has been reported by Burg and his co-workers,[4] for the trimeric P-dimethylphosphinoborane and the trimeric As-dimethylarsinoborane it is very stable for a boron–nitrogen compound containing two active hydrogens per boron. It is unaffected after weeks in contact with moist air and is hydrolyzed only very slowly by cold water.

The pyrolysis of methylamine-borane has been studied by a number of previous investigators[5] but this initial pyrolysis product never has been characterized.

Experimental

A. **Preparation of Trimeric N-Methylaminoborane.**—In a typical preparation, 3 mmoles of diborane was condensed with liquid nitrogen, together with a small excess of anhydrous methylamine (7 millimoles). The mixture was then allowed to warm up to room temperature over a period of about three hours. A small amount of hydrogen was produced in this preparation of methylamine borine. Air was then admitted to the system and the tube was removed from the vacuum line, stoppered with a calcium sulfate drying tube, and heated on a steam-bath for two hours. The liquid in the tube changed into a crystalline mass after the first hour of heating. This white solid was then placed in a clean tube, which was replaced on the vacuum line. A beaker of boiling water was placed around the bottom of the tube and the trimeric N-methylamino-borane sublimed under high vacuum. The product collected as a ring of fine needles on the walls of the tube just above the surface of the bath. The tube was removed from the line and broken on each side of the ring. The long white needles were then scraped from the walls; yield about 0.22 g. or 85%.

The analysis of the product is summarized in Table I.

TABLE I

Anal. for (CH₃NHBH₂)₃, %	Obsd.	Calcd.
Carbon	28.00	28.00
Hydrogen	14.02	14.10
"Active" hydrogen	4.35	4.70
Boron	25.0	25.23
Nitrogen	32.78	32.66

B. **Molecular Weight Determinations.**—The molecular weight of the solid was estimated from the freezing point depressions of benzene and nitrobenzene solutions using a standard Beckmann apparatus. The results indicated molecular weights of 121 and 141 for two trials in benzene and 134 for nitrobenzene.

The molecular weight was also determined by the vapor pressure lowering of liquid ammonia solutions. The apparatus designed by D. R. Schultz[6] was modified by using a large slush bath of ethylene chloride as the constant temperature medium. A molecular weight of 127 was obtained.

A trimer of CH₃NHBH₂ has a calculated molecular weight of 128.7.

C. **Decomposition into 1,3,5-Trimethylborazene.**—A quantity, 0.2364 g., of (CH₃NHBH₂)₃ was placed in an evacuated sealed tube and heated at 200° for four hours. Upon opening the tube, 5.96 mmoles of hydrogen, identified by a molecular weight of 2.1, was found. This gives a ratio of hydrogen per mole of starting material of 3.24. The 1,3,5-trimethylborazene was purified by vacuum condensation, the portion collecting in a trap at −45° being retained. A 74% yield was obtained based on the equation

$$(CH_3NHBH_2)_3 \xrightarrow{200°} 3H_2 + (CH_3NBH)_3 \quad (2)$$
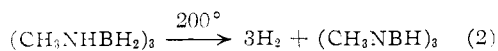
The 1,3,5-trimethylborazene produced was characterized by vapor pressure measurements over the temperature range 50 to 75°, and by vapor phase molecular weight measure-

(4) A. B. Burg and R. I. Wagner, THIS JOURNAL, 75, 3872 (1953); P. G. A. Stone and A. B. Burg, ibid., 76, 386 (1954).

(5) H. I. Schlesinger, D. M. Ritter and A. B. Burg, ibid., 60, 1926 (1938); E. Wiberg, K. Hertwig and A. Bolz, Z. anorg. Chem., 256, 177 (1948); G. W. Schaeffer and E. R. Anderson, THIS JOURNAL, 71, 2143 (1949); A. B. Burg and L. C. Randolph, ibid., 71, 3451 (1949).

