Phase Transitions of the Ammonium Nitrate–Magnesium Nitrate System

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Crystal transition between Form IV and Form III ammonium nitrate was studied by hot stage microscopy, hot stage x-ray and differential thermal analyses. A method was developed to move the IV → III transition from 32° to 55° and to stabilize the transition at 55°. The phase diagram for the anhydrous system, NH_4NO_3-$Mg(NO_3)_2$, was determined and two compounds were found $NH_4Mg(NO_3)_3$ and $(NH_4)_3Mg(NO_3)_5$.

TRANSITIONS of ammonium nitrate have been the subject of many scientific investigations. The salt experiences four crystal transitions in the temperature range between −20° C. and its melting temperature at 169° C. Much of the previous work has been centered about the transition between Forms IV and III, which is generally accepted as occurring near 32° C. The attention to this particular transition has resulted from the problems the transition causes during the storage of ammonium nitrate.

The 32° C. transition is in the ambient temperature range of the temperate zone and causes swelling, caking, and particle deterioration of stored ammonium nitrate when the transition occurs. The practical advantage of eliminating all transitions of ammonium nitrate under normal storage conditions is obvious. The following work describes how this was achieved as well as the interpretation of the data which led to a dimensionally stabilized ammonium nitrate.

Behn discovered that when ammonium nitrate is exhaustively dried the transition at 32° C. disappears, and it is replaced by a transition at about 50° C. Generally it is conceded the transition at 50° C. to 55° C. is a metastable transition between Forms IV and II and therefore eliminates Form III from the ammonium nitrate phase diagram (*1, 2, 6, 8, 10–17*).

This interpretation implies that the transition between Forms IV and III at 32° C. and the transition between Forms III and II near 82° C. have been traded for a single transition near 50° C. Also implied is that the transition temperature between Form IV and either of the higher temperature forms is a discontinuous function of the concentration of water in ammonium nitrate.

Two methods of influencing the temperature of the transition from Form IV to Form III ammonium nitrate have been studied in detail. Ammonium nitrate which has been coated with acid magenta (*4*) will transform from Form IV to Form III, but the kinetics of the transformation are greatly reduced. A second method depends upon lowering the temperature of the transition by the addition of a soluble salt to the ammonium nitrate. Potassium nitrate is typical and the temperature of the IV → III transition is lowered about 6° C. for each per cent of potassium nitrate which is added to the ammonium nitrate (*5*).

Small quantities (1% or less) of foreign salts will stabilize ammonium nitrate crystals in a temperature range in which they are not normally stable—e.g., Form II nitrate may be stabilized at room temperature by the addition of cesium nitrate to the ammonium nitrate (*7*). This observation suggests that very small quantities of properly chosen foreign salts should have a very large influence on the transition temperature of ammonium nitrate.

EXPERIMENTAL

The chemicals used were reagent grade except for the ammonium nitrate, which was a commercial sample manufactured by the Monsanto Chemical Co. and was better than 99.6% pure ammonium nitrate. The principal impurity in the ammonium nitrate was water.

Four techniques were employed to determine the transition temperatures of the ammonium nitrate samples. Differential thermal analyses were performed by the more or less standard techniques. A small pot furnace was used as a heat source and the rate of temperature rise was controlled with a variable transformer.

The reference sample, pure magnesium oxide, and the ammonium nitrate samples were completely sealed in glass vials to protect them from atmospheric water. The vials contained a thin thermocouple well which coincided with the axis of the vials. These wells were made in the vials by heating the bottoms of the vials to a temperature above the softening point of the glass and then forcing a sharply pointed carbon rod down the axis of the vial. The diameter of the vials was reduced at the mouth of the vial by pulling the neck of the vial to as small a diameter as possible while allowing easy entry of the samples into the vial. This allows easy sealing of the vial after the sample has been introduced without unnecessary heating of the sample.

When the vials were filled, sealed and cooled, they were placed in a steel block in which two holes had been drilled to allow a snug fit between vials and the block. The block had been machined to fit into the cavity of the furnace and was placed in the furnace. Chromel-Alumel thermocouples were fitted tightly in the wells of the vials and the furnace was closed with a stoneware cover.

The sample temperature was graphed as the x component and the difference in the sample temperature and reference temperature was graphed as the y component with a Mosely x-y recorder. This arrangement was employed for both the transition studies and the determination of the $Mg(NO_3)_2$-NH_4NO_3 phase diagram.

The sample size used during most of the work was about 10 grams and a heating rate near 2° C. per minute was found satisfactory. This rate is low enough to allow the sample to remain near equilibrium, yet high enough to yield easily detectable thermal changes at transition points.

