Summary.

1. A new all-glass manometer has been devised in which a platinized glass diaphragm is arranged to close an electrical indicating circuit. A measured air pressure was thus balanced against the unknown pressure, without the aid of optical systems.

2. A convenient method for preparing pure nitrogen pentoxide has been described.

3. The vapor pressures of nitrogen pentoxide have been determined by a static method in which corrections were made for the decomposition occurring in the gaseous phase. The results agree at the lower temperatures with those of Russ and Pokorny obtained by a different method, and extend to higher temperatures than they were able to employ. The vapor pressures of nitrogen pentoxide are conveniently given by the empirical formula:

$$\text{Log } P_{\text{mm.}} = \frac{1244}{T} + 34.1 \log T - 85.929.$$

4. The sublimation point and heats of sublimation of solid nitrogen pentoxide have been calculated.

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ADDITION COMPOUNDS OF AMMONIA WITH THE AMMONIUM HALIDES.

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The fact has long been noted in the literature[1] that the majority of the salts of ammonium are exceptionally soluble in anhydrous liquid ammonia, and a great deal of work has been done in the examination of the nature of such solutions. The most familiar case is that of ammonium nitrate, which absorbs ammonia readily at ordinary temperatures to form a mobile liquid known as Divers' solution.[2] Conflicting conclusions have been drawn regarding this system by different investigators. Raoult[3] deduced the existence of compounds of the formulas $NH_4NO_3, 2NH_3$, and $NH_4NO_3.NH_3$; Troost[4] claimed to have obtained 2 different compounds; $2NH_4NO_3.3NH_3$, and $NH_4NO_3.3NH_3$; while Kuriloff,[5] who first established the complete freezing point diagram, isolated only the latter compound—$NH_4NO_3,3NH_3$—which showed a m. p. of —40°.

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[1] See Franklin and Kraus, *Am. Chem. J.*, **20**, 820 (1898).

[2] Divers, *Proc. Roy. Soc.*, **21A**, 109 (1873).

[3] Raoult, *Compt. rend.*, **76**, 1261 (1873).

[4] Troost, *ibid.*, **94**, 789 (1882).

[5] Kuriloff, *Z. physik. Chem.*, **25**, 107 (1898).

Ammonium thiocyanate is also extremely deliquescent in ammonia. Bradley and Alexander[1] have succeeded in obtaining a whole series of addition compounds in this system, further data regarding which have recently been published by Foote and Hunter.[2]

For the remaining salts few results of any value are available. Troost[3] has stated that ammonium chloride forms with ammonia the compounds $NH_4Cl.3NH_3$ (m. p. +7°) and $NH_4Cl.6NH_3$ (m. p., —18°). Ammonium bromide and ammonia have been investigated by Troost[4] and Roozeboom;[5] compounds of the formulas NH_4Br, NH_3; $NH_4Br.3NH_3$ (m. p., +8.7°) and $NH_4Br.6NH_3$ (m. p., —20°) have been deduced.

In the present article the results of an examination of the freezing-point curves of ammonium chloride, bromide and iodide with ammonia over the whole of the available concentration range are recorded. Ammonium fluoride was found to be practically insoluble in liquid ammonia[6] and to form no compounds. The curve for the system NH_4NO_3–NH_3 was also redetermined in part, but since the data of Kuriloff were duplicated within the limits of experimental error, the results need not be repeated here.

Experimental.

The whole work was carried out in sealed glass bulbs, as described by Smith and Eastlack.[7] Anhydrous ammonia was obtained by warming a concentrated aqueous solution, drying the gas given off by means of quicklime and fused potassium hydroxide, and condensing in a tube surrounded by liquid air. The salts were C. P. products, recrystallized before use.

Mixtures of known composition were made by adding liquid ammonia to a weighed quantity of the powdered salt in an unsealed bulb, sealing at once and weighing again. A handle was fused to the bulb and complete admixture of its contents brought about by warming and shaking. Solidification was induced by rapid cooling in liquid air and the bulb, with a thermometer, was then immersed in a bath, the temperature of which was slowly raised until the point of disappearance of the last few crystals was noted. By careful repetition of this procedure the exact freezing point of the mixture was obtained.

