide.

The complex cupriammonia salt and the cupriammonia base are also probably electrolytically dissociated according to

$$\mathrm{Cu4HN_3.SO_4} \rightleftarrows \mathrm{Cu\overset{+}{4}NH_3} + \mathrm{\overset{-}{S}O_4} \qquad (4)$$

and

$$\mathrm{Cu2NH_3.(OH)_2} \rightleftarrows \mathrm{Cu\overset{+}{2}NH_3} + 2(\mathrm{\overset{-}{O}H}) \qquad (5)$$

Increase in the concentration of the $SO_4$ ions by the addition of sodium sulphate solution would influence the first ionic equilibrium so as to produce greater concentration of the undissociated salt, but the ammonium sulphate, which is one of the components on the other side of the equilibrium equation (3), is also influenced in the same manner, and as a consequence the addition of sodium sulphate may have but slight influence on this equilibrium. As regards the molecular species of which the ammonia is a dissociation product, we may suppose that these are the ionic complexes $Cu4NH_3$ and $Cu2NH_3$, dissociating according to the scheme

$$\mathrm{Cu2\overset{+}{N}H_3} \rightleftarrows \mathrm{\overset{+}{C}u} + \mathrm{2NH_3} \qquad (6).$$

This last equation is really nothing else than equation (2) written in ionic language, for the hydroxyl ion is common to both sides.

According to the views brought forward, increasing concentration of the ammonia in the ammoniacal copper oxide solution will result finally in the fixing of 2 molecules of ammonia per atom of copper, and in the ammoniacal copper salt solution of 4 molecules of ammonia per atom of copper.

Reychler's observation that the freezing point of copper sulphate solution is only lowered to a comparatively small extent by the addition of 4 molecules of ammonia per molecule of salt would seem to indicate that the reaction represented by equation (3) has taken place to a considerable extent from left to right with the formation of $Cu4NH_3.SO_4$, for only in this case can the correspondingly small increase in the number of molecules or ions in the solution be explained.

The fact that addition of alcohol to an ammoniacal copper sulphate solution results in the precipitation of $CuSO_4,4NH_3,H_2O$ is also capable of being explained on the above theory. Equation (3) also possibly explains the circumstance that, at the same concentration of copper, less ammonia per atom of copper is required for complete solution in the case of the salts than in the case of the solution free from an acid radicle.

The behaviour of the ammoniacal copper oxide and salt solutions on titration with decinormal acid should be noticed. At first deep blue, the ammoniacal copper oxide solution gradually becomes paler in colour and a precipitate is formed, the disappearance of which occurs just when the end point is reached. The acid probably reacts in the first place on the free ammonia present in the solution, converting this into ammonium ions, and diminishing in this way the product of the concentrations of the dissociation products on the left-hand side of equation (2), or (with reference to the ions) on the right-hand side of equation (6). The consequence of this is further dissociation of the complex, and attainment of the limit of solubility of copper hydroxide which is then precipitated, being afterwards dissolved by the last portions of acid. It appears probable that solutions supersaturated with regard to copper hydroxide are obtained, and that separation only takes place slowly under certain circumstances. As has been pointed out, a clear 0·08 normal solution of copper oxide containing about 7 molecules of ammonia per molecule of copper oxide gave a considerable precipitate on standing for 24 hours.

Similar phenomena are observed on titrating ammoniacal solutions of copper salts, and these can be explained in the same manner as in the case of the oxide. In both instances, the dilution resulting from the addition of the acid solution will aid in the precipitation of the copper hydroxide.

What has been said in regard to the copper sulphate solutions probably holds good for the salts of the other metals investigated: copper chloride, zinc sulphate, cadmium iodide, and nickel sulphate. It has been shown that under the same conditions, and for the concentrations used by us, the number of molecules of ammonia fixed per molecule of salt is the same in every case. The fact that increasing quantities of ammonia are required for the production of a clear solution with zinc sulphate, cadmium iodide, and nickel sulphate suggests that the dissociation of the complex formed in these solutions proceeds to a greater extent than that of the copper salt solution, but the relative solubility of the hydroxides must also be taken into account.