A polarizing microscope equipped with a Thomas-Kofler hot stage was also employed to visually check the transitions. A photo-multiplier tube was used on the microscope in conjunction with an El Dorado photometer and a 10-mv. recorder to check automatically the transitions of thin films

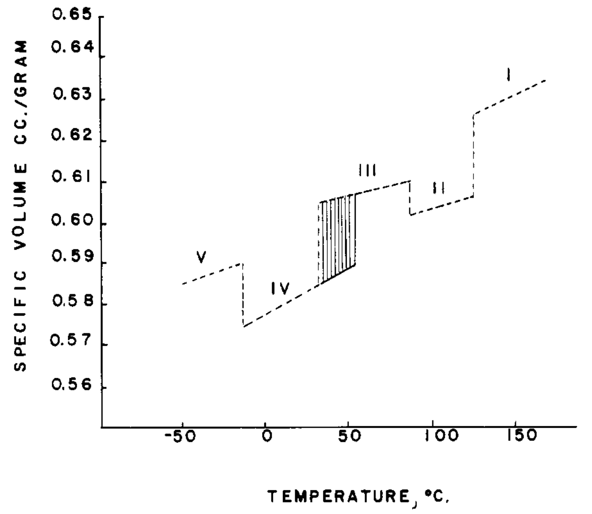

Figure 1. The specific volume of ammonium nitrate demonstrates the unlimited number of paths between Form IV and Form III when Form IV is heated

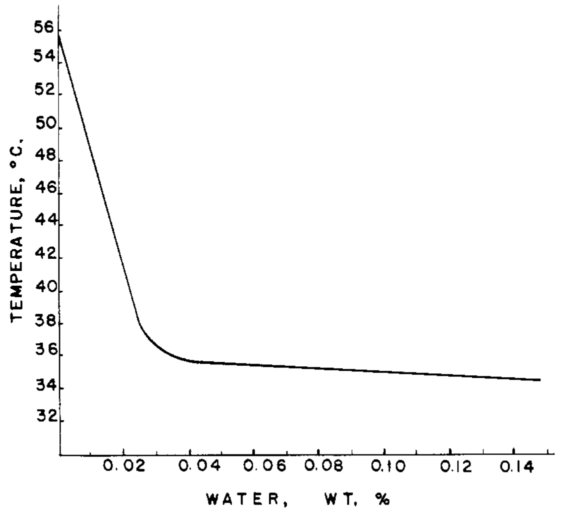

Figure 2. The influence of water on the IV ⟶ III transition of pure ammonium nitrate

of the ammonium nitrate systems. The temperature of the hot stage was either read directly with a thermometer or was recorded by a separate recorder similar to the recorder used with a photometer. The final method used to check the transitions was based upon hot stage x-ray patterns. The x-ray equipment was a Phillips unit equipped with a hot stage obtained from the Robert L. Stone Co.

The water contents of the ammonium nitrate samples were determined by titrations with Karl Fischer reagent delivered by a Beckman automatic titrimeter. Magnesium concentrations in the ammonium nitrate samples were checked by titration with the sodium salt of ethylenediamine tetraacetic acid solutions employing a Sargent-Malmstadt Spectro-Electric titrator (*9*).

The samples used in the phase diagram work were prepared by weighing 100 grams of pure ammonium nitrate into a round-bottomed flask and then heating the flask until the ammonium nitrate was molten. The desired quantity of magnesium oxide was added to the ammonium nitrate in small increments, allowing sufficient time for the complete reaction of magnesium oxide before more was added. The mixtures were heated with a Glas Col heating mantle placed over a large size magnetic stirrer. Glass covered stirring bars were employed. The samples were heated until all evidence of any reaction disappeared. Several hours are sometimes required for the complete reaction between magnesium oxide and molten ammonium nitrate. An inactive form of magnesium oxide gave better results when preparing systems rich in magnesium. When the reaction was complete the melts were sparged with anhydrous ammonia for 15 minutes and then allowed to cool slowly to a crystalline solid while dry nitrogen was passed through the flask. When cool, the pH of a 10% aqueous solution was measured as well as the percentage water in the crystals. Samples in the mixed salts systems which exceeded 0.3% moisture were discarded. The samples were then bottled and stored until ready for use. In most cases the thermal measurements on the samples were made the same day the sample was prepared; but there were occasions when several days elapsed between the time the samples were prepared and the time at which the samples were studied. When there was any doubt of a sample's storage stability, the samples were kept in sealed glass vials.

