Included in Fig. 3 for purposes of comparison are the data of Hill and Kaplan[5] for the ferric ammonium–aluminum ammonium system. The suggestion of Hill, Durham and Ricci that the distribution in this system is also a linear one in spite of the fact that the points tend to lie on a curve is therefore further supported by the two analogous systems here reported.

The relation

$$\log R_1 = \text{constant} + \log R_s \qquad (3)$$

thus found valid in all alum systems so far studied has been shown[1] to have a theoretical basis as a special case of

$$\log R_1 = \log K + \log (f_B/f_{B'}) - \log (\gamma_B/\gamma_{B'}) + \log R_s \qquad (4)$$

where f_B and $f_{B'}$ are the rational activity coefficients of the interchanging ions in the solid solution and γ_B and $\gamma_{B'}$ their practical activity coefficients in the coexisting liquid solution. To reduce this to (3) requires that $f_B/f_{B'}$ and $\gamma_B/\gamma_{B'}$ shall be constant at all points across the diagram and Hill, Durham and Ricci propose that in systems where m is unity both ratios are not only constant but unity. This assumption is, of course, necessary if the intercepts of Fig. 3 are to be identified with $\log K$.

It is possible to raise an objection to the identification of the intercepts with $\log K$ in the light of data of ref. 6 as applied to the chromic potassium–chromic ammonium alum pair.[3] The values of the molal solubilities of these alums are 0.817 and 0.603, respectively, in which solutions the respective mean ion activity coefficients are 0.0358 and 0.0465. This gives $\log K = \log (0.817 \times 0.0358/0.603 \times 0.0465)^4 = 0.07$. The intercept on the $\log R_1$ *vs.* $\log R_s$ plot is given[1] as 0.20 which equals the sum of the first three terms on the right side of (4). This means that $\log (f_K/f_{NH_4}) - \log (\gamma_K/\gamma_{NH_4}) = 0.13$, a finite constant for all proportions of the two alums. It is very unlikely that as one passes across the diagram the f and γ ratios both alter in such a way that the difference of their logarithms is constant; it is more reasonable to suppose that they are both constant, but then both could not be unity. It is interesting to note that if f_K/f_{NH_4} is regarded as unity then $\log (\gamma_K/\gamma_{NH_4})$, becomes -0.13 which may be compared with that estimated as follows: The ratio of the mean ion activity coefficient of chromic potassium sulfate to that of chromic ammonium sulfate is reasonably constant (about 0.88) over the range of ionic strengths of the isotherm. If the activity coefficients of chromic and sulfate ions are assumed to be the same in solutions of single alums as they are in mixed alums of the same ionic strength then $\log (\gamma_K/\gamma_{NH_4})$ should be given roughly by $\log (0.88)^4 = -0.22$. On the other hand, the uncertainties involved in the evaluation of the activity coefficients of the alums may have combined to produce a large error in $\log K$ thus invalidating the above argument.

Summary

1. The systems chromic ammonium sulfate–ferric ammonium sulfate–water and chromic ammonium sulfate–aluminum ammonium sulfate–water have been investigated at 25°.
2. Both systems exhibit a complete series of solid solutions at this temperature, and, as the distribution of the components follows the relation $\log R_1 = \text{constant} + \log R_s$, they are assigned to Type I of the Roozeboom classification. The values of the constant for each system compare favorably with the values estimated from the individual solubilities of the component alums.
3. A possible objection is raised to the assumption of a value of unity for the ratio of the activity coefficients of the interchanging ions in the liquid.

WINNIPEG, CANADA RECEIVED NOVEMBER 12, 1947

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS UNIVERSITY]

The System Ammonium Nitrate–Ammonium Sulfamate[1]

BY JACK H. THELIN[2] AND P. A. VAN DER MEULEN

The present research represents the initial investigation of the phase equilibria in the reciprocal salt pair system sodium nitrate–ammonium sulfamate. This included the phase diagram of the binary system ammonium nitrate–ammonium sulfamate.

Ammonium nitrate is known to exist in five crystalline modifications. Early and Lowry[3] have re-examined the transition temperatures of the various modifications and have summarized the results. Two of the transition points are of importance in the present investigation. They are the transition temperatures of 125.2° at which the cubic changes to the tetragonal and 84.2° at which the tetragonal changes to the monoclinic modification. There are no published records concerning possible polymorphism of ammonium sulfamate.

Experimental Method

Purification of Materials.—Merck ammonium nitrate was crystallized twice from distilled water and dried under

---

(1) Based on a thesis submitted by Jack H. Thelin to the graduate faculty of Rutgers University in partial fullfillment of the requirements for the degree of Doctor of Philosophy.

(2) Present address: American Cyanamid Co., Calco Chemical Division, Bound Brook, N. J.

