381. *An X-Ray Diffractometric Study of the Ammonium Nitrate–Potassium Nitrate System*

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An *X*-ray diffractometer has been used to study the system ammonium nitrate–potassium nitrate over the temperature range 20—130°. The following solid solutions were identified: KNO_3 in NH_4NO_3 III, NH_4NO_3 II, and NH_4NO_3 I; and NH_4NO_3 in KNO_3 III, KNO_3 II, and KNO_3 I. It has been found that KNO_3 III containing NH_4^+ ions is stable over a very wide range of temperature and composition. Mechanisms for the phase changes and reasons for the stability of NH_4^+-substituted KNO_3 III are proposed and discussed.

AMMONIUM NITRATE and potassium nitrate have considerable industrial importance and have been extensively studied. Of particular interest to the physical chemist are the various polymorphs of these two salts. There are five known polymorphs of ammonium nitrate and three of potassium nitrate, one of which only occurs on cooling. In the mixed system of these two salts the phase changes which occur and the temperatures at which they take place are complicated because the ammonium and potassium ions are very similar in size and can therefore readily replace each other in their respective crystal lattices.

Ando[1] found, from solution composition studies, that NH_4^+ would replace K^+ in potassium nitrate, and that K^+ would replace NH_4^+ in ammonium nitrate, and he quoted some limits of solution close to those accepted today.[2] Jänecke *et al.*,[3] also from solution composition studies, reported an ammonium-containing phase which they considered to be derived from potassium nitrate III, the metastable high-temperature phase. Karnaukhov *et al.*[4] confirmed from their solution studies that such a phase did exist and that its composition was variable, and isolated it at ambient temperatures. Morand[5] studied this system by differential thermal analysis and reported that his results were checked by *X*-ray powder diffraction analysis, but no details are given. He did not realise that many of his transitions were complicated by the variable distribution of NH_4^+ and K^+ between the phases, and, in particular, by the stability of the NH_4^+-substituted potassium nitrate III over the wide temperature range reported by Jänecke and Karnaukhov and their co-workers. Coates and Crewe[6] suggested limits of composition of the potassium nitrate III phase containing NH_4^+, and published *X*-ray powder diffraction data for the limiting solid solutions.

Most of the earlier work suffered from the disadvantage of not observing the existence of various crystallographic phases directly, *i.e.*, by *X*-ray diffraction analysis, but has inferred their existence from solution phase studies or differential thermal analysis. In the work to be described, solid solutions of ammonium nitrate in potassium nitrate II, and potassium nitrate in ammonium nitrate III, have been used as starting materials. (Ammonium nitrate III is stable at room temperature if $>2\%$, by weight, of potassium nitrate is present.[2]) These solid solutions have been heated by a hot-air blast and analysed by *X*-ray powder diffraction at many elevated temperatures up to a maximum of 135°. The phase changes which occurred on heating and cooling were thereby observed directly. This has removed the doubt and confusion arising from the solution phase and differential thermal analysis studies which did not characterise the exact solid phases present. Our own differential thermal analysis studies, carried out in conjunction with this work,[7] showed clearly how ambiguous results could be obtained.

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[1] K. Ando, *Mem. Coll. Sci., Kyoto Univ.*, 1925, **8**, 284.
[2] R. V. Coates and G. D. Woodard, *J. Sci. Food Agric.*, 1963, **14**, 398.
[3] E. Jänecke, H. Hamacher, and E. Rahlfs, *Z. anorg. Chem.*, 1932, **206**, 357.
[4] A. S. Karnaukhov and O. S. Zotova, *Doklady Akad. Nauk S.S.S.R.*, 1953, **90**, 549.
[5] J. Morand, *Ann. Chim. (France)*, 1955, **10**, 1018.
[6] R. V. Coates and J. M. Crewe, *Nature*, 1961, **190**, 1190.
[7] P. Doran, personal communication.