DISCUSSION AND RESULTS

Form IV (orthorhombic) ammonium nitrate is the room temperature form of this salt. When Form IV ammonium nitrate is heated a transition will occur between 32° and 55° C., depending upon the concentration of water in the ammonium nitrate. If the temperature of the transition occurs in the neighborhood of 32° C., the transition is generally accepted to be a transition from Form IV to Form III (orthorhombic); but if the transition occurs near 55° C., it is considered to be a transition from Form IV to Form II (tetragonal). Most of the data obtained in this work strongly suggests that the transition which occurs during the heating of Form IV ammonium nitrate is between Forms IV and III throughout the temperature range from 32° to 55° C. One or two samples which were studied had a phase transition at 55° C. but no transition at 82° to 90° C. This is the expected behavior for a transformation from Form IV to Form II. The 82° C. transition occurs when Form III ammonium nitrate converts to Form II. If the transition at 55° C. is the conversion of Form IV to Form II, there can be no transition at 82° C. because this is the transition of Form III to Form II, and the Form II conversion had already occurred at a lower temperature, 55° C.

Form II ammonium nitrate changes into Form I (cubic) near 125° C. and the Form I melts at 169° C. The melt is a transparent, colorless liquid similar to water in appearance.

The transition profile of ammonium nitrate is shown in Figure 1. The specific volume data were obtained from Hendricks and others (*6*), but the paths of the transition in the temperature range between 32° and 55° C. were modified by the author. Figure 2 shows that the transition from Form IV to Form III may occur anywhere in the temperature range between 32° and 55° C., depending upon the quantity of water in the sample. The very dry samples used in Figure 2 were obtained by heating finely ground nitrate at 90° C. for 8 hours in a forced air oven, and then transferring the ammonium nitrate for analyses while it was hot. A sample was considered to have zero water content when a 10-gram sample of the ammonium nitrate required one drop or less of Karl Fischer reagent to deactivate the automatic titrator. In each instance the ammonium nitrate was sealed in a hot glass vial and allowed to return to room temperature before the transition temperature was determined. The significant information of Figure 2 is the fact that the transition from Form IV to Form III is a continuous function of the percentage of water contained in the nitrate. This would hardly be the case if there were a change in mechanism and Form IV were converted to Form II instead of Form III at some intermediate temperature between 32° and 55° C.

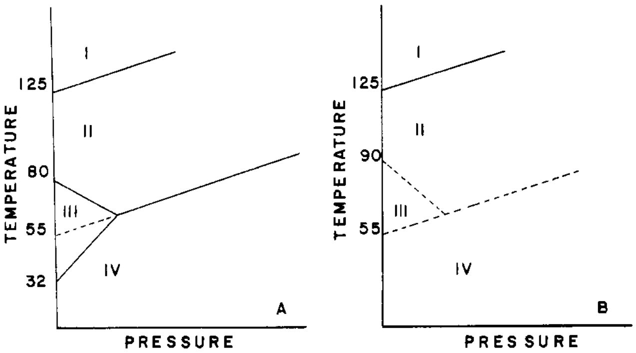

Figure 3. A. Bridgman's original data with an extrapolation added
B. The data obtained with stabilized nitrate at atmospheric pressure suggest that for very dry ammonium nitrate the curve of Bridgman should be similar to curve B

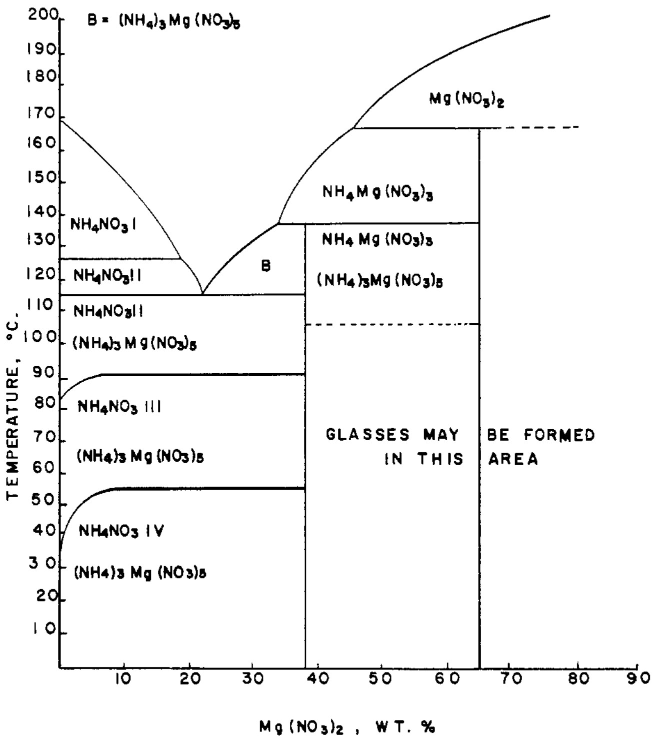

Figure 4. The phase diagram for the anhydrous system $NH_4NO_3-Mg(NO_3)_2$

Some salts were found to overcome the influence of dehydrating the ammonium nitrate. When as little as 0.1% sodium nitrate was added to molten ammonium nitrate and the mixture cooled to room temperature, the transition from Form IV to Form III occurred at 32° C., even for the driest ammonium nitrate the author could prepare. On the other hand, if the temperature of the IV → III transition were stabilized at 55° C. by the addition of 1.84% magnesium nitrate to the system, the addition of 0.1% sodium nitrate to the system was without detectable influence on the temperature of the transition at 55° C.

