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CHEMISTRY OF BORON HYDRIDES AND RELATED HYDRIDES

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CHEMISTRY OF BORON HYDRIDES AND RELATED HYDRIDES

I. THE PROPOSED INVESTIGATIONS

The work herein reported represents an extension of previously described[1] investigations in the following general areas: (1) a tracer study of the reaction between sodium and the diammoniate of diborane, (2) metathesis reactions in liquid ammonia with particular emphasis on the preparation of new borohydrides, (3) a physicochemical study of NH_4BH_4, its decomposition product $(BH_3NH_3)_n$, and the classical diammoniate of diborane, and (4) the reaction between hydroxylamine and diborane. Topic 4 has been extended to include the reaction between alkyl substituted hydroxylamines and diborane. To assist in interpretation of the data, the basic constants for the alkyl substituted hydroxylamines in water solution have been evaluated.

In addition to the above extensions, the reactions between lithium aluminum hydride and the chlorides of phosphorus have been studied as routes to the alkyl phosphines. The reactions between aluminum hydride and the phosphines have also been studied briefly in the course of this investigation.

Each area of investigation is described below under a separate heading.

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[1] Parry, R. W., Campbell, D. H., Schultz, D. R., Girardot, P. R., and Taylor, R. C., "Final Report, Chemistry of Boron Hydrides and Related Hydrides," Univ. of Mich., Eng. Res. Inst. Project M966-U.S. Air Force Contract AF 33(616)-8, E.O.R.-464 Br-1, 1952.

II. A TRACER STUDY OF THE REACTION BETWEEN SODIUM AND THE DIAMMONIATE OF DIBORANE

A. BACKGROUND

The structural formula to be assigned to the diammoniate of diborane has long been the subject of controversy. Stock and Wiberg[2] assumed that two of the hydrogens of diborane are acidic in character, this assumption leads to the representation of the diammoniate as an ammonium salt, $[(NH_4)_2B_2H_4]$.

Schlesinger and Burg[3] questioned the formulation of Stock and Wiberg and proposed instead the formula $NH_4[H_3BNH_2BH_3]$. This new representation, showing only a single ammonium ion and requiring no acid hydrogens for diborane, was based on the fact that only one equivalent of hydrogen was liberated when they allowed sodium to react with $B_2H_6 \cdot 2NH_3$ in liquid ammonia at -77°C.

Additional evidence bearing on the question of acid hydrogens in diborane was presented by Burg[4]. It has been shown that when the Brönsted-Lowry acid NH_4Cl is dissolved in liquid ammonia, a rapid interchange of protons between the acid and the solvent molecule occurs.[5] Burg conducted experiments with ND_3 and $B_2H_6 \cdot 2NH_3$ which showed that H-D interchange occurs only with the hydrogen of the ammonia and not with that of the B_2H_6 in the diammoniate. He interpreted his results as proof of the assumption that the hydrogens of diborane have no acidic character. Insofar as exchange experiments can be accepted as a criterion of acidic character, Burg's evidence is convincing. It appeared, however, that an independent and more drastic method for evaluating acidic character would yield interesting results; hence, a tracer study of the reaction between sodium and the diammoniate of diborane has been carried out in an effort to determine whether boron-hydrogen bonds, boron-nitrogen bonds, or both are broken when sodium reacts with the diammoniate in liquid ammonia.

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[2] (a) Stock, A., and Pohland, E., Ber. 58, 657 (1925); (b) Stock, A., Hydrides of Boron and Silicon Cornell Univ. Press, Ithaca, N. Y., 1933, p. 159.

[3] Schlesinger, H. I., and Burg, A., J. Am. Chem. Soc. 60, 290 (1938).

[4] Burg, A. B., J. Am. Chem. Soc. 69, 747 (1947).

[5] Nyman, C. J., Si Chang Fung, and Dodger, H. W., J. Am. Chem. Soc. 72, 1033 (1950).

The tracer-study results described earlier[1] can be summarized by the following four equations:

$$(1)\ B_2H_6 \cdot 2NH_3 + Na \xrightarrow{\text{liq. } NH_3} \text{solid residue} + H_2$$

$$(2)\ B_2D_6 \cdot 2NH_3 + Na \xrightarrow{\text{liq. } NH_3} \text{solid residue} + H_2$$

$$(3)\ B_2H_6 \cdot 2ND_3 + Na \xrightarrow{\text{liq. } ND_3} \text{solid residue} + D_2,\ HD,\ H_2\ (65\%D - 35\%H)$$

$$(4)\ ND_3 + Na \xrightarrow{Fe_2O_3} NaNH_2 + D_2\ (94\%D)$$

Equations 1 and 2 indicate that only nitrogen-hydrogen bonds are broken, but the results for equations 3 and 4 are more complex and are subject to any one of three different explanations.

First, the deuterium obtained in reaction 3 could have been contaminated with hydrogen during handling or analysis. Although the samples for run 3 and the standard (run 4) were handled in the same manner, the handling and analysis of pure D_2 in the mass spectrometer is recognized as a very difficult operation[6] and the possibility of contamination must be carefully considered.

According to a second explanation, the results could be real and the hydrogen obtained in reaction 3 could have arisen from the breaking of boron-hydrogen bonds when the hydrogens on ammonia were replaced by the less acidic deuterium. This would assume a fundamental difference in the mode of reaction of sodium with $B_2H_6 \cdot 2ND_3$ and $B_2H_6 \cdot 2NH_3$.

A third explanation could be based on the assumption that reactions 3 and 4 proceed by different mechanisms. If, then, the rate-controlling step in the catalytic reaction 4 did not involve a marked difference in reaction velocity when D was substituted for H, no appreciable fractionation of the ND_3 and ND_2H would result (ND_3 was not 100% deuterated). The resulting gas used as a standard (equation 4) would thus show no enrichment in the light isotope. If, on the other hand, the rate-controlling step in reaction 3 involved a marked difference in velocity when D was substituted for H, preferential liberation of H from the incompletely deuterated ND_3 would be expected. The result would then be as found in equation 3.

In order to obtain an unequivocal decision as to the correct explanation, the work previously described has been repeated by a new observer, using redesigned and rebuilt equipment.

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[6] Kirschenbaum, I., Murphy, G., and Urey, H., Physical Properties and Analysis of Heavy Water, McGraw-Hill Book Co., New York, 1951, p. 225.

A second questionable point arising from the preceding investigation concerned the stoichiometry of the reaction between sodium and the diammoniate of diborane in liquid ammonia. Schlesinger and Burg[3], in studying the reaction described by equation 1, had little difficulty in consistently obtaining 1 equivalent of hydrogen per mole of diborane. Their formulation of the compound as $[NH_4][H_3BNH_2BH_3]$ was based in large measure on this stoichiometry. It was therefore somewhat disconcerting to find in the earlier work from this laboratory that only 0.57 to 0.64 equivalents of hydrogen per mole of B_2H_6 was liberated by sodium in liquid ammonia. In view of this observation, the stoichiometry of the reactions between sodium and several weak acids in liquid ammonia, including $B_2H_6 \cdot 2NH_3$ has been investigated. Effects due to changes in the acid as well as effects due to experimental conditions have been carefully studied.

B. EXPERIMENTAL

1. The Stoichiometry of Reactions of Some Acids with Sodium in Liquid Ammonia

The acids studied included (1) NH_4CN, (2) $NH_4[CO_2NH_2]$, (3) H_3BO_3 + NH_3 and (4) $B_2H_6 \cdot 2NH_3$.

a. Materials. (1) Ammonia: Commercial tank NH_3 was dried over sodium metal before distillation into the vacuum line.

(2) Boric Acid: Before use, reagent-grade H_3BO_3 was out-gassed under vacuum for 12 hours at a temperature of 25°C to remove excess water. No water of constitution is lost under these conditions.

(3) Carbon Dioxide: CO_2 gas was obtained from dry ice and dried by passing it through a trap which was immersed in a CS_2 slush bath (-111.6°C).

(4) Hydrogen Cyanide: Dry HCN was kindly donated by Dr. Arthur Nersasian of this laboratory.

(5). Diborane: B_2H_6 was prepared by the reaction between $LiAlH_4$ and excess BF_3 etherate in ether solution[7]. The vapor pressure of the product, purified by low-temperature trap-to-trap distillation, was 225 mm at -111.6°C.

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[7] Shapiro, I., Weiss, H. G., Schmich, M., Sholnik, S., Smith, G. B. L., J. Am. Chem. Soc. 74, 901 (1952).

(6) Sodium: Sealed, evacuated, glass bulbs about 2 cm in diameter and containing 0.5-0.75 gm of sodium metal were prepared by standard techniques[8].

b. Apparatus. (1) Bulb Crusher: All reactions were run in the bulb crusher depicted in Fig. 1. A bulb containing sodium was placed in the crusher, which was then evacuated. It was possible to distill reactants into the dried and evacuated reaction tube A (Fig. 1), crush the bulb by rotating the movable arm, and drop the contents of the bulb into the reaction mixture by rotating the crusher around its own axis, B, thereby allowing the reaction to proceed without ever having exposed the system to the atmosphere after the initial evacuation.

(2) Toëpler Pump and Buret System: These have been adequately described previously[1,5].

c. Procedure. (1) Preparation of the Liquid Ammonia Solution of the Acid: The procedure used for the addition of the acid to the reactor was dependent on the physical properties of the acid. Gaseous CO_2 and HCN were measured out at room temperature in a trap of known volume attached to a manometer. The number of moles of gas added was then calculated by means of an appropriate equation of state* and the entire sample was then distilled into the reaction vessel.

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*The ideal gas law was satisfactory for CO_2, but since HCN forms some dimers and trimers in the gaseous state, it was necessary to use the equation of H Sinoski and R. Hara[9]:

$$\frac{PV}{nT} = R - bP - cP^2 ,$$

where

$$n = \text{number of moles of gas}$$

$$(\log b)^2 = -2.6393 + 0.010449T$$

$$-\log C = -4.4533 + 0.029123T$$

[8] Sanderson, R. S., Vacuum Manipulation of Volatile Compounds, John Wiley and Sons, New York, 1948, p. 72.

[9] Sinoski, H., and Hara, R., Tech. Rpts. Tohohu Imp. Univ. 8, No. 3 19 (1929); C. A. 23, 4860 (1929).

