AN INVESTIGATION OF AMMONIO-SILVER COMPOUNDS IN SOLUTION.

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I. INTRODUCTION.

This investigation was begun and in large part executed nearly three years ago at a time when much uncertainty existed in regard to the constitution of the ammonio-silver compounds in solution. Its completion and publication was, however, unavoidably delayed, and in the meantime other investigations have been published, which leave no reasonable doubt that these compounds have the formula $(Ag(NH_3)_2)^{\cdot}Cl'$, etc., the silver existing in dilute solution almost wholly in the form of the complex cation $Ag(NH_3)_2^{\cdot}$. This conclusion is confirmed by experiments based on a variety of different principles. Reychler[1] showed that the freezing-point of silver nitrate or sulphate solution is almost unaffected by the addition of ammonia until 2 mols have been added for each atomic weight of silver present, and that subsequent additions then produce the normal lowering, the same as in pure water. Konowalow[2] and Gaus[3] found that silver nitrate and chloride added to a solution of ammonia reduced the partial pressure of the ammonia gas to a value equal to that of a solution of pure ammonia of a concentration less by 2 mols of ammonia for each atomic weight of silver present. Berthelot and Delepine[4] proved by mixing dilute silver nitrate and ammonia solutions that no heat effect resulted upon adding either compound in excess of the amount corresponding to the ratio $1AgNO_3:2NH_3$. Finally Bodländer and Fittig[5] have made a thorough investigation of the solubility of silver chloride and bromide in ammonia solutions of various concentrations and that of the former salt in solutions containing both ammonia and potassium chloride or ammonia and silver nitrate, and by application of the Mass Action Law to the results have shown that the silver is present almost exclusively in the form of the compound $Ag(NH_3)_2^{\cdot}R'$ and its ions. They also

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[1] *Ber. d. chem. Ges.*, **28**, 555 (1895).

[2] *Ztschr. phys. Chem.*, **28**, 558 (1898).

[3] *Ztschr. anorg. Chem.*, **25**, 236 (1900).

[4] *Compt. Rend.*, **129**, 326 (1899).

Ztschr. phys. Chem., **39**, 597 (1901).

confirmed this conclusion by measuring the electromotive force of concentration elements composed of silver electrodes in two solutions containing the same concentration of silver nitrate or chloride and different concentrations of ammonia, or the reverse. From both the solubility and electromotive force values they derived the dissociation-constant of the complex ion with reference to its components (Ag and NH_3), and found it to be extremely small.

In spite of these numerous investigations on the subject, it has seemed to us that our own experiments were worthy of publication; first, because they furnish further evidence of the formation of the ion $Ag(NH_3)_2^{\cdot}$ by an entirely independent method—that of electrical transference; second, because many of the experiments involving principles previously applied were made with silver hydroxide instead of with silver salts, so that the data are new ones; and third, because, even when the same compounds and methods were used the confirmation of quantitative data by independent investigators is always of some value.

II. TRANSFERENCE EXPERIMENTS.

Since the conductivity and dissociation of ammonium hydroxide is very slight, and that of the silver and ammonio-silver compounds is comparable with that of other salts, the simple or complex silver ions will alone migrate to an appreciable extent when a solution containing both ammonia and silver salt is electrolyzed. If, therefore, such a solution is placed at the anode end of an electrolysis tube, the rest of which is filled with some other electrolyte (like sodium nitrate), and a current is passed through, and if after a sufficient time the ratio of silver to ammonia is analytically determined in the adjoining and more remote portions of the solution which originally contained neither of these substances, the composition of the complex ion can be determined, provided that only a single kind is formed, and that this does not undergo a considerable dissociation in the absence of its dissociation products.

