149. *Electrometric Studies of the Precipitation of Hydroxides. Part IX. The Action of Ammonia on Solutions of Mercuric Chloride.*

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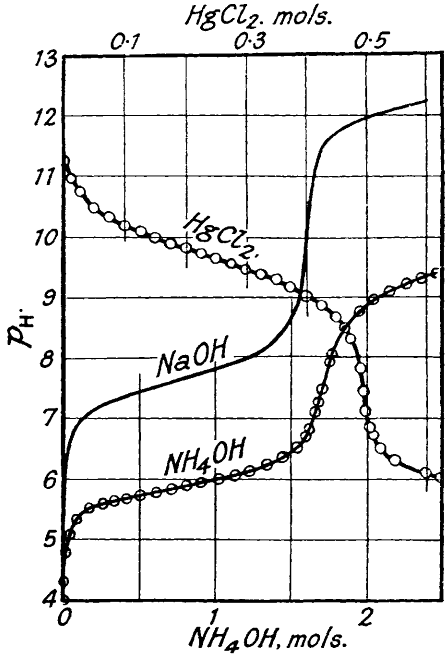
The fact that the precipitates obtained by the interaction of ammonia with mercuric chloride in aqueous solution contain ammonia has given rise to much conjecture regarding their constitution (Kane, *Phil. Mag.*, 1836, **8**, 495; 1837, **11**, 458; *Annalen*, 1838, **18**, 201; Rammelsberg, *J. pr. Chem.*, 1888, **38**, 558; Pesci, *Gazzetta*, 1889, **19**, 509; 1890, **20**, 485; *Z. anorg. Chem.*, 1899, **21**, 361; Hofmann and Marburg, *Annalen*, 1899, **305**, 191; Franklin, *J. Amer. Chem. Soc.*, 1907, **29**, 35; François, *Ann. Chim.*, 1927, **8**, 341), the general view being that the mercury enters into either the ammonia molecule or the ammonium radical; Rammelsberg and Pesci further consider that many precipitates are double compounds of complex mercury ammonia salts and ammonium chloride. Although the chemistry of mercuric compounds is in many ways anomalous, it is highly probable that the formulæ usually assigned to these precipitates do not represent their constitution.

Unlike previous investigations, which have dealt mainly with the preparation and analysis of precipitates, the work here described has been carried out to study the mode of precipitation from mercuric chloride solutions with ammonia, and if possible to correlate it with our previous work (Part VII; J., 1932, 2550) dealing with precipitation with sodium hydroxide. It shows that the constitution of the complexes is simpler than the earlier workers supposed.

Experimental.

1. *Glass-electrode Titrations.*—These titrations were performed with the ballistic galvanometer as described by Britton and Robinson (*Trans. Faraday Soc.*, 1932, **28**, 531). Fig. 1 gives the variation in p_H when (*a*) 100 c.c. of $0{\cdot}025M$-$HgCl_2$ are titrated by $0{\cdot}1027N$-NH_4OH at 12° (lower curve), (*b*) 100 c.c. of $0{\cdot}100N$-NH_4OH are slowly titrated by $0{\cdot}1M$-$HgCl_2$ at 16° (upper curve). The middle curve, being that of a titration of aq. $HgCl_2$ by NaOH under comparable conditions, is reproduced from Part VII.

Fig. 1.



In (*a*), a very pale yellow bulky ppt. was formed immediately and did not readily settle. During the addition of 1·66—2·0 mols. of NH_4OH the ppt. changed to a white, heavy, granular form and settled rapidly. The p_H values prevailing during this pptn. were about 2 units lower than those with NaOH. Although pptn. was complete with 1·75 mols. of NH_4OH, it is evident that, coupled with the act of pptn., some other process was occurring, apart from the possible pptn. of a basic mercuric chloride as was the case when NaOH was used.

The p_H values at which pptn. takes place on the addition of NH_4OH approximate very closely to those established when sufficient time and agitation have been given to get the ppt. into a state of equil. with the mother-liquor; *e.g.*, on addition of 0·4 mol. of NH_4OH, the p_H immediately set up was 5·68, but it became 5·50 after the ppt. had stood 4 days with the solution. It should be emphasised, however, that the inflexion of the p_H curve corresponding to equilibrium conditions occurred exactly at 2 mols. of NH_4OH, the reaction then being complete.

