

The following are the results obtained:

PH ₄ Br.			
Temp.	Press. in mm. Hg.	Temp.	Press. in mm. Hg.
-80°	1	6.4°	91
-50	3	6.8	93
-36	4	7.5	101
-24	8	9.8	118
-14.2	17	11.0	126
-9.8	25	14.4	159
-8.0	30	19.0	222
-4.8	37	20.5	250
0	56	23.0	291
1.4	63	27.6	396
2.0	65	31.6	507
4.6	80	34.3	602
5.2	83	38.8	794
PH ₄ I.			
0°	8	42.2°	231
11.4	24	43.6	286
15.0	32	47.0	309
18.5	47	48.8	348
22.0	57	51.8	417
24.4	74	52.2	426
31.4	117	56.2	535
34.2	141	56.4	536
34.4	144	56.8	557
40.2	206	59.8	651
40.4	207	61.0	708

The curves obtained are shown in Fig. 2. The dotted curve shows the values obtained by Tammann for phosphonium chloride. Below -41° this salt exists in two modifications, crystallin and amorphous, the former being the unstable form with the higher dissociation pressures. A similar occurrence was not observed in the case of either the bromide or iodide.

From the curves, PH₄Br and PH₄I have dissociation pressures of 1 atmosphere at 38° and 62°, respectively.

Although it is probable that all three salts are practically completely dissociated in the state of vapor the only one investigated is PH₄Cl.¹ No comparisons of the heats of dissociation can be made. An investigation leading to the necessary data is being undertaken.

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THE MIXED CRYSTALS OF AMMONIUM CHLORIDE WITH NICKEL, COBALT AND COPPER CHLORIDES.

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The fact that ammonium chloride can crystallize from solutions con-

¹ Briner, *J. chim. phys.*, 4, 476 (1906).

taining various chlorides of bivalent and trivalent metals, forming homogeneous mixed crystals with the latter, was first clearly recognized by Lehman¹ and later confirmed by Retgers.² The mixed crystals were of such a curious type that Roozeboom³ investigated those formed with ferric chloride from the standpoint of physical chemistry and was able to demonstrate that they resembled ordinary isomorphous mixtures in their solubility relations. He obtained crystals containing over 7% of ferric chloride; but the amount of the latter was so small that he could not determine with certainty what hydrate was present. The same system was studied later by van der Kolk⁴ and by Mohr,⁵ their results adding nothing very essential to what was already known. A somewhat extended study of mixed crystals of this type was also made by Johnsen,⁶ chiefly from a crystallographic standpoint.

Except for the case first investigated by Roozeboom, our knowledge regarding the mixed crystals which ammonium chloride forms with other metallic chlorides is almost entirely of a qualitative nature. To what extent mixed crystals form in other cases, and what hydrates are present, has not been settled. In the present investigation, we have determined the solubility of various mixtures of ammonium chloride with nickel, cobalt and copper chlorides at 25°, analyzing both residues and solutions. From a series of such results, it is possible to determine with a fair degree of accuracy, to what extent mixed crystals form. This solubility method has been used repeatedly in this laboratory for determining double salts. When the latter are present instead of mixed crystals, a series of results showing variable solubility and constant residue indicates a pure double salt. If mixed crystals form instead of a double salt, a series of determinations shows both variable residue and variable solubility.

Ammonium Chloride and Nickel Chloride.

A double chloride of nickel and ammonium, $\text{NH}_4\text{Cl} \cdot \text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, has been described by Adams and Merrick.⁷ It has also been obtained by Johnsen.⁸ A sample of the mixed chlorides was also analyzed by Johnsen who found 3.63% of nickel chloride as the dihydrate. Retgers⁹ states that the crystals are anhydrous.

Recrystallized ammonium and nickel chlorides were used in the experiments. Varying mixtures of the two were dissolved in water and

¹ *Z. Kryst.*, 8, 438 (1883).

² *Z. physik. Chem.*, 9, 312, 385 (1892); 10, 550 (1892).

³ *Ibid.*, 10, 145 (1892).

⁴ *Ibid.*, 11, 167 (1893).

⁵ *Ibid.*, 27, 193 (1898).

⁶ *N. Jahrb. Min.*, 2, 93 (1903).

⁷ *Chem. News*, 25, 187 (1872).