(6) D. R. Schultz, Ph.D. thesis, University of Michigan, 1954.

ments based on vapor density (obsd. = 126; theor. = 122.5). The melting point of the solid was 0 to −1° as compared to −9° reported by Wiberg, Bolz and Buckheit[2] and −7 to −8° reported by Schaeffer and Anderson.[5] It is believed that the higher value of 0 to −1° indicates greater purity of the sample studied and does not negate the characterization of the borazene.

D. **Properties of Trimeric N-Methylaminoborane.** The compound may be recrystallized from methyl or ethyl alcohol as long white fibrous needles. An analysis for boron and "active" hydrogen on this recrystallized material demonstrated that the composition was unchanged. In addition to the above solvents, the compound is very soluble in acetone and liquid ammonia. It is moderately soluble in benzene, ether and chloroform and is insoluble in carbon tetrachloride, petroleum ether and water. The insolubility in water may be primarily a wetting problem.

The density of the compound is 0.90 g./ml. as determined by centrifuging a few crystals in a series of mixtures of carbon tetrachloride and kerosene. The crystals would remain suspended in the mixture with a density of 0.90 g./ml.

A sample of the solid was allowed to stand exposed to the moist air of the laboratory for three weeks, during which time no noticeable hydrolysis occurred. A portion placed in cold water will float for hours but will disappear after about a day. A 20% solution of hydrochloric acid must be heated to boiling to bring about rapid hydrolysis.

E. **X-Ray Power Diffraction Data for Trimeric N-Methylaminoborane.**—In Table II are listed the interplanar spacings (d values) and the relative line intensities found to be characteristic of the compound. The powder patterns were taken with copper Kα radiation in a cylindrical camera of 57.3 mm. diameter. The low absorbing glass capillaries used to hold the sample had a diameter of 0.2 mm. and a wall thickness of 0.01 mm.

TABLE II

d	I	d	I	d	I
7.1	VS	2.68	VW	1.20	VW
4.26	VS	2.29	W	1.88	VW
4.00	MS	2.27	W	1.77	VW
3.45	M	2.19	W	1.70	VW
3.06	VW				

The System Ba(NO₃)₂-KNO₃; Characterization of the Double Salt Ba(NO₃)₂·2KNO₃[1]

BY MEYER M. MARKOWITZ, JOHN E. RICCI AND PAUL F. WINTERNITZ

The literature referring to the phase relationships in the system Ba(NO₃)₂-KNO₃ is contradictory. Harkins and Clark[2] characterized the system as being of a simple eutectic type on the basis of an investigation at liquidus temperatures. Ricci[3] in replotting their data demonstrated indications for the presence of the binary compounds 2Ba(NO₃)₂·

(1) This work was performed under Contract No. DAI-28-017-501-ORD-(P)-1247. Project No. TU2-2M. Dept. of Army Project No. 517-06-002. The support and permission to publish are gratefully acknowledged.

(2) W. D. Harkins and G. L. Clark, THIS JOURNAL, 37, 1816 (1915).

(3) J. E. Ricci, ibid., 59, 1763 (1937).

KNO₃ and Ba(NO₃)₂·2KNO₃. More recently, Protsenko and Bergman[4] have reported the system as a simple eutectic at liquidus temperatures. The aqueous ternary system at 9.1, 21.1 and 35.0°[5] and at 25.0 and 50.0°,[6] however, shows the formation of the incongruently soluble, anhydrous double salt Ba(NO₃)₂·2KNO₃, which, though isolated,[7] has never been characterized. It is, therefore, the intent of the present investigation to clarify the nature of the Ba(NO₃)₂–KNO₃ system. Pursuant to this, the complete phase diagram has been determined as well as some of the properties of the double salt Ba(NO₃)₂·2KNO₃.

Materials and Methods.—The barium nitrate and the potassium nitrate were C.P. materials found to be 99.9 and 99.6% pure, respectively. Analysis was based on the determination of barium through precipitation as barium chromate and iodometric titration of the precipitate with standard thiosulfate solution, and on the gravimetric determination of potassium by conversion to potassium sulfate.

