

to confirm the existence of the monohydrate. It is a white crystalline substance, having a density of 1.48, freezing at  $-15.35^{\circ}$ , and resembling ammonium chloride in general character. It is very soluble in water but very slightly in hydrogen chloride. Since it is in equilibrium with the hydrogen chloride phase, or very nearly so, at its melting point, its vapor pressure at that temperature must be nearly equal to that of the liquid, which is in turn practically equal to that of the pure hydrogen chloride. This according to Faraday is 17.3 atmospheres.

The density of solutions and of their vapor have been determined up to the saturation point at the temperatures  $-15^{\circ}$ ,  $0^{\circ}$ ,  $20^{\circ}$  and  $35^{\circ}$ .

The density of liquid and of gaseous hydrogen chloride have been determined at temperatures from  $+51^{\circ}$  to  $-50^{\circ}$ .

In conclusion, I wish to acknowledge my obligations to Dr. H. P. Cady for his kindly interest and valuable suggestions during this work.

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## THE SOLID HYDRATES OF AMMONIA.

BY FRANK F. RUPERT.

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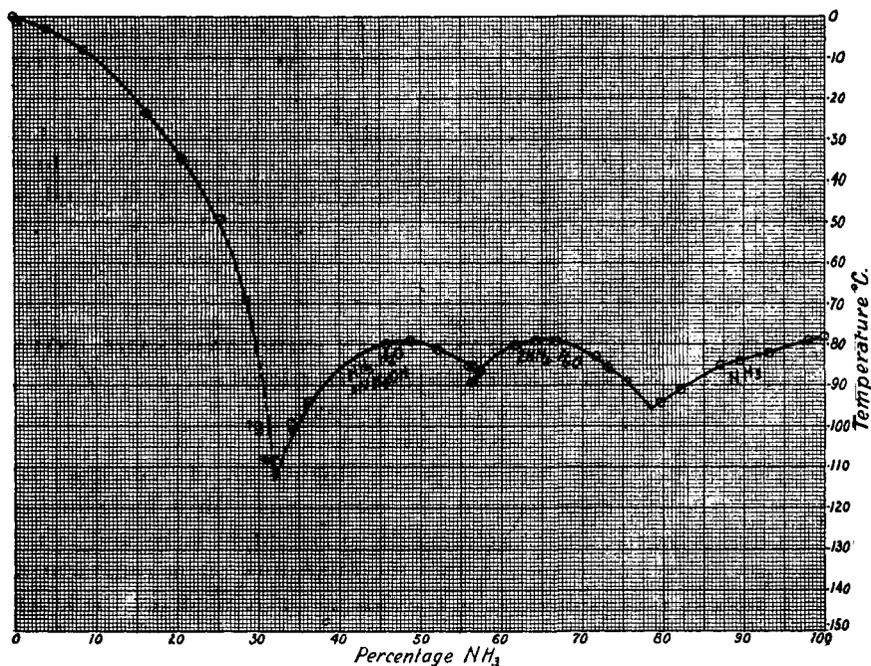
In connection with the work on the system hydrogen chloride and water it was noticed that there are several similar systems on which little work has been done in the matter of freezing points and the search for solid compounds. One of these is the system ammonia and water. It is familiar to all that the monohydrate of ammonia, or ammonium hydroxide, has been regarded as a compound by practically all chemists for many years from the resemblance of the properties of a solution of ammonia to those of hydroxides, but it never has been obtained as a solid.

The method for investigating ammonia was very much simpler than that necessary in the case of hydrogen chloride, as liquid ammonia and water are miscible in all proportions, and solutions in all concentrations can be prepared whose vapor pressure is less than one atmosphere. Weighed quantities of water and of ammonia were introduced into a large test tube containing a stirring rod and toluene thermometer. When it was necessary to keep this below room temperature when weighing, the tube was inserted through a cork into a vacuum jacketed tube previously cooled with liquid air, and the whole weighed. To find the freezing point the tube was immersed in a bath as described in the paper on hydrochloric acid, except that gasoline has been found more satisfactory as a bath liquid at the temperatures used. The bath was cooled and freezing points found in the ordinary way.

The following measurements of percentage composition and freezing points have been made.