Experiments of this nature have been made by us on ammonio-silver nitrate and sulphate, with solutions of each salt having two different ratios of ammonia to silver in the anode part of the tube. The apparatus used in these experiments has been previously described by A. A. Noyes.[1] It consists of two large glass U-tubes which have one of their arms bent at right angles and which are joined beyond the bends by a piece of soft rubber tubing. The inside arms were completely filled, and the outside arms were charged for about 1 cm. in one tube and 4 cm. in the other tube above the top of the lower bends, with a solution of the sodium salt, nitrate or sulphate, having a concentration of one-tenth mol per liter. On the side having the least solution, about 50 cc. of an ammonio-silver solution of known ratio of ammonia to silver and of a concentration in ammonia of 1 mol per liter was now added; and this, owing to its greater specific gravity, immediately sank into the bend. Methyl orange, which had been previously added to the ammonio-silver solution to color it yellow, showed the line of demarkation between the sodium salt solution and the ammonio-silver salt solution and served to give an indication of any possible stirring during the electrolysis. In the case of the nitrate, nitric acid and ammonia were added to the cathode and anode sides respectively, as the electrolysis proceeded, to neutralize the products of the electrolysis, while with the sulphate enough sulphuric acid and ammonia were added at first to neutralize all products which might be formed. Both of these methods of neutralizing the products of electrolysis were tested by electrolyzing a sodium salt solution alone, without the addition of the ammonio-silver solution; in these tests in the arm adjoining the anode the portions were found to remain entirely neutral. When after five hours the electrolysis was stopped, the portions numbered 1-3 were taken from the inside arm beginning Portion 1 about 1 cm. above the line of demarkation. These were analyzed by first titrating the ammonia with nitric acid and then precipitating the silver as chloride, filtering on Gooch crucibles and weighing after drying at 150°. The experimental data are given in Tables I and II. The ratios of the ammonia to silver are expressed in equivalents. The temperature was 25° in all cases. The current used was between 0.15 and 0.20 ampere.

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[1] This Journal, **23**, 42 (1901).

TABLE I.—TRANSFERENCE EXPERIMENTS WITH AMMONIO-SILVER NITRATE.

Expt. No.	Initial ratio $C_{NH_3} : C_{Ag}$ at anode.	Portion. No.	Weight of portion.	Weight of AgCl obtained.	Cc. 0.4625 N HNO_3 used.	Ratio $C_{NH_3} : C_{Ag}$.
1	2.5	1	50	0.5729	17.84	2.065
		2	50	0.5517	17.06	2.051
		3	54	0.3062	9.27	2.008
2	2.5	1	45	0.4784	14.85	2.059
		2	57	0.5921	18.27	2.046
		3	71	0.4850	14.93	2.042
3	3.5	1	40	0.3873	11.99	2.052
		2	48	0.4193	12.79	2.023
		3	61	0.2003	6.19	2.054
4	3.5	1	45	0.4613	14.59	2.097
		2	49	0.5016	15.85	2.096
		3	61	0.4929	15.48	2.082
5	3.5	1	38	0.3990	12.48	2.074
		2	49	0.4882	15.29	2.077
		3	57	0.3722	11.57	2.062

TABLE II.—TRANSFERENCE EXPERIMENTS WITH AMMONIO-SILVER SULPHATE.

Expt. No.	Initial ratio $C_{NH_3} : C_{Ag}$. at anode.	Portion No.	Weight of portion.	Weight of AgCl obtained.	Cc. 0.2006 N HNO_3 used.	Ratio. $C_{NH_3} : C_{Ag}$.
1	2.5	1	41	0.5065	37.34	2.121
		2	67	0.4862	34.47	2.040
		3	68	0.1034	7.24	2.015
2	2.5	1	41	0.4032	29.57	2.110
		2	59	0.5485	38.44	2.017
		3	68	0.1637	11.29	1.985
3	2.5	1	56	0.5173	37.32	2.075
		2	58	0.4065	28.10	1.989
		3	74	0.0414	2.81	1.95
4	3.5	1	49	0.1700	13.83	2.289
		2	48	0.1377	10.78	2.258
		3	67	0.0616	4.46	2.083
5	3.5	1	45	0.2352	19.91	2.435
		2	44	0.2032	14.95	2.117
		3	62	0.0631	4.47	2.038
6	3.5	1	65	0.5041	40.92	2.335
		2	57	0.3976	29.32	2.121
		3	69	0.0757	5.57	2.117

The atomic ratio of ammonia to silver in each experiment with the ammonio-silver nitrate is almost the same in all portions, but it does have a slightly larger value in the portion nearest the ammonio-silver solution at the anode. This mean value of the ratio is 2.045 when the original ratio is 2.5, and 2.069 when it is 3.5.