To avoid confusion, throughout this Paper a solid solution will be defined as: a solid chemical compound in which one ion has been partly replaced over a continuously variable range by another of similar radius, the crystal space-group remaining that of the original, pure compound.

EXPERIMENTAL

X-*Ray Apparatus, Specimen Preparation, and Heating Procedure.*—The crystallographic phase changes were observed with a Geiger-counter diffractometer of 25 cm. radius with CuK_α radiation (Ni filter) at 30 kv, 20 mA, and a scanning speed of 1° Bragg/min. Full details of specimen-preparation and the specimen-heating apparatus have been described.[8] Every time the sample temperature was changed the sample was soaked for ¼ hr. to enable the equilibrium composition of the phases present to be approached.

Below 120°, the temperatures of the transitions were usually measured to within 5°, and above 120° to within 1°. The reasons for these two standards are as follows. (i) Below 120° the transitions are widely separated, and therefore location to within 5° is sufficiently accurate when a smoothed curve is to be drawn through the temperatures; above 120° greater accuracy is needed because of the proximity of the ammonium nitrate II $\longrightarrow$ I and potassium nitrate III $\longrightarrow$ I transitions. (ii) As explained later in the Discussion section, when new phases form, the ammonium nitrate : potassium nitrate ratios of the phases existing alter irreversibly from that of the initial sample. Thus, at the transition temperature there is a small uncertainty as to the precise composition ratio. Moreover, these irreversible changes make temperature-cycling of the specimen impossible, and to obtain 1° accuracy over the whole temperature range the specimen would have to be heated in 1° steps with the 15 min. soaking at each step.

Preparation of Ammonium Nitrate Containing Potassium Ions.—Mixtures of ammonium nitrate and potassium nitrate, containing up to 30% by weight of potassium nitrate, were dissolved in water and evaporated to dryness on a steam-bath. The product was ammonium nitrate III, stabilised at room temperature by potassium.

Preparation of Potassium Nitrate Containing Ammonium Ions.—Mixtures of potassium nitrate and ammonium nitrate, containing up to 70% by weight of ammonium nitrate, were dissolved in water at room temperature. When a small amount of crystallisation had occurred the mixture was filtered and the solid analysed for ammonium content. The filtrate was allowed to crystallise further, and refiltered. The product was potassium nitrate II and contained up to 13·3 wt.% of ammonium nitrate, which is comparable to the limiting value of solid solution reported by Ando.[1]

RESULTS

The transitions in pure ammonium and potassium nitrates are given to facilitate comparisons.

Ammonium nitrate:[9] (heating undried AnalaR salt) IV $\longrightarrow$ III 32°, III $\longrightarrow$ II 86°, II $\longrightarrow$ I 126°; (cooling from phase I) I $\longrightarrow$ II 125°, II $\longrightarrow$ IV 50°.

Potassium nitrate:[2] (heating) II $\longrightarrow$ I 127°; (cooling) I $\longrightarrow$ III 127°, III $\longrightarrow$ II 115°.

Phase Transitions in Mixed Ammonium–Potassium Nitrates.—(i) *Ammonium nitrate III containing potassium.* The temperatures of some of the phase transitions on heating are shown graphically in Figure 1. Additional changes, and those on cooling, are described below for each composition, expressed as a weight percentage. All the phases mentioned below are mixed ammonium and potassium nitrates with the crystal structure of the pure phase mentioned.

98% NH_4NO_3, 2% KNO_3. The quantity of potassium nitrate III increased steadily up to 125°. At this temperature, ammonium nitrate I was formed from ammonium nitrate II and the potassium nitrate III dissolved in it. On cooling, the reverse changes occurred at 125°. Ammonium nitrate III appeared at 115° but some ammonium nitrate II still remained down to 90°. Below 100° potassium nitrate III decreased, and at 70° only ammonium nitrate III remained.

