

The ionic refraction of the alkali ions is also plotted against Δ_v/ϕ_v in Fig. 3, the Δ_v/ϕ_v values being increased 0.1 to prevent overlapping. It is obvious that the same sort of systematic relationship exists. The function Δ_v/ϕ_v is, therefore, a useful index to the polarizability of the ions.

Summary

1. The ionic potentials of the inert-gas type ions have been recalculated to volts and compared with ionizing potentials.
2. It is indicated that the valence electron of alkali and alkaline earth ions comes within the crystal radius with ions 0.3 Å. and 0.2 Å. larger than cesium and barium ions, respectively.
3. The ionic polarizability by light or by electrons varies systematically with the fractional difference between the ionic and ionizing potentials, which therefore may be used to estimate the polarizability.

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[CONTRIBUTION FROM THE FRENCH BATTERY COMPANY, MADISON, WISCONSIN]

THE REACTIONS OF AMMONIA ON THE SYSTEM $\text{ZnCl}_2\text{-NH}_4\text{Cl-H}_2\text{O}$

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The literature contains much information relating to the composition and preparation of the zinc-ammonium chloride double salts and the oxy and hydroxy forms as well, but little or no attention seems to have been given to the mechanism of the reactions, especially in relation to hydrogen ion concentration.

It is the object of this investigation to study the formation of insoluble salts in aqueous solution where the ammonium chloride, zinc chloride, ammonia or ammonium hydroxide concentrations are varied. The actual experimental work covered the following ground: (1) determination of the *PH* of aqueous zinc chloride-ammonium chloride solutions in the range of solubility at 20°; (2) determination of the approximate quantity of ammonia which the solutions absorb to the point of formation of a permanent precipitate; (3) determination of *PH* of the supernatant liquors in equilibrium with these precipitates; (4) analysis of the precipitates obtained.

Experimental Procedure

The range of possible concentrations of zinc chloride-ammonium chloride in water at 20° (without supersaturation) was first shown graphically by plotting the aqueous solubilities of zinc chloride-ammonium chloride mixtures on triangular coordinate paper (Fig. 1). The solubility values were as determined by Meerburg.¹ Concentrations were selected to cover the entire range of possible solutions.

¹ Meerburg, *Z. anorg. Chem.*, **37**, 206 (1903).

The stock zinc chloride and ammonium chloride for these solutions were prepared as follows. (1) A stock solution of zinc chloride was prepared from the technical fused salt and the solution allowed to stand for several days, after which it was filtered through asbestos fiber. It analyzed 67.88% ZnCl_2 and 0.077% Fe. (2) The ammonium chloride was obtained by recrystallizing the white commercial 99% grade and drying for twenty-four hours at 105° . The recrystallized salt showed no trace of iron with ammonium sulfocyanate reagent.

The solutions (160 g. of each) were carefully made up from the stock zinc chloride solution, recrystallized ammonium chloride and distilled water. They were not subsequently analyzed.

The P_H measurements were made with the hydrogen electrode and a Type K Leeds and Northrup potentiometer.

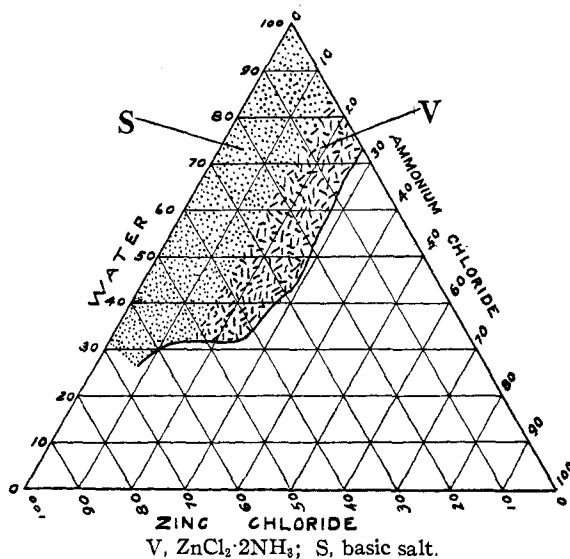


Fig. 1.—Showing solubility range of $\text{ZnCl}_2\text{-NH}_4\text{Cl}$ mixtures in water at 20° , and areas in which ammonia precipitates $\text{ZnCl}_2\cdot 2\text{NH}_3$ and the basic salt.