In the case of ammoniacal solutions of calcium chloride, the much smaller quantity of ammonia fixed at corresponding concentrations would point to a much higher degree of dissociation of the complex as compared with those of the above metal salts. The absence of any precipitation is accounted for by the much greater solubility of calcium hydroxide. It should finally be noted that the values obtained for the amount of ammonia fixed per molecule of salt agree completely with those obtained by Konowaloff (*loc. cit.*) from determinations of the partial pressure of ammonia over ammoniacal salt solutions.

All the above experiments were carried out at 20°; we have also investigated the influence of temperature on the dissociation equilibrium in ammoniacal salt solutions.

Experiments have been made at 25° and at 30° with *zinc sulphate solutions*, and the results are tabulated below:

At 25°, $k$ = 24·9 (see page 1243):

| Total $NH_3$ in original solution. Gram-mol. per litre. | Concentration of $NH_3$ in $CHCl_3$. Gram per litre. | Concentration of $NH_3$ in aqueous part. Grams per litre. | Coefficient. $k$. |
|---|---|---|---|
| With 0·1 normal: | | | |
| 0·466 | 0·1878 | 7·761 | 41·2 |
| 0·657 | 0·3090 | 10·910 | 35·3 |
| With 0·05 normal: | | | |
| 0·468 | 0·2499 | 7·744 | 31·0 |
| 0·562 | 0·3061 | 9·294 | 29·7 |
| 0·655 | 0·3715 | 10·800 | 29·1 |
| With 0·025 normal: | | | |
| 0·280 | 0·1518 | 4·629 | 30·5 |
| 0·375 | 0·2138 | 6·181 | 28·9 |
| 0·469 | 0·2754 | 7·728 | 28·0 |
| 0·566 | 0·3450 | 9·309 | 26·9 |
| 0·652 | 0·4071 | 10·723 | 26·4 |
| 0·653 | 0·4046 | 10·746 | 26·6 |

At 30°, $k$ = 23·2 (see page 1243):

| Total $NH_3$ in original solution. Gram-mol. per litre. | Concentration of $NH_3$ in $CHCl_3$. Gram per litre. | Concentration of $NH_3$ in aqueous part. Grams per litre. | Coefficient. $k$. |
|---|---|---|---|
| With 0·1 normal: | | | |
| 0·573 | 0·2738 | 9·512 | 34·7 |
| 0·669 | 0·3375 | 11·088 | 32·8 |
| 0·765 | 0·4096 | 12·648 | 30·9 |
| With 0·05 normal: | | | |
| 0·384 | 0·2033 | 6·342 | 31·2 |
| 0·480 | 0·2703 | 7·925 | 29·3 |
| 0·573 | 0·3366 | 9·442 | 28·1 |
| With 0·025 normal: | | | |
| 0·193 | 0·1006 | 3·183 | 31·6 |
| 0·383 | 0·2339 | 6·309 | 27·0 |
| 0·575 | 0·3652 | 9·445 | 25·9 |

A comparison of the numbers obtained at these higher temperatures with those for 20° shows that the nature of the equilibrium in solution has undergone no change. The calculation of the quantity of fixed ammonia from the above experimental data shows that for 1 molecule of salt there are from 3 to 4 molecules of ammonia combined. As at 20°, also, increasing concentration of ammonia tends to make this molecular ratio approximate gradually to the limiting value of 4.

At corresponding concentrations of salt and ammonia, increase of temperature is accompanied by a decrease of the distribution-coefficient, as was also found to be the case for pure water. The variation is, moreover, of the same relative order of magnitude in the two cases, in consequence of which the question as to the influence of temperature on the dissociation of the molecular complexes in solution cannot be deduced with certainty from the experiments. We hope, however, as the result of further investigations, to be able to ascertain this influence of temperature.

YORKSHIRE COLLEGE,
LEEDS.