95% NH_4NO_3, 5% KNO_3. The quantity of potassium nitrate III increased slowly up to 115° and then more rapidly. Above 125° it increased slightly at the expense of ammonium

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[8] R. V. Coates and G. D. Woodard, *J.*, 1964, 1780.

[9] R. N. Brown and A. C. McLaren, *Proc. Roy. Soc.*, 1962, *A*, **266**, 329.

nitrate I. Above 130°, potassium nitrate III changed sluggishly into potassium nitrate I. On cooling, the potassium nitrate I $\longrightarrow$ III transition was rapid by 130°, and the ammonium nitrate I $\longrightarrow$ II transition was between 120 and 125°. Ammonium nitrate III formed at 90° and potassium nitrate III began to decrease, but some remained down to room temperature.

90% NH_4NO_3, 10% KNO_3. The quantity of potassium nitrate III increased steadily from 100 to 130°. The potassium nitrate III $\longrightarrow$ I transition was again very slow, still being incomplete at 135°. On cooling, the ammonium nitrate I $\longrightarrow$ II transition was at the normal temperature of 125°. Ammonium nitrate III appeared at 100°. The potassium nitrate III phase decreased from 90° onwards, but some remained at room temperature.

85% NH_4NO_3, 15% KNO_3. The quantity of potassium nitrate III increased steadily above 90°. The ammonium nitrate II $\longrightarrow$ I transition did not occur normally; it was very slow and was not complete until 135°. Ammonium nitrate III formed on cooling at 100° and increased at the expense of potassium nitrate III down to room temperature.

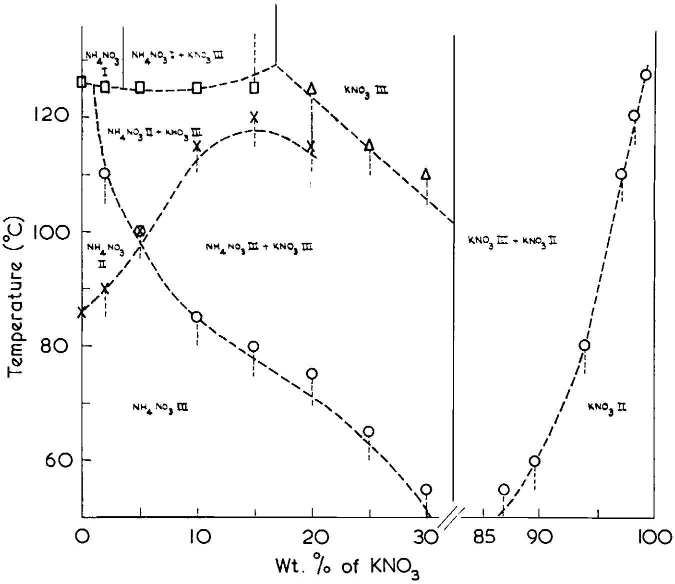


FIGURE 1. Transition temperatures, and phases which occur on heating ammonium–potassium nitrate solid solutions

×, NH_4NO_3 III $\longrightarrow$ II transition temperature (heating); □, NH_4NO_3 II $\longrightarrow$ I transition temperature (heating); ○, Temperature at which first KNO_3 III appears; △, Temperature at which all phases are converted into KNO_3 III.

80% NH_4NO_3, 20% KNO_3. Potassium nitrate III increased steadily in quantity until at 125° it was the only phase present. On cooling, ammonium nitrate III formed from potassium nitrate III at 95°.