It was first attempted to pass measured quantities of pure gaseous ammonia into the solutions, but this was found impracticable due to the rapid clogging of the end of the delivery tube with insoluble salts. The introduction of ammonia was finally effected by bubbling definite volumes of carbon dioxide-free air through a large volume of ammonia water maintained at 20° , thence through glass wool vapor traps and finally into the solutions. The apparatus was calibrated, *i. e.*, the ammonia content of a definite volume of the air passed through this train was determined after each three or four runs. This method was quite crude but was found to be within 10% accuracy.

The various solutions tried absorbed all ammonia passed into them; *i. e.*, no appreciable quantity of ammonia escaped as determined by leading the air through a known quantity of standard acid solution after passing through the solutions studied.

The introduction of ammonia was stopped when the first trace of a permanent precipitate occurred. The solutions, which were in Erlenmeyer flasks, were stoppered and allowed to remain for at least twenty-four hours before P_H measurements were made on the supernatant liquor by the method mentioned heretofore.

The solutions were separated from the precipitates by filtering through an asbestos fiber layer in a Gooch crucible. Each precipitate was washed with from 15 to 25 cc. of 95% alcohol, followed by 10 cc. of ether. They were then dried at 100° for two to four hours. The precipitates obtained from the more concentrated solutions were removed from the crucible, suspended in about 20 cc. of 95% alcohol and again filtered. There was no trouble in separating the precipitates from the asbestos fiber as the washed and dried precipitates "poured" out quite readily after gently tapping them loose with a glass rod. The weight of the precipitate obtained was 2 to 3% of the total weight of solution taken. No analysis was made of the supernatant liquors after the addition of ammonia.

Results

Table I shows the composition of the solutions before adding ammonia, the *P_H* before and after the addition of ammonia, grams of ammonia absorbed up to the point of the first permanent precipitate, analysis of precipitate and nature of precipitate.

TABLE I
COMPOSITION AND *P_H* OF SOLUTIONS, AMMONIA ABSORBED AND ANALYSIS OF
PRECIPITATES

No.	ZnCl ₂ , %	NH ₄ Cl, %	H ₂ O, %	<i>P_H</i>	<i>P_H</i> after adding NH ₃	G. of NH ₃ added per 100 g. of soln.	Analysis of ppts.			Precipitate
							Zn, %	Cl, %	NH ₃ , %	
1	0	26.9	73.1	4.66	..	0	None
2	5.0	15.0	80.0	4.60	6.19	.9	38.22	41.87	19.86	ZnCl ₂ ·2NH ₃
3	5.0	5.0	90.0	4.93	5.41	.3	58.10	15.45	...	Basic
4	15.0	27.6	57.4	4.43	5.52	.7	38.37	41.63	20.00	ZnCl ₂ ·2NH ₃
5	15.0	20.0	65.0	4.34	5.54	1.0	38.19	41.89	19.80	ZnCl ₂ ·2NH ₃
6	15.0	10.0	75.0	4.48	5.56	1.3	51.72	24.01	7.10	Basic
7	15.0	0	85.0	4.97	4.82	0 ^a	54.70	Basic
8	25.0	15.0	60.0	4.09	5.07	1.2	38.09	41.91	...	ZnCl ₂ ·2NH ₃
9	26.0	29.0	45.0	4.29	5.02	0.6	38.21	41.79	19.53	ZnCl ₂ ·2NH ₃
10	30.0	20.0	50.0	3.86	5.04	1.2	38.58	41.54	19.79	ZnCl ₂ ·2NH ₃
11	30.0	5.0	65.0	4.03	4.64	0.6	61.14	13.37	.09	Basic
12	40.0	20.0	40.0	3.22	4.66	1.6	38.65	41.61	19.68	ZnCl ₂ ·2NH ₃
13	40.0	10.0	50.0	3.22	4.33	1.2	56.65	17.43	3.02	Basic
14	43.2	26.0	30.8	3.08	4.59	2.1	38.26	41.86	19.88	ZnCl ₂ ·2NH ₃
15	50.0	10.0	40.0	2.39	3.67	1.4	54.65	19.46	2.93	Basic
16	53.2	14.5	32.3	1.89	3.43	1.8	55.74	18.32	3.13	Basic
17	60.0	5.0	35.0	1.27	2.67	1.3	57.85	15.99	0.39	Basic
18	60.0	0	40.0	1.44	2.46	0.2	57.55	15.13	0.20	Basic
19	66.6	7.9	25.5
20	62.0	9.0	29.0	1.05	2.47	1.1	48.44	32.26	6.60	Basic
21	33.3	0	66.7	4.05
22	50.0	0	50.0	2.71

^a Precipitate formed on standing without addition of ammonia.