The atomic ratio in the experiments with ammonio-silver sulphate is always higher in the portion adjoining the anode portion than in the more remote ones and considerably larger than 2.0. It is doubtful whether this has any significance, however, for that portion may have been influenced mechanically by the anode portion. The mean value of the ratio in Portions 2 and 3 is 2.000 in the experiments where the original ratio at the anode was 2.5, and 2.122 in those where that ratio was 3.5.

It is evident from all these results that the ammonio-silver ion must have the formula $Ag_n(NH_3)_{2n}$. This is therefore a confirmation of the conclusion drawn from the results by other methods. These experiments furnish, of course, no indication as to the value of *n* in the formula.

III. FREEZING-POINTS OF SOLUTIONS OF SILVER HYDROXIDE AND AMMONIA.

The silver oxide, used in the freezing-point and conductivity experiments, was prepared from clear crystals of silver nitrate and chlorine-free potassium hydroxide. It was precipitated from boiling solution and washed with boiling water. Its freedom from silver chloride was proved by dissolving it in nitric acid and subsequently diluting. The ammonia used was made by diluting the commercial chemically pure ammonia of specific gravity 0.90.

The freezing-point determinations were made with the Beckmann apparatus, the usual precautions with reference to the quantity of ice separated and the temperature of the outer bath being observed. The solutions used in the experiments numbered 1-15 in the following table were obtained by saturating ammonia solutions of various concentrations with silver oxide at 25° ; the analytical data in regard to them will be found in Table V under the section on Solubility Experiments. The solutions used in the experiments numbered 21 and 22 were not saturated, and were prepared especially for the freezing-point work.

The first column in the table gives the experiment numbers, which correspond to those in Table V. The second and third columns contain the concentrations in mols of silver and ammonia per 1000 grams of water, calculated on the assumption that the silver exists as $Ag(NH_3)_2OH$ and the remaining ammonia as NH_4OH. The fourth column contains the actual freezing-point of the ammonio-silver solution, while in the fifth column is the freezing-point of the ammonia solution of equivalent concentration, calculated with the constant, 18.6. The rise in freezing-point caused by the addition of silver oxide is given in column 6; and the corresponding decrease in the number of mols present, calculated by using 18.6 as the molecular lowering, is given in column 7.

TABLE III.—FREEZING-POINTS OF AQUEOUS SOLUTIONS OF SILVER HYDROXIDE AND AMMONIA.

			Freezing-points.			
Experiment No.	Mols AgOH per liter.	Mols NH_3 per liter.	Ammonio-silver solution.	Pure ammonia solution.	Difference.	Decrease of mols present.
1	0.0654	0.214	0.378	0.395	0.017	0.009
2	0.0658	0.220	0.388	0.407	0.019	0.010
3	0.134	0.458	0.838	0.846	0.008	0.004
4	0.140	0.469	0.856	0.866	0.010	0.005
5	0.205	0.671	1.228	1.238	0.010	0.005
6	0.205	0.684	1.244	1.261	0.017	0.009
9	0.251	0.811	1.460	1.496	0.036	0.019
10	0.248	0.827	1.506	1.527	0.021	0.011
11	0.242	0.830	1.500	1.531	0.031	0.017
12	0.257	0.876	1.588	1.616	0.028	0.015
13	0.278	0.899	1.616	1.659	0.043	0.023
15	0.299	0.999	1.820	1.843	0.023	0.012
21	0.111[1]	0.405[1]	0.734	0.748	0.014	0.008
22	0.151[2]	1.063[2]	1.948	1.964	0.016	0.009

A consideration of the magnitude of the values given in column 6 shows that the freezing-point is only very slightly raised even by the addition of considerable quantities of silver oxide. A comparison of columns 3 and 7 shows that the number of molecules, which have disappeared on the addition of silver hydroxide is only, in the extreme case, 4 per cent. of the total number of molecules present. This change is so small that the number of

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[1] Ten grams of this solution required 10.67 cc. of 0.4715 normal hydrochloric acid for its neutralization and yielded 0.1554 gram of silver chloride.

