

CXI.—*The Properties of Ammonium Nitrate. Part III.*
Ammonium Nitrate and Sodium Nitrate.

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AMONGST the saline impurities commonly found in commercial ammonium nitrate, the most important is sodium nitrate, left behind by the incomplete conversion of the sodium salt into the ammonium salt in the process of manufacture. In the course of the experiments on the freezing point of ammonium nitrate (T., 1919, 115, 1381), a few samples of commercial ammonium nitrate, in which the saline impurity was almost entirely confined to sodium nitrate, came under examination, and their freezing points were determined in the same way as for the pure salt, with the following results.

	Sodium nitrate present.	Freezing point (after drying).	Depression of freezing point.	Depression by 1 per cent. of NaNO_3 .
Sample 1	8.8 per cent.	145.5°	24.1°	2.7°
" 2	4.0 " "	155.5	14.1	3.5
" 3	1.7 " "	164.0	5.6	3.3

These three samples show a depression of about 3° for every 1 per cent. of sodium nitrate, but the values are probably too high on account of the presence of small quantities of ammonium chloride, of which, for example, sample No. 3 contained 0.16 per cent. In order to secure exact information as to the influence of pure sodium nitrate on pure ammonium nitrate, an equilibrium diagram was plotted from 0 to 40 per cent. of sodium nitrate, and this diagram has been compared with that of silver nitrate and ammonium nitrate, for which data have been given by Zawidski (*Z. physikal. Chem.*, 1904, 47, 721). These diagrams are of interest on account of the relationships which are involved between the various forms of the polymorphous nitrates.

EXPERIMENTAL.

Freezing Points of Mixtures of Pure Ammonium and Sodium Nitrates.

In the present series of experiments the freezing points of mixtures of ammonium and sodium nitrates, containing up to 40 per cent. of the latter salt, were determined. The apparatus was similar to that described in Part I for the determination of the freezing point of ammonium nitrate, except that the outer hot-water jacket was dispensed with, the air-jacket between the large and small boiling-tubes serving to prevent the over-rapid cooling of the contents of the smaller tube. This arrangement had the advantage that the fine crystals first appearing in the "melt" could be detected much more readily than when an outer bath of liquid was used.

The method of experiment was as follows. Ammonium nitrate was weighed into the inner boiling-tube, and the exact quantity of sodium nitrate corresponding with a mixture of the required composition was weighed on a piece of glazed paper, the weight of the two salts being about 20 grams in each experiment. The ammonium nitrate was melted over a small flame with constant stirring, and when completely molten the sodium nitrate was added slowly, and dissolved by continuous stirring and gentle heating. The tube and stirrer were clamped within the larger tube, a standard thermometer (graduated from 0° to 200° in fifths) inserted, and the space between the two tubes closed at the top with cotton-wool. The "melt" was stirred and the temperature at which fine crystals first appeared noted. The rate of cooling

was then recorded, in order that any subsequent "arrest" might be detected; and stirring was continued until brought to a stop by the accumulation of solid matter in the tube. The separation of the eutectic was usually preceded by overcooling, but the maximum temperature following crystallisation could be observed easily. The observations were repeated after remelting carefully the contents of the tube before these had cooled to the transition temperature at 84.2° , where an expansion occurs which often bursts the tube.

The results, which generally agreed within 1° in the case of the initial freezing points, and within one- or two-tenths of a degree in the case of the eutectic arrests, are given in Table I and are shown graphically in Fig. 1.

FIG. 1.

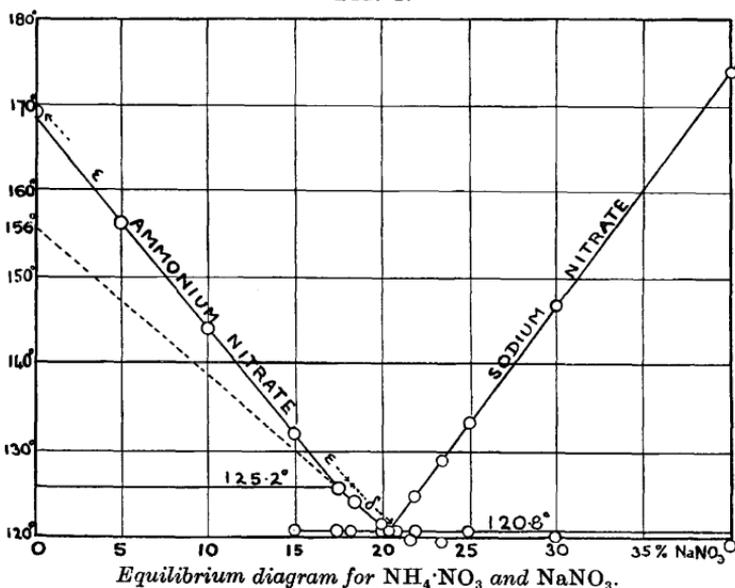


TABLE I.