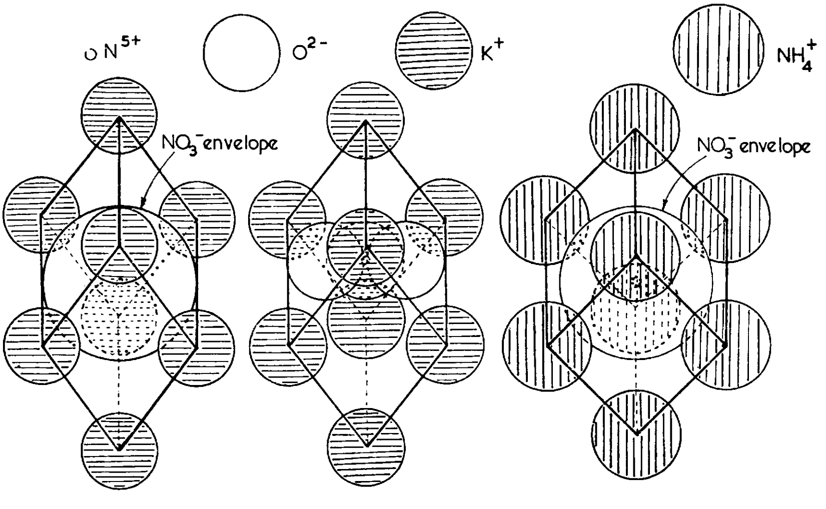
75% NH_4NO_3, 25% KNO_3. On cooling, ammonium nitrate III formed between 100 and 105° and increased steadily down to room temperature.

(ii) *Potassium nitrate containing ammonium ions.* The phase transitions occurring in this system with up to 13·3% of ammonium nitrate are shown graphically in Figure 1.

DISCUSSION

The temperatures of the transitions of pure ammonium nitrate and pure potassium nitrate are given at the beginning of the Results section. Brown and McLaren [9] reported that forms I, II, and IV of ammonium nitrate are very similar and the transitions are associated with small changes in the position and size of the nitrate ion accompanied by a volume increase. In form IV there is no rotation of the nitrate ion, in form II the nitrate ion is oscillating in its own plane between two bound orientations, and in form I the nitrate ion is rotating freely to assume spherical symmetry. Form III is not related to the other forms, as the nitrate ion is six-fold co-ordinated compared to eight-fold for the other forms. The presence of water is necessary for the II $\longrightarrow$ III transition to occur, probably because the mechanism involves a solution phase recrystallisation.

In potassium nitrate I, the nitrate ion assumes spherical symmetry, as in ammonium nitrate I, giving a rhombohedral cell containing one formula unit (see Figure 2a and Table). When potassium nitrate I changes on cooling into the metastable form III, the nitrate ion ceases to have spherical symmetry, merely rotating in its own plane. The cell remains rhombohedral with one formula unit but the mean position of the nitrate ion departs slightly from the geometrical centre of the cell (see Figure 2b and Table). It can be seen that potassium nitrates I and III can be considered as having distorted CsCl cells and thus closely resemble ammonium nitrate I, which is a true cubic CsCl type (see Figure 2c and Table). Hence, replacement of potassium ions by ammonium ions can be expected to occur over a wide compositional range with associated modification of the rhombohedral cell constants (see Table).



(a) (b) (c)

FIGURE 2. Unit-cells of (a) KNO_3 I at 130°, (b) KNO_3 III at 120°, and (c) NH_4NO_3 I above 130° (see also Table)

Material	Temp. (°c)	*a* (Å)	α	Space group	Volume (Å^3)	Ref.
KNO_3 I	130	4·54	73° 24′	*R*$\bar{3}$*m*	75·03	**6**
KNO_3 III	120	4·42	76° 42′	*R*3*m*	74·74	**6**
$(NH_4)_{0·25}K_{0·75}NO_3$	20	4·38	77° 42′	*R*3*m*	74·21	**6**
$(NH_4)_{0·5}K_{0·5}NO_3$.........	20	4·42	77° 54′	*R*3*m*	76·56	**6**
NH_4NO_3 I	150	4·40	90° 00′	*Pm*3*m*	85·24	*

* C. Finbak and O. Hassel, *Z. phys. Chem.*, 1937, **35**, *B*, 25.