Thermal analyses were performed by heating 20-g. samples at a constant heating rate of 10°/minute in a small furnace. A chromel–alumel thermocouple used in conjunction with an ice-bath constituted the temperature sensing element. E.m.f. readings were made every 30 seconds on a Leeds–Northrup Precision Potentiometer. The accuracy of the thermocouple was periodically checked against known temperature standards and a suitable calibration curve was prepared. All such measurements reported here have been corrected and are felt to be correct within plus or minus 3°.

The Preparation of Ba(NO₃)₂·2KNO₃.—254.9 g. of potassium nitrate and 117.6 g. of barium nitrate were dissolved in 627.4 g. of water, with stirring, at 95°. The complex was placed in a water-bath at 25° (plus or minus 0.1°) and equilibrated with continuous, vigorous agitation. Equilibration was checked by density determinations, which gave the values 1.1738 and 1.1737 after 9.5 and after 24 hours of stirring, respectively. The saturated solution was found to contain 75.12% H₂O, 3.06% Ba(NO₃)₂ and 21.82% KNO₃ (by difference). These figures agree well with the data from the 25.0° isotherm for the Ba(NO₃)₂–KNO₃–H₂O system as obtained by Glasstone and Riggs. Filtration of the double salt was performed by use of a filtering flask and fritted glass funnel immersed in water at about 32°. The double salt was sucked dry from its mother liquor by aspiration for 1.5 hours. This gave an almost free-flowing material which was then dried overnight at 110°.

Anal. Calcd. for Ba(NO₃)₂·2KNO₃: Ba(NO₃)₂, 56.36. Found: Ba(NO₃)₂, 56.03.

Because of the incongruent solubility relations of the double salt in the aqueous system, in which it is stable as a solid phase only in contact with solutions containing excess of potassium nitrate, the product is always contaminated with some potassium nitrate deriving from the mother liquor.

The X-Ray Powder Pattern of Ba(NO₃)₂·2KNO₃.—The X-ray powder pattern of Ba(NO₃)₂·2KNO₃ differs in inter-

TABLE I

X-RAY POWDER DATA FOR Ba(NO₃)₂·2KNO₃, "d" FOLLOWED IN PARENTHESES BY RELATIVE INTENSITY (s, STRONG; m, MEDIUM; w, WEAK; v, VERY)

5.84(m), 5.54(s), 4.12(w), 3.84(vw), 3.41(w), 3.32(vs), 3.22(m), 2.92(m), 2.82(s), 2.60(m), 2.46(m), 2.33(vvs), 2.20(m), 2.16(w), 2.15(w), 2.07(w), 1.94(s), 1.89(vvw), 1.85(m), 1.83(m), 1.76(m), 1.72(m), 1.67(m), 1.62(m), 1.59(m), 1.56(vvw), 1.51(w), 1.47(w), 1.43(m), 1.41(m), 1.40(m), 1.37(m), 1.34(m), 1.32(vw)

(4) P. I. Protsenko and A. G. Bergman, *J. Gen. Chem. (USSR)*, **21**, 1731 (1951).

(5) A. Findlay, I. Morgan and I. P. Morris, *J. Chem. Soc.*, **105**, 799 (1914).

(6) S. Glasstone and E. J. Riggs, *ibid.*, **127**, 2846 (1925).

(7) H. W. Foote, *Amer. Chem. J.*, **32**, 251 (1904); W. K. Wallbridge, *ibid.*, **30**, 154 (1903).

planar spacings and line intensities from the patterns obtained from potassium nitrate, from barium nitrate and from a stoichiometric mechanical mixture of the two simple salts.

Thermal Behavior.—Heating of potassium nitrate shows an endothermic break occurring at 126° which was found to persist upon cooling and reheating. This break corresponds to a reversible crystallographic transition of potassium nitrate.[8] Heating of barium nitrate to 325° shows no indications of heat effects other than a smooth steady temperature rise.

Heating of the double salt Ba(NO₃)₂·2KNO₃ showed the occurrence of two endothermic processes, one at 201° (at the 10°/minute heating rate) and the other at 288°. This behavior was consistently reproducible. There was no liquid formation observed at the 201° break but liquid was evident at the 288° break. Cooling of the material after heating above either 201 or 288° and subsequent thermal analysis showed a new behavior. The break at 201° had disappeared but now a break at 126° was present. The break at 288°, nevertheless, remained.