⁸ *Loc. cit.*

⁹ *Z. physik. Chem.*, 9, 388.

allowed to crystallize. The difficulty of establishing equilibrium between solution and solid, when mixed crystals form, has often been noted and was to be expected in the present case. Roozeboom, and afterward Mohr found, for instance, that the amount of ferric chloride in the crystals did not increase regularly with increase of iron in solution, but varied irregularly. To insure equilibrium in the present case, the crystals were crushed in a mortar and transferred, with most of the mother liquor, to bottles and shaken in a thermostat, usually for several days. The bottles contained glass rods to assist in reaching equilibrium, an arrangement which has been described previously.¹ A weighed sample of the solution for analysis was removed through a filter of glass wool. The residues were dried quickly between filter papers. They were rather finely divided and were of necessity somewhat contaminated with the solution. On the other hand, there is every reason to believe that equilibrium was reached between the residues and solutions. Ammonia was determined in the usual manner by distilling with sodium hydroxide, absorbing the ammonia in standard acid and titrating the excess. Nickel was precipitated in the hot ammoniacal solution by an alcoholic solution of dimethylglyoxime; the precipitate after standing was filtered on a Gooch crucible and dried at 100–120° before weighing. The results obtained by this method were entirely satisfactory. Water was calculated by difference.

The following results were obtained:

TABLE I.—SOLUBILITY OF MIXTURES OF AMMONIUM CHLORIDE AND NICKEL CHLORIDE IN WATER AT 25°.

No.	Per cent NH ₄ Cl in solution.	Per cent NiCl ₂ in solution.	Per cent NH ₄ Cl in residue.	Per cent NiCl ₂ in residue.	Per cent H ₂ O in residue (by difference).	Residue contains.
1	26.07	3.10	undet.	0.32	undet.	} Mixed crystals of NH ₄ Cl.xNiCl ₂ .2H ₂ O
2	22.27	8.04	"	0.83	"	
3	20.68	10.32	"	0.94	"	
4	17.43	15.01	"	3.14	"	
5	11.22	26.93	"	12.13	"	
6	10.21	30.56	75.79	17.37	6.84	
7	9.90	32.82	71.25	21.69	7.06	
8	9.64	34.00	63.80	27.01	9.19	
9	9.16	35.70	55.59	32.06	12.35	
10	7.98	37.41	43.62	39.40	16.98	} Mixed crystals and NiCl ₂ .6H ₂ O
11	8.07	37.73	34.67	44.03	21.30 ²	
12	8.23	37.45	21.82	46.63	31.55	
13	8.17	37.64	16.03	48.93	35.04	
14	7.51	37.19	trace	54.64	undet.	} NiCl ₂ .6H ₂ O
15	3.06	37.98	trace	54.04	"	
16	0	37.53 ³	0	pure hydrate	"	

¹ THIS JOURNAL, 33, 1033 (1911).

² Residue dried over night and effloresced.

³ Determined by Mr. J. A. Ambler.

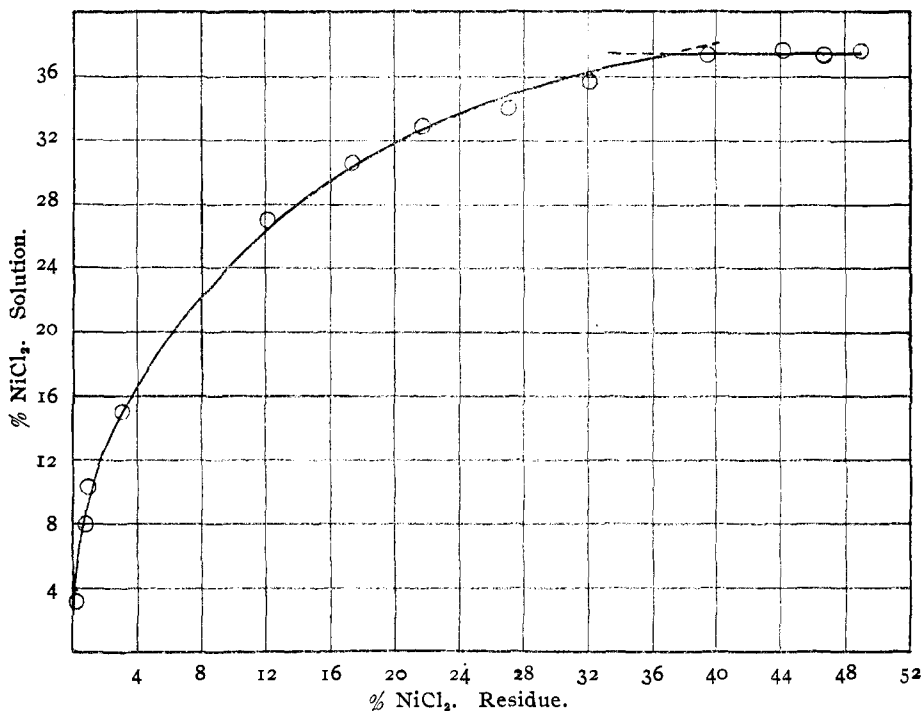
The residues in Nos. 1-9 were all of a light yellow color which deepened somewhat toward the nickel end. The results show variable residue and variable composition of solution, indicating mixed crystals. Nos. 10-13 have a nearly constant solubility and variable residue, indicating a mixture of two solids. With a lens, the different phases could be seen very clearly on account of their different colors, one phase being yellow mixed crystals and the other, green nickel chloride. In Nos. 14 and 15, pure nickel chloride was present.

