

nitrate is added to ammonium nitrate. There is no change in the crystal structure of the ammonium nitrate, however, because the x-ray powder pattern of ammonium nitrate is identical before and after the addition of magnesium nitrate to the system, except for the appearance of a second phase,  $(\text{NH}_4)_3\text{Mg}(\text{NO}_3)_5$ , in the diagram.

The phase diagram for the system  $\text{Mg}(\text{NO}_3)_2\text{-NH}_4\text{NO}_3$  is shown in Figure 4. Ammonium nitrate which exhibited a transition near 35° C. was chosen as a raw material for the preparation of the systems to be investigated. The rise in the temperature of the transition between Forms IV and III is a continuous function of the concentration of magnesium nitrate contained in the system until the transition temperature reaches 55° C. The temperature of the III → II transition is also influenced by the magnesium nitrate but not as strongly as in the case of the IV → III transitions.

Calcium nitrate also extends the stability of Form IV ammonium nitrate but the maximum temperature obtained for the IV → III transition was 50° C. While magnesium nitrate has considerable influence on the temperature of the III → II transition and will raise the temperature from 82° to 90° C., calcium nitrate has very little influence on the temperature of the III → II transition.

Two compounds,  $\text{NH}_4\text{Mg}(\text{NO}_3)_3$  and  $(\text{NH}_4)_3\text{Mg}(\text{NO}_3)_5$ , were formed in the concentration range of the  $\text{NH}_4\text{NO}_3\text{-Mg}(\text{NO}_3)_2$  phase diagram. Both compounds have unique x-ray patterns and both melt incongruently. When as little as 5% magnesium nitrate has been formed in the ammonium nitrate by the reaction of magnesium oxide and ammonium nitrate the compound  $(\text{NH}_4)_3\text{Mg}(\text{NO}_3)_5$  can be detected in the x-ray patterns of the system.

Table I. Analyses of Compounds in the Phase Diagram

		Wt. %; Theory	Wt. %; Found
	$(\text{NH}_4)_3\text{Mg}(\text{NO}_3)_5$		
Total nitrogen		28.84	28.58
Ammoniacal nitrogen		10.81	10.94
Magnesium oxide		10.37	10.20
	$\text{NH}_4\text{Mg}(\text{NO}_3)_3$		
Total nitrogen		24.52	24.92
Ammoniacal nitrogen		6.13	6.91
Magnesium oxide		17.64	17.59

The compositions which are very rich in magnesium nitrate are difficult to prepare, and the melting temperature is not very reliable because the system decomposes at high

temperatures. Attempts to prepare samples containing more than about 85% magnesium nitrate were abandoned because the samples must be heated to temperatures high enough to cause decomposition of the system.

Glasses rather than crystalline products can be easily prepared in the system in the region near 65% magnesium nitrate. They form more easily when the melt is not ammoniated before cooling. Once a glass has been formed it will crystallize upon reheating to 110° C. and a large quantity of heat is evolved during the crystallization.

It is impossible to state that the IV → II transition does not occur when Form IV ammonium nitrate is heated to temperatures above 55° C.; but none of the evidence supports the IV → II concept. The hot stage x-ray patterns were never completely clean and two phases, IV and III, usually co-existed; but in no instance was Form II detected below 80° C. when pure Form IV had been heated. It is therefore concluded that a II → IV transition may occur on cooling, but that IV → III transition occurs on heating ammonium nitrate, whether the transition temperature is 32° C. or 55° C.

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#### LITERATURE CITED

- (1) Behn, U., *Proc. Roy. Soc. (London)* **A80**, 444 (1908).
- (2) Bowen, N.L., *J. Phys. Chem.* **30**, 724 (1926).
- (3) Bridgman, P.W., *Proc. Am. Acad. Arts Sci.* **51**, 581 (1916).
- (4) Butchart, A., Whetstone, J., *Disc. Faraday Soc.* **1949**, p. 254.
- (5) Campbell, A.N., Campbell, A.J.R., *Can. J. Research* **24B**, 93 (1946).
- (6) Hendricks, S.B., Posnjak, E., Kracek, F.C., *J. Am. Chem. Soc.* **54**, 2766 (1932).
- (7) Hocart, R.J., Mathieu-Sicard, A., *Disc. Faraday Soc. No. 5*, 237 (1949).
- (8) *Ibid.*, 289 (1949).
- (9) Kaelble, E.F., Monsanto Chemical Company, St. Louis, Missouri, Private Communication, October 27, 1958.
- (10) Leskovich, I.A., *Zhur. Fiz. Khim.* **28**, 2255 (1954).
- (11) Makhnatkin, M.P., *Ibid.*, 552 (1954).
- (12) Morand, J., Michel, A., *Bull. Soc. Chem. France* **1953**, p. 913.
- (13) Morand, J., *Ann. Chim. (Paris)* **10**, 1018 (1955).
- (14) Tanko, K., Fukuyama, I., *J. Phys. Soc. Japan* **8**, 428 (1953).
- (15) Trimeyer, R., *Z. Krist.* **97**, 386 (1937).
- (16) Val'fkovich, S.L., Rubenchik, S.M., Kozhin, V.M., *Izvest. Akad. Nauk.S.S.R., Otdel Khim. Nauk* **1954**, p. 209.
- (17) Whetstone, J., *Acta. Cryst.* **7**, 697 (1954).

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#### CORRECTIONS

In the article, "Mass Transfer Studies in Perforated-Plate Extraction Towers," by M. Raja Rao [*J. Chem. Eng. Data* **7**, No. 4, 471(1962)] a figure caption was omitted. "Figure 1. Extraction of benzoic acid from toluene to water. Comparison of the present mass transfer data with that reported in the literature" should have been inserted in the first column below the first graph. The second graph is part a of Figure 2.

In the article, "Equilibrium Vapor Compositions of *p*-Dichlorobenzene-*p*-Dibromobenzene and *p*-Dichlorobenzene-*p*-Bromochlorobenzene Solid Solutions at 50° C., by Sister J.E. Callanan and N.O. Smith [*J. CHEM. ENG. DATA* **7**, No. 3, 374 (1962)] an omission occurred in Table I. Between the fourth and fifth rows of data, the following heading should appear:

The System *p*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>-*p*-C<sub>6</sub>H<sub>4</sub>BrCl