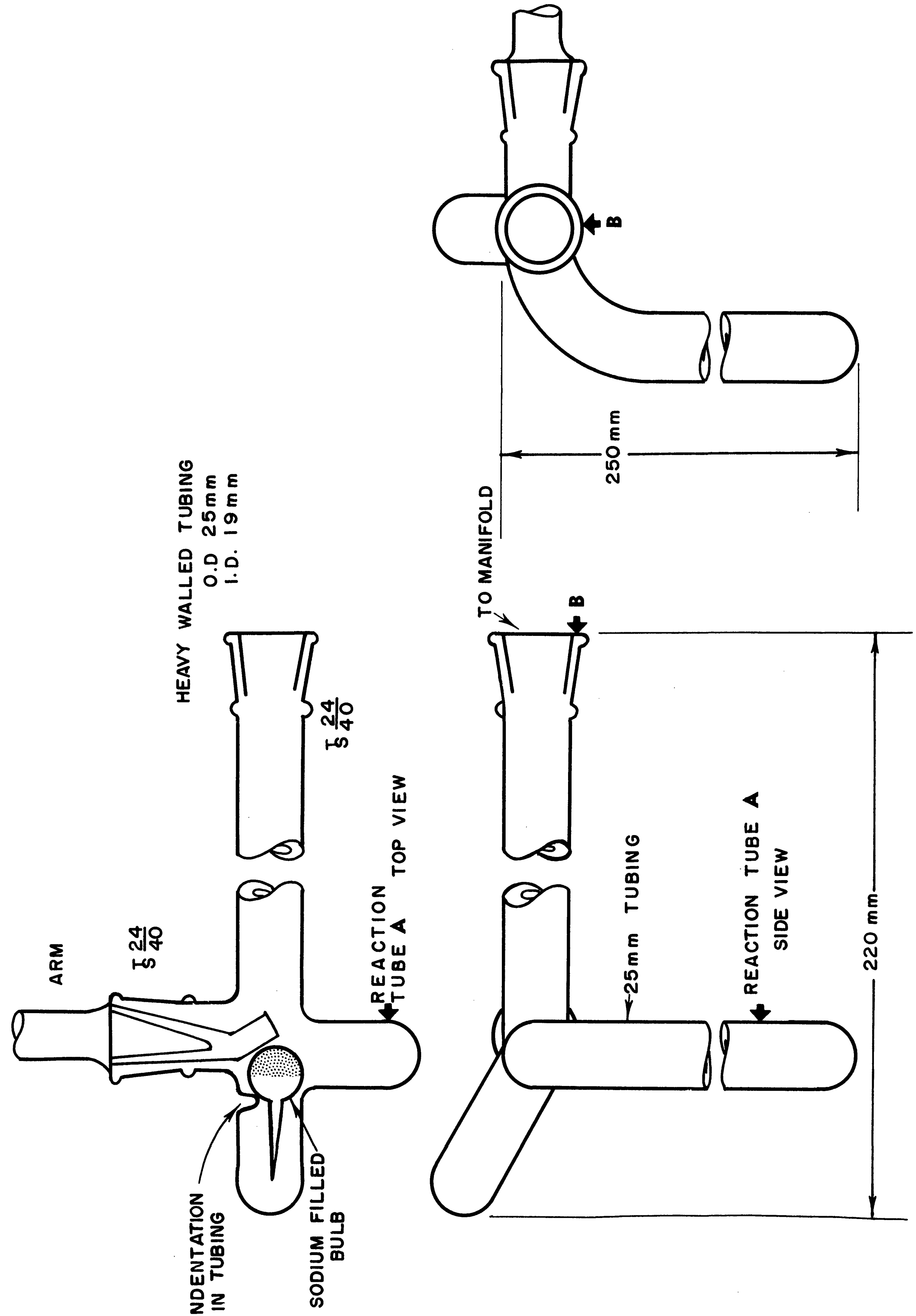

Fig. 1. Bulb Crusher

For solid H_3BO_3 a small glass bucket about 1 cm long was made out of 8-mm glass tubing. It was filled with dry boric acid crystals, weighed, and then lowered into the bulb crusher on a fine thread. When the bucket was on the bottom of the reactor tube of the bulb crusher, it was tipped by pulling a second thread attached to its bottom. The boric acid spilled into the bottom of the reactor tube, and the bucket was withdrawn and reweighed. The liquid ammonia solution of each of the above acids was prepared by freezing 3-5 ml of ammonia on top of each acid.

The $B_2H_6 \cdot 2NH_3$ solutions were prepared in two different ways, and there is abundant evidence to indicate that the result obtained is dependent on the mode of preparation.

The first method consisted of condensing a ring of diborane (2 millimoles) above a thin layer of ammonia which coated the sides and bottom of the reactor (1 ml of liquid ammonia). The reactor was immersed in a bath of mixed pentanes at -130°C, which was then allowed to warm up to -80°C, causing the diborane to melt and run onto the solid ammonia. Compound formation was indicated by a decrease in the pressure in the system. The excess ammonia was removed after reaction had occurred, leaving a white, amorphous solid. Ammonia was then condensed on the solid until the total volume was 3-5 ml.

The second method was essentially the same as the first with the very important exception that ammonia was never removed. Instead, more ammonia was condensed in the reactor to bring the volume up to 3-5 ml.

(2) Reaction between Sodium and an Acid: The solution was frozen, the sodium-containing bulb was crushed and dropped on the reaction mixture and about 1 ml of ammonia was condensed on the crushed bulb. The system was thermostated using a dry ice - isopropyl alcohol bath (-78.5°C) and the ammonia melted, thereby allowing the reaction to proceed. From time to time the reaction was quenched by immersion in liquid nitrogen and the evolved hydrogen gas was pumped into the gas burette with a Toepler pump. Data are summarized in Table I, on p. 18.

2. Tracer Study

a. Materials. (1) Magnesium Nitride: High-purity Mg_3N_2 was prepared by passing pure, dried nitrogen over highest-purity Dow magnesium heated to 650°C. The reaction was carried out in a stainless-steel tubular furnace (Fig. 2) and the gas flow was maintained for a period of 12 hours.

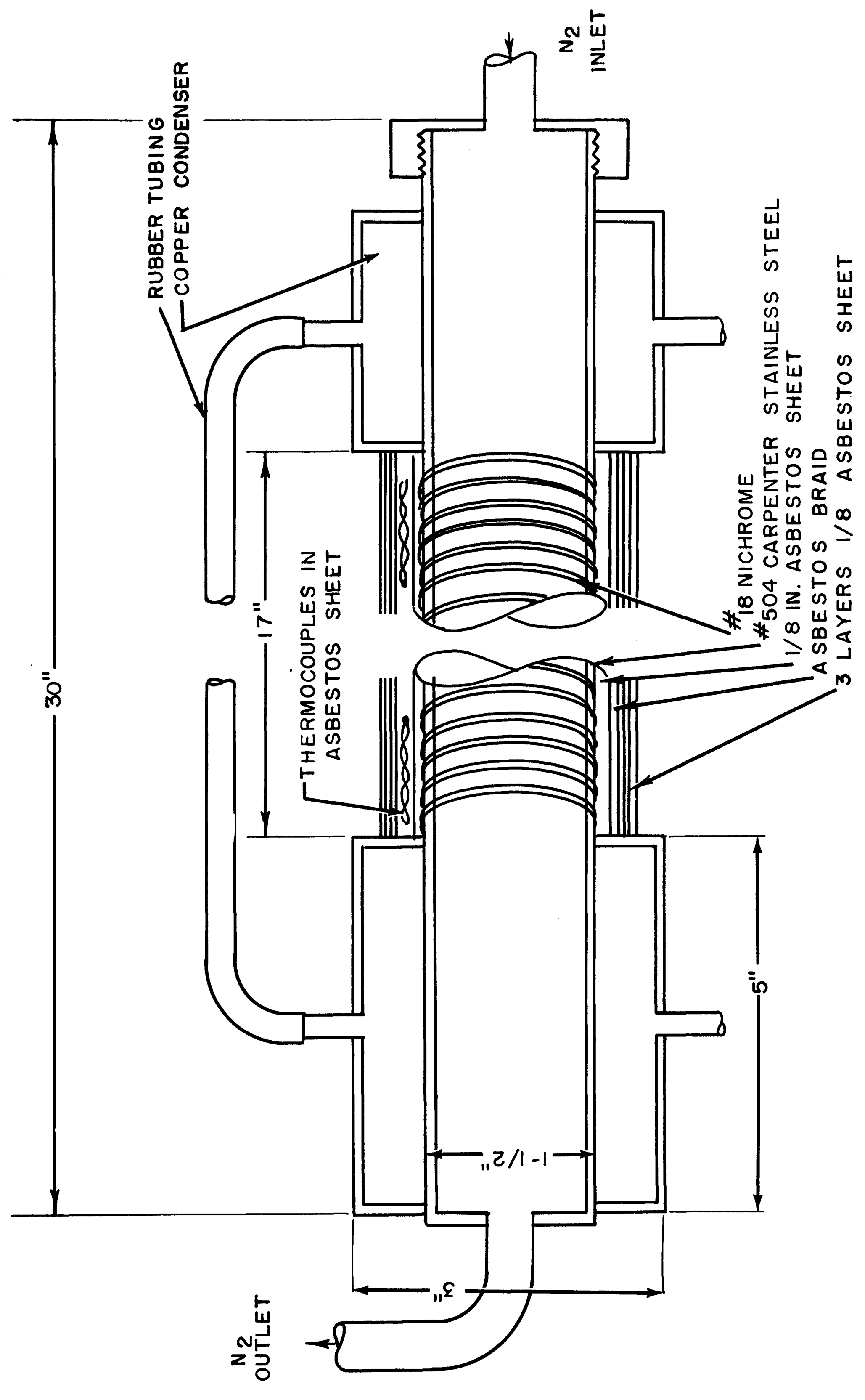

Fig. 2. Furnace for Preparing Magnesium Nitride

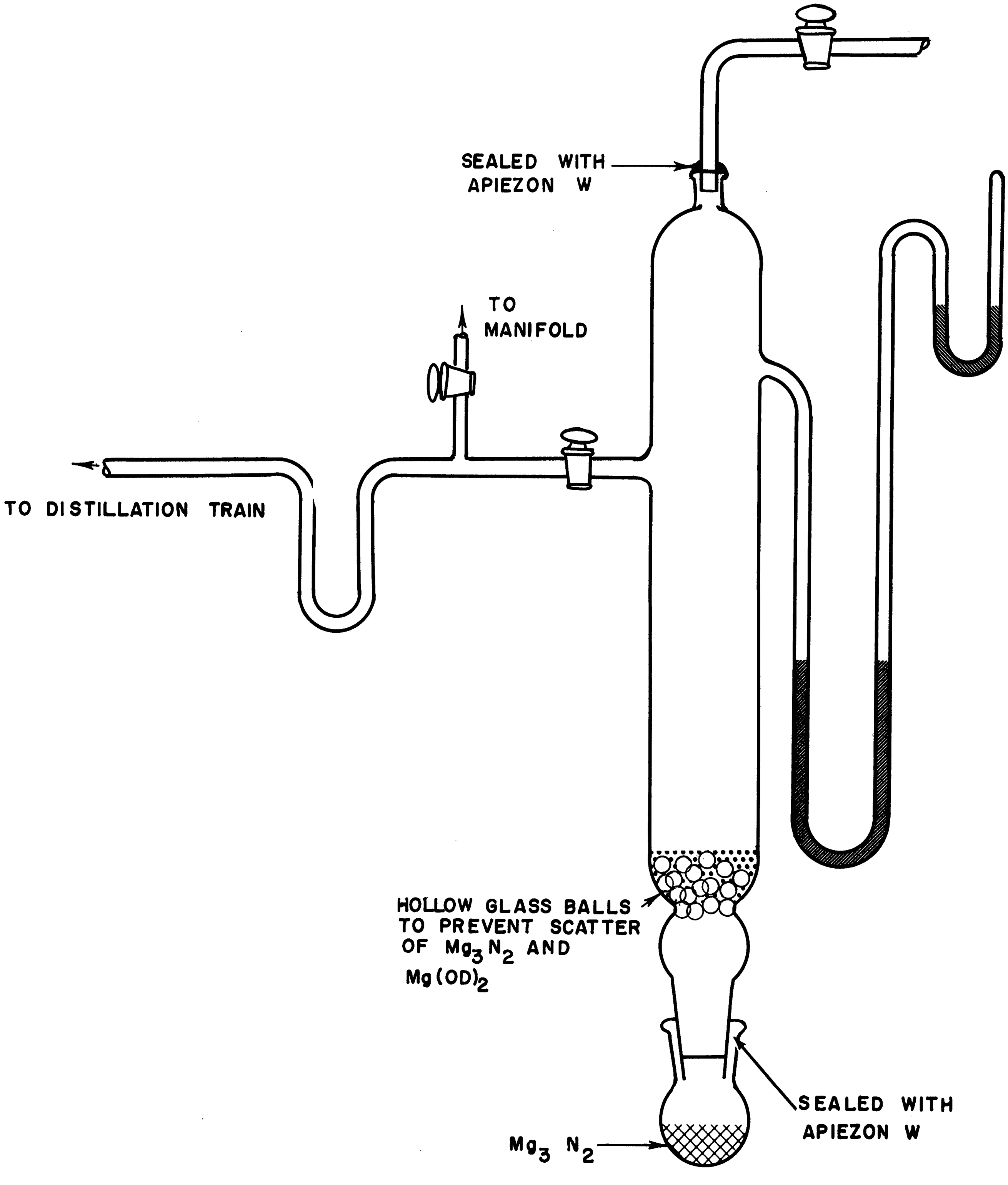

Fig. 3. System for Preparing and Collecting Deuteroammonia

(2) Deuteroammonia: ND_3 was prepared by distilling small amounts of D_2O onto an excess of Mg_3N_2, allowing the mixture to warm up slowly to room temperature, and then distilling the ND_3 from the reaction vessel. The amount of D_2O added at any one time was such that the final ND_3 pressure never exceeded one atmosphere. The gas generator is depicted in Fig. 3.

ND_3 was dried by passing it through two traps at -78°C and then distilling it from distilled, hydrogen-free sodium, its vapor pressure at -63.5°C was 111 mm as compared to a reported value of 110 mm[10].