Morand [5] proposed the following mechanisms for the changes in the transition temperatures of ammonium nitrate when some of the ammonium ions are replaced by potassium ions. The cation : anion radius ratio for ammonium nitrate is 0·76. This value closely approaches the ratio of 0·73 below which salts of the type $R(MX_3)$ are stable in a six-fold co-ordinated NiAs structure, which is the structure type of ammonium nitrate III. The radius of the potassium ion is 1·33 Å compared with 1·48 Å for the ammonium ion, and hence, replacement of NH_4^+ by K^+ favours the NH_4NO_3 III structure. This is evident as a steady fall in the ammonium nitrate IV ⟶ III transition temperature as the replacement of ammonium ions by potassium ions increases. We found that, with above 2 wt. % of potassium nitrate, ammonium nitrate III is stable down to room temperature.[2]

The replacement of ammonium ions by potassium ions in ammonium nitrate III decreases its unit-cell size and this hinders the onset of oscillation of the nitrate ion which causes the III ⟶ II transition. Thus, as the concentration of potassium ions increases, the nitrate ion oscillation is more hindered and the III ⟶ II transition temperature rises.

The II ⟶ I transition takes place when full spherical rotation of the nitrate ion occurs, and its transition temperature is unaffected by the substitution of potassium ions for ammonium ions.

As can be seen from Figure 1, our results for the III ⟶ II and II ⟶ I transition temperatures are in fair agreement with those of Morand. However, our II ⟶ I curve at first falls slightly and then begins to rise; the transition at 15 wt. % of potassium nitrate is very sluggish but is definitely not less than 125°, whereas Morand obtained a steady decline levelling off at 14 wt. % of potassium nitrate to 117°. Morand's curve for the III ⟶ II transition flattens considerably above 6 wt. % of potassium nitrate and reaches a steady maximum of 106° between 20 and 30 wt. % of potassium nitrate, whereas our curve shows a maximum of 120° at 15 wt. % of potassium nitrate. This peaking is an illusory effect as the composition of the ammonium nitrate III phase is unknown because of the formation from it of potassium nitrate III. This phase seemingly went undetected by Morand but it is of overwhelming importance in the study of this system. Though Morand says he checked his differential thermal analysis results by *X*-ray analysis we assume that this analysis must have been done at room temperature and some time after the thermal analysis. We believe that only with these conditions could the potassium nitrate III phase have gone undetected in his work.

The transitions and conversions at the potassium nitrate and ammonium nitrate ends of the system are discussed separately, with particular reference to the formation of the potassium nitrate III-based phase.

Potassium Nitrate End of System.—When potassium nitrate I is cooled, potassium nitrate III is formed as a metastable phase between 125 and 115°, and can be preserved at room temperature by raising the pressure,[10] by quenching,[11] or by incorporating ammonium ions.[6] As can be seen from Figure 1 the temperature at which potassium nitrate III is first formed falls rapidly at each end of the compositional range. Between 30 and 87 wt. % of potassium nitrate it was impossible to investigate the nucleation temperature of potassium nitrate III because, either it was present in the initial material, or the initial material contained a mixture of the two phases at each end of the system.

The II ⟶ I potassium nitrate transition needs a sufficient volume increase to permit complete spherical rotation by the nitrate ion, whereas the II ⟶ III transition needs only a sufficient volume change to permit the nitrate ion to oscillate in its own plane. In pure potassium nitrate, the II ⟶ III transition does not occur on heating presumably because the energy needed to interconvert between these two dissimilar phases necessitates a high temperature, and thus when the conversion does occur the nitrate ion has sufficient energy to rotate, and potassium nitrate I is formed. On cooling, the potassium nitrate I ⟶ III transition occurs easily since forms I and III are structurally related (see Figure 2 and Table). The replacement of potassium ions by ammonium ions in potassium nitrate II contributes some of the necessary increase in volume for the nitrate ion to oscillate and the II ⟶ III transition to occur. The conversion becomes possible when only 0·8 wt. % of ammonium nitrate is present and the temperature of potassium nitrate III nucleation rapidly falls as the ammonium ion concentration increases, until, at 13·3 wt. % of ammonium nitrate, the temperature is 55°. It has been shown [6] that, over the range 25—50% of

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[10] T. Barth, *Z. phys. Chem.*, 1939, **43**, *B*, 448.