The density of the double salt before heating was determined to be 2.772. After fusion, the material had a density of 2.609. This latter value is in good agreement with the density calculated for a mechanical mixture of 56.03% barium nitrate and 43.97% potassium nitrate.

The Binary System.—Mixtures of barium nitrate and potassium nitrate were prepared varying in composition from 0 to 60 mole per cent. barium nitrate. The mixtures were fused to yield a clear liquid and then cooled slowly with stirring to the first appearance of solid (the liquidus temperature). Stirring was done by means of a calibrated nitrogen-filled mercury thermometer. All temperatures reported have been corrected. The data obtained are summarized in the second column of Table II. These results agree well with those of Protsenko and Bergman and do indeed show the non-existence of any double salts at liquidus temperatures.

TABLE II

LIQUIDUS CURVE OF THE SYSTEM Ba(NO₃)₂–KNO₃; RELATIVE MAGNITUDE OF ARRESTS IN THE SYSTEM

Mole % Ba(NO₃)₂	Liquidus temp., °C.	126° arrest	288° arrest	Mole % Ba(NO₃)₂	Liquidus temp., °C.	126° arrest	288° arrest
0.00	335	7.5	0.0	33.33	433	4.0	9.0
5.00	319	7.0	8.0	35.00	443	4.0	..
10.00	297	6.0	12.0	40.00	457	4.0	8.5
12.68	286 (eutectic)	6.0	13.0	45.00	479	3.0	8.0
15.00	309	6.0	12.0	50.00	489	2.0	..
20.00	354	5.0	11.5	55.00	503	1.0	7.0
25.00	387	5.0	11.0	60.00	517	1.0	6.0
30.00	415	4.0	10.0	100.00	596	0.0	0.0

Heating curves were then run on the cooled powdered mixtures of Table II. Except for pure potassium nitrate and pure barium nitrate, each sample showed but two endothermic breaks, namely, at 126° and at 288°. Table II gives the relative magnitude of each arrest. These conform to the behavior anticipated for a simple binary

(8) R. G. Early and T. M. Lowry, *J. Chem. Soc.*, **121**, 963 (1922).

eutectic system. Thus, the 126° break corresponds to the potassium nitrate crystallographic transition and the 288° break corresponds to the eutectic temperature for the system.

The non-appearance of any evidence for the existence of $Ba(NO_3)_2 \cdot 2KNO_3$ above the eutectic temperature indicates that the double salt is stable only below the eutectic. Thus, the 201° break observed for the double salt must correspond to the decomposition into its simple component salts at the 10°/minute heating rate. It was found that the apparent decomposition temperature varied with the heating rate. At heating rates of 10, 8.5, 6.9, 5.6, 4.5, 3.2, 2.2 and 0.5°/minute, the corresponding decomposition temperatures were 201, 200, 198, 197, 196, 195, 194 and 187°, respectively. However, heating the double salt for 2 days at 168° brings about decomposition, whereas if it is maintained at 165° for 11 days the salt persists as determined by the presence or absence of this decomposition arrest in the heating curve. Hence, the true or equilibrium decomposition temperature lies between 165 and 168°. The thermal analysis gives a temperature which corresponds to a rapid rate of decomposition and not the true equilibrium temperature, a temperature at which the rate is evidently quite slow. This particular case is therefore another instance of the uncertainty of thermal analysis when applied to slow reactions.

Attempts at nucleation of the double salt with admixtures of up to 50 weight per cent. of the previously decomposed material or by rapid heating of the double salt to 195° and then cooling did not result in any change of the observed decomposition temperature. Rather the observed decomposition temperature was that characteristic of the heating rate.