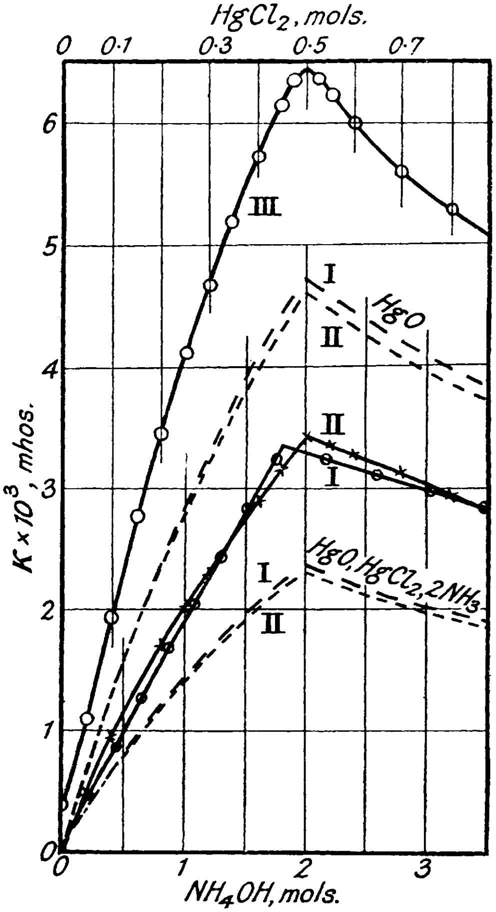
The $[H^{\cdot}]$ after pptn. had become complete was such as would be produced by the buffering of the added excess NH_3 by the NH_4Cl formed during the pptn. The free NH_3 and NH_4Cl were estimated in aliquot portions of the filtrates obtained after various excess amounts of $0{\cdot}1N$-NH_4OH had been added in titrations of type (*a*). Table Ia gives (in mol. or at. proportion)

TABLE III.

$HgCl_2$ added, c.c.	mols. per $1NH_3$.	p_H.	p_{OH}.	$[NH_4Cl]/[NH_4OH]$.	NH_4Cl in soln., mols.	Combined with Hg. Cl.	NH_3.
10·0	0·10	10·18	4·02	0·21	1·65	0·35	0·35
20·0	0·20	9·81	4·39	0·49	1·47	0·53	0·53
30·0	0·30	9·47	4·73	1·07	1·43	0·57	0·57
40·0	0·40	9·05	5·16	2·88	1·44	0·56	0·56

The last col. gives an average for the Cl and NH_3 contents of 0·50, and thus the ppt. must have been $HgCl_{0·5}(OH)_{1·5},0·5NH_3$ or, expressed in accordance with the above equation, $3HgO,HgCl_2,2NH_3$.

FIG. 2.



2. *Conductometric Titrations.*—Fig. 2 gives the conductometric curves of (*a*) 50 c.c. of $0·025M$-$HgCl_2$ with $0·1085N$-NH_4OH (curve I), and (*b*) 100 c.c. of $0·100N$-NH_4OH with $0·1M$-$HgCl_2$. Both titrations were performed at 25° in the cell described by Britton and German (J., 1930, 1249). Pptn. began immediately. In the direct titration curve the "break" occurs with 1·75—1·8 mols. of NH_3, which agrees with the corresponding p_H curve in Fig. 1. The inflexion in the second curve occurs at 0·5 mol. $HgCl_2$ to 1 mol. NH_3, as would be expected from the previous observations.

As the conductivity of $HgCl_2$ solutions is negligibly small, it follows that the sp. conductivities established during the first titration must have been caused by the NH_4Cl in the solution as the result of the pptn. It has been proved experimentally that the conductivities of the NH_4Cl formed and the $HgCl_2$ present in these titrations were additive—complex formation thus having no effect as far as the total conductivities were concerned. Assuming that each successive addition of NH_3 caused a proportional pptn. of the Hg, and knowing that under the conditions of expt. 1·75 mols. of NH_3 cause complete pptn., we can calculate the mol. proptns. of Cl and NH_3 retained by the ppt. throughout the whole course of the reaction. Table IV records the obs. values of κ and the calc. comp. of the ppt. For the purpose of computing the concn. of NH_4Cl from the obs. sp. conductivities, the data published in the International Critical Tables (1929, Vol. VI, p. 232) were used. The conductivity of the excess NH_3 is negligible.