[11] J. P. Nolta and N. W. Schubring, *Phys. Rev. Letters*, 1962, **9**, 285.

ammonium ion replacement for potassium ion, the potassium nitrate III phase is stable at room temperature.

Ammonium Nitrate End of System.—Beyond the 70 wt. % of ammonium nitrate composition we are dealing with the formation of the potassium nitrate III phase from ammonium nitrate III, not from potassium nitrate II. The limit of potassium nitrate solubility in ammonium nitrate III is 25% replacement of the ammonium ions by potassium ions, and therefore, on complete conversion into potassium nitrate III, each nitrate ion on the average is surrounded by 6 ammonium ions and 2 potassium ions. This occurs at 110°. In fact, nucleation of the potassium nitrate III phase begins at 55° but at this temperature it is almost certain that the potassium nitrate III contains a higher percentage of potassium ions than does the ammonium nitrate III from which it is formed. From 55 to 110° the concentration of ammonium ions in the potassium nitrate III increases steadily. As the potassium ion concentration in the ammonium nitrate III decreases, both the nucleation temperature and the temperature of complete formation of the potassium nitrate III phase rise. We suggest that this is because the very high ammonium ion concentration in the potassium nitrate III is now hindering rather than assisting the nitrate ion oscillations. Each nitrate ion is surrounded by 4 or more ammonium ions, and these, by virtue of their size relative to that of the potassium ions, interfere with the nitrate ion oscillation. This hypothesis is further confirmed by the very wide temperature range over which the potassium nitrate III phase changes into potassium nitrate I, the spherical rotation of the nitrate ion being blocked by the ammonium ions. The maximum replacement of potassium ions by ammonium ions for complete formation of potassium nitrate III corresponds to 80 wt. % of ammonium nitrate, and at this composition each nitrate ion is surrounded, on average, by $6\frac{2}{3}$ ammonium ions.

Above 80 wt. % of ammonium nitrate, the conversion into potassium nitrate III is never complete. The residual ammonium nitrate III changes into ammonium nitrate II and then into ammonium nitrate I. The distribution of ammonium and potassium ions between the ammonium nitrate III and potassium nitrate III phases is not known, but as the temperature rises the quantity of the potassium nitrate III phase increases and, almost certainly, the concentration of ammonium ions in it increases. This explains the peak in the ammonium nitrate III $\longrightarrow$ II transition curve. At 20 wt. % of potassium nitrate, the potassium nitrate III phase is richer in potassium ions than the nominal, and therefore the ammonium nitrate III phase is deficient in potassium ions and changes into ammonium nitrate II at an appropriately reduced temperature.

Below 5 wt. % of potassium nitrate, the ammonium nitrate III $\longrightarrow$ II transition is below the nucleation temperature for the potassium nitrate III phase. In ammonium nitrate II the nitrate ion is already oscillating, and this fact, coupled with the hindering effect of the increased ammonium ion concentration in any potassium nitrate III phase formed, results in a rapid increase in the potassium nitrate III phase nucleation temperature until, below 2 wt. % of potassium nitrate, it ceases to appear at all. More complete discussion of the ammonium nitrate II phase $\longrightarrow$ potassium nitrate III phase conversion is impossible owing to the lack of complete structural information for ammonium nitrate II.

The unknown composition of the various phases on cooling prevents any useful discussion of cooling conversion-temperature results. However, it should be noted that, from the 95 wt. % of ammonium nitrate 5 wt. % of potassium nitrate starting material, the potassium nitrate III phase has become sufficiently rich in potassium ions so that it can exist at room temperature.

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