249. *Electrometric Studies of the Precipitation of Hydroxides. Part XI. The Constitution of Ammoniacal Solutions of* (a) *Silver Nitrate,* (b) *Silver Oxide.*

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THE present paper is a continuation of the earlier work of Britton (J., 1925, **127**, 2956), in which an attempt was made to follow by means of oxygen electrodes, the variations in p_H caused during precipitation and complex-ion formation when ammonia is added to solutions of silver nitrate. By using the more accurate glass electrode, it is now shown that not only does the complex kation $Ag(NH_3)_2^{\cdot}$ exist in ammoniacal silver nitrate solutions, but that the salt $Ag(NH_3)_2NO_3$ is formed, which is not materially decomposed by an excess of free ammonia. Such a salt should therefore be that of a base $Ag(NH_3)_2OH$, which is appreciably stronger than ammonium hydroxide. Glass-electrode titrations of ammoniacal solutions of silver oxide prove conclusively that such a base is formed, and moreover, that it is considerably stronger than ammonia. Other evidence has been obtained from solubility and conductivity determinations, and measurements of the potentials of silver electrodes immersed in the complex solutions.

EXPERIMENTAL.

In the previous paper it was shown that the addition of ammonia to silver nitrate solution in equivalent proportions caused maximum precipitation of silver oxide, which, however, was only 7·3%. As it was not then realised that the particular concentrations used had any effect on the extent of precipitation, the estimations were performed on more concentrated solutions than those used in the oxygen-electrode titrations. From solutions of the concentrations, 0·02*N*-silver nitrate and 0·10*N*-ammonia, the precipitation at any stage never becomes more than a faint cloudiness, which could not be estimated with accuracy. Table I gives the percentage amounts of silver oxide precipitated by using (*a*) 0·1*N*- and (*b*) *N*-solutions of each reagent. The estimations were made by filtering off silver oxide and precipitating the silver as chloride from the mother-liquors.

TABLE I.

$\frac{\text{Mols. } NH_4OH}{\text{Mols. } AgNO_3}$	0·10	0·25	0·50	0·75	1·00	1·25	1·50	1·75	1·90	2·0
% Ag pptd. (*a*)	5·35	5·99	7·68	8·72	8·83	8·68	8·16	6·41	3·37	0
% Ag pptd. (*b*)	—	—	7·81	—	9·68	—	7·95	—	—	0

The p_H during the progressive addition of sodium and ammonium hydroxides to silver nitrate solutions has been measured by means of glass electrodes, a condenser and ballistic galvanometer being used. Curves I and II in Fig. 1 give the changes during the titration of 100 c.c. of (I) 0·02*N*- and (II) 0·1*N*-silver nitrate with 0·1*N*-sodium hydroxide at 18°, and by calculating the silver-ion concentration at different stages on the basis of α derived from Kohlrausch and Steinwehr's conductivity data (*Sitzungsber. Berlin Akad.*, 1902, 581) and the hydroxyl-ion concentration from the observed p_H values, it has been found that the two curves correspond to the values $1{\cdot}29 \times 10^{-8}$ and $1{\cdot}20 \times 10^{-8}$ respectively, for the solubility product $[Ag^{\cdot}][OH']$ (cf. Britton and Robinson, *Trans. Faraday Soc.*, 1932, **28**, 539). The remaining curves in Fig. 1 refer to glass electro-titrations of 100 c.c. of silver nitrate (curve III, 0·02*N*-; curve IV, 0·1*N*-; curve V, 0·1*N*-silver nitrate + 0·0109*M*-ammonium nitrate) with 0·1*N*-ammonia. The uppermost curve shows the variation in specific conductivity after the attainment of equilibrium at 25° of a series of solutions, 0·05*M* with respect to silver nitrate, and containing different amounts of ammonia corresponding to various stages of the reaction. The bottom curve corresponds to a similar set of solutions and gives the variations in silver-ion concentration, measured by means of the combination

$$Ag \mid 0{\cdot}05N\text{-}AgNO_3 + xM\text{-}NH_4OH \mid \text{Satd. } KNO_3 \mid N\text{-}Hg_2Cl_2$$

(see also Table II)

