[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

Solubility Relations of the Ternary System Magnesium Nitrate–Nitric Acid–Water at 25°

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This further investigation[1] was undertaken to confirm the existence of certain hydrates of magnesium nitrate; and to determine methods of preparation of these salts for calorimetric and vapor pressure measurements, which are being made in this Laboratory. Malquori[2] investigated this system at 20°, but gives only fragmentary data up to 59.38% nitric acid.

Experimental

The procedure was to make saturated solutions, and to analyze both the solution phase and the moist crystal phase for nitric acid and for zinc nitrate.

Materials.—C. P. magnesium nitrate was prepared as previously described.[1] C. P. nitric acid was prepared by distilling from a mixture of two volumes of sulfuric acid and one volume of nitric acid. The distillate was redistilled in a still having a long fractionating column and a controlled reflux. The fraction distilling over at 82° was collected. This brown acid which distilled over was decolorized by blowing dry air through it at 70°. The acid thus purified analyzed 99–100% acid. A good grade of distilled water was used.

Preparation of Saturated Solutions.—Mixtures of the proper concentrations were made by weighing out requisite amounts of the three constituents. These were placed in two ounce tincture bottles having carefully ground glass stoppers. These bottles were then sealed with paraffin. The samples were then revolved in a water-bath at 25 ± 0.02° for six hours. The concentration did not change after the third hour. The saturated solution phase was then removed and analyzed. The moist residues were analyzed in enough cases to establish the nature of the solid phase.

The saturated solutions were withdrawn by either of two methods. For the non-viscous solutions, where the crystals settled out rapidly leaving a clear solution, the solution was pipetted off. In other cases, a filtering apparatus was used. It consisted of a wide-mouthed bottle having a two-holed rubber stopper. One hole contained a suction tube, and the other hole contained a tube having a sintered glass filter plate at the end. This tube, at 25°, was placed in the solution and suction was applied. This caused the saturated solution to be transferred to the wide-mouthed bottle.

Method of Analysis.—The magnesium nitrate content was determined by igniting duplicate samples to the oxide. The acid content was determined by diluting duplicate samples to one liter each and titrating 25-ml. portions with 0.1 *N* carbonate free potassium hydroxide. Either brom thymol blue or brom cresol green was used as the indicator. To ensure that the stoichiometric equivalent of base was used, the 25-ml. samples were diluted with water containing the indicator. The acidity of this diluting water had been adjusted to the indicator end-point and the diluted sample was then titrated to the same color. The amount of water was obtained by the difference between the weight of sample and the sum of the weights of the other two constituents.

Results

The data obtained are tabulated in Table I, and are plotted in Fig. 1. The solutions lying along portion AB of the curve are in equilibrium with

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[1] Ewing, Brandner, Slichter and Griesinger, THIS JOURNAL, **55**, 4822 (1933).

[2] Malquori, *Gazz. chim. ital.*, **58**, 209 (1928).

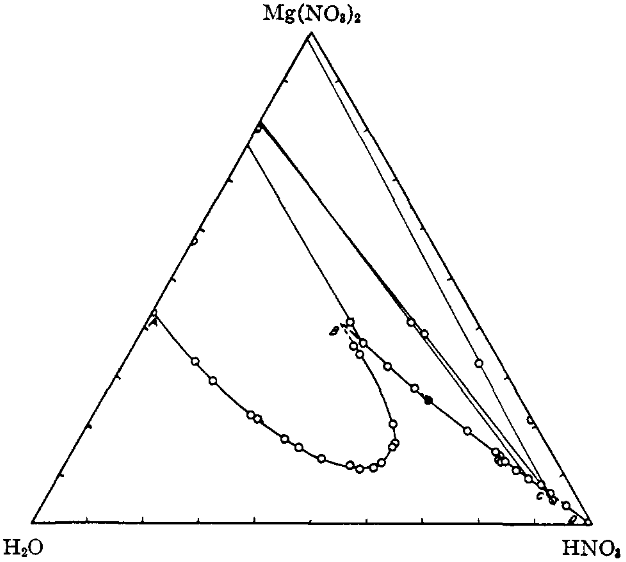

Fig. 1.—Ternary diagram of magnesium nitrate–nitric acid–water.

hexahydrate crystals, along BC with dihydrate crystals and along CD with anhydride crystals.

TABLE I

COMPOSITION OF SATURATED SOLUTIONS

%HNO_3	%$Mg(NO_3)_2$	Solid phase[c]	%HNO_3	%$Mg(NO_3)_2$	Solid phase[c]
0.0	42.5	VI	40.9	34.3	VI
12.6	33.2	VI	41.0	34.3	VI
17.9	29.0	VI[a]	41.5	34.7	VI
17.9	29.1	VI	39.6	36.0	VI
18.5	28.6	VI	41.0	36.7	II[b]
18.6	28.5	VI	47.4	32.2	II
28.1	22.0	VI	47.6	32.1	II
28.1	22.1	VI	54.8	27.6	II
29.7	21.2	VI	58.4	25.2	II
29.9	21.2	VI	68.5	19.0	II
36.7	17.1	VI	75.8	14.7	II
36.8	17.2	VI	77.0	13.0	II
37.4	16.7	VI	77.0	13.7	II
40.4	15.4	VI	77.6	12.8	II
45.4	13.2	VI	78.3	13.0	II
51.1	11.7	VI	81.2	11.0	II
53.0	11.3	VI[a]	81.9	10.6	II
55.4	11.5	VI	84.4	9.4	II[b]
55.5	11.5	VI	87.1	8.1	II[b]
56.1	12.6	VI	89.5	6.4	II
56.2	12.6	VI	89.7	6.2	II

TABLE I (*Concluded*)

%HNO_3	%$Mg(NO_3)_2$	Solid phase[c]	%HNO_3	%$Mg(NO_3)_2$	Solid phase[c]
56.7	15.9	VI	91.0	4.7	0[b]
56.7	16.5	VI	93.9	3.8	0
56.8	16.6	VI	99.6	0.2	0[b]
54.6	20.2	VI[a]			

[a] Dried crystals analyzed. [b] Residue analyzed. [c] VI = hexahydrate, II = dihydrate. 0 = anhydride.

The nature of the solid phase was determined by two methods. In the case of the hexahydrate, the moist residues in three instances were centrifuged, and the crystals analyzed. The values obtained were 6.16, 6.2 and 6.0 molecules of water per molecule of magnesium nitrate. The dihydrate and the anhydride were so hygroscopic that this method was not feasible. Here the "tie line" method was used. The total residue was dissolved in a weighed amount of water, and its composition determined by analysis. The "tie lines" are plotted on Fig. 1, and indicate the existence of the solid phases mentioned above.

Summary

The equilibrium diagram for the ternary system magnesium nitrate–nitric acid–water at 25° has been established.

The forms of magnesium nitrate in stable equilibrium with nitric acid at 25° are the hexahydrate, the dihydrate and the anhydride.

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The Temperature-Composition Relations of the Binary System Zinc Nitrate–Water

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Mention is made of several hydrates of zinc nitrate in the literature:[1] namely, hydrates containing one, one and one-half, two, three, four, five and one-half, six and nine molecules of water. The existence of the enneahydrate and the hexahydrate have been thoroughly substantiated by previous investigators. Comprehensive solubility data are given in "International Critical Tables" for the enneahydrate and the hexahydrates. The data indicate that the next lower form is the trihydrate.

In connection with vapor pressure and calorimetric work which is being carried out in this Laboratory, it became necessary to establish definitely

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[1] Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, Vol. IV, p. 651, 1923.