(3) Catalytic Mixed Oxides: $Fe(NO_3)_3 \cdot 9H_2O$ was thermally decomposed at 300°C. The resultant Fe_2O_3 was heated at 700°C for 2 days, to remove water. The mass was pulverized; a little PtO_2, about 10%, was thoroughly mixed with the Fe_2O_3 and the mixture heated for another day at 700°C. Then it was transferred to a bulb crusher and heated in vacuo at 300-400°C until it was used (at least 24 hours).

(4) Diborane: The diborane previously described was used (p. 4).

(5) Sodium: Since sodium in bulbs prepared by standard techniques may contain hydrogen[11], the metal was refluxed and distilled in vacuum using a modification of a procedure described by Strong[11]. The apparatus is shown in Fig. 4. Prior to distillation, material in the still pot was refluxed under vacuum for 20 hours at about 300°C. During the distillation, which was carried out at 480 ± 20°C, sodium collected above the constrictions leading to the bulbs. With gentle heating and tapping the metal melted and ran through the constriction into the bulb. The evacuated bulbs were then sealed off.

b. Apparatus. (1) The Bulb Crusher: See p. 5 and Fig. 1.

(2) Sample Bulbs: Samples of gas were collected in calibrated bulbs (Fig. 5), which were then sealed at the constriction. To open a bulb for mass spectrometer analysis of its contents, it was sealed to the spectrometer manifold and a glass-enclosed iron weight, which was suspended by a magnet, was dropped on the break seal.

(3) Glass Sheath for Introducing Heavy Water into the Vacuum Line: A small vial containing 1-5 gm of D_2O was sealed into a glass sheath (Fig. 6) with Apeizon W wax. The sheath, which was connected to the vacuum line through a stopcock, was evacuated and then immersed in liquid nitrogen.

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[10] Kirschenbaum, I., and Urey, H.C., J. Chem. Phys. 10, 706 (1942).

[11] Strong, J. S. et. al., Procedures in Experimental Physics, Prentice Hall Inc., New York, 1938, p. 534.

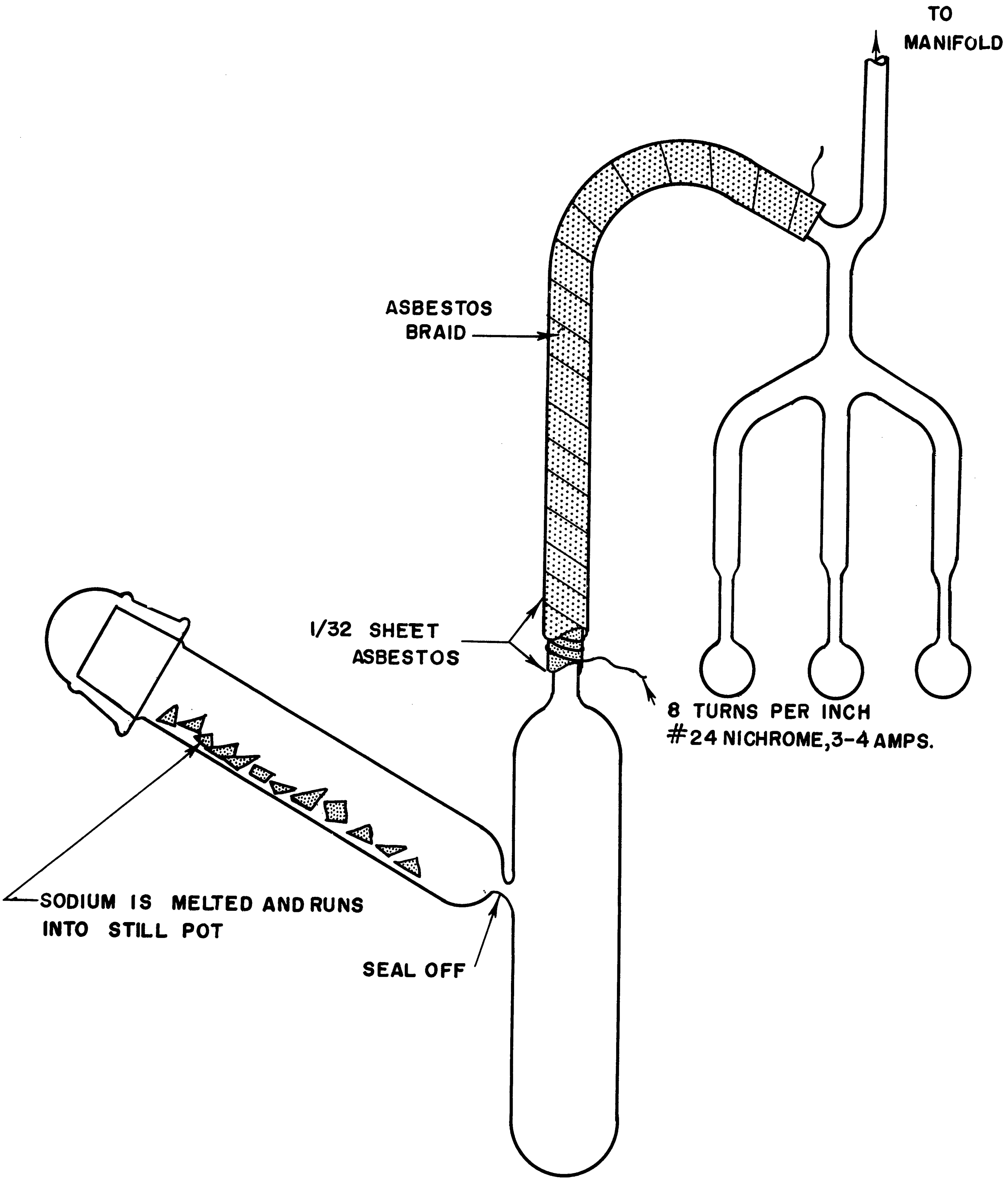

Fig. 4. Sodium Still

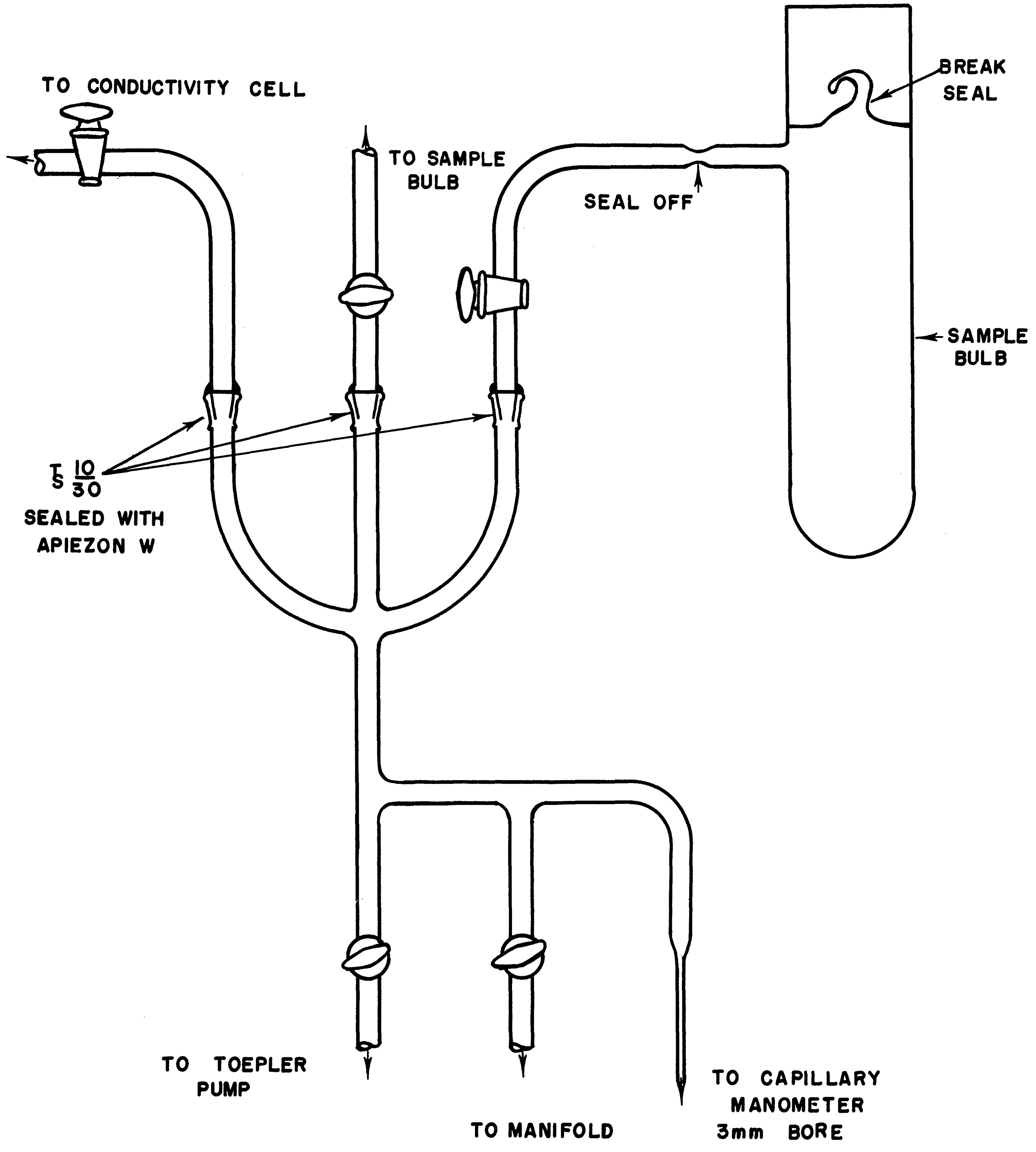

Fig. 5. System for Analyzing and Collecting Gas Samples

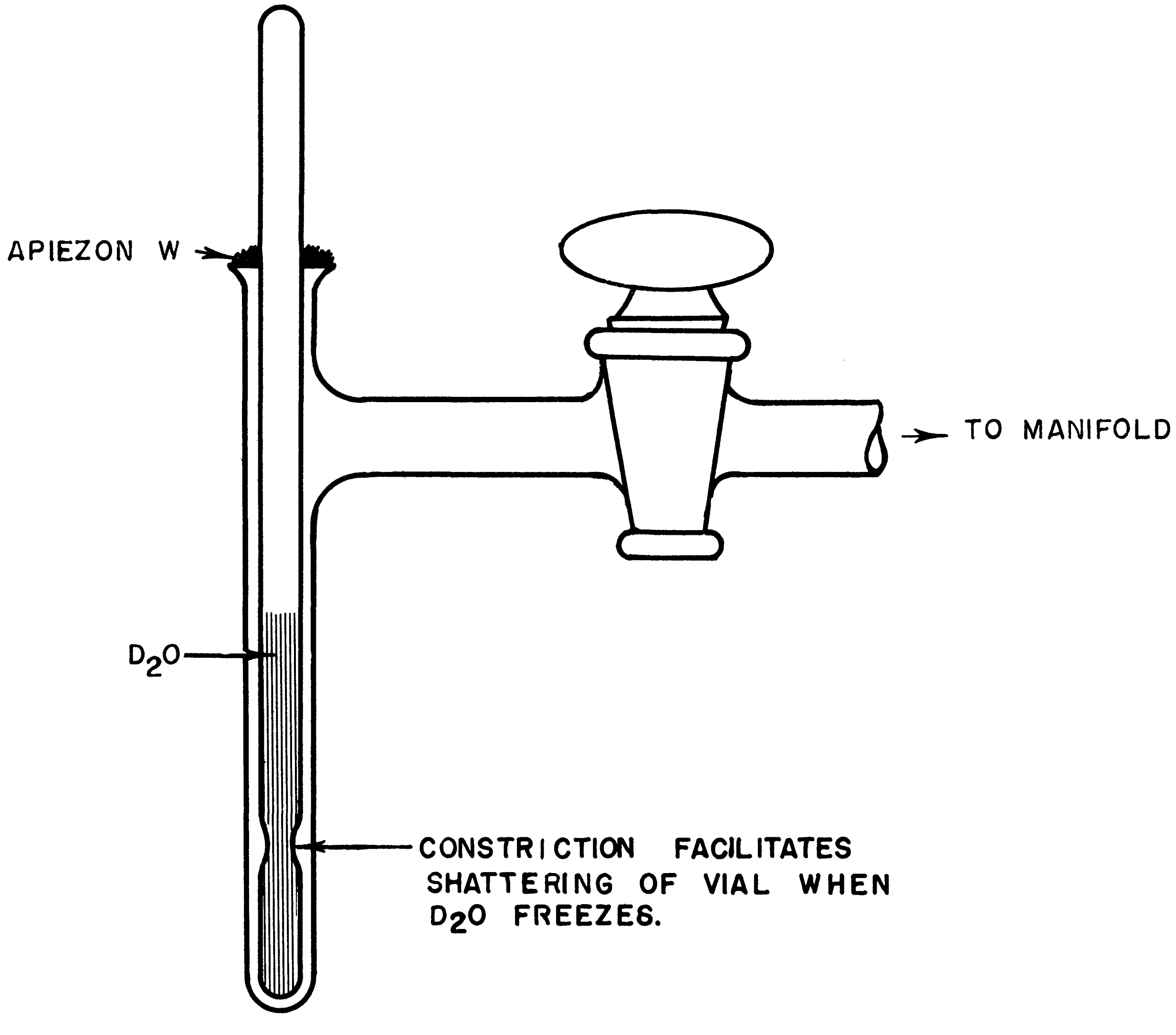

Fig. 6. Glass Sheath for Introducing Heavy Water into the Vacuum Line

D_2O expanded on freezing and cracked its containing vial, thereby gaining admittance to the sheath and vacuum line.