The ppt. first formed was

$$HgCl_{1·0}(OH)_{1·0},0·75NH_3,$$

but as pptn. proceeded it gradually acquired the composition $HgCl_{0·72}(OH)_{1·28},0·47NH_3$. After pptn. had ended, the Cl content of the ppt. fell to 0·5, and the NH_3 to 0·25 mol. These calculations are, however, based on the assumption that no NH_3 reacts after 1·75 mols. of NH_3 have been added, whereas Table I shows that subsequently upwards of 0·25 mol. of NH_3 becomes incorporated in the ppt., and thus it appears that when a relatively small excess of NH_3 had been added, the ppt. was $HgCl_{0·5}(OH)_{1·5},0·5NH_3$.

Curve II in Fig. 2 represents the sp. conductivities of mother-liquors under equil. conditions produced by adding various amounts of $0·100N$-NH_4OH to 50 c.c. of $0·025M$-$HgCl_2$ and keeping the mixture at 25° until const. conductivities were established. Table V gives some observations obtained.

TABLE IV.

NH_4OH c.c.	2·5	5·0	7·5	10·0	12·5	15·0	17·5	20·0	22·5	23·5	30·0	35·0	40·0
NH_4OH mols. per $1HgCl_2$	0·22	0·43	0·63	0·87	1·08	1·30	1·52	1·74	1·95	2·04	2·60	3·04	3·47
$\kappa \times 10^4$	4·28	8·84	12·69	16·68	20·43	24·08	27·83	31·79	32·85	32·60	31·05	29·84	28·65
$[NH_4Cl] \times 10^3$	3·0	6·3	9·2	12·0	14·7	17·3	20·1	22·8	23·7	23·5	22·3	21·5	20·7
Precipitate : To 1Hg Cl	1·0	0·87	0·86	0·84	0·81	0·79	0·75	0·72	0·62	0·62	0·57	0·54	0·51
Precipitate : To 1Hg NH_3	0·75	0·62	0·61	0·59	0·56	0·54	0·50	0·47	0·37	0·37	0·32	0·29	0·25

TABLE V.

NH_4OH added,		$\kappa \times 10^3$,	$C_{NH_4Cl} \times 10^3$,		Combined with Hg.	
c.c.	mols.	mhos.	obs.	total.	Cl.	NH_3.
10·0	0·8	1·696	12·1	16·6	0·54	0·54
20·0	1·6	2·874	20·6	28·5	0·55	0·55
25·0	2·0	3·430	24·6	33·3	0·52	0·52
30·0	2·4	3·268	23·4	31·2	0·50	0·50

From the obs. conductivities, the concns. of NH_4Cl (C_{NH_4Cl}) have been obtained, and these are compared with the concns. that would have been produced if HgO alone had been pptd. Curve II in Fig. 2 gives a definite " break " with 2 mols. of NH_3, and by assuming that 2 mols. of NH_3 are necessary for pptn. under equil. conditions, the comp. of the ppt. has been ascertained, the average being $HgCl_{0{\cdot}53}(OH)_{1{\cdot}47},0{\cdot}53NH_3$.

The broken lines in Fig. 2 show the variations in κ that would have occurred if either HgO or infusible white ppt. had been pptd. Some of the observations of the reverse titration, Curve III, Fig. 2, are recorded in Table VI, together with an analysis of the data.

TABLE VI.

$HgCl_2$,		$\kappa_{obs.} \times 10^3$,	$\kappa_{NH_4OH} \times 10^3$,	$\kappa_{NH_4Cl} \times 10^3$,	$C_{NH_4Cl} \times 10^3$,		Combined with Hg.	
c.c.	mols.	mhos.	mhos.	mhos.	obs.	total.	Cl.	NH_3.
0	0	0·368	0·368	0	0	0	—	—
10	0·10	1·923	0·023	1·900	13·6	18·2	0·51	0·51
20	0·20	3·436	0·009	3·427	24·5	33·3	0·53	0·53
30	0·30	4·667	0·004	4·663	33·7	46·2	0·54	0·54
40	0·40	5·684	0·002	5·682	41·7	57·1	0·54	0·54
50	0·50	6·380	0	6·380	47·5	66·6	0·57	0·57

Once again the ppt. had the approx. composition $HgCl_{0{\cdot}5}(OH)_{1{\cdot}5},0{\cdot}5NH_3$. That pptn. took place in accordance with the equation on p. 602, and that the assumptions involved in Table VI were correct, was proved by titrating the free NH_3 and NH_4Cl present in the mother-liquor at different stages. The analytical figures corresponded even more closely to the given composition.

