Solid-Liquid Equilibria for the Ammonium Nitrate and Monoammonium Phosphate Binary System

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THE PHASE diagram for the ammonium nitrate-monoammonium phosphate system was drawn using data accumulated as a part of a study of the properties of this system. Figure 1 shows a simple eutectic diagram for the region between 50° and 200° C. at atmospheric pressure. The eutectic composition for the system is 86% ammonium nitrate and 14% monoammonium phosphate. The eutectic temperature is 148° C. No compound formation in the system was observed.

The solidus line was determined using the standard differential thermal analysis technique. A linear heating rate of 60° C. per hour was used and all temperatures were measured with iron-constantan thermocouples to an accuracy of ±2° C. The liquidus curve between 0 and 90% ammonium nitrate was plotted from values measured by Bergman (*1*). These values were verified in this laboratory to the accuracy given above, and the curve was extended to 100% ammonium nitrate. The temperatures were determined by visually observing the point at which the last crystals in a solution would disappear. The solids were heated until a slurry formed and then this slurry was stirred and heated at a rate not exceeding 2° C. per minute until a clear melt was obtained.

The dashed lines on the diagram indicate the temperatures at which the ammonium nitrate moved from one of its crystal forms to another. The areas on the diagram representing the solid portion are labeled with the respective nitrate crystal form. The lines are very near the transition temperatures for pure nitrate and indicate little or no interaction between the two salts.

The samples were prepared from ground and dried reagent grade ammonium nitrate and monoammonium phosphate. The powdered compounds were weighed to the nearest milligram and thoroughly mixed. No sample analyzed more than 0.03% water by Karl Fischer titration.

Analyses (*2*) were made for the formation of higher condensed phosphates which form as the orthophosphate loses water on heating. Only about 1% of the orthophosphate in a mixture containing 90% monoammonium phosphate was converted to more condensed phosphates upon heating the mixture to its melting point. Formation of different compounds was not felt to be a serious problem on heating; however, the formation of higher condensed phosphates at solution temperature occurs rapidly enough to make it a serious problem on cooling the mixture. The diagram shown in Figure 1 does not describe the freezing behavior of melts of ammonium nitrate and monoammonium phosphate if these mixtures have been maintained for more than 3 to 5 minutes in the molten state.

Some 40 to 60% of the orthophosphate was converted to pyro-, tripoly-, and trimetaphosphate after the clear melts were heated for periods of 1 to 2 hours. A typical analysis for a melt initially containing 90% mono-ammonium phosphate is given in Table I. These more condensed phosphates which are formed on heating completely distort the simple phase diagram shown in Figure 1, since it is for a binary system, and after the clear melts have been heated for a period of time, at least five components will be present in the melt. The problem at this point becomes one not easily resolved as glass formation was observed, and this phenomenon is not amenable by the phase rule. No particular problem is posed by the five components and only a slight problem by the fact that the system is changing. The phase rule is applicable at any instant in a changing system; for this particular system the changes taking place can be made small relative to the cooling rate. Sample history has a very strong effect on the crystallizing behavior of melts of monoammonium phosphate and ammonium nitrate.

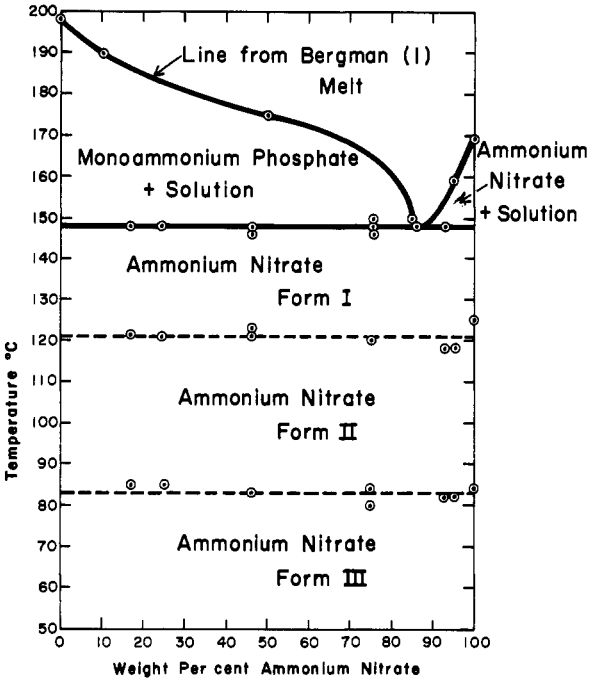

Figure 1. Monoammonium phosphate and ammonium nitrate phase diagram

Table I. Analysis of a 10% Ammonium Nitrate–90% Monoammonium Phosphate Mixture After Heating

Compound	Weight % of Total Phosphate	
	At melting point	After heating 2 hours
Orthophosphate	98.93	61.29
Pyrophosphate	Trace	32.04
Tripolyphosphate	1.06	4.90
Trimetaphosphate	Trace	1.75

Two mixtures, one containing 50%, and the other 10% ammonium nitrate initially, had freezing points after heating of 133 and 153° C., respectively. The normal temperatures at which crystals first appear for such mixtures would be 175° and 190° C. In other instances glass formation and subsequent slow rates of crystallization occurred. A tacky, very viscous liquid formed, and, when held at 25° C., periods of up to 24 hours elapsed before the mass crystallized.

The above information is of interest in the manufacture of high analysis fertilizer materials by processes such as prilling, graining, or the Stengel method, which proceed via crystallization of an essentially anhydrous melt. The formation of the more condensed phosphates greatly complicates the simple picture shown in Figure 1. It is advisable to keep the heating time of the melts to a minimum.

LITERATURE CITED

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(2) Kolloff, R.H., *Anal. Chem.* **33**, 373 (1961).