[2] Fifty grams of this solution required 122.71 cc. of 0.4715 normal hydrochloric acid for its neutralization and yielded 1.0294 grams of silver chloride.

molecules may be said to be unchanged by the solution of silver oxide in the solution. It is evident that this fact is consistent with the formation of the compound $Ag(NH_3)_2OH$ only under the assumption that the dissociation of this compound is substantially complete. In that case for every 2 molecules of ammonia which disappear, 2 new molecules, $Ag(NH_3)_2^{\cdot}$ and OH', are formed. As there were no existing data on the conductivity of ammonio-silver hydroxide, we have investigated it in this direction.

IV. CONDUCTIVITY OF AMMONIO-SILVER HYDROXIDE.

The saturated solution of Experiment 15 (Tables III and V) and four dilutions of it made outside of the resistance cell by means of graduated flasks were used for the conductivity measurements. The ratio $NH_3:Ag$ in this solution was 3.35. As the ammonio-silver hydroxide proved to be a highly dissociated base, the excess of ammonia could have, in its presence, no appreciable conductivity of its own, and it served to reduce any tendency of the complex ion to dissociate into its components. The measurements were made by the usual method of Kohlrausch at a temperature of 24.75°. The conductivities are expressed in reciprocal ohms. The cell-constant determined by means of $^1/_{50}$ molar potassium chloride was 954.8. The results are presented in the following table.

TABLE IV.—EQUIVALENT CONDUCTIVITY OF AMMONIO-SILVER HYDROXIDE.

Liters per mol.	Actual conductivity.	Equivalent conductivity.
3.35	0.0610	194.8
6.69	0.0314	200.5
13.38	0.0159	203.3
26.75	0.00804	205.3
53.50	0.00403	205.8

The equivalent conductivity of completely dissociated silver hydroxide is at this temperature, according to Kohlrausch's values for the separate ion, 258.5.[1] This value is of the same order of magnitude as those given in the table, and it proves that the ammonio-silver hydroxide unlike ammonium hydroxide is a largely dissociated base. This conclusion is further confirmed by the fact that its equivalent conductivity changes only very slightly with increasing dilution. The difference between its value in

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[1] See *Sitzungsber. kön. preuss. Akad. der Wissenschaft*, (1901), p. 1031.

$^1/_{53\cdot 5}$ molar solution and that of completely dissociated silver hydroxide may well be wholly due to the slower rate of migration of the complex ion and to the usual small proportion of undissociated molecules present at such concentrations even in the case of highly dissociated bases like potassium hydroxide.

The facts that this complex base is nearly completely dissociated and that the freezing-point of ammonia solutions does not change on dissolving silver hydroxide in them show that the composition of the complex compound must be represented by the formula $Ag_n(NH_3)_{n+1}(OH)_n$; for when $(n+1)$ molecules of NH_4OH disappear through combination, this formula evidently requires that $(n+1)$ be reproduced, namely n molecules of OH' and 1 molecule of $Ag_n(NH_3)_{n+1}$.

V. SOLUBILITY OF SILVER OXIDE, CHLORIDE, AND BROMIDE IN AQUEOUS AMMONIA SOLUTIONS.

The silver oxide was prepared as described in Section 3. The silver chloride was prepared in a dark room from silver nitrate crystals by precipitation with potassium chloride, which had been previously twice crystallized from hot water. It was then washed free from chlorides. The silver bromide was made from potassium bromide, which had been boiled for half an hour with bromine to expel all iodine and then crystallized from solution. After washing it free from soluble bromides, it was rotated in a bottle with two successive portions of half-normal ammonia to dissolve any chloride present. The ammonia was made by the distillation from potassium hydroxide of commercial ammonia.

The solutions were saturated by rotating them for six hours or more in the solubility apparatus described by Noyes,[1] the temperature of the bath being kept constant within 0.05°. In the cases of the silver chloride and bromide experiments, the state of saturation was approached both from the undersaturated and the supersaturated side, the two procedures being distinguished by the letters *u* and *s* in the tables below. Since the solubility is greater the lower the temperature, in the former procedure the silver compound was added to the ammonia solution only after it had been brought to the temperature of the bath; in the latter, the solutions were first shaken at 18° for fifteen minutes with an

[1] *Ztschr. phys. Chem.*, 9, 606 (1892).

excess of the salt and then rotated in the thermostat. In the case of silver oxide, the oxide was added to the ammonia at room temperature and then immediately placed in the thermostat for rotation. The experiments were all made at 25°, except that two were made with silver oxide at 0° for the purpose of orientation.