(4) Thermal-Conductivity Cell: An established method for analyzing hydrogen-deuterium mixtures makes use of the difference in their thermal conductivities[12,13]. The cell depicted in Fig. 7 was constructed from a 25-watt G.E. light bulb and was patterned after the cell of Peri and Daniels[13]. It was calibrated by determining the change in electrical resistance of the filament when surrounded by pure D_2 and by pure H_2 at constant pressure. A linear change in resistance with composition was then assumed. The cell was thermostated at 0°C and the resistance of the filament was determined by means of a Wheatstone bridge.

Because the assumption of linearity in change of resistance with changing composition may not be entirely valid, and because of other potential errors in analysis, all samples are taken in duplicate (see p. 12). One of each pair is being sent to the Consolidated Engineering Corporation for a check analysis using an isotope-ratio mass spectrometer.

c. Procedure. (1) Conditioning the Vacuum Line: Contamination of the vacuum line by traces of residual water constitutes a serious problem in a tracer study of this nature, particularly when highly deuterated materials are being handled[6]. To minimize errors due to this source the system was conditioned as described below.

The line was out-gassed for one day under high vacuum using conventional techniques; then a small amount of D_2O from the glass sheath (Fig. 6) was admitted to the system and allowed to equilibrate with the traces of residual water for 1 day. Following equilibration the system was again outgassed under high vacuum, for a minimum of 3 days. This procedure guaranteed that any traces of water remaining in the vacuum system would be rich in deuterium and thus would not seriously contaminate the highly deuterated ND_3.

(2) The Tracer Reaction: If the hydrogen atoms attached to boron in the diammoniate of diborane are not liberated by reaction with sodium, the formal analogy indicated below in which B_2H_6 (regardless of its mode of operation) is considered as a catalyst for the reaction between sodium and ammonia, is valid.

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[12] Farkas, A., and Melville, H. W., Experimental Methods in Gas Reactions, Macmillan and Co. Ltd., London, England, 1939, pp. 190, 281.

[13] Peri, J. B., and Daniels, F., J. Am. Chem. Soc. 72, 424 (1950).

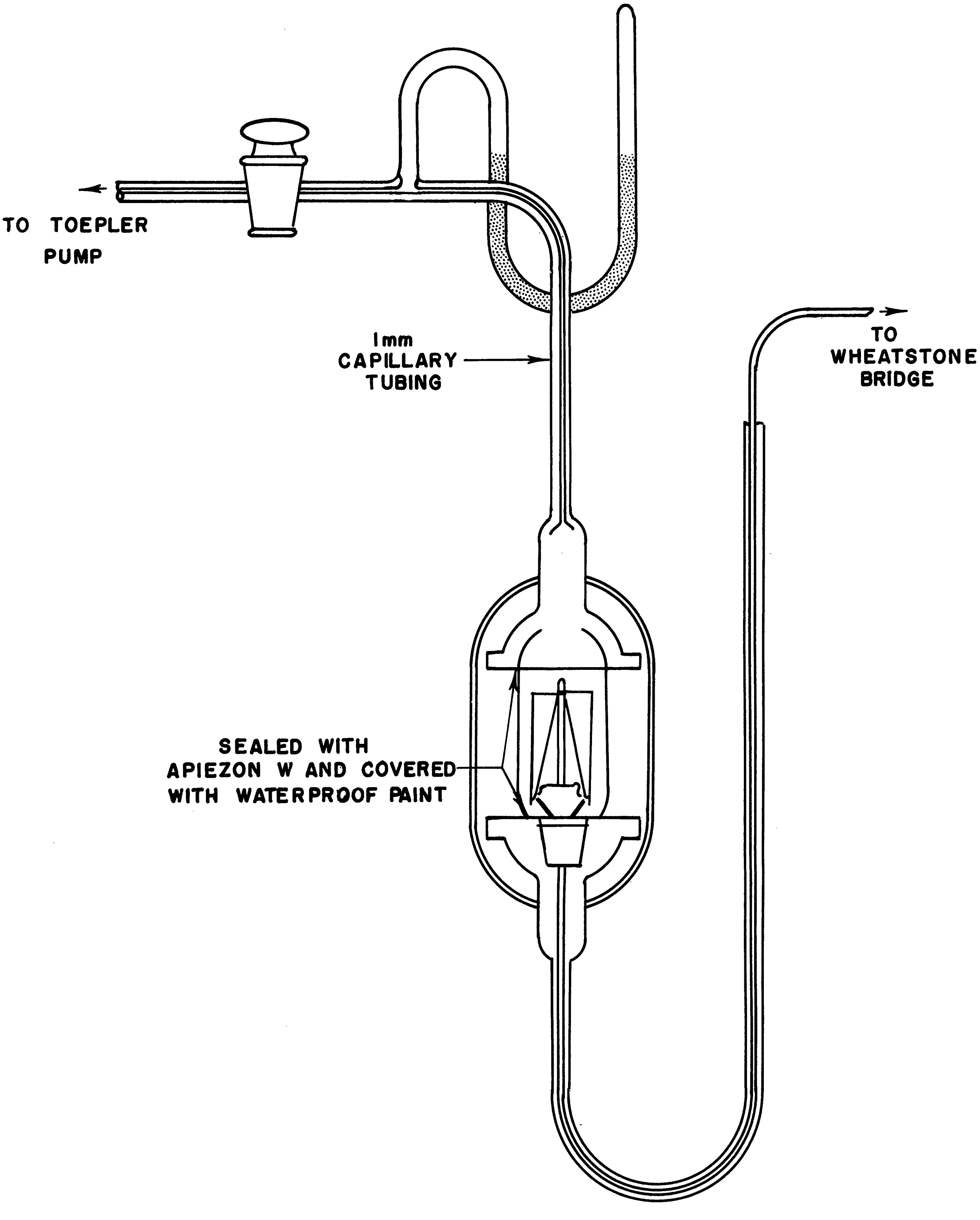


Fig. 7. Conductivity Cell

$$(1)\ 2Na + 2ND_3 \xrightarrow{Fe_2O_3-PtO_2} \begin{array}{c} 2NaND_2 + D_2 \\ + \\ Fe_2O_3 + PtO_2 \end{array}$$

$$(2)\ 2Na + 2ND_3 \xrightarrow{B_2H_6} \begin{array}{l} \text{solid residue} + D_2 \\ \text{including } B_2H_6 \end{array}$$

The "catalyst" remains attached to the solid residue in each case, although purification of the solid product is easier in case 1 than in case 2, because of the stability of the compound $NaND_2 \cdot B_2H_6$ formed in case 2. If reaction 2 shows more protium in the evolved gas than is found in reaction 1, three possibilities must be considered. These are: (1) boron-hydrogen bonds are being broken in the reaction. (2) preferential liberation of H_2 or HD from incompletely deuterated ND_3 is more rapid in case 2 than in case 1 because of differences in reaction mechanism, or (3) reaction 2 is being contaminated by residual hydrogen, while reaction 1 is not.

In order to eliminate possibility 3, the two reactions were conducted simultaneously using two separate bulb crushers attached to the same system. Both were thoroughly conditioned (sodium bulbs in place) prior to use (see p. 5). After conditioning, during which both units were open to the same systems, the gaseous reactants (ND_3 for reaction 1 and ND_3 +B_2H_6 for reaction 2) were distilled into the appropriate bulb-crusher reactors. At no time after conditioning of the system was either unit ever opened to the air or extraneous gases of any kind; thus foreign contamination, if any, should be the same in both cases.

The sodium bulb for the first reaction was broken as previously described (p. 5) and the reaction occurred at -78.5°C. The hydrogen gas evolved from the system was Toëplerized through a glass-helices packed U trap immersed in liquid air into the conductivity cell and then into one of the sample bulbs shown in Fig. 5. Since the volume of the cell and bulb was previously calibrated, the amount of hydrogen could be determined from PVT measurements. The resistance of the filament was determined, the stopcock on the sample bulb was closed, and the whole system was evacuated. The procedure was repeated for reaction 2, the gas sample being obtained in the second bulb attached to the ψ fitting (Fig. 5). After the stopcock on the second sample bulb was closed, both sample bulbs were sealed off. These are being sent to the Consolidated Engineering Corporation for a check analysis. Currently available data for the first of two runs are summarized in Table II.

C. DISCUSSION OF THE OBSERVATIONS ON THE STOICHIOMETRY OF THE REACTIONS BETWEEN ACIDS AND METALLIC SODIUM IN LIQUID AMMONIA

1. Data for NH_4CN, $B_2H_6 \cdot 2NH_3$, and $NH_4[O\overset{\overset{O}{\|}}{C}-NH_2]$

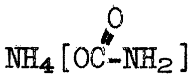
Results on stoichiometry are summarized in Table I. In general the results obtained for

NH_4CN

$B_2H_6 \cdot 2NH_3$

$B_2H_6 \cdot 2ND_3$,

and



$NH_4[O\overset{\overset{O}{\|}}{C}-NH_2]$

are in accord with previous studies[14,3,1,15] employing less extreme conditions. Extreme conditions such as a 10- to 15-fold excess of sodium and an unusually long reaction time were deliberately imposed in this investigation to measure the sensitivity of the stoichiometric measurements to experimental factors. A blank determination involving sodium and liquid ammonia without a catalyst was carried out to determine how much hydrogen is liberated as a result of noncatalyzed sodamide formation. Over a 2-week period at temperatures ranging from -78.5 to -51.6°C, the total amount of hydrogen never exceeded 5% of the amounts measured for the acid reactions. Accordingly, the maximum error from this source in the acid measurements probably does not exceed 5-8%. It will be noted in Table I that all runs except 4 and 8 show up to 14% excess hydrogen liberated on long standing.

One rather unexpected dependence of the result on experimental conditions is revealed by the data in Table I. In reaction 2 involving $B_2H_6 \cdot 2NH_3$, the excess ammonia was taken off the solid and then returned to the system as described earlier by Schlesinger and Burg[3]. About 0.97 equivalent of hydrogen per mole of B_2H_6 was obtained in less that 3 hours, in complete agreement with the results of Schlesinger and Burg for these conditions. On the other hand, in reaction 8 the excess ammonia was never distilled from the addition compound; instead sodium was added after the solution had been allowed to stand for a period of time equivalent to that required for removal and addition of ammonia in the previous case. This

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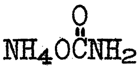
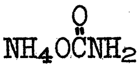
[14] Frank H. H., and Freitay, C., Z. angen. Chem. 39, 1430 (1926).

[15] Rengade, E., Bull. Soc. Chim., Paris, 31, No. 3, 565 (1904).