Attempts at the thermal preparation of $Ba(NO_3)_2 \cdot 2KNO_3$ by the annealing of intimate stoichiometric mixtures of the component salts were not successful. Tempering such mixtures at 147° for 15 days or at 160° for 14 days did not yield any double salt as ascertained by thermal analysis.
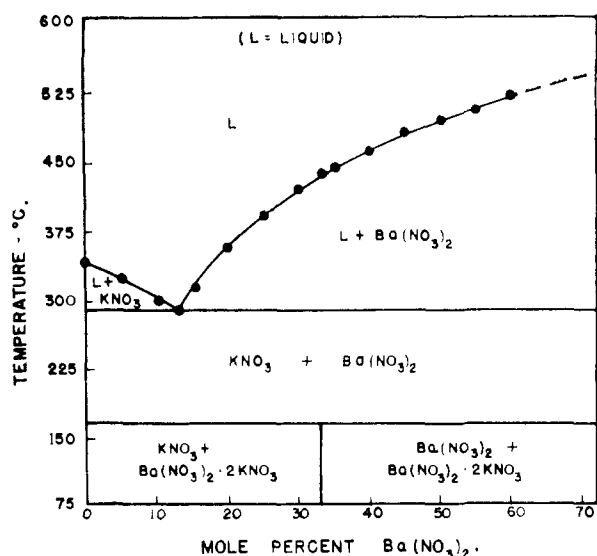
The composite results obtained in the course of this investigation are given in Fig. 1.

The double salt, then, is a stable solid phase in the binary system up to about 168°, although it does not form at any measurable rate from the anhydrous salts even at temperatures just below this decomposition temperature. In the presence of water it forms very readily even at room temperature, and its range of existence as a stable solid phase in the aqueous system, making its appearance at about 168°, increases with falling temperature.

DEPARTMENT OF CHEMICAL ENGINEERING AND
DEPARTMENT OF CHEMISTRY
NEW YORK UNIVERSITY
NEW YORK 53, NEW YORK

The Stability of Silver(I) Complexes of Some 3- and 4-Substituted Pyridines[1]

BY R. KENT MURMANN[2] AND FRED BASOLO

Pauling[3] has explained the greater stability of certain complexes of the transition elements compared to those of other metals on the basis of double bonding. He suggested that the transition elements can use for multiple bonding lower energy d orbital electrons which are not available to the non-transition elements. Although there is at present no direct proof of such double bonding in complexes, several experimental observations have been rationalized on this basis.[4] The stability constants of silver(I) complexes of some 3- and 4-substituted pyridines are reported here and the results obtained are also consistent with the concept of π-bonding.

Experimental

Pyridine, α-picoline, β-picoline and γ-picoline were redistilled over barium oxide and the middle portions used in these experiments. The physical constants of the amines are listed in Table I.

TABLE I

PHYSICAL CONSTANTS OF PYRIDINES

	B.p. or m.p., °C.
Pyridine	115.0–115.2
α-Picoline	127.5–128.0
β-Picoline	142.8–143.0
γ-Picoline	142.8–143.0
2-Methoxypyridine	142.5–143.0
3-Methoxypyridine	77–79 (15 mm.)
4-Methoxypyridine	72–73 (20 mm.)
Methyl picolinic ester	108–109 (22 mm.)
Methyl nicotinic ester	103–104 (20 mm.)
Methyl isonicotinic ester	100–102 (20 mm.)
Nicotinamide	M.p. 126–127
Isonicotinamide	M.p. 155–156
3-Cyanopyridine	M.p. 48–49
4-Cyanopyridine	M.p. 78–79

(1) This investigation was supported by a grant-in-aid from the National Institutes of Health, Grant No. G-3239C2. Taken in part from a thesis submitted by R. Kent Murmann in partial fulfillment of the requirements for the Ph.D. degree, Northwestern University, 1954.
(2) University of Connecticut, Storrs, Connecticut.
(3) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1948, p. 250.
(4) J. Chatt and R. A. Williams, J. Chem. Soc., 3061 (1951); R. S. Nyholm and F. H. Burstall, ibid., 3570, 3579 (1952).

Fig. 1.—The system $Ba(NO_3)_2$–KNO_3.