CXII.—*Metal-Ammonia Compounds in Aqueous Solution. Part IV. The Influence of Temperature on the Dissociation of Copper-Ammonia Sulphate.*

By H. M. Dawson and J. McCrae.

It has already been shown (this vol., p. 496) that the distribution of ammonia between water and chloroform at 20° is not quite independent of the concentration, and the variation is exhibited by the distribution coefficient curve on p. 497. In our first communication (Trans., 1900, 77, 1239), we have shown that a complex compound, probably $Cu4NH_3{\cdot}SO_4$, is formed when excess of ammonia is added to a solution of copper sulphate; this complex compound is dissociable, and only when there is a large excess of ammonia in the solution does the number of fixed ammonia molecules per atom of copper approximate to four. We have been able to follow the extent of this dissociation at constant temperature with decreasing total ammonia concentration, and now we have endeavoured to ascertain the influence of temperature on the dissociation.

On account of the method which we employ, it was impossible to use a temperature much above the ordinary, and we have not deemed it advisable to work above 30°, which is our upper limit. For lower temperatures, we are only limited by the freezing point of the solution, but the lowest temperature at which we found it convenient to work was 10°. This gives us a range of 20°, and it was expected that the extent of dissociation at the lower and higher temperatures would be sufficiently different to indicate the temperature influence.

Distribution of Ammonia between Water and Chloroform at varying Temperatures.

The method of experimentation was exactly as has been described in our previous communications (*loc. cit.*). In order to ascertain the amount of ammonia fixed by the salt in solution from the distribution coefficient determined with this solution, it is necessary to know the distribution ratio between pure water and chloroform, and since this varies very considerably with the temperature, determinations of the latter had to be carried out at different temperatures. The temperatures chosen were 10° and 30°, and the following results were obtained :

Concentration of NH_3 in aqueous part. Grams per litre. c_1.	Concentration of NH_3 in the chloroform. Gram per litre. c_2.	Distribution coefficient, $\frac{c_1}{c_2}$. k.
Temperature 10° :		
5·211	0·1686	30·91
6·974	0·2261	30·84
8·123	0·2633	30·84
8·701	0·2847	30·57
12·835	0·4253	30·18
17·370	0·5854	29·67
17·428	0·5862	29·73
Temperature 30° : *		
5·092	0·2250	22·63
6·658	0·2949	22·57
8·497	0·3751	22·65
10·203	0·4558	22·39
11·660	0·5232	22 29
13·601	0·6133	22·18
16·660	0·7575	22·00

---

* In a previous publication (Trans., 1900, **77**, 1243), we have given the coefficient at 30° as 23·2, but we prefer to take the numbers given above for the reason pointed out on p. 496.

These figures show exactly the same relationships as those previously obtained for the distribution coefficient at 20° (this vol., p. 496), namely, for solutions less than 0·5 normal with respect to ammonia the distribution coefficient remains practically constant at constant temperature, but with more concentrated solutions this ratio diminishes with increasing concentration of the ammonia. The variation of the distribution coefficient within the same limits of ammonia concentration is very nearly the same at the three temperatures, consequently the curve given on p. 497 may be used to express the results obtained at 10° and 30° if we add to the ordinate 4·54, or subtract from it 3·66. In other words, the three curves representing the dependence of the distribution coefficient on the ammonia concentration at the different temperatures are almost parallel.

It is evident that the distribution coefficient at constant ammonia concentration is not a linear function of the temperature, for the difference in the coefficient for 10° (from 20° to 30°) is in one case 3·66 units, whilst in the other case, for 10° (from 10° to 20°), it is 4·54.

The results obtained have been plotted as curves (not reproduced here), and from these the values at any concentration of ammonia can be read off.

Experiments at 10° *and* 30° *with Copper Sulphate Solutions.*

At 10° and 30°, experiments were made with 0·1 normal copper sulphate solutions, and at 10° with 0·05 normal solutions. The results so obtained are recorded below, and they may be compared with those which we have previously found at 20°.