Initial and Final Freezing Points for Mixtures of Ammonium Nitrate and Sodium Nitrate.

Percentage of sodium nitrate.	Initial freezing point.	Eutectic arrest.	Percentage of sodium nitrate.	Initial freezing point.	Eutectic arrest.
0.0	169.6°	None	18.5	124.3°	120.8°
		observed.	20.0	121.9	120.8
5.0	156.5	None	22.0	124.8	120.8
		observed.	23.0	126.6	120.6
10.0	144.2	None	23.5	129.1	120.7
		observed.	25.0	133.4	120.8
15.0	132.0	120.6°	30.0	147.0	120.2
17.5	126.3	120.6	40.0	174.2	119.0

The composition of the mixture of ammonium and sodium nitrates of lowest melting point, as deduced from the curve, is as follows :

Ammonium nitrate . . .	79.5 per cent.
Sodium nitrate . . .	20.5 „ „

The constant freezing point of this mixture may be taken as 120.8° , which is the mean of the six highest values recorded in Table II. The lower values are probably less accurate on account of the liability to overcooling, more especially in mixtures the compositions of which are more removed from that of the eutectic.

Melting Point of the δ -Form of Ammonium Nitrate.

Fig. 1 is interesting in two respects, (i) in the straightness of the branches, and (ii) in the presence of a distinct break in the left-hand branch at about 126° , corresponding with the transition temperature at 125.2° . Zawidski records a similar break at about 125° in the curve showing the initial crystallising points of mixtures of ammonium nitrate and silver nitrate. The latter diagram shows two eutectic points connected by a convex curve, corresponding with the separation of the compound $\text{NH}_4\cdot\text{NO}_3\cdot\text{AgNO}_3$; but the two intersecting lines which show the separation, above and below 125° , of the ϵ - and δ -forms of ammonium nitrate, and the line which shows the separation of silver nitrate at concentrations above 50 mols. per cent. AgNO_3 have the same rectilinear form as the three sections of the freezing-point curve in Fig. 1. If the line between 125° and the first eutectic point (101.5°) on Zawidski's curve is produced back to the temperature axis, it cuts this at about 155° ; similar treatment of the corresponding (but shorter) branch in Fig. 1 gives an intercept at 156° approximately. The experimental evidence appears therefore to justify the view that the extension of this branch to cut the ammonium nitrate axis, as shown by a broken line in Fig. 1, would give the temperature at which the metastable δ -form of ammonium nitrate would separate from the molten salt, and that the melting point of this form, which is ordinarily stable only between 84.2° and 125.2° , would be at 155 — 156° , if it could be heated to this temperature without undergoing polymorphous change.

Experiments on the Isopolymorphism of Ammonium and Sodium Nitrates.

The univalent nitrates are remarkable for their readiness to appear in several crystalline forms. Thus, ammonium nitrate is pentamorphous; lithium, rubidium, and thallium nitrates are trimorphous; potassium, caesium, and silver nitrates are dimor-

phous; and sodium nitrate alone does not exhibit polymorphism. The crystalline forms in which the various nitrates are known are set out below, together with the transition temperatures at which the various forms change into a new form on cooling.

	Am.	Tl.	Li.	Na.	K.	Ag.	Rb.	Cs.
Melting point	170°	205°	253°	312°	336°	209°	?	414°
?	—	—	—	—	—	—	?	—
Cubic	ε 125.2°	ε 142.5°	ε	—	—	—	ζ 219°	ε 161°
Tetragonal ...	δ 84.1°	—	—	—	—	—	—	—
Rhombo-								
hedral	γ* 32.1°	γ 72.8°	γ	γ	γ 126°	γ 159.6°	γ	γ
Orthorhombic	β — 16°	—	β	—	β	β	—	—
Tetragonal ...	α —	—	—	—	—	—	—	—

* Perhaps monosymmetric.

Although sodium nitrate is known only in one form, this belongs to a system in which every one of the eight nitrates crystallises, with the possible exception of ammonium nitrate. It might therefore be expected that it would form isomorphous mixtures with most of the other nitrates; but there is in fact no case in which a complete series of isomorphous mixtures of sodium nitrate with another nitrate is known. Thus, silver nitrate forms two series of isomorphous mixtures, giving rise to a broken freezing-point curve (Hissink, *Z. physikal. Chem.*, 1900, **32**, 537). In the case of potassium nitrate, two series of isomorphous mixtures are also formed, containing up to 12 per cent. of KNO_3 or 20 per cent. of NaNO_3 , but these form a eutectic mixture with one another (Hissink, *loc. cit.*). With thallium nitrate and lithium nitrate, no isomorphous mixtures appear to be formed.