(3) R. G. Early and T. M. Lowry, *J. Chem. Soc.*, **115**, 1387 (1919).

vacuum with phosphorus pentoxide at 40° with frequent grinding. Heating was found to be necessary to obtain the accepted freezing point of 169.6° as given by Early and Lowry.[3] Samples dried for two months at room temperature under vacuum with phosphorus pentoxide gave a freezing point of only 169.2°. In all experiments the ammonium nitrate used in this research had a freezing point of 169.5–169.6° (cor.).

The ammonium sulfamate was obtained from E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware, and was their technical grade. It was recrystallized twice from distilled water with care taken not to heat above 60°. An odor of ammonia was plainly noticeable at 80°. The freezing point obtained by us after two crystallizations from water and drying under vacuum with phosphorus pentoxide with intermittent heating to 100° on a water-bath was 132.9° (cor.). Gordon and Cupery[4] report a melting point of 131°. The purity was established by reaction of the ammonium sulfamate with potassium nitrite to form the sulfate and subsequent determination as barium sulfate. Two determinations gave 28.17 and 28.15% sulfur (calcd. 28.07). Dilatometric measurements using a high boiling kerosene fraction as medium showed no transition within the temperature range of 47° and the melting point.

Apparatus Used.—The freezing point apparatus is shown in Fig. 1. The oil-bath consisted of a one-liter Griffin-type beaker filled with Nujol in which the jacketed freezing point tube was placed. The inner tube which held the melted salts was made from a small Pyrex test-tube (13 × 100 mm.). The platinum wire used to agitate the melt was driven by a suitable mechanism at 120 strokes per minute. A loop of glass tubing through which water could be circulated was suspended in the oil-bath to aid cooling at temperatures below 100°. When the flame under the oil-bath was adjusted so that no variation of the oil-bath temperature was noted, the flowing of a few milliliters of water through the coil lowered the temperature of the melt as little as 0.05° a minute. Such slow cooling was advantageous in treating melts which had a strong tendency to supercool.

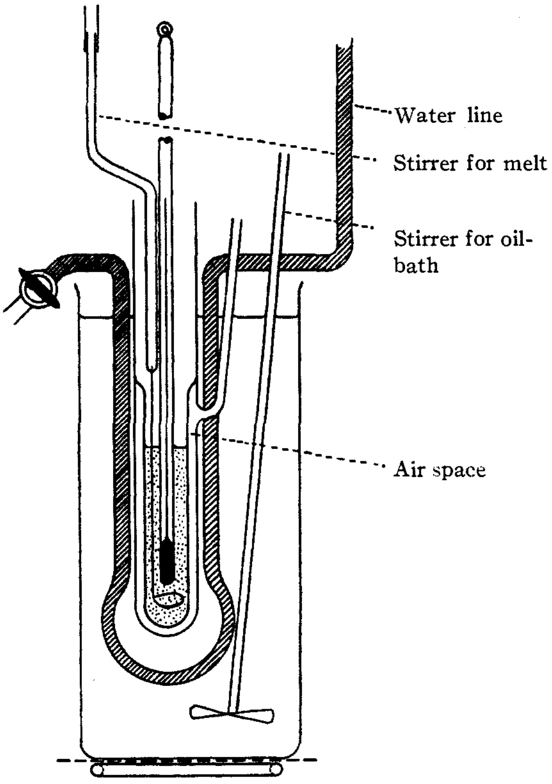

Fig. 1.

The thermometers were graduated in fifths of a degree and were standardized against thermometers recently checked by the Bureau of Standards. Corrections for emergent stem were made.

Technique.—The salt charge of approximately 4 g. was weighed by difference, placed in the aluminum boat of the apparatus shown in Fig. 2, and dried under vacuum at 56° (boiling acetone) for one to two hours with phosphorus pentoxide. In this way any moisture absorbed while weighing was removed. After drying, the mixtures were quickly transferred to the freezing point tube and placed in the previously heated oil-bath.

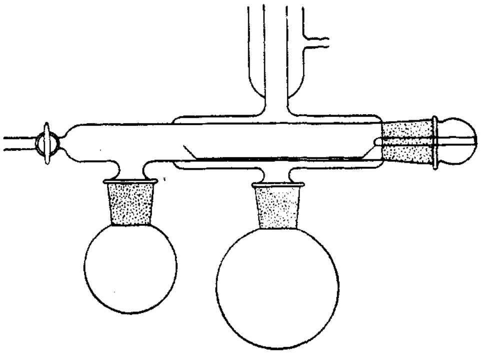

Fig. 2.—Modified Abderhalden drying pistol.

The drying apparatus of Fig. 2 is a modification of the Abderhalden drying pistol. In the conventional type the vacuum pump connection, the phosphorus pentoxide bulb and the sample itself are all attached at the front of the apparatus. In the present modification the drying chamber is extended through to the rear and the vacuum connection and the phosphorus pentoxide bulb are attached at the back out of the way. The boat is fastened to the glass stopper by a short piece of glass rod.

The usual cooling rate was 0.2–0.4° per minute. Seeding was accomplished by dipping a platinum wire into the melt at one-minute intervals and allowing the melt clinging to the tip to solidify. Enough of the melt adhered to the wire to "seed" the melt on the next trial. All recorded temperatures represent visual observation of initial crystal formation.