In the table on p. 1075 we give the various data, the molecules of ammonia fixed per molecule of salt (or per atom of copper) being calculated from the formula $\frac{c_1 - kc_2}{17{\cdot}07} \cdot \frac{2}{n}$, in which k is the distribution coefficient for pure water at the same concentration of ammonia in the chloroform, c_1 and c_2 the observed ammonia concentrations in the aqueous and chloroform layers, and n the normality of the salt solution. We are unable to take account of the physical action of the dissolved material, but, as already stated (p. 511), we believe this to be, in the case of copper salts, very small.

When the distribution coefficient attains a high value, corresponding to a small amount of free ammonia in the salt solution, the error in the determination of the fixed ammonia may be relatively large on account of the small quantity of acid used in the titration of the chloroform. Further, if the coefficient is not much greater than that for pure water, the accuracy is not great, since the calculation involves the difference between these two values. The most accurate values are those obtained when the concentration of ammonia in the aqueous phase is between 6 and 9 grams per litre. As no extreme accuracy can be claimed for the individual figures, we have drawn smoothed curves representing the molecular amount of ammonia fixed per atom of copper in 0·1 *N* solution at 10°, 20°, and 30° with varying ammonia concentration. The numbers for 20° have been recalculated in accordance with the later determina-

Concentration of NH_3 in aqueous layer. Grams per litre. c_1.	Concentration of NH_3 in $CHCl_3$. Gram per litre. c_2.	Distribution coefficient. k'.	Coefficient corresponding to c_2 for water. k.	Molecular ratio of $CuSO_4$: fixed NH_3. $\frac{c_1 - kc_2}{17\cdot07} \cdot \frac{2}{n}$.
Temperature 10°.				
0·1 *N* copper sulphate :				
5·427	0·0765	70·92	30·94	1 : 3·52
6·688	0·1153	58·01	30·91	3·66
7·171	0·1317	54·45	30·89	3·64
8·322	0·1679	49·56	30·88	3·68
8·931	0·1872	47·71	30·87	3·69
10·675	0·2446	43·65	30·82	3·67
13·130	0·3273	40·12	30·57	3·66
0·05 *N* copper sulphate :				
3·580	0·0666	53·76	30·94	3·56
5·347	0·1224	43·68	30·90	3·66
7·095	0·1786	39·73	30·87	3·70
9·800	0·2679	36·58	30·75	3·66
Temperature 30°.				
0·1 *N* copper sulphate :				
5·347	0·1072	49·86	22·66	3·42
7·062	0·1790	39·45	22·64	3·53
8·650	0·2441	35·44	22·62	3·66
10·310	0·3170	32·55	22·60	3·68
11·960	0·3915	30·55	22·52	3·68
13·720	0·4699	29·21	22·39	3·76

tions of the distribution coefficient between pure water and chloroform at this temperature. Instead of reproducing these curves, we have constructed the table given on p. 1076 indicating points on the curves.

As would be expected, the figures indicate that, at constant ammonia concentration, the extent of dissociation increases as the temperature rises, and it may be stated that if a comparison be made between the numbers obtained with 0·05 *N* copper sulphate solutions at 10° and 20°, the same conclusion is evident. The differences between the numbers obtained at the different temperatures are, however, too small to admit of any quantitative statement as to the influence of

Table showing the number of molecules of ammonia fixed per atom of copper in 0·1 *N solution.*

Concentration of NH_3 in the aqueous phase.	10°.	20°.	30°.
6 grams per litre	3·55	3·46	3·42
7 ,, ,, ...	3·63	3·55	3·51
8 ,, ,, ...	3·67	3·61	3·58
9 ,, ,, ...	3·70	3·67	3·62

temperature on the dissociation of the complex copper ammonia sulphate.

THE YORKSHIRE COLLEGE,
LEEDS.