Ammonium nitrate, on the other hand, forms a complete series of solid solutions with thallium nitrate, giving rise to a continuous freezing-point curve, corresponding with the separation of cubic crystals throughout. These crystals break up when the ammonium nitrate changes into the tetragonal form; but since the transition points of ammonium nitrate at 84° and of thallium nitrate at 80° are mutually lowered when both salts are present, it is probable that the rhombohedral and the orthorhombic forms of the two salts may also be isomorphous (Boks, *Diss.*, Amsterdam, 1902). Potassium nitrate, on the other hand, lowers the transition point at 32° (Müller, *Z. physikal. Chem.*, 1899, **31**, 354), showing that this salt is isomorphous with ammonium nitrate in the rhombohedral γ -form, but tends to separate from it on passing to the orthorhombic β -form; this fact is important, since ammonium nitrate, when prepared from Chile saltpetre, carries down with it most of the potassium nitrate of the raw material.

No complete investigation appears to have been made of the possible isopolymorphism of the ammonium and sodium salts.

The results of our experiments on the temperature of arrest of cooling in mixtures of ammonium and sodium nitrates are set out in Table II.

TABLE II.

Arrest Points in Mixtures of Ammonium Nitrate and Sodium Nitrate.

Percentage of sodium nitrate.	Arrests in cooling from		
	ϵ to δ .	δ to γ .	γ to β .
(a) <i>Anhydrous salts.</i>			
0	125.2°	84.2°	32.2°
5	125.4	83.6	—
10	125.5	83.3	31.6
20.5	—	82.0	31.4
25	—	82.5	—
(b) <i>In presence of water.</i>			
Pure AmNO_3	—	—	31.5
+ 10% NaNO_3	—	—	31.45
+ 0.5% KNO_3	—	—	30.2

The transition temperatures of the anhydrous mixtures of salts were determined on blocks which had crystallised from the "melt," and were therefore subject to much more overcooling than in the case of the sludge of powdered ammonium nitrate with an organic liquid which was used in determining the transition temperatures of the pure salt. It will be seen that the arrest at 125.2° is not lowered by the presence of sodium nitrate, up to 17 per cent. of NaNO_3 , where this arrest falls below the melting point of the mixture. The arrest at 84.2° is lowered by about a degree, but this is no more than the lowering by overcooling in pure ammonium nitrate when allowed to cool as a block instead of as a sludge. It is therefore clear that neither the ϵ - nor the δ -form of ammonium nitrate takes up enough sodium nitrate from the melt to affect its transition into the δ - or γ -form on cooling.

The experiments on the cooling of blocks from the melt do not, however, afford any real information as to the possible isomorphism of sodium nitrate with γ - or β -ammonium nitrate, since if these two salts crystallise from the melt as separate phases they will remain separate at lower temperatures, and no alteration of the 32° transition point can be expected. In order to get the ammonium nitrate to crystallise out in the γ - or β -form from a mixture containing sodium nitrate it is necessary to make use of a solvent. A sludge of ammonium nitrate and water was therefore cooled from about 80° and its transition temperature at 32° determined as in Müller's experiments on potassium nitrate (*loc. cit.*). The use of alcohol instead of water in making the sludge increased the overcooling, and no improvement was effected by adding ammonia; but a definite diminution of overcooling was effected by adding

nitric acid to the water used in making the sludge. The table shows an overcooling of 0.6° in the case of pure ammonium nitrate, but this was only increased by 0.05° by the presence of 10 per cent. of sodium nitrate, whereas 0.5 per cent. of potassium nitrate lowered the transition temperature by 1.3° . It is therefore clear that sodium nitrate is not isomorphous with the γ -form of ammonium nitrate; and since it is well known that ammonium nitrate does not carry down sodium nitrate when it separates from water below 32° , there is also no isomorphism with the β -form of the salt.

Summary.

1. An equilibrium diagram has been plotted for ammonium nitrate and sodium nitrate from 0 to 40 per cent. of NaNO_3 .

2. The freezing-point curve consists of three accurately rectilinear sections corresponding with the crystallisation of two forms of ammonium nitrate and the one form of sodium nitrate.

3. If the line which shows the temperature of crystallisation of the δ -form of ammonium nitrate is produced, it cuts the axis of temperature at $+156^{\circ}$. A similar value can be deduced from the freezing-point diagram for ammonium nitrate with silver nitrate. This temperature may therefore be taken as the melting point of the metastable δ -form of ammonium nitrate.

4. The eutectic point for the two salts has been located at 120.8° , and 20.5 per cent. of sodium nitrate.

5. No evidence of isomorphism between the two salts has been discovered.

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