The first conclusion which may be drawn from the results is that no double salt formed. The double salt $\text{NH}_4\text{Cl} \cdot \text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ has, however, been described. It contains 18.38% NH_4Cl and 44.5% NiCl_2 . The composition, therefore, is not very different from that of the residue in No. 12, which was clearly a mixture, as were Nos. 10, 11 and 13. That these were mixtures was shown both by the fact that two different solids could be seen and also by the constant solubility of the series. We therefore conclude that the double salt does not form at 25°. We were successful, however, in preparing it at a lower temperature. In one case, a solution left at room temperature over night deposited some large greenish crystals which were supposed to be nickel chloride. Analysis showed 18.55% of NH_4Cl , which is nearly theoretical for the double salt. On standing with the solution in a room slightly above 20°, the salt disappeared leaving the ordinary mixed crystals. Another crop of double salt was obtained at a considerably lower temperature. The crystals contained 17.87% NH_4Cl . They yielded mixed crystals when shaken in the thermostat with the solution, at 25°. A sample placed in a specimen tube with the temperature slightly above 20° slowly changed to a yellow, moist mass, evidently consisting chiefly of mixed crystals. There seems to be no doubt, therefore, that a transition temperature exists, probably slightly below 20°. Above this temperature, the double salt decomposes into a mixture of hydrated nickel chloride and mixed crystals.

The amount of nickel chloride which can enter the mixed crystals is surprising and considerably greater than has been observed before. The largest amount actually found was 32.06% in No. 9. This, however, is not the maximum amount which can be taken up. This maximum can be approximately determined by plotting the results in the table and determining the point of intersection of the solubility curves for Nos. 1-9 and 10-13. In the figure, the percentage of nickel chloride in the residues is plotted as abscissa; and in the solutions, as ordinate. The two curves meet at a point indicating approximately 37% NiCl_2 in the residue, which represents very nearly the composition of the saturated mixed crystals at 25°. Undoubtedly this limiting value changes with the temperature.¹

¹ *Am. Chem. J.*, 27, 345 (1902).

Nickel chloride appears to be present in the mixed crystals as the dihydrate and not in the anhydrous condition. The analyses always showed somewhat more water than corresponded to this hydrate, due apparently to the difficulty of freeing the residues completely from solution. The



latter on drying left the excess of nickel chloride as hexahydrate. The greatest error as regards water appears to be in No. 9, where the empirical composition of the hydrate is $\text{NiCl}_2 \cdot 2.8\text{H}_2\text{O}$. The solutions rich in nickel were very syrupy. Johusen, from an analysis of one sample, also concluded that the dihydrate was present while Retgers assumed they were anhydrous.

Ammonium Chloride and Cobalt Chloride.

Only five determinations were made in this series but they were sufficient to fix the mixing limit with fair accuracy. Recrystallized salts were used, but the cobalt contained a trace of iron which was not entirely removed. Cobalt was determined either electrolytically or by evaporating the solution with excess of sulphuric acid, heating cautiously and weighing cobalt sulfate. The results are given in Table II.

Nos. 3 and 4 in the table were very nearly alike, but in the residue of No. 3, none of the crystals of pure cobalt chloride could be seen, while

TABLE II.—SOLUBILITY OF MIXTURES OF AMMONIUM CHLORIDE AND COBALT CHLORIDE IN WATER AT 25°.