Hitherto attention has been confined to the reaction in dil. solution. By using more conc. solns. less basic ammoniated chlorides are obtained. For instance, calculation shows that the method given in the British Pharmacopœia (1914, p. 177) for the prepn. of infusible white ppt. involves the interaction of stoicheiometric amounts by the gradual addition of $0{\cdot}18M$-$HgCl_2$ to approx. N-NH_4OH. Strömholm (*Z. anorg. Chem.*, 1908, **57**, 73), however, used much more dil. aq. $HgCl_2$ but more conc. aq. NH_3 added in excess. André (*Compt. rend.*, 1899, **108**, 233, 290) took equiv. amounts of $0{\cdot}125M$-$HgCl_2$ and $0{\cdot}25N$-NH_4OH and obtained a mixture of infusible white ppt. with a large amount of the chloride of the so-called Millon's base, but larger vols. of NH_3 soln. led to a preponderance of the former, and conc. aq. NH_3 gave this ppt. alone (see also de Fourcroy, ***Ann. Chim. Phys.***, 1792, **14**, 47; Franklin, *J. Amer. Chem. Soc.*, 1905, **27**, 820; Saha and Choudhuri, *Z. anorg. Chem.*, 1910, **67**, 358).

As with dil. solutions, we have found that on addition of conc. aq. $HgCl_2$ to conc. aq. NH_3, reactions become complete when $HgCl_2 : NH_3 = 1 : 2$. It would thus appear that any variations caused by the use of more conc. solns. must lie in the value of x in the comp. of the ppt. (see p. 602). Pptn. occurred in this way during progressive addition of $0{\cdot}2M$-$HgCl_2$ to 25 c.c. of $1{\cdot}00N$-NH_4OH, as found by determination of the free NH_3 in the different filtrates. The concns. of

NH_4Cl were also estimated volumetrically, and hence the amount of Cl which had been pptd. was calculated, the comp. of the ppt. at various stages of the reaction being as follows :

$HgCl_2$.		C_{NH_4Cl},	Combined with Hg.	
c.c.	mols. per mol. of NH_4OH.	mols./l.	Cl.	NH_3.
15·6	0·125	0·081	0·95	0·95
31·25	0·250	0·114	0·97	0·97
46·9	0·375	0·133	0·98	0·98
62·5	0·500	0·135	1·06	1·06

The concns. are similar to those advocated in the Pharmacopœia, and the table shows that both the ppts. had the composition, $HgNH_2Cl$, usually assigned to infusible white ppt.

A preparation made according to those directions was tested by dissolving the ppt. in aq. KI and titrating the liberated alkali electrometrically by means of the glass electrode with 0·1045*N*-HCl, instead of with 0·1*N*-HCl and methyl-orange, as prescribed. 25·7 C.c. of 1·001*N*-NH_4OH were added to 3·494 g. of $HgCl_2$ in 75 c.c. of H_2O. The ppt. was separated, washed, dissolved in KI aq., the solution diluted to 500 c.c., and 100 c.c. used for titration. The curve so obtained showed two " breaks " : one when approx. 24 c.c. had been added, and the other after 49·2 c.c., the first corresponding to the free KOH and the second to the NH_4OH set free in the reaction $x\mathrm{HgO} + (1 - x)(\mathrm{HgCl_2,2NH_3}) + 4\mathrm{KI} = \mathrm{K_2HgI_4} + 2x\mathrm{KOH} + 2(1 - x)\mathrm{NH_4OH} + 2(1 - x)\mathrm{KCl}$.