TABLE I

SUMMARY OF RESULTS ON STOICHIOMETRY OF HYDROGEN LIBERATION

Run	Reactant	Acid	Eq. Na / Mole Reactant	Time, hrs (cumulative)	Temp., °C	Eq. H / Mole Reactant (cumulative)
1	HCN	NH_4CN	10-15	7	-78.5	1.07
				11	-45.2	1.14
2	B_2H_6	$B_2H_6 \cdot 2NH_3$[a]	10-15	3	-78.5	0.97
				6	-63.5	1.03
				13	-43.7	1.14
3	CO_2	 $NH_4O\overset{O}{\overset{\|}{C}}NH_2$	10-15	3	-78.5	1.06
	[NH_3 removed, then replaced on solid before reaction with Na]			7	-63.5	1.06
				14	-45.2	1.12
4	CO_2	 $NH_4O\overset{O}{\overset{\|}{C}}NH_2$	1.01	24	-78.5	0.35
				48	-78.5	0.60
	[NH_3 not removed and replaced on solid before reaction with Na]			72	-78.5	0.78
				96	-78.5	0.88
				120	-78.5	0.89
				126	-63.5	0.92
				132	-63.5	0.95
				144	-63.5	1.00
5	H_3BO_3	$[aH_3BO_3+bNH_3]$[b]	10-15	5	-78.5	0
				8	-63.5	0.92
				11	-63.5	1.30
				23	-63.5	1.74
6	H_3BO_3	$[aH_3BO_3+bNH_3]$[c]	10-15	11	-51.6	1.81
				21	-51.6	1.85
7	H_3BO_3	$[aH_3BO_3+bNH_3]$	10-15	11	-78.5	1.01
				23	-51.6	1.64
				35	-51.6	1.69
				47	-45.2	1.76
				59	-45.2	1.82
8 Tracer Study	B_2H_6	$B_2H_6 \cdot 2ND_3$	10-15	4	-78.5	0.55
				756	-78.5	1.04

[a] This was treated in a different manner than prescribed in the procedure. After the formation of the acid, excess NH_3 was removed, leaving a white residue. NH_3 was distilled back onto the residue and the reaction with sodium was undertaken.

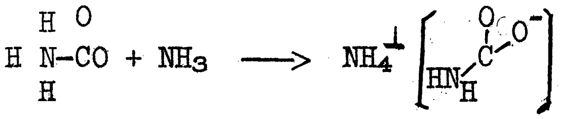
[b] The addition product was maintained at -63.5°C for 1/2 hour before the addition of sodium.

[c] The addition product was maintained at -51.2 for 2 hours before the addition of sodium.

duplicates the conditions employed in the earlier tracer study reported from this laboratory by Girardot[1]. Under these conditions only 0.55 equivalent of hydrogen per B_2H_6 was liberated in 4 hours. In the previous study of Girardot, 0.53 equivalent of hydrogen was liberated in about 5 hours. After standing 4-1/2 weeks* at -78.5°C, 1.04 equivalents of hydrogen per B_2H_6 were finally obtained from run 8, indicating that the results are ultimately the same as those of run 2, but a much longer time interval is required if the ammonia has never been distilled off to obtain the solid product before reaction begins.

It is interesting to note that the same type of phenomenon occurred for CO_2 in runs 3 and 4 and had been observed earlier by Rengade[15], although he failed to recognize the removal of the excess ammonia from the solid prior to reaction as the significant variable.

One interpretation of the results for CO_2 can be based on the assumption that complete proton transfer in accordance with the equation



$$\mathrm{H}\,\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{N}}}\text{-}\mathrm{C}\overset{\mathrm{O}}{\mathrm{O}} + NH_3 \longrightarrow NH_4^{+}\left[\underset{\mathrm{H}}{\mathrm{HN}}\text{-}\overset{\mathrm{O}}{\mathrm{C}}\text{-}\mathrm{O}^{-}\right]$$

is slow in solution at -78.5°C and is facilitated by removal of excess ammonia and formation of solid crystals. A similar postulate for B_2H_6 would require the existence of B_2H_6 in solution without reaction in accordance with the equilibrium

$$B_2H_{6\,(soln)} + 2NH_3 \longrightarrow [NH_4][BH_3NH_2BH_3] \quad \text{or}$$

$$[H_3NBH_2NH_3][BH_4]\ .$$

Such an equilibrium would be consistent with the dimenic molecular weight which has been accepted for low temperatures[16] and would be analogous to the equilibrium assumed for NH_3 in water solution (i.e., $NH_3 + H_2O \longrightarrow NH_4^+ + OH$).

Two forms of the diammoniate are included in the above equation. The first is classical formulation of Schlesinger and Burg, whereas the

---

*An interval somewhere between 1 and 4-1/2 weeks may be adequate; 4-1/2 weeks was simply a matter of experimental convenience in this case.

[16] Rathjens, G. W. Jr. and Pitzer, K. S., J. Am. Chem. Soc. 71, 2783-85 (1949).

second is the borohydride form which is favored in this laboratory. A large amount of experimental evidence in favor of the latter representation is given by Schultz[17].

2. The Nature of H_3BO_3 in Liquid Ammonia

As seen in Runs 5, 6, and 7, the reaction between solid boric acid suspended in liquid ammonia and metallic sodium dissolved in this solvent produced from 1.74 to 1.85 equivalents of hydrogen per mole of boric acid. The results can be interpreted if the following reactions are assumed.

$$4\ H_3BO_3 \xrightarrow[NH_3]{liq.} H_2B_4O_7 + 5\ NH_4OH$$

$$5\ Na + 5\ NH_4OH \xrightarrow[NH_3]{liq.} 5\ NaOH + \frac{5}{2}\ H_2$$

$$H_2B_4O_7 + 2\ Na \longrightarrow Na_2B_4O_7 + H_2$$

According to the above equations, 7 equivalents of hydrogen would be liberated for each 4 moles of boric acid or 1.75 equivalents of H/mole B_2H_6. The agreement with experiment is excellent and deviations are well within the limits of error observed with NH_4CN, $NH_4[CO_2NH_2]$, and $B_2H_6 \cdot 2NH_3$.

To check the validity of the postulates in the first of the above equations, ammonia was condensed on a known amount of solid boric acid at -45.2°C (C_6H_5Cl slush); after 1-1/2 hours, excess ammonia was removed by distillation at -45.2°C and then the solid residue was allowed to warm up under dry air. The sample was dissolved in water; ammonia was determined by Kjeldahl; and boron was determined by titration with NaOH in the presence of manitol (see p. 38). The analytical values are:

	% N	% B
Observed	6.40	19.6
Calculated for $NH_4HB_4O_7 \cdot 2\text{-}1/2\ H_2O$	6.39	19.73

The isolation of $NH_4HB_4O_7$ offers strong support for the above interpretation of the stoichiometric data.

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[17] Schultz, D. R., Ph.D. Thesis, Univ. of Mich., 1954.

D. DISCUSSION OF THE RESULTS OBTAINED FOR THE TRACER STUDY OF THE REACTION BETWEEN METALLIC SODIUM AND THE DIAMMONIATE OF DIBORANE

In Table II results of the earlier tracer study of Girardot[18] are summarized along with the more recent results obtained by Shore in the completely independent investigation described in the experimental section. Although the absolute values for the deuterium analysis in the last sudy may be refined somewhat by subsequent calibrations, the relative values are considered reliable. It is significant that the results of the two studies agree. It then becomes apparent that the protium enrichment in the reaction

$$B_2H_6\cdot 2ND_3^* + Na \xrightarrow[ND_3]{\text{liq.}} \text{solid residue} + H_2,\ HD,\ D_2$$

is real and is very significantly greater than the protium enrichment in the control reaction

$$ND_3 + Na \xrightarrow[\text{liq } ND_3]{Fe_2O_3\ +\ PtO_2} NaND_2 + H_2,\ HD,\ D_2$$

Because of the design of the experiment and the care taken in all manipulations, it is extremely unlikely that these differences could arise from accidental contamination of the evolved gas by protium. It is, then, fairly certain that the results represent a real phenomenon.

Two explanations for the results can be offered: (1) protium enrichment could result from the breaking of boron-hydrogen bonds in $B_2H_6\cdot 2ND_3$ as a result of accumulated favorable isotope effects, or (2) protium could be liberated preferentially from the incompletely deuterated ND_3. Since different mechanisms are undoubtedly involved, the H-D separation factor for the reaction:

$$ND_3^* + Na \xrightarrow[Fe_2O_3\ +\ PtO_2]{\text{liq. } ND_3} NaND_2 + \underbrace{H_2,\ HD,\ D_2}_{}$$

would differ from that for the reaction with the diammoniate, which can be formally represented as

$$ND_3 + Na \xrightarrow[B_2H_6]{\text{liq. } ND_3} NaND_2 + H_2,\ HD,\ D_2 \quad .$$

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*In both cases the ND_3 was not completely deuterated, but was about 95% D.

[18] Girardot, P. R., PhD. Dissertation, Univ. of Mich., 1952.

TABLE II

SUMMARY OF THE DATA FOR THE REACTION BETWEEN ISOTOPICALLY SUBSTITUTED $B_2H_6 \cdot 2NH_3$ AND SODIUM METAL

A. Study of Girardot previously reported from this laboratory[1]

Run	Isotopic Composition of Diammoniate	Time and Temp. of Formation	Equiv. Na Used	Equiv. B_2H_6 Used	Time and Temp. of Na Reaction	Ml. H_2 Evolved S.T.P.	Ratio H atoms/B_2H_6 mol.	Isotopic Analysis	Total % D
1	$B_2H_6 \cdot 2NH_3$	14 hrs -150 to -100°C	2.3	2.3	105 mins. at -81°C	14.98	0.573	.04% HD 99.64% H_2	.02
2	$B_2H_6 \cdot 2NH_3$	5 hrs -133 to -109°C	.52	.51	160 mins. -80 to -50°C	3.66	0.64	.02% HD 99.98% H_2	.01
3	$B_2H_6 \cdot 2ND_3$*	4.5 hrs -135 to -110°C	.99	.97	100 mins. -79°C	5.42	0.50	53.72% HD 3.19% H_2 43.09% D_2	70.0
4	$B_2H_6 \cdot 2ND_3$*	4.75 hrs -129 to -95°C	1.57	1.7 (excess)	40 mins. -79°C	9.27	0.527	41.31% HD 3.04% H_2 55.65% D_2	76.3
5	$B_2D_6 \cdot 2NH_3$	6.5 hrs -135 to -101°C	1.55	1.55	50 mins. -81°C	10.24	0.59	0.50% HD 99.50% H_2	0.25
6	$NH_3 + Fe_2O_3$ catalyst	used K metal		-	-	-	-	90.40% D_2 7.93% HD 1.70% H_2	94.4
	Control	To determine composition of ND_3							

*Not completely deuterated, see run 6

TABLE II (cont.)

B. Study of Shore to check earlier results of Girardot. (This report.)

Run	Isotopic Composition of Diammoniate	Time and Temp. of Formation	Equiv. Na Used x 10^3	Equiv. B_2H_6 x 10^3	Time and Temp. of Na Reaction	Ml. H_2 Evolved S.T.P	Ratio $\frac{\text{H atoms}}{B_2H_5 \text{ mol.}}$	Isotopic Analysis	Total %D by Thermal Conductivity
1a	$B_2H_6 \cdot 2ND_3^*$	-130 to -80°C	excess	1.96	4 hours -78.5°C 750 hours -78.5°C 754 hrs. total	12.1 10.8 22.9 total	0.55 0.49 1.04 total	not yet available from Consolidated Engineering	70% **
2a	$ND_3+Fe_2O_3+PtO_2$ +Na		excess		-45°C				90% **

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*ND_3 was approximately 95% deuterated

**Absolute value subject to revision by recalibration of cell, but relative values are reliable.

A separation factor of 1 or slightly above for the heterogeneous catalytic reaction and a value of about 5 for the homogeneous reaction involving B_2H_6 would account for the observed facts. It is of interest that the high separation factor for the diborane reaction would imply that the diammoniate of diborane is a weak acid in liquid ammonia[19], a conclusion which is also in agreement with the lower rate of hydrogen evolution obtained for those samples from which ND_3 had never been quantitatively removed (see p. 19). A separation factor of 5 for the homogeneous reaction is certainly not unreasonable.

To obtain an unequivocal choice between the above two possibilities, two experiments are in progress. In the first the compound $B_2D_6 \cdot 2ND_3$ is being allowed to react with sodium. If the observed protium contamination arises from the breaking of B-H bonds, little protium enrichment should be observed, but if there is preferential liberation of protium from incompletely deuterated ND_3, the enrichment should be comparable to that observed earlier and recorded in Table II. The second experimental approach to the problem involves preparation of samples containing known ratios ND_3 and NH_3. From the ratios and the postulated separation factor the composition of the evolved gas can be calculated if protium enrichment arises from preferential liberation of the lighter isotope.