In general, the p_H values set up directly the ammonia was added showed but very little difference, if any, from those that had been measured after the reaction mixtures had been agitated for several days. Curve III shows that higher p_H values than in the corresponding sodium hydroxide reaction (Curve I) were set up, whereas with the more concentrated solutions represented by IV and II no such difference in p_H was observed. Both III and IV indicate that after 1 mol. of ammonia had reacted with 1 mol. of silver nitrate there was a slightly more rapid increase in p_H until 2 mols. had been added, whereupon fairly definite increases occurred. These corresponded to the dissolution of the little silver oxide that had been precipitated, and also to the formation of the complex salt, $Ag(NH_3)_2NO_3$, in solution. The solution used to give Curve V had included in it just sufficient ammonium nitrate to prevent any precipitation of silver oxide occurring, and it will be seen that this is reflected in the lower p_H values prevailing during the addition of 2 mols. of ammonia. The inflexion at 2 mols., however, reveals that the same complex salt had been formed. The p_H values established in each of these titrations after the addition of 2 mols. of ammonia were due almost entirely to the added ammonia, for calculations always showed that less than 6% of the ammonium nitrate which would have been produced if simple metathesis had resulted from the interaction of ammonia with silver nitrate was actually formed. This will be seen from Table II, in which are recorded the specific conductivity, p_{OH}, and p_{Ag} of a series of solutions, 0·05*N*-silver nitrate and *xM*-ammonia, in which equilibrium had been attained.

FIG. 1.

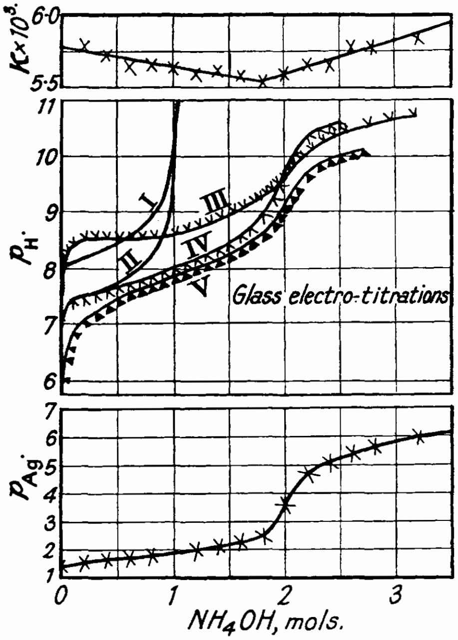

FIG. 2.

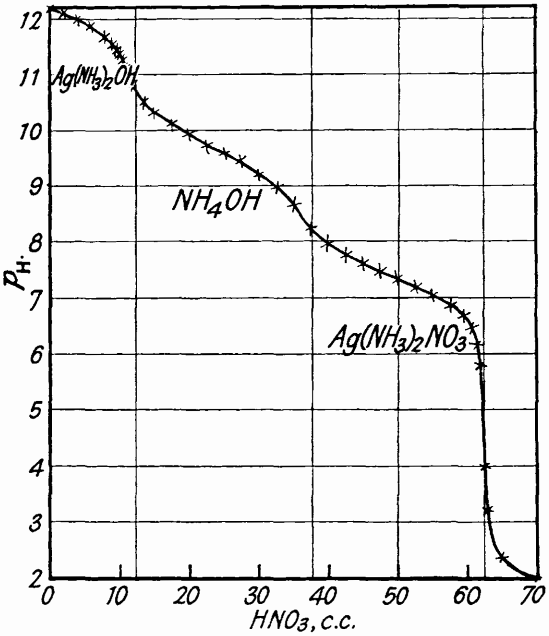

TABLE II.

x	0·02	0·04	0·06	0·08	0·10	0·12	0·14	0·16	0·18	0·20
NH_4OH, mols.	0·4	0·08	1·2	1·6	2·0	2·4	2·8	3·2	3·6	4·0
$\kappa\times10^3$, mhos	5·74	5·71	5·59	5·58	5·58	5·65	5·78	5·84	5·88	5·98
p_{OH}	6·43	6·26	6·03	5·65	4·43	3·72	3·48	3·38	3·31	3·17
$[NH_4NO_3]/[NH_4OH]$	—	—	—	—	—	0·105	0·060	0·048	0·041	0·030
NH_4NO_3, %	—	—	—	—	—	4	5	5	7	6
E_{Ag} (H=0) mv.	708	699	688	673	597	515	480	460	443	435
p_{Ag}	1·64	1·79	2·00	2·24	3·57	5·01	5·63	5·97	6·27	6·42
p_{Ag} (calc.)	1·48	1·65	1·88	2·26	3·48	—	—	—	—	—
p_K	—	—	—	—	—	7·11	7·13	7·13	7·17	7·12