The first end-point was more accurately determined by boiling off the free NH_3 and titrating with HCl (methyl-orange); this indicated the correct " break " at 23·7 c.c. Whence,

$$\frac{\mathrm{HgO}}{\mathrm{HgCl_2,2NH_3}}\ (\text{in ppt.}) = \frac{x}{1 - x} = \frac{23{\cdot}7}{49{\cdot}2 - 23{\cdot}7} = \frac{23{\cdot}7}{25{\cdot}5} = \frac{0{\cdot}929}{1{\cdot}000}.$$

The ppt. is therefore $0{\cdot}929\mathrm{HgO,HgCl_2,2NH_3}$, or, expressed as before, $\mathrm{Hg(OH)_{0{\cdot}96}Cl_{1{\cdot}04},1{\cdot}04NH_3}$.

DISCUSSION.

We have previously shown (J., 1932, 2550) that sodium hydroxide precipitates a basic chloride of the composition $3HgO,HgCl_2$. It is now shown that the same concentration of ammonium hydroxide gives the same chloride except that 2 molecules of ammonia are associated with one of mercuric chloride (or one with each atom of chlorine) in $3HgO,HgCl_2,2NH_3$. This might have been expected from its probable relationship to fusible white precipitate, $HgCl_2,2NH_3$. The precipitate contains the three elements in the ratios N : Hg : Cl = 1 : 2 : 1, and thus corresponds to the chloride of the so-called Millon's base.

An extraordinary number of ammoniated basic mercuric chlorides have been described (see, *e.g.*, Franklin, *J. Amer. Chem. Soc.*, 1907, **29**, 35), and, although it is highly probable that at room temperature only the two above-mentioned can be regarded as definite chemical individuals, yet as a rule they express the composition of precipitates that have actually been obtained under different conditions (cf. Table IV). The following figures give the various molecular ratios of Cl : NH_3 for each atom of Hg in these precipitates : 1·5 : 1·5; 1·5 : 0·5; 1 : 1; 0·5 : 0·5; 1·2 : 0·4; 0·83 : 0·83; 0·75 : 0·75; 0·6 : 0·6; 0·6 : 0·2; 0·56 : 0·56; 0·4 : 0·4; 0·33 : 0·33. Hence, with very few exceptions, they show that the ammonia content is exactly the same as that of the chlorine, *i.e.*, that each molecule of mercuric chloride corresponds to two of ammonia. Previous theories regarding the constitution of some of these precipitates have been based on the erroneous contention (cf. Pesci, *Z. anorg. Chem.*, 1899, **21**, 361) that some of the ammonia was bound in such a way that it could not be expelled by boiling with alkali solutions, and moreover there is little support for the view that some of it is held by such a weak base as mercuric oxide in the form of an amide.

As Fig. 1 shows, there is an appreciable difference between the p_H values (about 2 units) during precipitation by ammonium hydroxide and by sodium hydroxide. This is unexpected if both precipitates are essentially basic chlorides of similar composition. Calculations show that the hydrolysis of the ammonium chloride formed is not responsible for the p_H impressed upon the solution. The diminution in hydrogen-ion concentration in the latter stage of the precipitation was evidently caused by hydroxyl ions originating from the precipitate, probably from both the basic part and the combined ammonia.

The fact that ammonia causes precipitation at a lower p_H, and therefore a lower hydroxyl-ion concentration, indicates that the entrance of ammonia into the precipitate gives it a lower solubility. Attempts have been made to calculate the ionic product, $[Hg^{\cdot\cdot}][OH']^2$, corresponding to different stages of precipitation both in the titration and in the cases where equilibrium had been reached between the precipitate and the mother-liquor. The mercury electrode could not be employed to measure the mercuric-ion concentrations on account of its reaction with the mercuric salt in solution, but it can be shown that complex formation between mercuric and ammonium chlorides is too slight to affect the mercuric-ion concentration appreciably, so the equilibrium $HgCl_2 \rightleftharpoons Hg^{\cdot\cdot} + 2Cl'$ alone need be considered, the chlorine ion being derived from the ammonium chloride. Using the data given on p. 601, the concentrations of ammonium chloride being based on conductivity determinations (Table V), and taking $K = [Hg^{\cdot\cdot}][Cl']^2/[HgCl_2] = 1 \times 10^{-14}$ (Morse, *Z. physikal. Chem.*, 1901, **36**, 385), we have calculated the values of p_{Hg} given below.