III. METATHESIS REACTIONS IN LIQUID AMMONIA

A. BACKGROUND

The metathesis reaction between sodium borohydride and ammonium fluoride in liquid ammonia was described in the preceding report[1]. Metathesis reactions of this type can give interesting information concerning the structure of those boron compounds which are soluble in liquid ammonia and, in addition, offer a method for producing many compounds which might have interesting and valuable properties.

The ammonium borohydride previously described represents borohydric acid in liquid ammonia. The molecule is unstable and loses hydrogen at about -35°C because of the presence of protonic and hydridic hydrogens in the same molecule.

It has been observed that the stability of the alkali-metal borohydrides inqreases as the size of the cation increases. Thus it seemed to be relevent to determine the stability and characteristics of borohydrides

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[19] Halpern, O., J. Chem. Phys. 3, 456 (1935)

with large cations. The hexammine metal (III) ions suggested the possibility of a haxammine metal (III) borohydride which would have a very large cation and also protonic hydrogens in the cation.

The remote possibility of putting the borohydride ion in the coordination sphere seemed worthy of investigation, and the possibility of obtaining interesting metal-nitrogen-boron polymers offered some additional justification for the study.

B. STATEMENT OF THE PROBLEM

The work described involves the preparation of the hexammine chromium (III) borohydride and the hexammine cobalt (III) borohydride and a study of the thermal decomposition of these compounds. The preparation of the corresponding hexammine fluorides is also described, since these compounds are needed intermediates.

C. EXPERIMENTAL

1. Materials

a. Sodium Borohydride. Commercial sodium borohydride from Metal Hydrides, Inc. was recrystalized once from liquid ammonia using a vacuum-line filtration assembly. The resulting $NaBH_4$ was approximately 100% pure as indicated by the hydrogen liberated on acid hydrolysis.

b. Liquid Ammonia. Commercial tank ammonia was dried over sodium metal before distillation into the vacuum line.

c. Hexammine Cobalt (III) Fluoride. The complex fluoride was prepared from hexammine cobalt (III) chloride. The preparation of this compound will be described in detail.(see p. 35).

d. Haxammine Chromium (III) Fluoride. The chromium complex was prepared from haxammine chromium (III) chloride and will be described in detail (see p.37).

2. Apparatus and Procedure

The apparatus used for preparing the hexammine metal (III) borohydrides is shown in Fig. 8.

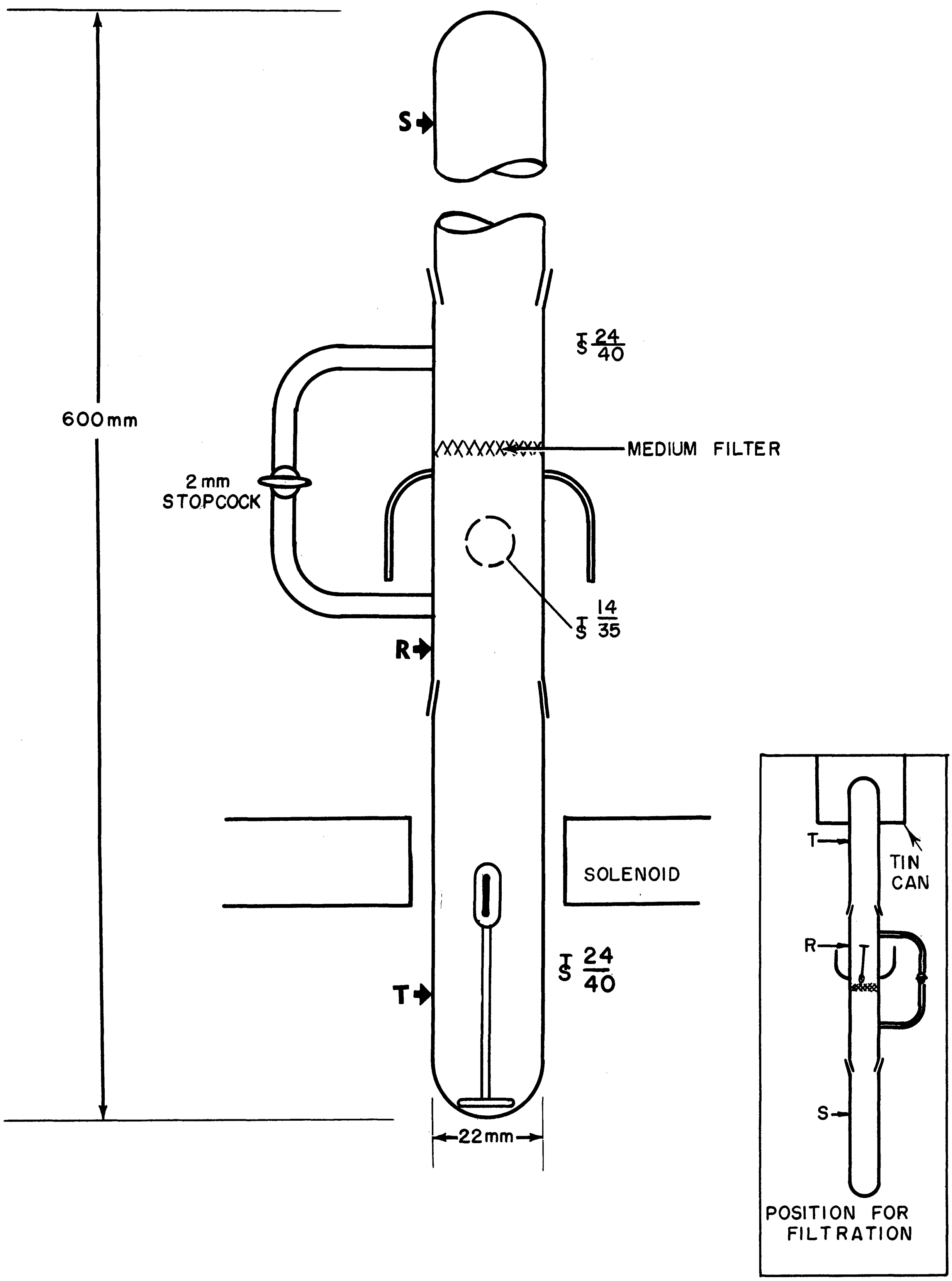

Fig. 8. Apparatus for the Preparation of Hexammine Metal(III)Borohydrides

A simple metathesis reaction was assumed; therefore, stoichiometry would require 3 moles of sodium borohydride per mole of complex fluoride. Both the complex fluoride and the sodium borohydride were weighed out in a controlled-atmosphere gloved box and placed in tube T. The remaining portion of the apparatus had previously been attached to the vacuum line at the ₮ 14/35 joint. Final assembly of the tube T to the rest of the apparatus was made as rapidly as possible to avoid contact with the atmosphere. After evacuation, ammonia was condensed into tube T, and the reaction was carried out at -65 to-45°C. The mixture was agitated by an electromagnetic plunger-type stirrer which was actuated 60 times per minute. The reaction was allowed to proceed from 3 to 5 hours, and the mixture was then frozen with liquid nitrogen. The apparatus was inverted by turning through 180° about the ₮ 14/35 joint. At this time, the solenoid was removed, and a metal can, with a hole cut in the bottom, was placed on the inverted tube T. The hole in the can was just large enough to permit a snug fit around the tube, and was placed about 1-1/2 inches from the end of the tube. Dry ice and i-propyl alcohol were placed in this can and in the cup on R. The remainder of T was wrapped with glass wool.

The solid reaction mixture gradually melted, ran down the sides, and was held on the filter frit in R. As the pressure increased, a dry ice - i - propyl alcohol bath was placed around section S and the solution filtered through the frit. Effective washing of the precipitate and the sides of the reactor could be accomplished by placing an empty Dewar flask around S, opening the stopcock in R, and adding more dry ice to the can on T. Then the stopcock on the bypass was closed, and when S was cooled, the solution would filter again. Usually, five washes were required to extract all the product. The solvent ammonia was then carefully evaporated off, leaving the complex borohydride in S.

3. Hexammine Cobalt (III) Borohydride and Hexammine Chromium (III) Borohydride

Preparation of these complex borohydrides involved the reaction between hexammine cobalt (III) fluoride or hexammine chromium (III) fluoride and sodium borohydride in liquid ammonia. The metathesis reaction is

$$[Co(NH_3)_6]\,F_3 + 3NaBH_4 \xrightarrow[NH_3]{liq.} [Co(NH_3)_6]\,(BH_4)_3 + 3NaF\downarrow$$

or

$$[Cr(NH_3)_6]\,F_3 + 3NaBH_4 \xrightarrow[NH_3]{liq.} [Cr(NH_3)_6]\,(BH_4)_3 + 3NaF\downarrow.$$

The complex fluorides are yellow salts which are insoluble in liquid ammonia. This is indicated by the fact that no color is imparted to a mixture of liquid ammonia and $M(NH_3)_6F_3$ (where M is cobalt or chromium). However, a mixture of $NaBH_4$, $M(NH_3)_6F_3$, and liquid ammonia yields an intensely yellow-colored solution at -63.5°C, in about 15 minutes. A white gelatinous precipitate appears which was qualitatively identified by fluorine analysis as sodium fluoride. Ordinarily, an excess of $M(NH_3)_6F_3$ was used in the reaction. Hexammine metal (III) borohydride is apparently very soluble in liquid ammonia; after filtration, washing, and evaporation of the solvent ammonia, a yellow salt was obtained. Typical analyses for the salts are given in Table III.

TABLE III
COMPOSITION OF HEXAMMINE METAL (III) BOROHYDRIDES

$Cr(NH_3)_6\ (BH_4)_3$	Obs.	Calc. for $Cr(NH_3)_6\ (BH_4)_3\cdot 0.5\ NH_3$
Cr	25.3%	25.1%
NH_3	53.3%	53.3%
B	15.6%	15.7%
Active H:*	5.7%	5.8%
Cr/12H	1.03	$NH_3/Cr = 6.45$
NH_3/12H	6.67	$B/Cr = 2.96$
B/12H	3.07	$H/Cr = 11.7$
$Cr(NH_3)_{6.5}B_{2.96}H_{11.7}$		
	Obs.	Calc. for $Co(NH_3)_6\ (BH_4)_3\cdot 1.0\ NH_3$
Co	26.6%	26.4%
NH_3	53.8%	53.5%
B	14.2%	14.6%
Active H:*	5.0%	5.4%
Co/12H	1.09	$NH_3/Co = 7.00$
NH_3/12H	7.63	$B/Co = 2.90$
B/12H	3.16	$H/Co = 11.0$
$Co(NH_3)_{7.00}B_{2.90}H_{11.0}$		

*Active hydrogen, determined by hydrolysis, tends to give low results in the presence of NH_3.

It was not determined whether or not the excess ammonia was bound as a definite solvate. The last traces of ammonia were not removed because decomposition occurs if this is done.

4. Decomposition and Stability of Hexammine Metal (III) Borohydride

The fact that hexammine chromium (III) complexes tend to form red polymeric oils in neutral or slightly alkaline solution is well known to all who have worked with the chromium ammines. This is in marked contrast to the stability of hexammine cobalt (III) complexes, which usually remain crystalline without polymer formation. Even the strongly alkaline hexammine cobalt (III) hydroxide may be formed and titrated in water solution without serious decomposition, yet the corresponding hexammine chromium (III) hydroxide gives off ammonia and decomposes rapidly just as soon as it is formed[20]. It is, then, a matter of some interest to note the complete reversal of the stability order in the case of the hexammine borohydrides.

Dry hexammine cobalt (III) borohydride loses ammonia and undergoes irreversible decomposition when the ammonia pressure is reduced below 50 mm at 25°C. In contrast, the dry hexammine chromium (III) borohydride is remarkably stable at 25°C even under high vacuum: the decomposition under these conditions was less than 2% as measured by H_2 evolution. When the chromium complex is heated in vacuum to 60°C, its decomposition becomes comparable to that of the cobalt complex at 25°C. This reversal is attributed solely to a decrease in the stability of the cobalt borohydride and not to an increase in the stability of the chromium compound.

Data now available indicate that the instability of the cobalt complex is to be associated with the strong reducing properties of the borohydride group and with the fact that $Co(NH_3)_6^{+3}$ is reduced more easily than its chromium counterpart. This fact is indicated by the value for the standard electrode potential of the oxidation reaction:

$$Co(NH_3)_6^{+2} \longrightarrow Co(NH_3)_6^{+3} + e \qquad E_0 = -0.1$$

The value for the corresponding chromium couple is not available, but qualitative considerations indicate that it must be more positive than +0.5 since ammoniacal solutions of $Cr(NH_3)_6^{+2}$ liberate hydrogen rapidly from water in the presence of finely divided platinum[21].