The results are given in Tables V to VII, which are sufficiently explained by the headings.

It will be seen that in the experiments with silver oxide the ratio $C_{NH_3} : C_{Ag}$ is constant within the experimental error throughout the whole range of concentration, even though that of the ammonia varied from about 0.2 to 1.5 molar. In other words, within these limits of concentration the quantity of silver dissolved is almost exactly proportional to the quantity of ammonia in the solution. It has already been shown by Bodländer and Fittig[1] that, assuming the complex compound to be completely dissociated into its two ions, this constancy of the ratio is predicted by the Mass Action Law for any compound of the formula $Ag_n(NH_3)_{n+1}R_n$ and only for one of that formula. As the conductivity measurements of Table IV show that the undissociated portion is relatively small, this constant ratio shows beyond a doubt that the compound in question has this general formula.[2] The mean value of the ratio is 3.314.

In the case of the silver chloride the ratio $C_{NH_3} : C_{Ag}$ varies continuously in value from 13.5 when the ammonia is 2.0 molar to 20.0 when it is 0.028 molar. However, as the solution becomes more and more dilute the values become more nearly constant; and by plotting them a limiting value of 20.20 for the ratio in very dilute solution was obtained.

These results agree fairly well with those of Bodländer and Fittig, who found for 0.1 molar ammonia the ratio 19.7 (our

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[1] *Ztschr. phys. Chem.*, **39**, 598.

[2] It is true, to be sure, that the constancy of the ratio $C_{NH_3} : C_{Ag}$ is much more perfect than would be expected theoretically; for a few per cent. of the undissociated compound must be present even in the most dilute saturated solution, and the absolute quantity of this should increase proportionally to the $(n + 1)$ power (instead of the first power) of the concentration of the free ammonia, and thus diminish the value of the ratio. That it does not do so is probably to be attributed partly to the same cause, whatever it may be, that makes strong electrolytes deviate in the same sense from the theoretical dilution law. It may be due in part to a compensation of the theoretical solubility increase by a decrease in solvent power in the more concentrated solutions. How considerable this last may be is shown by the experiments of Konowalow (*Ztschr. phys. Chem.*, **35**, 376) and of Rothmund and Wilsmore (*Ibid.*, **41**, 619).

TABLE V.—SOLUBILITY OF SILVER OXIDE IN AQUEOUS AMMONIA SOLUTIONS.

Expt. No.	Weight of solution analyzed.	Weight of AgCl obtained.	Cc. of 0.4715 N HCl used.	C_{Ag} = atomic weights of silver per liter.	C_{NH_3} = mols NH_3 (total) per liter.	Ratio $C_{NH_3}:C_{Ag}$.
1	9.18	0.0850	5.37	0.0654	0.214	3.272
2	9.87	0.0917	5.90	0.0658	0.220	3.351
3	10.04	0.1877	12.26	0.134	0.458	3.420
4	9.99	0.1943	12.53	0.140	0.469	3.361
5	10.09	0.2847	18.00	0.205	0.671	3.275
6	9.97	0.2807	18.03	0.205	0.684	3.343
7	14.66	0.4531	28.11	0.225	0.720	3.196
8	13.15	0.4049	25.54	0.224	0.733	3.264
9	10.10	0.3462	21.68	0.251	0.811	3.236
10	10.14	0.3432	22.41	0.248	0.827	3.336
11	14.25	0.4717	30.84	0.242	0.830	3.424
12	14.36	0.5025	32.80	0.257	0.876	3.402
13	10.07	0.3800	23.80	0.278	0.899	3.237
14	9.97	0.3730	23.82	0.276	0.915	3.320
15	25.48	1.0294	66.11	0.299	0.999	3.344
16	10.08	0.4640	29.80	0.343	1.147	3.343
17	10.55	0.6312	40.10	0.454	1.498	3.298
18	10.73	0.6612	41.40	0.470	1.522	3.235
19[1]	....	1.0382	54.02	....	....	2.519
20[1]	....	0.7894	41.39	....	....	2.545

TABLE VI.—SOLUBILITY OF SILVER CHLORIDE IN AQUEOUS AMMONIA SOLUTIONS.