Below 0° the bath employed was an unsilvered Dewar flask containing alcohol previously cooled by liquid air. Above 0° a water bath was substituted. For temperatures below —35° a toluene thermometer was used, standardized at the freezing points of mercury and pure ethyl

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[1] Bradley and Alexander, THIS JOURNAL, **34**, 15 (1912).

[2] Foote and Hunter, *ibid.*, **42**, 69 (1920).

[3] Troost, *Compt. rend.*, **88**, 578 (1879).

[4] Troost, *ibid.*, **92**, 715 (1881).

[5] Roozeboom, *Z. physik. Chem.*, **2**, 460 (1888).

[6] Compare Franklin and Kraus, *loc. cit.*

[7] Smith and Eastlack, THIS JOURNAL, **38**, 1262 (1916).

acetate.[1] Above —35° a standardized mercury thermometer was employed. The freezing points recorded below may be regarded as of the following accuracy: from —80 to —35°, possible error 0.5° to 1.0°; above —35°, possible error 0.2° to 0.5°.

It was found impossible to carry the curves much above ordinary temperatures owing to the enormous ammonia pressures there exerted. Persistent efforts to obtain more points merely resulted in the sudden transference of the apparatus to the ceiling of the laboratory. However, since in all cases the neutral salt had already been reached as solid phase, no compounds have been missed by this incomplete examination of the systems.

The results obtained are given in the tables below and in the accompanying diagram. The significance of the curves need not be elaborated upon here; it is sufficient to state that each break indicates a change in solid phase and that the composition of each compound isolated is automatically determined by its maximum point on the curve.

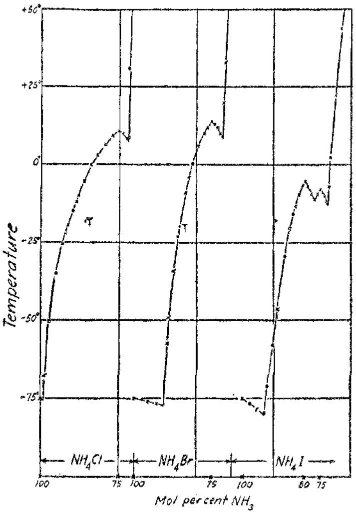

Fig. 1.

Ammonia-Ammonium Chloride:

(*a*) Solid phase, NH_3.

Mol. % NH_3...	100
T............	—74.8

(*b*) Solid phase, $NH_4Cl.3NH_3$.

Mol. % NH_3...	98.8	97.4	95.5	93.1	92.2	91.3	89.8	88.6	87.9
T............	—67.4	—50.5	—35.0	—25.6	—22.0	—19.6	—15.0	—11.9	—10.0
Mol. % NH_3...	86.0	83.9	81.9	79.0	77.1	75.0	74.0		
T............	—5.1	0.0	3.2	6.6	9.5	10.7	10.0		

(*c*) Solid phase, NH_4Cl.

Mol. % NH_3...	72.3	71.5
T............	9.1	31.0

Ammonia-Ammonium Bromide:

(*a*) Solid phase, NH_3.

Mol. % NH_3...	100	95.6	92.9
T............	—74.8	—76.0	—76.7

(*b*) Solid phase, $NH_4Br.3NH_3$.

Mol. % NH_3...	89.5	88.9	87.6	85.9	83.4	82.4	81.3	79.7
T............	—57.4	—49.0	—34.0	—23.1	—9.0	—4.1	0.4	6.0
Mol. % NH_3...	77.8	76.2	75.0	74.3	73.1	72.8	72.2	
T............	10.1	12.1	13.7	13.1	11.7	10.9	9.7	

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[1] Compare Kendall and Booge, THIS JOURNAL, 38, 1718 (1916).

(*c*) Solid phase, NH_4Br.

Mol. % NH_3...	71.8	71.4	70.7	69.9	68.6
T............	9.2	20.0	32.6	53.0	87.0

Ammonia-Ammonium Iodide:

(*a*) Solid phase, NH_3.

Mol. % NH_3...	100	97.5	95.4
T............	—74.8	—76.8	—78.6

(*b*) Solid phase, $NH_4I.4NH_3$.

Mol. % NH_3...	92.8	92.0	90.2	88.8	86.8	85.1	84.0
T............	—79.5	—71.0	—58.0	—46.2	—29.5	—20.2	—16.0
Mol. % NH_3...	83.2	82.0	80.0	79.2	77.9	77.0	
T............	—13.2	—9.4	—5.1	—6.8	—9.2	—10.9	

(*c*) Solid phase, $NH_4I.3NH_3$.