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[20] Parry, R. W., and McCall, M. G., Unpublished results, 1952.

[21] Parry, R. W., and Berman, D. A., To be published.

It is also of some interest to note that the reducing properties of the borohydride group cause a different type of thermal decomposition than is observed with the hexammine complexes containing a nonreducing anion. The thermal decomposition of hexammine cobalt (III) chloride may be represented by the equations

$$[Co(NH_3)_6]\,Cl_3 \xrightarrow{\Delta} [Co(NH_3)_5Cl]\,Cl_2 + NH_3\uparrow$$

$$3[Co(NH_3)_5Cl]\,Cl_2 \xrightarrow[\Delta]{} 3CoCl_2 + 3NH_4Cl + 14NH_3\uparrow + 12N_2\uparrow\,,$$

in which ammonia is oxidized to give elemental nitrogen. The hexammine cobalt (III) fluoroborate, which is formally analogous to the complex borohydride, decomposes in accordance with the equation[22].

$$6[Co(NH_3)_6](BF_4)_3 \xrightarrow{\Delta} 6CoF_2 + 12BF_3NH_3 + 6NH_4BF_4 + N_2 + 16NH_3 \;.$$

The thermal decomposition of the dry hexammine metal (III) borohydrides differs from that described in that the borohydride group is oxidized rather than ammonia. Otherwise certain elements of similarity may be noticed. Although the decomposition is complex, the equation for the main process is:

$$[M(NH_3)_6]\,(BH_4)_3 \longrightarrow \underbrace{M_aB_{a+b}N_bH_x}_{\substack{\text{solid mixture}\\ \text{perhaps}\\ aMB\,+\,b(NBH_{\frac{x}{b}})}} + [BH_3NH_3]_2 + NH_3 + H_2 \;.$$

The H_2 and ammonia were identified positively as gaseous decomposition products. The compound $[BH_3NH_3]_2$ was extracted from the solid residue with liquid ammonia and its nature indicated by analysis. The overall composition of the solid black residue suggested a mixture of metal boride and polymeric BNH_x where $x = 0$ to 4 (see note on p. 31).

Unequivocal identification of separate phases or compounds in this solid was never achieved. Experimental evidence for these conclusions is given in the note at the end of this section.

The hexammine metal (III) borohydrides of both chromium and cobalt crystallize from liquid ammonia solution as long yellow needles which can be dissolved in water to give yellow solutions. The solution of the cobalt complex decomposes rapidly to give a black ferromagnetic precipitate which yields cobalt (II) ion when acidified. The same black solid is also observed when sodium borohydride is added to a hexammine cobalt (III) chloride solution.

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[22] Balz, Von Günther, and Zinser, Werner, *Z anorg. allgem. Chem. 221*, 225-48 (1935).

The chromium complex borohydride reacts more slowly with water and no precipitate appears. In the absence of air the blue chromous ion is produced when the solution is acidified. It is consistent with the above observation to note that hexammine chromium (III) chloride and sodium borohydride gave no apparent reaction in water solution except for slow liberation of hydrogen. Data for the overall hydrolysis reactions of both complex borohydrides are consistent with the following equation:

$$[M(NH_3)_6]\,(BH_4)_3 + 11\,H_2O \longrightarrow M^{+2} + 3\,BO_2^- + \overbrace{5\,OH^- + 6\,NH_4^+}^{NH_3\ +\ H_2O} + 11\tfrac{1}{2}\,H_2$$

Note: The schemes for the decomposition of the hexammine metal (III) borohydrides are indicated in Tables IV and V. This decomposition was carried out in the apparatus shown in Fig. 8. Apiezon T was used to grease the stopcocks and joints and was found to be very satisfactory at elevated temperatures. The sample was placed in section T. Decomposition was accomplished by increasing the temperature or by pumping off the gases with a Toepler pump, i.e., reducing the pressure over the salt. Then liquid ammonia was condensed into tube T and the ammonia-soluble portion was filtered and washed through the frit in R by rotating the system. After distilling off the solvent ammonia, the two portions were hydrolyzed and analyzed.

In the case of the chromium complex, the ammonia-insoluble portion contained 0.88 mM Cr, 2.42 mM N, and 3.29 mM B. If it is assumed that CrB is formed, then 3.29-0.88 = 2.41 mM B left, which would indicate that the decomposition yields CrB and BNH_x, where x is less than 6.

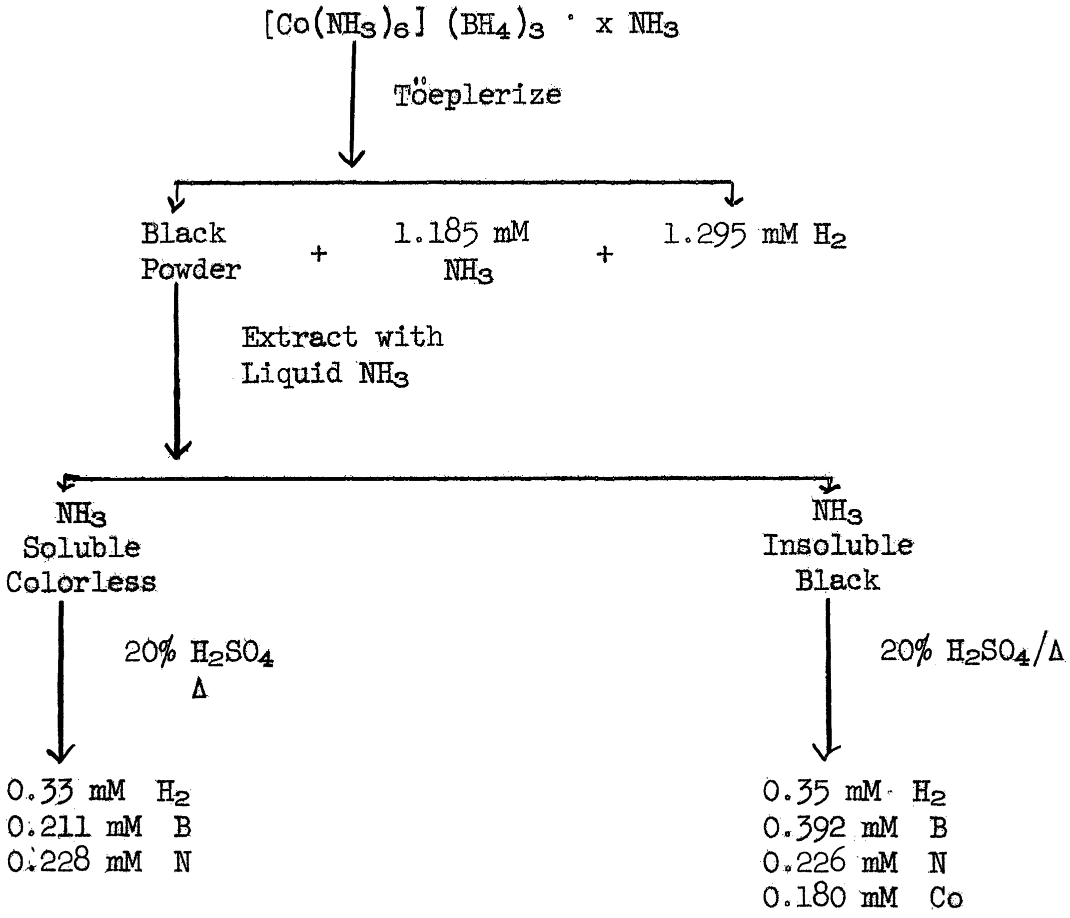
In the chromium complex decomposition, the ammonia-soluble portion contained some undecomposed $[Cr(NH_3)_6]\,(BH_4)_3$. If all of this chromium were present as the complex, 0.049 mM/Cr, 0.147 mM B, and 0.294 mM N would be required. This would leave 0.356 mM B and 0.349 mM N, or approximately 0.35 mM BNH_x. Since this portion is the ammonia-soluble portion, BNH_2 and BNH_4 would be ruled out. If the compound were BNH_6, the total hydrogen content would be about 17.3% and Cr, B, N, and H would total 99.4%.

In the case of the decomposition of the cobalt complex, the formation of 0.18 mM CoB would result in 0.392-0.18 = 0.212 mM B as compared with 0.226 mM N. Thus, the decomposition of the cobalt complex also indicates the formation of CoB and BN.

The ammonia soluble portion of the decomposed cobalt complex yields the same data: 0.211 mM B in combination with 0.228 mM N

TABLE IV

DECOMPOSITION OF $[Co(NH_3)_6](BH_4)_3$

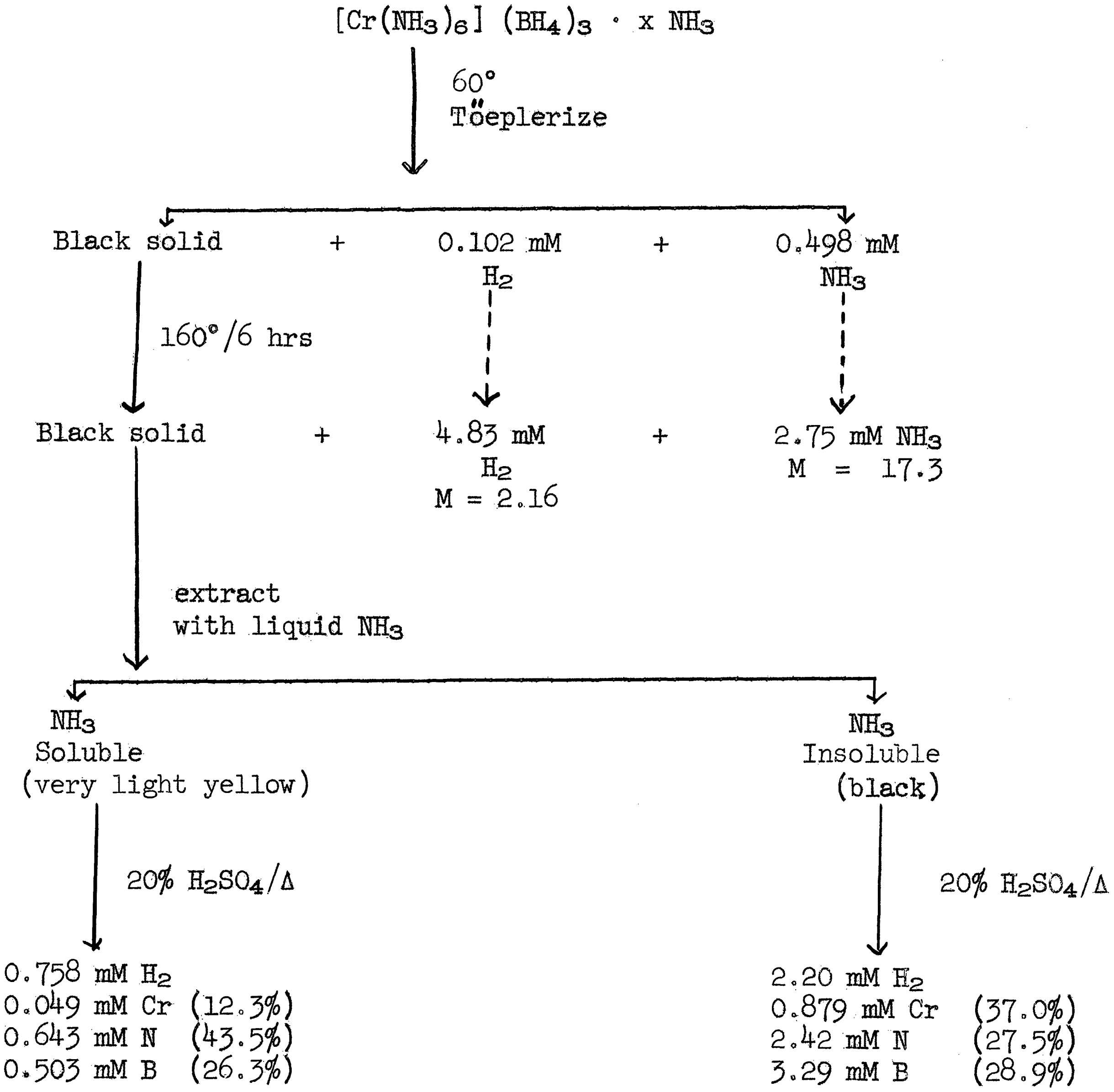


indicates a compound of the type BNH_x, and in all probability x = 6. Table IV also indicates that the hydrolysis of BNH_6 or the diammoniate of diborane fails to give the theoretical amount of hydrogen on hydrolysis.