Expt. No.	Weight of solution analyzed.	Weight of AgCl obtained.	Cc. of 0.4625 N HNO_3 used.	C_{NH_3} = mols NH_3 (total) per liter.	C_{Ag} = atomic weights of silver per liter.	Ratio $C_{NH_3}:C_{Ag}$.	Method of saturation.
1	47.81	0.9471	193.83	2.042	0.151	13.57	*u*
2	47.01	0.9264	188.76	2.017	0.149	13.51	*u*
3	48.05	0.9431	192.23	2.013	0.149	13.51	*s*
4	46.48	0.9026	184.10	1.991	0.147	13.51	*s*
5	49.24	0.4189	98.51	0.961	0.0616	15.59	*u*
6	47.76	0.3849	91.23	0.916	0.0583	15.71	*u*
7	47.69	0.3850	90.49	0.909	0.0584	15.59	*u*
8	47.93	0.3797	90.37	0.903	0.0572	15.78	*s*
9	48.71	0.3838	91.08	0.896	0.0569	15.73	*s*
10	49.76	0.3825	90.78	0.873	0.0555	15.73	*u*

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[1] These two experiments were made at 0° instead of 25°.

Expt. No.	Weight of solution analyzed.	Weight of AgCl obtained.	Cc. of 0.4625 N HNO_3 used.	C_{NH_3} = mols NH_3 (total) per liter.	C_{Ag} = atomic weight of silver per liter.	Ratio C_{NH_3} : C_{Ag}	Method of saturation.
11	48.63	0.3487	83.95	0.863	0.0541	15.97	*s*
12	49.16	0.3507	84.27	0.818	0.0514	15.93	*s*
13	74.52	0.2618	67.95	0.428	0.0249	17.23	*s*
14	76.19	0.2582	67.63	0.416	0.0240	17.37	*s*
15	72.02	0.2338	61.72	0.411	0.0235	17.50	*u*
16	74.89	0.2403	63.43	0.397	0.0227	17.51	*u*
17	144.6	0.2880	78.54	0.253	0.0140	18.08	*u*
18	141.8	0.2830	76.89	0.253	0.0140	18.02	*s*
19	143.7	0.2867	77.66	0.252	0.0140	17.95	*s*
20	142.0	0.2819	76.68	0.252	0.0139	18.04	*u*
21	525.8	0.4656	308.9	0.118	0.00621	18.82	*s*
22	529.1	0.4685	310.1	0.118	0.00621	19.04	*u*
23	504.7	0.4451	295.4	0.118	0.00619	19.09	*u*
24	515.0	0.4590	300.2	0.118	0.00625	18.82	*s*
25	548.6	0.2380	160.8	0.0590	0.00304	19.43	*u*
26	538.0	0.2287	157.6	0.0589	0.00297	19.73	*s*
27	551.9	0.2370	160.5	0.0585	0.00300	19.49	*s*
28	521.2	0.1114	74.73	0.0288	0.00149	19.31	*s*
29	517.8	0.1060	74.01	0.0287	0.00143	20.09	*u*
30	549.3	0.1115	77.96	0.0285	0.00142	20.12	*s*
31	518.1	0.1047	72.73	0.0282	0.00141	19.99	*u*

TABLE VII.—SOLUBILITY OF SILVER BROMIDE IN AQUEOUS AMMONIA SOLUTIONS.

Expt. No.	Weight of solution analyzed.	Weight of AgBr obtained.	Cc. of 0.2002 N HNO_3 used.	C_{NH_3} = mols NH_3 (total) per liter.	C_{Ag} = atomic weights of silver per liter.	Ratio C_{NH_3} : C_{Ag}.	Method of saturation.
1	605.6	0.1901	1483.0	0.450	0.00170	293.9	*u*
2	591.5	0.1740	1440.0	0.497	0.00159	311.9	*u*
3	617.9	0.1082	817.4	0.268	0.000941	284.7	*u*
4	616.1	0.1223	831.2	0.273	0.00107	256.2	*u*
5	622.3	0.0455	355.8	0.115	0.000391	294.7	*u*
6	625.5	0.0451	365.3	0.118	0.000386	298.3	*u*
7	611.9	0.0316	232.2	0.0764	0.000276	277.0	*u*
8	613.1	0.0303	236.8	0.0777	0.000264	294.5	*u*

value 19.1); for 0.5 molar, the value 18.8 (our value 17.0); for 1.0 molar, the ratio 15.8 (our value 15.5); and for 1.9 molar the ratio 14.0 (our value 13.7).

