

The physical constants of the other hexanol are being measured at present and their values will be reported in later communications.

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

## The Temperature-Composition Relations of the Binary System Magnesium Nitrate-Water

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Mention is made of several hydrates of magnesium nitrate in the literature:<sup>1</sup> namely, the ennea, hexa, tri, di and monohydrates and the anhydride. The purpose of this investigation was to establish definitely which of these forms actually occur in order that they might be prepared for calorimetric and vapor pressure measurements which are being made in this Laboratory. The existence of the ennea, the hexa, and the dihydrate and the anhydride has been confirmed and the conditions under which they exist are indicated by the accompanying data.

**Experimental Method.**—The freezing point method was used. An approximate preliminary freezing point was first determined outside the apparatus. The accurate freezing point was then determined in the apparatus, with only a fraction of a degree of supercooling. This was repeated until the accurate temperature was definitely established. The apparatus used has been described in a previous article.<sup>2</sup>

The following modifications were used. For temperatures below 0° a platinum resistance thermometer was used. The resistance was measured by means of a Mueller type temperature bridge made by Eppley Laboratory, Inc. The bath surrounding the freezing point tube consisted of alcohol cooled by means of solid carbon dioxide. For the higher temperatures the bath surrounding the freezing point tube consisted of oil. It contained a resistance coil extending from the top to the bottom of the oil. The oil was stirred by a stream of air bubbling through it.

C. p. magnesium nitrate was thrice recrystallized as hexahydrate from water. These crystals were dried over 60% sulfuric acid. The dihydrate was prepared by drying the hexahydrate over phosphorus pentoxide. It was possible to remove still more water by drying over phosphorus pentoxide at 110°.

The composition of the samples was determined by igniting to the oxide and weighing.

(1) Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, Vol. IV, pp. 379-381, 1923.

(2) Ewing, Krey, Law and Lang, *THIS JOURNAL*, **49**, 1958 (1927).

## Results

The data obtained are tabulated in Table I and are plotted in Fig. 1. The composition of the hexahydrate and the dihydrate follows from the

TABLE I

TEMPERATURE-COMPOSITION RELATIONS					
Mg(NO <sub>3</sub> ) <sub>2</sub> , % <sup>a</sup>	Temp., °C.	Solid <sup>b</sup> phase	Mg(NO <sub>3</sub> ) <sub>2</sub> , %	Temp., °C.	Solid phase
0.50	- 0.232	Ice	52.4	77.6	VI
1.96	- 0.476	Ice	54.0	84.3	VI
2.87	- 1.29	Ice	55.8	87.8	VI
6.58	- 2.49	Ice	57.8	89.9	VI <sup>c</sup>
12.09	- 5.07	Ice	61.2	87.6	VI
15.04	- 6.84	Ice	64.2	81.2	VI
18.8	-10.09	Ice	64.7	74.8	VI
22.2	-13.82	Ice	66.4	64.5	VI
25.5	-17.88	Ice	66.8	62.3	VI
27.5	-20.17	Ice	67.2	56.9	VI
29.3	-22.58	Ice	69.0	40.4	VI <sup>d</sup>
31.06	-25.66	Ice		52.7	VI-II
32.37	-31.87	Ice IX	68.7	52.9	II
32.8	-30.5	IX	68.4	61.1	II
33.6	-25.0	IX	69.3	65.9	II
36.6	-15.3	IX	69.4	68.6	II
37.1	-14.7	IX-VI	70.0	71.8	II
36.7	-23.7	VI <sup>d</sup>	71.4	82.3	II
38.4	- 4.8	VI	71.4	85.4	II
39.6	+ 2.7	VI	73.0	96.5	II
40.4	10.2	VI	74.9	114.4	II
42.5	25.0	VI	76.1	119.7	II
43.2	32.4	VI	77.5	125.8	II
45.0	43.1	VI	79.8	130.0	II
46.7	49.3	VI	81.1	130.9	II <sup>c</sup>
47.8	56.2	VI	82.4	130.0	II <sup>d</sup>
48.4	60.0	VI	81.9	130.5	II-0
49.2	63.3	VI	82.1	137.7	0
50.2	66.8	VI	82.4	144.6	0
51.5	74.1	VI			

<sup>a</sup> % = g. Mg(NO<sub>3</sub>)<sub>2</sub> per 100 g. of solution. <sup>b</sup> IX = enneahydrate, VI = hexahydrate, II = dihydrate, 0 = anhydride. <sup>c</sup> = freezing point of hydrate. <sup>d</sup> = metastable solid phase.

diagram. The composition of the enneahydrate was determined experimentally by analysis. While this investigation was being carried out, Sieverts and Petzold<sup>3</sup> published results on the same system. Their data are also plotted in Fig. 1. The general shapes of the curves are similar. The discordances in results are indicated by the following comparisons, in which the first data are by the present authors and the second by Sieverts and Petzold.

(3) Sieverts and Petzold, *Z. anorg. allgem. Chem.*, **205**, 113 (1932).

Composition	Freezing points, °C.	
Cryohydric point	-31.9	-31.5
Ennea-hexa transition	-14.7	-17.1
Hexahydrate	89.9	89.2
Hexa-di eutectic	52.7	55.6
Dihydrate	130.9	129.3
Di-anhydride eutectic	130.5	127.7

In addition to the above forms they report a metastable tetrahydrate freezing just below the hexa-di eutectic and forming hexa-tetra and tetra-di transition points. We did not find such a phase either by freezing point or vapor pressure methods.

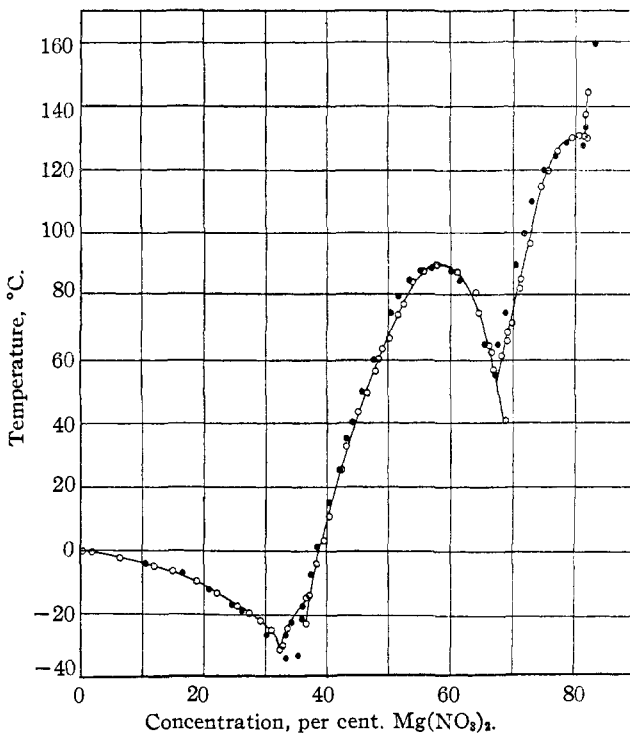


Fig. 1.—Freezing point-composition diagram of the system magnesium nitrate-water; ○, Ewing, Brandner, Slichter, and Griesinger; ●, Sieverts and Petzold.

### Summary

The temperature-composition diagram of magnesium nitrate-water has been investigated.

The existence of the ennea, the hexa and the dihydrates, and of the anhydride of magnesium nitrate has been confirmed.

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