These results are given graphically in the accompanying curve, which

shows maximum freezing points at about 49 per cent., freezing point  $-79^{\circ}$ , and 65 per cent., freezing point  $-79^{\circ}$ . The theoretical composition of ammonium hydroxide is 48.59 per cent. ammonia; of  $2\text{NH}_3\cdot\text{H}_2\text{O}$ ,



*Freezing points of ammonia solutions.*

65.40 per cent. Eutectic points probably appear at 32 per cent. about  $-115^{\circ}$ , 57.5 per cent.,  $-86.5^{\circ}$  and 78.5 per cent.,  $-96^{\circ}$ . The temperature of the second was found experimentally.

Per cent. $\text{NH}_3$ .	Freezing point $^{\circ}$ .	Per cent. $\text{NH}_3$ .	Freezing point $^{\circ}$ .
4.1	$-2.9$	61.6	$-81.0$
8.2	$-8.1$	64.3	$-79.3$
16.2	$-23.1$	66.7	$-79.6$
20.7	$-34.9$	71.7	$-82.9$
25.3	$-49.8$	73.4	$-85.5$
28.5	$-69.2$	75.4	$-88.8$
30.0	not at $-98$	79.8	$-94.2$
33.9	not at $99.6$	82.3	$-91.6$
36.2	$-94.1$	87.1	$-86.2$
46.3	$-80.0$	89.6	$-84.2$
48.9	$-79.6$	93.2	$-82.2$
52.3	$-81.0$	97.8	$-79.1$
56.3	$-85.5$ and $-89.5$	100.0	$-78.0$
56.7	$-85.1$		.....

Ammonium hydroxide forms very small colorless crystals which suggest those of sodium and potassium hydroxides; those of  $2\text{NH}_3 \cdot \text{H}_2\text{O}$ , which may be called ammonia semi-hydrate, or may possibly be written  $(\text{NH}_4)_2\text{O}$ , ammonium oxide, are much larger, transparent and needle-shaped. Solutions containing from about 25 to 60 per cent. ammonia are very viscous at temperatures below about  $-60^\circ$ . At  $-100^\circ$  the 33 per cent. solution can hardly be stirred.

The weighings are subject to some small error from accumulated moisture and other causes. Another series of freezing points will be found, with more accurate weighings and with points nearer together, and possibly other properties of the system will be investigated.

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## THE VELOCITY OF HYDROLYSIS OF AN INORGANIC SALT, POTASSIUM RUTHENIUM CHLORIDE.

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1. *Introduction.*—The kinetics of the hydrolysis of inorganic salts has been relatively little studied for two reasons. Most inorganic salts which hydrolyze in aqueous solution do so instantaneously, and in those cases where the rate is measurable, the difficulties of measurement and the number of factors influencing the velocity have rendered the kinetics so complex that, as far as we are aware, a satisfactory kinetic equation has not been established for the hydrolysis of a single purely inorganic salt. On the other hand, the equilibria of salt hydrolyses have been extensively studied and shown by the investigations of Arrhenius,<sup>1</sup> Walker,<sup>2</sup> Shields,<sup>3</sup> and others, to be in accord with the Guldberg-Waage Law of Mass action.

Among the inorganic salts composed of a weak base and a strong acid and which hence liberate acid on hydrolyzing, several cases of time reaction have been observed and studied by means of the rise in electrical conductivity. Among others should be mentioned  $\text{FeCl}_3$  (H. M. Goodwin, *Z. physik. Chem.*, **21**, 1);  $\text{AuCl}_3$ ,  $\text{SnCl}_4$ ,  $\text{PtCl}_4 \cdot \text{H}_2\text{O}$  (F. Kohlrausch, *Ibid.*, **33**, 257, and *Wied. Ann.*, **64**, 423);  $\text{AuCl}_3$  (Hittorf and Salkowski, *Ibid.*, **28**, 546). There is, however, in general, one marked difference between organic and inorganic hydrolyses aside from their extreme differences in rate, namely that, while the presence of acid accelerates the velocity of the former it retards that of the latter. Also in the former, the equilibrium is unaffected, but in the latter is shifted by the presence

<sup>1</sup> Arrhenius, *Z. physik. Chem.*, **5**, 16; **13**, 407.

<sup>2</sup> Walker, *Ibid.*, **4**, 333.

<sup>3</sup> Shields, *Ibid.*, **12**, 167.