Table II shows the composition of the basic precipitates recalculated on the basis of zinc, chlorine and oxygen only. It was assumed that the ammonium ion was present as ammonium chloride uncombined with the other constituents. There is also a possibility of free zinc chloride being

present. The basicity was determined by dissolving a 0.2-g. sample in an excess of normal sulfuric acid and titrating back with half normal sodium hydroxide. The basicity was computed as "O."

TABLE II

COMPOSITION OF BASIC PRECIPITATES RECALCULATED ON BASIS OF Zn, Cl AND O ONLY

Precipitate no.	Zn, %	Cl, %	O, %	Moles per 100 grams		
				Zn	Cl	O
6	72.30	12.90	14.80	1.10	0.36	0.93
11	70.90	15.27	13.83	1.08	.43	.86
13	71.51	14.05	14.44	1.09	.40	.90
15	69.68	17.02	13.30	1.05	.48	.83
16	71.22	15.07	13.72	1.09	.43	.86
17	69.12	18.14	12.74	1.06	.51	.80
18	69.47	17.77	12.76	1.06	.50	.80
20	65.03	24.85	10.12	0.99	.70	.63
Average ^a				1.08	.44	.85

^a Values for precipitate No. 20 are omitted from the average due to their considerable deviation from the other values.

Figure 1 shows the range of possible concentrations of zinc chloride and ammonium chloride in water at 20° (without supersaturation) and also the areas in which $ZnCl_2 \cdot 2NH_3$ and the basic precipitate are obtained when ammonia is added.

Discussion

The data show that two kinds of precipitates were formed, *viz.*, $ZnCl_2 \cdot 2NH_3$ and basic zinc chloride.

The identity of the $ZnCl_2 \cdot 2NH_3$ compound is unmistakably shown by (1) the analysis, which checks closely with the theoretical 38.37% Zn, 41.63% Cl and 20.00% NH_3 , (2) definite crystal form, (3) milky appearance when treated with water and (4) the evolution of ammonia with no ammonium chloride fumes when gently heated, leaving fused zinc chloride.

All basic precipitates when heated gave off water vapor and some ammonium chloride fumes, after which the mass became sticky, congealing to a hard vitreous mass on cooling. A mixture of zinc oxide and zinc chloride in about equal proportions acted in the same way. This combination is sometimes used as a cement.

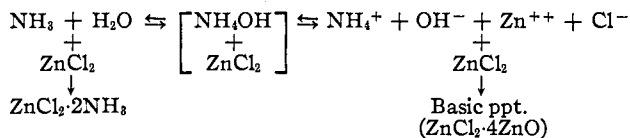
A study of the results of analysis of the basic precipitates and the conditions of their formation indicates that they consist of a basic zinc chloride with the admixture of free zinc chloride and ammonium chloride. The data in Table II were obtained by deducting the percentage of ammonium and the theoretical percentage of chlorine combined with it to form ammonium chloride, then computing the percentage composition with the basicity figured as oxygen. It was not possible to determine the admixed zinc chloride. The results, however, show closer agreement than the original analysis but there is still considerable variation. However, the average

moles of zinc, chlorine and oxygen per 100 g. of basic precipitate (Table II) point to the formula $ZnCl_2 \cdot 4ZnO$.

The experimental data show that if the ammonium chloride content is 15% or above, regardless of the zinc chloride content (above at least 5%), the compound $ZnCl_2 \cdot 2NH_3$ is precipitated by adding ammonia. Below 15% ammonium chloride the basic compound is thrown down.

Obviously a preponderance of dissolved gaseous ammonia would favor the formation of $ZnCl_2 \cdot 2NH_3$, while excessive hydroxyl ions would throw the reaction in favor of $ZnCl_2 \cdot 4ZnO$, or some other similar basic compound.

The reactions can be represented by the chemical equations



The addition of ammonium chloride drives equilibrium to the left since ammonium ions from ammonium chloride repress the ionization of ammonium hydroxide. When the ammonium chloride content is less than 15%, the hydroxyl ions can be made sufficiently concentrated (by addition of ammonia, forming ammonium hydroxide) to exceed the solubility product for the basic zinc salt ($ZnCl_2 \cdot 4ZnO$).

Conclusions

When ammonia is added to zinc chloride-ammonium chloride solutions at 20°, $ZnCl_2 \cdot 2NH_3$ is precipitated when the ammonium chloride content is about 15% or above, and a basic precipitate, probably $ZnCl_2 \cdot 4ZnO$, is precipitated when the ammonium chloride content falls below 15%.

The mechanism of the reaction in the system $NH_3-ZnCl_2-NH_4Cl-H_2O$ is explained by the concentrations of the various constituents and the effect which ammonium chloride has upon the extent of ionization of these constituents.

MADISON, WISCONSIN