The ratios $[NH_4NO_3]/[NH_4OH]$ were calculated from the usual mass-law expression and $p_{K_{NH_4OH}} = 4·70$. In arriving at the percentage amounts of ammonium nitrate, it was considered that the total reaction came to an end with 2 mols. of ammonia and that therefore all the additional ammonia existed in solution as such.

The *E.M.F.* data with the silver electrode were obtained at 15°, and the normal electrode potential (H = 0) of the electrode used was 0·799 volt. As the mother-liquors during the reaction with the first 2 mols. of ammonia had reached equilibrium with precipitated silver oxide, it appeared that one factor governing the hydroxyl-ion concentration was the solubility product $[Ag^{\cdot}][OH']$. From the average value, $1{\cdot}24 \times 10^{-8}$, given above, and the different p_H values, the p_{Ag} values were calculated. These are given in the lower part of Table II, and are in fair agreement with those actually measured. On comparing the $[Ag^{\cdot}]$ curve in Fig. 1 with the titration curve in Fig. 1 in the previous paper, it will be observed that, by allowing time for the attainment of equilibrium, as shown by the present curve, there results a better defined inflexion with 2 mols. of ammonia. Moreover, an almost identical curve was obtained when sufficient ammonium nitrate was included in the solution to prevent precipitation (cf. Glasstone, J., 1932, 2849).

The figures for p_K in Table II are those of the " instability constant," $K = [Ag^{\cdot}][NH_3]^2/[Ag(NH_3)_2^{\cdot}]$, for the dissociation of the kation, $Ag(NH_3)_2^{\cdot}$. The average p_K value, 7·13, though of the same order, is somewhat greater than the value previously obtained, possibly on account of equilibrium being obtained. A similar value, *viz.*, p_K 7·18, was obtained with solutions in which the ammonium nitrate had been included. Moreover, the p_{OH} values corresponding to the addition of an excess of ammonia to a 0·1*N*-silver nitrate + 0·0109*N*-ammonium nitrate solution revealed that very little ammonium nitrate had been formed as the result of the reaction. Thus on addition of 2·6 mols. of ammonia the p_{OH} was 4·05, and therefore $[NH_4NO_3]/[NH_4OH] =$ 0·22, the total ammonium nitrate = 0·134 mol. (*i.e.*, per mol. of silver nitrate), whence it follows that 0·025 mol. of ammonium nitrate had been formed in the reaction.

The conductivity data in Table II, plotted in Fig. 1, show that a small but gradual diminution in specific conductivity resulted from the reaction with the first 2 mols. of ammonia, after which further ammonia caused a slight increase. As these conductivities refer to solutions, the silver content of which was kept at 0·05*M*, and if $Ag(NH_3)_2NO_3$ is formed by the addition of 2 mols. of ammonia, it follows that this increase should be caused by the added ammonia.

The specific conductivity caused by the excess ammonia was computed from the p_{OH} values, these giving the concentration of hydroxyl ion and therefore of ammonium ion originating from the dissociation of the ammonium hydroxide; Λ_0 at 25° of ammonium hydroxide was taken as 270. Col. 4 of Table III gives the specific conductivity due to the $Ag(NH_3)_2NO_3$ alone, whilst col. 5 gives the equivalent conductivity at the existing dilution, *viz.*, 20, and col. 6 Λ_0, it being assumed that the ionisation of the complex salt in 0·05*M*-solution is the same as that of 0·05*M*-silver nitrate, *viz.*, 86%. The last col. gives the ionic mobility of the $Ag(NH_3)_2^{\cdot}$ kation, the ionic mobility of the nitrate ion at 25° being 70·5 (International Critical Tables, 1929, Vol. 6, p. 230).

TABLE III.