The fact that this considerable variation in the value of the ratio takes place with the chloride, while there is practically no variation with the oxide, is difficult of explanation. Since ammonium hydroxide is very slightly dissociated and both ammonio-silver hydroxide and ammonium chloride are strongly dissociated, not more than 2-3 per cent. of these latter compounds could be formed by metathesis; and this could therefore not account for the variation. The formation of undissociated ammonio-silver chloride might explain it; but it would be necessary to assume a much larger proportion of it than is usual with di-ionic salts, since the maximum concentration of the complex salt is only 0.15 molar.

In the case of silver bromide where the concentration of the dissolved silver is very small, the ratio shows no progressive variation with the concentration of the ammonia, though this varied from 0.08 to 0.45 molar. Thus for this salt the constancy required by the formula $Ag(NH_3)_{n+1}(OH)_n$ is fulfilled. The mean value of the ratio is 288.8. Bodländer and Fittig, who carried the determinations up to a higher concentration, obtained for the ratio the constant value 321 for ammonia concentrations between 0.193 and 0.574 molar, while for 1.97 molar and for 3.02 molar, the values found were 284 and 260 respectively.

We will next compare the results obtained with the three different silver compounds. It has been shown by Bodländer and Fittig (p. 604 of their article) that, if the electrolytic dissociation is complete and the formula of the complex ion is $Ag(NH_3)_2$, and only in the case of this formula, will the constant ratio of dissolved silver to uncombined ammonia, that is, the ratio $C_{Ag} : (C_{NH_3} - 2C_{Ag})$, in the case of different silver salts, be directly proportional to the solubility of the salts in pure water. And they showed that the results with silver chloride and bromide conformed to this requirement of the theory. As we have investigated a third compound (silver oxide), it is of interest to make a similar comparison in the case of the three compounds. From our values of the ratio $C_{NH_3} : C_{Ag}$ which are 3.314, 20.20, and 288.8 for the oxide, chloride, and bromide, respectively, we get for the ratio $C_{Ag} : (C_{NH_3} - 2C_{Ag})$ the values $^1/_{1.314}$, $^1/_{18.20}$, and $^1/_{286.8}$. These ratios have been divided by one another in pairs, and the quotients are given in the column headed "ammonia solution" in the table below. The corresponding quotients for the solubilities in pure water are given in the column headed "pure water". The values of the separate solubilities which are used are for silver oxide[1] 216×10^{-6}, for silver chloride,[2] 15.0×10^{-6}, and for silver bromide,[3] 0.71×10^{-6}.

	Ammonia solution.	Pure water.
AgOH : AgCl	13.86	14.40
AgOH : AgBr	218.3	304.2
AgCl : AgBr	15.76	21.13

The agreement of the two values is fairly close in the case of the AgOH:AgCl ratio. In the other ratios, which involve silver bromide, the values are more discordant, owing undoubtedly mainly to an error in the value of the solubility in pure water of this very difficultly soluble salt. If, conversely, this solubility is calculated from those of the other two silver salts in pure water and the ammonia solution ratios, it is found to be $0.99 \times 10^{\;6}$ when the silver oxide is used as a basis, and 0.95×10^{-6} when the silver chloride is so used. The agreement is remarkably good. The mean of these values (0.97×10^{-6}) is probably nearer the truth than that obtained by the conductivity method. Bodländer and Fittig's results and calculations on the relative solubilities in ammonia of the bromide and chloride lead to the value 0.86×10^{-6}, if the solubility of the chloride in water is taken as 15.0×10^{-6}. By the conductivity measurements, Holleman (1893) found 3.3×10^{-6}, Kohlrausch and Rose 2.1×10^{-6}, and Kohlrausch and Dolazalek (1901) 0.71×10^{-6}. By electromotive force measurements Goodwin (1894) found 0.66×10^{-6} and Thiel (1900) 0.81×10^{-6}.