Experimental.—The data given in Table I were obtained as described under Experimental Method. Each recorded temperature represents a freshly prepared melt.

Figure 3 is a plot of the data with temperature as ordinates and composition as abscissas. The composition indicated by the intersection of the liquidus curves is 54.8% $NH_4SO_3NH_2$. Supercooling effects were observed, however, so that the eutectic temperature of 75.3° finally obtained with all mixtures is higher than the temperatures indicated by the intersection of the two liquidus curves. This leaves the precise composition of the eutectic mixture in doubt to the extent of about 1% of ammonium sulfamate. An enlarged plot of the curve gave 125.7° for the transition temperature of $NH_4NO_3(I) \rightleftarrows NH_4NO_3(II)$. Early and Lowry give 125.2° as the transition point for pure ammonium nitrate. Holmes and Revinson[5]

---

(4) W. E. Gordon and M. E. Cupery, *Ind. Eng. Chem.*, **31**, 1237 (1939)

(5) E. C. Holmes, Jr., and D. Revinson, THIS JOURNAL, **66**, 453 (1944)

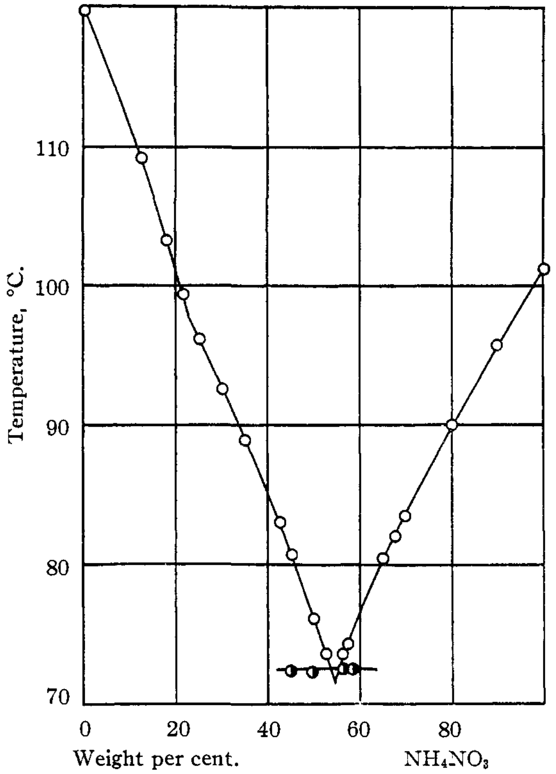

Fig. 3.—Freezing point of mixtures of $NH_4SO_3NH_2$ and NH_4NO_3

report 126.2° from a reinvestigation of the system ammonium nitrate–sodium nitrate. Perman and Harrison[6] report the transition temperature as 122° from a study of the system lithium and ammonium nitrates. The absence of the inversion point at 84.2° has been reported previously[7] in a study of the solubility of ammonium nitrate in water.

Howells,[8] on the basis of a study of the system urea–ammonium nitrate also states that no inversion point was obtained at 83°.

TABLE I

FREEZING POINTS OF MIXTURES OF AMMONIUM NITRATE (A) AND AMMONIUM SULFAMATE (B)

	% B by weight	F. p., °C.	Eutectic, °C.
Solid phase A	0.0	169.6	..
	12.5	148.3	..
	17.5	136.4	..
	18.0	135.5	..
	20.0	131.2	..
	21.0	128.9	..
	25.0	122.1	..
	30.0	115.4	..
	35.0	107.8	..
	42.5	96.0	..
	45.0	91.4	75.0
	50.0	82.1	74.5
	52.5	77.2	75.4
	53.8	75.4	75.4
Solid phase B	56.2	76.6	75.3
	57.5	78.7	75.3
	60.0	83.2	..
	65.0	91.0	..
	67.5	93.9	..
	70.0	97.0	..
	80.0	110.1	..
	90.1	121.4	..
	100.0	132.9	..

Summary

1. The freezing point of ammonium sulfamate is 132.9°.
2. Dilatometric measurements indicate that ammonium sulfamate exists in only one crystalline modification in the temperature range from 47° up to the melting point.
3. The binary system NH_4NO_3–$NH_4SO_3NH_2$ has a eutectic point at 75.3° and *ca.* 54.8% ammonium sulfamate with NH_4NO_3 and $NH_4SO_3NH_2$ as the solid phases.
4. The transition from NH_4NO_3(I) to NH_4NO_3(II) takes place at 125.7°.

NEW BRUNSWICK, N. J.

RECEIVED JANUARY 19, 1948

---

[6] E. P. Perman and W. R. Harrison, *J. Chem. Soc.*, **125**, 1709 (1924).

[7] A. Findlay, "The Phase Rule," Longmans, Green and Co., New York, N. Y., 1938, p. 174.

[8] W. J. Howells, *J. Chem. Soc.*, 910 (1929).