Mol. % NH_3...	76.9	75.9	75.0	74.3	73.8	73.2
T............	—10.9	—9.1	—8.0	—8.9	—10.0	—11.5

(*d*) Solid phase, NH_4I.

Mol. % NH_3...	72.4	71.5	69.8	68.0	66.8
T............	—7.0	2.5	22.6	44.2	57.0

Discussion of Results.—From the diagram it will be seen that the existence of the following compounds has been demonstrated:

	M. p.
(*a*) $NH_4Cl.3NH_3$.............................	10.7°
(*b*) $NH_4Br.3NH_3$.............................	13.7°
(*c*) $NH_4I.3NH_3$.............................	—8.0°
(*d*) $NH_4I.4NH_3$.............................	—5.1°

The melting points of the first 2 of these compounds are considerably higher than the values recorded by previous workers. The other 2 compounds have not been isolated before.

No evidence was obtained in support of the compounds, $NH_4Cl.6NH_3$ and $NH_4Br.6NH_3$, claimed by Troost.[1] From the position of the melting points given by him for these compounds, as referred to the general curves (see the 2 points marked T in the diagram), it appears that their existence is extremely improbable. In the same way no indication was given of compounds of the type $NH_4Br.NH_3$. While no actual analyses were carried out upon the solid phases separating out at ordinary temperatures from the mixtures, yet their crystal habit was in each case identical with that of the neutral salt.

When we compare the curves among themselves, we note a regular increase in the extent and stability of compound formation as we pass upwards through the series of halogens. Ammonium fluoride forms no compounds at all with ammonia. The chloride forms a compound $NH_4Cl.3NH_3$, which is appreciably dissociated into its components on fusion, as is shown by the relative flatness of the curve in the region of its maximum. The compound $NH_4Br.3NH_3$ is much more stable, as may be seen by the

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[1] Troost, *loc. cit.*

sharper maximum on the diagram. With ammonium iodide, finally, not only is there obtained a stable compound of the regular type, $NH_4I.3NH_3$, but also a second very stable compound of the composition $NH_4I.4NH_3$.

The stability of these compounds, indeed, is so unexpectedly high that it is evident that their existence at higher temperatures and even in the vapor phase cannot be entirely left out of consideration in any exact study of the ammonium halides. For example, Smith and Lombard[1] have found that the vapor density of ammonium iodide at temperatures below 350° is greater than the value required by the formula NH_4I, and have suggested that any dissociation into ammonia and hydrogen iodide is outbalanced by association into complex molecules of the type $(NH_4I)_2$. The present investigation indicates an alternative and very plausible explanation, namely that complex molecules of the type $NH_4I.nNH_3$ (and perhaps, too, of the type $NH_4I.nHI$, since ammonium nitrate has been shown by Ditte[2] and by Groschuff[3] to form stable addition compounds with nitric acid) are existent in the vapor phase, raising the observed density above the normal value. The possibility of the presence of such compounds in the vapor phase also adds a new complication to the discussion between Wegscheider[4] and Smith[5] on the abnormalities in the vapor densities of dried and undried ammonium chloride.

Summary.

The freezing point curves of the ammonium halides with ammonia have been determined throughout the whole available composition range.

Compounds of the following formulas have been isolated: $NH_4Cl.3NH_3$ (m. p., 10.7°), $NH_4Br.3NH_3$ (m. p., 13.7°); $NH_4I.3NH_3$ (m. p., —8.0°); $NH_4I.4NH_3$ (m. p., —5.1°). Other compounds of these systems previously recorded in the literature are probably non-existent.

The stability of the addition compounds with ammonia increases regularly as we ascend the series of the ammonium halides. Some consequences of the probable persistence of these compounds in the vapor phase have been briefly indicated.

NEW YORK, N. Y.

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[1] Smith and Lombard, THIS JOURNAL, **37**, 66 (1915).

[2] Ditte, *Ann. chim. phys.*, **18**, 320 (1879).

[3] Groschuff, *Ber.*, **37**, 1486 (1904).

[4] Wegscheider, *Z. anorg. Chem.*, **103**, 207 (1918).

[5] Smith, Eastlack and Scatchard, THIS JOURNAL, **41**, 1961 (1919).