NH_4OH, mols.	$\kappa \times 10^3$, mhos. Obs.	NH_4OH.	$Ag(NH_3)_2NO_3$.	Λ of 0·05*M*-$Ag(NH_3)_2NO_3$.	Λ_0 of $Ag(NH_3)_2NO_3$.	Λ_0 of $Ag(NH_3)_2$.
2·2	5·65	0·03	5·62	112·4	130·8	60·3
2·4	5·65	0·05	5·60	112·0	130·2	59·7
2·6	5·77	0·07	5·70	114·0	132·5	62·0
2·8	5·78	0·09	5·69	113·8	132·2	61·7
3·2	5·84	0·11	5·73	114·6	133·2	62·7
3·6	5·88	0·13	5·75	115·0	133·9	63·4
4·0	5·98	0·18	5·80	116·0	134·9	64·4

The specific conductivity obtained for the 0·05*M*-$Ag(NH_3)_2NO_3$ exhibits a distinct tendency to increase with the addition of ammonia. This may be due to enhanced stability of the complex kation. The values of the ionic mobility, average 62·0, show that it is a little smaller than that of the silver ion, *viz.*, 62·4.

To ascertain whether the complex base, $Ag(NH_3)_2OH$, actually exists in solution, freshly precipitated silver oxide was dissolved in aqueous ammonia and titrated in the presence of the glass electrode with nitric acid. Fig. 2 gives a typical titration curve. It refers to the titration of 100 c.c. of a solution, 0·04757*N* with respect to ammonia and 0·01174*N* with respect to silver oxide, with 0·0952*N*-nitric acid at 14°. If the base, $Ag(NH_3)_2OH$, were formed, then the solution would be 0·01174*N* with respect to it, and 0·04757*N* − 2(0·01174)*N* = 0·02409*N* with respect to free ammonia. Hence, if the base, $Ag(NH_3)_2OH$, were appreciably stronger than ammonia, its neutralisation should be complete with 12·34 c.c. of 0·0952*N*-nitric acid, after which the ammonia should come into play and end with (25·38 + 12·34) = 37·72 c.c. of nitric acid. Fig. 2

shows that this is the case, and both end-points are marked by the appearance of definite inflexions. The final branch of the curve corresponds to the reaction with the 2 mols. of ammonia contained in the complex salt, thus : $Ag(NH_3)_2NO_3 + 2HNO_3 \longrightarrow AgNO_3 + 2NH_4NO_3$.

The p_H values prevailing during the neutralisation of the $Ag(NH_3)_2OH$ reveal that it ionises to an extent similar to that of sodium hydroxide, and those during the third stage of the titration are similar to those indicated in Fig. 1, corresponding to the production of the complex salt.

DISCUSSION.

Although the p_H values of ammoniacal solutions of silver nitrate indicate that relatively small amounts of ammonium ion are present, they show that the silver exists almost entirely in the form of the complex salt, $Ag(NH_3)_2NO_3$. This is in accord with the fact that $Ag(NH_3)_2OH$ is a strong base, as is definitely proved in Fig. 2. That such a base probably existed in ammoniacal solutions of silver oxide became apparent from the conductivity measurements of Euler (*Ber.*, 1903, **36**, 1854), Bonsdorff (*ibid.*, p. 2322), and Whitney and Melcher (*J. Amer. Chem. Soc.*, 1903, **25**, 69). Whilst Bonsdorff's data are vitiated mainly by the comparatively large proportions of ammonia in his solutions, those of Euler at 18° and of Whitney and Melcher at 24° point to the existence in the solutions of a complex having an exceptionally large equivalent conductivity. Thus, the latter workers investigated solutions at dilutions ranging from 3·35 to 53·5 litres containing 3·35 mols. of ammonia and 1 mol. of silver hydroxide, *i.e.*, $Ag(NH_3)_2OH + 1{\cdot}35NH_4OH$. Assuming the conductivity due to the excess of ammonia to be negligible in the presence of the strong complex base, they obtained equivalent conductivities varying from 194·8 to 205·8 mhos. The foregoing glass electro-titrations thus afford decisive proof of Whitney and Melcher's view, and, like their data, reveal that the strength of the base is of the same order as that of sodium hydroxide. The similarity of the ionic mobility, 62·0, of the $Ag(NH_3)_2^{\cdot}$ ion, given in Table III, to that of the silver ion, 62·4, also explains why only small changes in specific conductivity occurred when ammonium hydroxide was added to silver nitrate solution.

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