$\frac{NH_4OH}{HgCl_2}$, mols.	Titration.			Equilibria.		
	p_{OH}.	p_{Hg}.	$p_{[Hg^{\cdot\cdot}][OH']^2}$.	p_{OH}.	p_{Hg}.	$p_{[Hg^{\cdot\cdot}][OH']^2}$.
0·4	8·66	11·26	28·58	8·89	11·38	29·16
0·8	8·45	12·02	28·92	8·68	12·10	29·46
1·2	8·22	12·64	29·02	8·43	12·55	29·41
1·6	7·61	13·47	28·69	7·84	13·09	28·77

This table shows that the ionic product $[Hg^{\cdot\cdot}][OH']^2$, corresponding to the precipitation of $3HgO,HgCl_2,2NH_3$, is approximately 10^{-29}. This is 1000 times smaller than the solubility product of mercuric hydroxide. As will be shown in a subsequent paper, it is this condition which enables ammonia to cause precipitation from Nessler's solution, whereas, owing to its greater solubility product, mercuric oxide is not precipitated therefrom by the large concentration of sodium hydroxide present.

If the magnitudes of $[Hg^{\cdot\cdot}]$ and $[OH']$ are determining factors in precipitation with ammonia, as would be the case if the precipitates were ammoniated basic chlorides, then it would appear that the magnitude of the dissociation constant of ammonium hydroxide will determine whether the requisite p_H can be established at which the ionic product 10^{-29} can be exceeded. Now, although mercuric chloride forms analogues of fusible white precipitate with many organic bases, *e.g.*, ethylamine, aniline, pyridine, quinoline, and urea, yet the last four are too weak to give basic chloride precipitates (containing the organic base) when added directly to mercuric chloride, evidently because they cannot maintain p_H values high enough for basic precipitation to take place. By adding concentrated alkali and alkali carbonate solutions to solutions of mixtures of mercuric chloride and urea, however, Pesci (*Z. anorg. Chem.*, 1897, **15**, 232) prepared the urea analogues of infusible white precipitate and of the so-called chloride of Millon's base.

The precipitation of a less basic chloride, $HgO,HgCl_2,2NH_3$ (*i.e.*, hydrated infusible white precipitate) by use of a more concentrated solution of ammonia may appear to be at variance with the views expressed above. Two influences, however, come into play: (1) the diminished ionisation of the ammonium hydroxide, due to the increased concentration, and consequent production of a relatively smaller $[OH']$ and greater $[NH_3]$; (2) the solubility of mercuric oxide in saline solutions (cf. Part VIII, this vol., p. 9) including those of ammonium salts. If the concentration of ammonium chloride formed during the reactions at higher concentrations exceeds that with which the particular final solid phase is in equilibrium (cf. Strömholm, *Z. anorg. Chem.*, 1908, **57**, 80) it will dissolve mercuric oxide from the complex basic precipitate, $HgO + 2NH_4Cl \longrightarrow HgCl_2,2NH_3$, and the product is ultimately reprecipitated.

Many of the methods of preparing fusible white precipitate, $HgCl_2,2NH_3$, make use of precipitation with concentrated solutions of ammonia from mercuric chloride solutions in which much ammonium chloride has been dissolved. The latter salt not only tends to dissolve the former but also forms a complex, $(NH_4)_2HgCl_4$, with it (see Part VII), so reducing the mercuric-ion concentration and raising the p_H at which precipitation occurs on addition of ammonia, and thus tending to counteract the precipitation of mercuric oxide in the product. Although fusible white precipitate and mercuric oxide are but sparingly

(i) the amount of NH_4OH added per mol. of original $HgCl_2$; (ii) and (iii) respectively the NH_3 and NH_4Cl found in the filtrates; from these data the figures in the remaining cols. were calculated, the last of which gives the proptns. of Cl and NH_3 retained in the ppt. by each atom of Hg.

TABLE I.