Hot stage x-ray analyses in the temperature range between 32° and 60° C. showed only Form IV and Form III crystals. This is not conclusive proof that a IV → II transition does not occur because it is very difficult to be certain that no water is absorbed in the surface crystals exposed to the x-rays, even though the sample was prepared for analysis in a dry-box and the chamber of the x-ray furnace was purged with dry nitrogen. The conclusions drawn from the above work are: the transition occurring near 55° C. is a transition between Forms IV and III; the transition at 55° C. is the equilibrium temperature for the transition from Form IV to Form III, and the 32° C. transition is the property of the binary system H_2O-NH_4NO_3; a transition from Form IV to Form II may occur on rare occasions but is not normal when the system is being heated, the transition from Form II to Form IV at 55° C. occurs because ammonium nitrate supercools easily and the transition between Forms II and III may be bypassed when cooling a sample.

The pressure-temperature phase diagram prepared by Bridgman (*3*) did much to support the theory that very dry ammonium nitrate transforms from Form IV to Form II without passing through Form III. Bridgman showed that Form III does not exist in the ammonium nitrate phase diagram at higher pressures and that a IV → II transition occurs. Because the ammonium nitrate used by Bridgman could not possibly have been anhydrous in direct contact with kerosine and because the extrapolation of the IV → II transition curves to atmospheric pressure indicates the IV → II transition should occur at 55° C.—provided the ammonium nitrate were anhydrous—some workers have accepted this phase diagram as additional proof that the IV → II transition occurs in dry ammonium nitrate at atmospheric pressure (*13*). It is this author's contention that had Bridgman's ammonium nitrate been exhaustively dehydrated, the range of stability of Form IV would have been extended from –17° C. to 55° C. and that the stable region of Form III would have been decreased to the limits from 55° C. to about 90° C. as shown in Figure 3.

Because it is much more difficult to superheat a crystal into a metastable region than to supercool it into a metastable region, heatingg curves were used throughout this work. Cooling was used only as a check on the heating. The importance of the use of heating curves is easily seen from the work on the phase diagram NH_4NO_3-$Mg(NO_3)_2$ in which glasses rather than crystals were often obtained when the samples were cooled from melt temperature to room temperature.

When magnesium oxide is added to ammonium nitrate and the mixture is heated above the melting temperature of the ammonium nitrate, a slow reaction occurs to produce ammonia, water, and magnesium nitrate. When as little as 0.1% magnesium oxide is added to ammonium nitrate, a noticeable change in the physical properties of the nitrate is observed and the temperature of the transition between Forms IV and III will move to a temperature near 40° C., even when the original ammonium nitrate contained enough water to experience a transition at 32° C. When the concentration of magnesium oxide is increased to 1% of the weight of the ammonium nitrate the transition is raised to 55° C. and a sample of the nitrate may be cycled in the temperature range between 20° C. and 45° C. hundreds of times without any transition occurring and without any change in the dimension of the particles occurring. Moreover, there is no caking or swelling of the sample when hundreds of cycles have been completed.

The magnesium nitrate formed from the magnesium oxide influences the ammonium nitrate in two ways. First, it dehydrates the ammonium nitrate and gives the nitrate a water-holding capacity; second, it changes the crystal habit of the nitrate. The crystals viewed under the microscope are smaller and more rounded at the ends when magnesium 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, $(NH_4)_3Mg(NO_3)_5$, in the diagram.

The phase diagram for the system $Mg(NO_3)_2$-NH_4NO_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, $NH_4Mg(NO_3)_3$ and $(NH_4)_3Mg(NO_3)_5$, were formed in the concentration range of the NH_4NO_3-$Mg(NO_3)_2$ 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 $(NH_4)_3Mg(NO_3)_5$ can be detected in the x-ray patterns of the system.

Table I. Analyses of Compounds in the Phase Diagram

	Wt. %; Theory	Wt. %; Found
$(NH_4)_3Mg(NO_3)_5$		
Total nitrogen	28.84	28.58
Ammoniacal nitrogen	10.81	10.94
Magnesium oxide	10.37	10.20
$NH_4Mg(NO_3)_3$		
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.

ACKNOWLEDGMENT

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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-$C_6H_4Cl_2$–p-C_6H_4BrCl