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

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

BY WARREN W. EWING, JOHN J. MCGOVERN AND GEORGE E. MATHEWS, JR.

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

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

which hydrates of zinc nitrate exist, and to determine methods for preparing them. The freezing point method was used, and the complete solubility relations determined from the hexahydrate to the monohydrate. From the data obtained, it may be seen that the stable forms existing at room temperature are the hexahydrate, the tetrahydrate, the dihydrate and the monohydrate.

Experimental Method

The apparatus used and the experimental technique have been described in a previous article.[2]

Materials.—A c. p. grade of zinc nitrate was recrystallized twice from water in the hexahydrate form. These crystals could be air dried on a day when the humidity was low. Desiccating the hexahydrate over concentrated sulfuric acid gave approximately the dihydrate composition. The process was very slow. Further desiccation over phosphorus pentoxide in a vacuum resulted in approximately the monohydrate composition. There was some decomposition as indicated by an insoluble residue when the salt was dissolved in water. Hence the following alternate rapid method was used to obtain the

Table I

Temperature–Composition Relations

$Zn(NO_3)_2$, %[a]	Temp., °C.	Solid phase[b]	$Zn(NO_3)_2$, %[a]	Temp., °C.	Solid phase[b]
56.1	25.1	VI	76.3	41.3	IV
56.3	25.9	VI	77.2	39.7	IV
56.9	27.3	VI	77.3	39.1	IV
57.6	28.8	VI	77.8	38.2	IV
57.7	29.1	VI	77.8	37.5	IV
58.2	29.7	VI	78.0[d]	37.2	IV–II
58.3	30.4	VI	79.0	32.2	IV[c]
59.1	31.4	VI	79.7	43.6	II
58.9	31.4	VI	79.8	44.9	II
59.2	31.6	VI	80.1	46.6	II
59.5	32.4	VI	81.6	50.6	II
60.3	33.3	VI	81.9	51.9	II
60.3	33.4	VI	84.0	55.4	II
60.8	34.1	VI	85.2	55.2	II
61.0	34.3	VI	86.0	53.8	II
63.4	36.1	VI	86.0	53.3	II
63.7	35.9	VI	86.3[d]	52.1	II–I
65.2	35.4	VI	86.6	52.8	I
66.2	34.6	VI–IV	86.6	54.1	I
67.4	33.1	VI[c]	87.6	59.2	I
67.9	40.0	IV	88.6	65.2	I
70.0	43.2	IV	89.0	66.9	I
72.5	44.7	IV	89.4	68.6	I
75.8	42.4	IV	89.8	70.3	I
			90.0	70.7	I

[a] % = g. $Zn(NO_3)_2$ per 100 g. of solution. [b] VI = hexahydrate, IV = tetrahydrate, II = dihydrate, I = monohydrate. [c] Metastable solid phase. [d] Determined graphically.

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(2) Ewing, Brandner, Slichter and Griesinger, This Journal, **55**, 4822 (1933).

very concentrated "melts." Hexahydrate crystals were melted and boiled until the boiling point reached 250°. There was considerable decomposition. The solution was cooled and carefully neutralized with 100% redistilled nitric acid. This neutralized sample left no insoluble residue when dissolved in water, and the solution was neutral to brom thymol blue.

Analysis.—The melts were analyzed by igniting to the oxide.

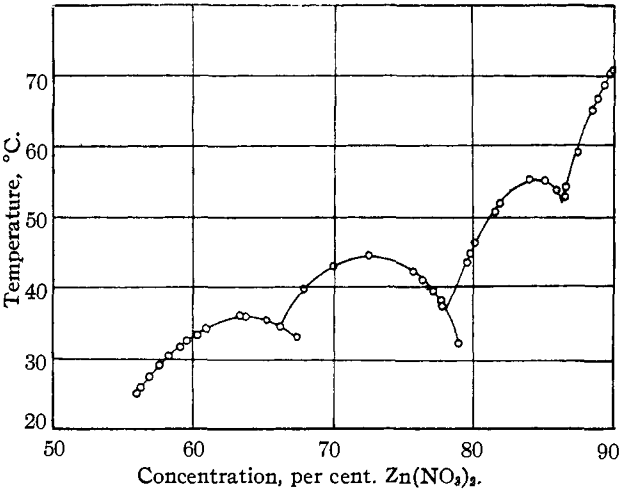

Fig. 1.—Freezing point–composition diagram of the system zinc nitrate–water.

Results

The data obtained are tabulated in Table I, and are plotted in Fig. 1. The data indicate that the hexahydrate, the tetrahydrate, the dihydrate and the monohydrate, melting respectively at 36.1, 44.7, 55.4 and 70.7°+ are the stable forms at room temperature. No evidence was obtained of the existence of the trihydrate. It is estimated that the data are acccurate to 0.1% for the hexahydrate and the tetrahydrate regions. For the higher concentrations, the accuracy is not quite so good due to the fact that these solutions decompose slowly at their melting temperatures. All the solutions which were studied can be easily supercooled to room temperature. At the higher concentrations the solutions were quite viscous. The freezing point method is not as accurate for highly viscous liquids due to the slow formation of the crystals, and the consequent slow evolution of heat. However, the solubility method is perhaps more inaccurate due to difficulty in filtering the highly viscous system.

Summary

The solubility–temperature diagram for the system zinc nitrate–water has been extended from the hexahydrate region to the freezing point of the monohydrate.

The existence of the hexahydrate, the tetrahydrate, the dihydrate and the monohydrate has been established.

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

BY WARREN W. EWING, ATWOOD J. RICARDS, WILLIAM J. TAYLOR, JR., AND DAVID W. WINKLER

This further investigation[1] was undertaken to confirm the existence of certain hydrates of zinc 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 for the hexahydrate and the tetrahydrate regions.

Experimental

The apparatus and the technique used have been described in a previous article.[3] The only change was to use glass wool instead of a sintered glass plate as the filter medium. This was necessitated by the viscous solutions encountered. The glass wool was packed in a bell-shaped portion extending beyond a constriction in the filtering tube. All solutions were filtered.

The methods of preparing and purifying the zinc nitrate and the nitric acid, and the methods of analysis, have been described in previous articles.[1,3] The compositions of the solid phases were established by analyzing the moist residues and plotting "tie lines."

TABLE I

COMPOSITION OF THE TERNARY SYSTEM $Zn(NO_3)_2$–HNO_3–H_2O AT 25°

Solution		Residue		
% HNO_3	% $Zn(NO_3)_2$	% HNO_3	% $Zn(NO_3)_2$	Solid phase[a]
0.0	56.1			VI
3.5	53.1			VI
9.5	49.4			VI
15.5	46.8			VI
16.6	47.6	6.1	57.8	VI
15.5	49.7	10.3	56.0	VI–IV
24.0	41.5			IV
36.7	34.6			IV
38.6	34.5	22.1	50.7	IV
39.2	35.0			IV

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[1] Ewing, McGovern and Mathews, THIS JOURNAL, **55**, 4827 (1933).

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

[3] Ewing and Klinger, THIS JOURNAL, **55**, 4825 (1933).