	NH_3 added.	NH_3 found.	NH_4Cl found.	NH_3 reacted.	Combined with Hg. Cl.	Combined with Hg. NH_3.
A	1·82	0·05	1·22	1·77	0·78	0·55
	2·00	0·15	1·28	1·85	0·72	0·57
	3·00	0·99	1·45	2·01	0·55	0·56
	4·00	1·90	1·52	2·10	0·48	0·58
	6·00	3·87	1·49	2·13	0·51	0·64
B	2·4	0·42	1·50	1·98	0·50	0·48
	3·2	1·17	1·50	2·03	0·50	0·53
	4·0	1·95	1·50	2·05	0·50	0·55

The data show that if the ppts. be regarded as basic chlorides containing NH_3, 1·8—2·0 mols. of NH_3 produced $HgCl_{0\cdot75}(OH)_{1\cdot25},0\cdot56NH_3$, and the average comp. of the ppt. obtained thereafter was $HgCl_{0\cdot53}(OH)_{1\cdot47},0\cdot59NH_3$.

If, however, the ppts. are shaken for some days with the mother-liquor containing excess of NH_3 until equil. is reached, they all acquire the same comp., *viz.*, $HgCl_{0\cdot50}(OH)_{1\cdot50},0\cdot5NH_3$. This is seen from section B of Table I.

It is possible to calculate the ratios of $[NH_4Cl] : [NH_4OH]$ that set up the p_H values on the addition of excess of NH_4OH in the first glass-electrode titration, from the expression

$$p_{OH} = p_{K_{NH_4OH}} + \log [NH_4Cl]/[NH_4OH].$$

As the available values of $p_{K_{NH_4OH}}$ had been derived from conductivity measurements, the value was redetermined by means of glass-electrode titrations of solutions of NH_3 by HNO_3. The value found was 4·70, in excellent agreement with the conductometric values (cf. Bredig, *Z. physikal. Chem.*, 1894, **13**, 289; Goldschmidt, *Z. anorg. Chem.*, 1901, **28**, 97). Col. 5 of Table II gives the values of $[NH_4Cl]/[NH_4OH]$, and, by assuming that no further NH_3 reacted after 1·75 mols. had been added, the number of mols. of NH_4Cl (*i.e.*, per mol. of $HgCl_2$) remaining in solution were calculated (col. 6) and also the amount of Cl that had been pptd. with the Hg (col. 7). Col. 8 represents the amount of NH_3 that must have passed into the ppt. upon the above assumption.

TABLE II.

NH_4OH added, c.c.	NH_4OH added, mols.	p_H.	p_{OH}.	$[NH_4Cl]/[NH_4OH]$.	NH_4Cl in soln., mols.	Combined with Hg. Cl.	Combined with Hg. NH_3.
50·0	2·05	8·96	5·38	4·79	1·44	0·56	0·31
60·0	2·47	9·35	4·99	1·95	1·40	0·60	0·35
70·0	2·88	9·55	4·79	1·25	1·39	0·61	0·36

Although the comp. of the ppt. thus found is only approx., owing to the considerable discrepancies introduced by very slight errors in the observed p_H, it indicates the nature of the ppt. immediately after its formation. The NH_3 content is somewhat lower than those recorded in Table I, but, as col. 4 of that table shows, the absorption of NH_3 by the ppt. continues somewhat after pptn. has been completed.

By carrying out the reverse process (*b*), it was considered that the absorption of NH_3 by the ppt. would be a max. The upper curve in Fig. 1 reveals that the reaction is accompanied by a buffered change in $[H^{\cdot}]$ which terminates by a very definite inflexion when exactly 1 mol. of $HgCl_2$ has been added to 2 mols. of NH_3 aq. The reaction can thus be represented by the equation

$$2xNH_4OH + 2(1 - x)NH_3 + HgCl_2 \longrightarrow xH_2O + 2xNH_4Cl + \underbrace{xHgO,(1 - x)(HgCl_2,2NH_3)}_{\text{precipitate}}$$

from which it would follow that if 2 mols. of NH_4OH are not required to form 1 mol. of HgO, 2 mols. of NH_3 must be taken up unattacked by each mol. of $HgCl_2$ that passes into the ppt. If pptn. takes place in this manner throughout the titration, then the amount of ammonia left unattacked is known at any stage, and as the value of $[NH_4Cl]/[NH_4OH]$ can be calculated from the p_H value, the $[NH_4Cl]$ in solution, and consequently the NH_3 and Cl present in the ppt., can be ascertained. Table III gives the details of such computations based on the titration of 100 c.c. of $0\cdot100N$-NH_4OH with $0\cdot1M$-$HgCl_2$ at 16°.

soluble in water at room temperature, both are more soluble in concentrated solutions of ammonia and especially if ammonium chloride is present.

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