In conclusion, attention may be called to the significance of the experiments on the solubility of silver oxide in ammonia at 0°. The ratio $C_{NH_3} : C_{Ag}$ was found by the two experiments recorded in Table V to have the value 2.53, which is much less than that

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[1] Noyes and Kohr: This Journal, **24**, 1146.

[2] Kohlrausch and Rose: *Ztschr. phys. Chem.*, **12**, 242 (1893).

[3] Kohlrausch and Dolazalek: *Sitzungsber. kön. preuss. Akad. der Wissenschaft* (1901), p. 1018.

(3.31) at 25°. In other words, the solubility of silver oxide in ammonia is much greater at 0° than at 25°. This might be due wholly or in part to an increase in the solubility of silver oxide in pure water with decrease of temperature: but this is not the case; for the heat of neutralization of silver oxide with dilute nitric acid is, according to Berthelot, 5,200 calories, while dissolved and completely dissociated bases give the value 13,700 calories, whence it follows that the heat of solution of silver oxide in water is attended by a large absorption of heat, and therefore that its solubility must increase with rise of temperature. The results at 0° therefore show that the complex ion $Ag(NH_3)_2$ is very much more stable at that temperature than at 25°. This is in agreement with the fact, established by Berthelot and Delepine,[1] that a considerable evolution of heat occurs upon mixing dilute silver nitrate and ammonia solutions.

VI. SUMMARY.

It has been shown by this investigation:

(1) That, when an electric current is passed from a solution containing ammonia and silver nitrate or sulphate into an adjoining solution of a neutral sodium salt, an ion of the formula $Ag_n(NH_3)_{2n}$ migrates into the latter solution.

(2) That the freezing-point of ammonia solutions is not changed by dissolving silver oxide in them.

(3) That the equivalent conductivity of ammonio-silver hydroxide is of such magnitude, and changes so slowly with increasing dilution as to show that this compound is nearly completely dissociated.

(4) That it follows from the two facts last stated that ammonio-silver hydroxide has the formula $Ag_n(NH_3)_{n \div 1}{}^{\cdot}(OH)_n$.

(5) That the solubility at 25° of silver oxide in ammonia solutions is almost exactly proportional to the concentration of the latter between the investigated limits of 0.2 and 1.5 molar; this fact also is consistent only with the formula given in 4. The ratio of the solubility to the ammonia concentration is 1:3.31, both being expressed in equivalents.

(6) That the ratio of the solubility of silver chloride to the concentration of the ammonia decreases (from the initial value

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[1] *Compt. Rend.*, **129**, 326 (1899).

1 : 13.5 at 2.0 molar) as the concentration of the latter decreases, but finally attains at a moderate dilution (about 0.025 molar) a nearly constant value (1 : 20.2).

(7) That the solubility of silver bromide as previously found byBodländer and Fittig is proportional to the concentration of the ammonia between the limits of 0.08 and 0.45 molar, and that the ratio has the value 1 : 289. The constancy of this ratio is in correspondence with the requirement of the formula $Ag_n(NH_3)_{n+1}Br'_n$.

(8) That the ratio of the solubilities in dilute ammonia of silver oxide and chloride is the same as the ratio of their solubilities in water, as the formula $Ag(NH_3)_2 \cdot R'$ alone requires.

(9) That the solubility of silver bromide in water at 25°, is found to be 0.99×10^{-6} and 0.95×10^{-6} when calculated under the assumption of proportionality, from the relative solubilities in ammonia of silver bromide and oxide on the one hand and of silver bromide and chloride on the other.

(10) That the solubility of silver oxide in ammonia is much greater at 0° than at 25°, though the reverse is true of its solubility in pure water; and that this is due to a much slighter dissociation-tendency of the complex ion into its components at the lower temperature.

It is our agreeable duty at this point to express our sincere thanks to Prof. A. A. Noyes for his very considerable assistance and continual interest in this investigation.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
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THE ELECTROLYTIC ESTIMATION OF BISMUTH AND ITS SEPARATION FROM OTHER METALS.[1]

BY ALFRED LEWIS KAMMERER.

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INTRODUCTION.

IN determining bismuth by the ordinary gravimetric methods many difficulties confront the analyst. These limitations led the author to give attention to the estimation of this metal in the electrolytic way.

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[1] From the author's thesis for the degree of Ph.D., 1901.