No.	Per cent NH ₄ Cl in solution.	Per cent CoCl ₂ in solution.	Per cent NH ₄ Cl in residue.	Per cent CoCl ₂ in residue.	Per cent H ₂ O in residue (by diff.).	Residue contains:
1	17.9	15.63	...	3.2	...	} Mixed crystals of NH ₄ Cl. <i>x</i> CoCl ₂ .2H ₂ O
2	13.59	25.19	83.01	13.52	3.47	
3	8.75	34.28	35.12	50.66	14.22	
4	7.45	35.24	34.02	49.64	16.31	} Mixed crystals and CoCl ₂ .6H ₂ O
5	7.62	34.61	7.07	55.27	37.66	

in No. 4, a few could be detected with the microscope on account of their very different color. The mixed crystals were lavender colored at the cobalt end. The discrepancy in the percentages of cobalt found in these two results was due to the great difficulty of properly drying the residues. No. 3 has very nearly the limiting composition. We know of no way to determine it more closely. It appears that ammonium chloride is capable of taking up more cobalt chloride than nickel chloride. The dihydrate is present, resembling nickel chloride in this respect. No indication of a double salt was found at 25° or at any other temperature where crystallization took place.

It appears impossible to decide at present in regard to the molecular condition of the nickel and cobalt chlorides in the mixed crystals. It is not unlikely that the residues are to be regarded as isomorphous mixtures of ammonium chloride and some double salt which is unstable in pure condition. Cases are known in which two single salts crystallize isomorphously to form a stable hydrate which neither salt yields when alone. For instance, copper and zinc sulfates together form a well known monoclinic heptahydrate which neither deposits singly. So it is not impossible that there is an unstable double salt here which becomes stable on forming mixed crystals with ammonium chloride. There is no evidence either for or against this view and it appears simpler to consider the crystals as isomorphous mixtures, leaving it uncertain as to whether there is actual chemical combination between the nickel or cobalt chlorides and a part of the ammonium chloride.

Ammonium Chloride and Copper Chloride.

The double salts of ammonium and copper chloride have been very thoroughly investigated in their solubility relations by Meerburg.¹ It has been shown, however, by Lehman and others that mixed crystals of the two salts form, though the extent to which mixing takes place has not been determined. It was evident from Meerburg's work that the amount of copper which could be taken up by ammonium chloride must be small, since the double salt at the ammonium end of the series is rather insoluble. Only the extreme ammonium end of the series of

¹ *Z. anorg. Chem.*, 45, 1 (1905).

possible saturated solutions was investigated as the rest has been done by Meerburg. The following results were obtained. The work was carried out by Mr. E. H. Norton.

TABLE III.—SOLUBILITY OF MIXTURES OF AMMONIUM CHLORIDE AND CUPRIC CHLORIDE IN WATER AT 25°.

No.	Per cent NH_4Cl in solution.	Per cent CuCl_2 in solution.	Per cent CuCl_2 in residue.	Residue contains.
1	28.13	0.83	1.08	Mixed crystals
2	27.90	1.41	1.35	
3	27.83	1.61	1.66	
4	27.74	1.79	14.50	Mixed crystals and double salt
5	27.70	1.87	37.39	

The solutions in Nos. 1–3 vary somewhat in composition and deposited only mixed crystals, while in Nos. 4 and 5, with constant solubility and variable residue, mixed crystals were present together with the well known double salt $2\text{NH}_4\text{Cl} \cdot \text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. All residues were examined under the microscope where the different solids were easily detected. The mixed crystals have only a faint tinge of blue. They become yellow when heated in the oven, so the dihydrate is evidently present as in the other cases. The mixed crystals in equilibrium with double salt contain only about 1.8% of cupric chloride.

Whether any of the substituted ammonium chlorides form mixed crystals similar to those of ammonium chloride is a matter of some interest. It has been shown by Retgers¹ that methylamine hydrochloride forms no such crystals with ferric chloride. Similar experiments have been tried in this investigation with aniline hydrochloride. A strong solution of nickel chloride was heated with enough of the hydrochloride so that the latter crystallized on cooling. The crystals formed in thin plates almost impossible to free completely from solution. They had a slight greenish—not yellow—tinge and contained 1.46% NiCl_2 . Some of this was undoubtedly due to contamination from the solution. It is safe to conclude, therefore, that little or no mixing occurs between these salts.

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BEHAVIOR OF POTASSIUM TRINITRIDE TOWARD MANGANESE DIOXIDE AT HIGH TEMPERATURES.

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In view of the analogy existing between nitrogen and oxygen, between ammonia and water,² and, therefore, perhaps also between the pernitrides

¹ *Z. physik. Chem.*, **9**, 393 (1892).

² Franklin, *THIS JOURNAL*, **27**, 820–51 (1905); *Am. Chem. J.*, **47**, 285–317 (1912).