In all cases there was more BNH_x than BNH_6, and more H_2 evolved than NH_3.

TABLE V

DECOMPOSITION OF $[Cr(NH_3)_6](BH_4)_3$



5. The Reaction between $NaNH_2$ and $Co(NH_3)_6(HF_2)_3$ in Liquid Ammonia to Form Cobalt Nitride

The compound $Co(NH_3)_6(HF_2)_3$ is relatively insoluble in water and can be precipitated easily from water solution containing excess HF. On the other hand, the complex $[Co(NH_3)_6]F_3$ is very soluble in water and is difficult to dry and crystallize. The following process seemed to offer a convenient way to prepare water-free $Co(NH_3)_6F_3$ in liquid ammonia:

$$[Co(NH_3)_6](HF_2)_3 + 3NaNH_2 \xrightarrow{\text{liq. } NH_3} [Co(NH_3)_6]\,F_3\downarrow + NaF\downarrow + 3NH_3 \quad .$$

Accordingly, $NaNH_2$ was prepared in reactor T of Fig. 8 from metallic sodium and liquid ammonia using Fe_2O_3 as a catalyst. Then $[Co(NH_3)_6](HF_2)_3$ was added, and ammonia was condensed on this mixture. The sodamide is relatively insoluble in liquid ammonia, so an excess of this reagent was used. The mixture was allowed to react at -65°C for 2 hours. Then the ammonia was removed at -65°C. The entire mass had the typical yellow color which is characteristic of the $[Co(NH_3)_6]^{+3}$; but as the reaction tube warmed up to room temperature, a gas was evolved and the mixture became brown. The gas was identified as ammonia by vapor-pressure and molecular-weight tests. A crude analysis of the solid mixture indicated cobalt and nitrogen.

By analogy, the following sequence of reactions might be expected:

(a) $2H_2O \rightleftarrows H_3O^+ + OH^-$

(b) $[Co(NH_3)_6]\,F_3 + 3OH^- \rightarrow [Co(NH_3)_6](OH)_3 + 3F^-$

(c) $[Co(NH_3)_6]\,(OH)_3 \rightarrow Co(OH)_3 + 6NH_3$

(d) $2Co(OH)_3 \rightarrow Co_2O_3 + 3H_2O$.

Thus in ammonia the reactions would be:

(a) $2NH_3 \rightleftarrows NH_4^+ + NH_2^-$

(b) $[Co(NH_3)_6]\,F_3 + 3NH_2^- \rightarrow [Co(NH_3)_6](NH_2)_3 + 3F^-$

(c) $[Co(NH_3)_6]\,(NH_2)_3 \rightarrow Co(NH_2)_3 + 6NH_3$

(d) $Co(NH_2)_3 \rightarrow CoN + 2NH_3$

The preparation of CoN by a modification of this technique has been reported by Schmitz-DuMont, Broja, and Piepenbrink[23] (found after the above experiment).

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[23] Schmitz-DuMont, Broja, H., and Piepenbrink, H. F., Z. anorg. Chem. 253 118-35 (1947).

6. Preparation of Hexammine Cobalt (III) Fluoride

The preparation of the hexammine cobalt (III) fluoride has been reported by Böhm[24] and by Birk and Biltz[25]. However, in both cases the instructions were rather vague. Considerable difficulty was experienced in preparing the neutral salt due to its tremendous solubility and hygroscopic nature. The bifluoride, however, is easily obtained from acid solution. The method which finally gave a pure neutral salt is indicated by the following reactions:

$$[Co(NH_3)_6]\,Cl_3 + \frac{3}{2}\underset{\text{(solid)}}{Ag_2O} + \frac{3}{2}H_2O \xrightarrow{0^\circ} 3AgCl\downarrow + [Co(NH_3)_6](OH)_3$$

$$[Co(NH_3)_6](OH)_3 + 3HF \xrightarrow{0^\circ} 3H_2O + [Co(NH_3)_6]\,F_3$$

a. Reagents. $Co(NH_3)_6Cl_3$: Prepared in this laboratory* by the method of Bjerrum and McReynolds[26].

NH_3: Found, 37.94%; calc., 38.10%.

$AgNO_3$: Merck and Co. C. P. reagent

NaOH: 50% solution, carbonate free

HF: B and A (A. C. S. reagent-grade) 48%.

b. Method. Silver nitrate (0.38 mole) was dissolved in distilled water and treated with 50% NaOH until no test for Ag^+ could be obtained. the precipitated Ag_2O was filtered on a Büchner funnel and washed thoroughly with distilled water. Hexammine cobalt (III) chloride (0.1 mole) was placed in a mortar which had been cooled in ice water and the wet Ag_2O filter cake was added. The mixture was ground for about 1 hour. During this time the mortar was placed in an ice-water bath. The mixture was then filtered and

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*We wish to express our appreciation to Mr. M. G. McCall for preparing the hexammine cobalt (III) chloride.

[24] Böhm, E., Z. anorg. Chem. 43, 338-40 (1905).

[25] Birk, E., and Biltz, W., Z. anorg. Chem. 153, 115-125 (1926).

[26] Fernelius, W. Conrad, Inorganic Synthesis, Vol. II, McGraw-Hill Book Company, Inc., New York, N. Y., 1946, p. 216.

washed on a Büchner. The filtrate was transfered to a polyethylene beaker, and reagent-grade HF was added until the filtrate had a pH = 7. A Beckman Model H-2 pH meter was used to follow the pH.

The neutral solution was then placed in a vacuum dessicator over concentrated sulfuric acid and periodically evacuated for 1 week. After 4 days crystals appeared, and at the end of a week just enough moisture was left to permit easy transfer of the salt. The crystals were filtered on a sintered glass frit using a drying train to exclude moisture. The crystals were washed with a very small amount of cold distilled water, and then with absolute alcohol. Finally, they were dried overnight at 105°C. The following analysis was obtained:

$Co(NH_3)_6F_3$

	Found, %	Calculated, %
Co:	26.9	27.02
NH_3:	46.6	46.84
F:	26.4	26.13
HF:	0.13	---

The presence of the $Co(NH_3)_6^{+3}$ was confirmed by comparing the absorption spectra of $Co(NH_3)_6F_3$ and $Co(NH_3)_6Cl_3$. A Beckman Model DU spectrophotometer was used for the comparison.

Control of the pH was very important in preparing the neutral salt. The effect of pH on the resultant salt is shown in Table VI.

TABLE VI

EFFECT OF pH OF SOLUTION ON $Co(NH_3)_6F_3$

Run	pH	% HF in Salt*
2	4.6	12.7
1	5.7	0.52
4	7.0	0.39
5	7.5	0.36
3	8.9	0.30

*Determined by titrating a weighed sample of complex to a pH of 7.0 (glass electrode) using standard NaOH.

7. Hexammine Chromium (III) Fluoride

Hexammine chromium (III) fluoride cannot be prepared in the same manner as the cobalt complex because the hydroxide is too unstable[20]. Therefore, the following reactions were used:

$$\frac{3}{2}\,Ag_2O + 3HF \rightarrow 3AgF + \frac{3}{2}\,H_2O$$

$$[Cr(NH_3)_6]\,Cl_3 + 3AgF \rightarrow [Cr(NH_3)_6]\,F_3 + 3AgCl \quad .$$

a. Reagents. Ag_2O: Mallinkrodt, purified

HF: B and A (A. C. S. reagent-grade)

$Cr(NH_3)_6Cl_3$: Prepared in this laboratory*.

b. Method. Hexammine chromium (III) chloride (0.034 mole) was dissolved in water in a polyethylene beaker. Silver fluoride solution was added until no Cl^- could be detected, nor could any Ag^+ be detected. The AgCl was filtered off and the resulting solution (pH = 6.3) was placed in a vacuum dessicator over concentrated sulfuric acid for 1 week. The crystals formed were filtered on a sintered glass frit with exclusion of air and dried in a vacuum dessicator over NaOH. The following analysis was obtained.

$Cr(NH_3)_6F_3$

	Found, %	Calculated, %
Cr:	24.1**	24.63
NH_3:	47.0**	48.38
F:	27.0	26.99
HF:	1.0	---

8. Analytical Methods

a. Hydrolysis. Active hydrogen in the borohydride compounds was determined by hydrolyzing the sample with 20% sulfuric acid in the vacuum line. The hydrogen evolved was measured by use of a Toepler pump and

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*The hexammine chromium (III) chloride was prepared by Mr. David Berman using the oxidation of $CrCl_2$ in the presence of NH_3. H_2 was liberated from the active platinum catalyst[21]. The salt contained 19.8% Cr. (theor. 19.96% Cr).

**The analytical data actually suggest contamination of the fluoride with a maximum of 10 mole % of the acid fluoride, $Cr(NH_3)_6(HF_2)_3$, and a formula of $0.9\ Cr(NH_3)_6F_3 + 0.1\ Cr(NH_3)_6(HF_2)_3$.

burette system. The acid was added to the system in the following manner. A tube (12 mm X 50 mm) was cooled in liquid nitrogen; then 20% H_2SO_4 was added to this tube drop by drop. The frozen tube was then placed in the reactor containing the sample. The reactor was rapidly attached to the vacuum line and liquid nitrogen was placed around it. Then the entire system was evacuated. After evacuation, the reactor was allowed to warm to room temperature, and hydrolysis proceeded. The solution could be warmed by placing a Dewar flash filled with hot water around the reactor. Final traces of gas were freed from the solution by using a freeze-thaw technique; i.e., the solution was carefully frozen with liquid nitrogen and then rapidly melted by placing hot (60°C) water about the reactor. The very rapid melting of the surface ice minimized the tendency to crack the glass vessel.

b. Nitrogen. Nitrogen was determined using the standard micro-Kjeldahl method. A Beckman Model F pH meter with a glass electrode was used to follow the titrations.

c. Cobalt. Cobalt was reduced to the cobaltous state and determined electrolytically on either a micro or a macro scale[27,28].

d. Chromium. Chromium was determined by oxidation to CrO_4^{--} and back-titrating with $FeSO_4^{--}$[29].

e. Fluorine. Fluorine was determined by the method of Willard and Winter[30].

f. Hydrofluoric Acid. The acid fluoride was determined by titrating with standard alkali to a pH of 7.0 using a glass electrode and a Beckman Model F pH meter.

g. Boron. The determination of small amounts of boron in the presence of various organic bases presented a problem, and some experimental work was directed toward obtaining a practical solution.

The usual volumetric determination of boron, by titrating boric acid in the presence of a poly-alcohol such as glycerol or mannitol, using phenolphthalein as an indicator, cannot be used in the presence of a weak

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[27] Brophy, Dorothy Hall, Ind. Eng. Chem., Anal. Ed. 3, 363 (1931).

[28] Hecht, Fredrich, and Donau, Julius, Anorganische Mikrogewichts Analyse, Julius Springer, Wien, 1940, p. 197-98.

[29] Willard, H. H., and Diehl, Harvey, Advanced Quantitative Analysis, D. Van Nostrand Company, New York, 1943, p. 229-47.

[30] Willard, H. H., and Winter, O. B., Ind. Eng. Chem., Anal. Ed. 5, 7-10 (1933).

acid such as ammonium chloride, since high results will occur due to partial neutralization of the acidic salt. A modification of the so-called identical-pH method proposed by Foote[31] was applied to this case for the micro determination of boron in nitrogen-containing derivatives of diborane. The basic procedure of this method is adjusting the solution to a pH value in the neighborhood of pH 7, then adding an amount of a complexing agent such as mannitol, and titrating back to the same pH.

A few elementary considerations will indicate which pH value to select (see Fig. 9). The pK_a of boric acid is 9.234[32], while that of the polyol complex in a saturated mannitol solution at 25°C is about 4.2 as determined from the pH of the half-neutralized solution. When the solution is adjusted to a pH near 7, a small amount of the boric acid is neutralized; while after adding the mannitol and titrating back to the identical endpoint, a small amount of the boric acid - mannitol complex is not neutralized. These two errors are in the same direction and make the value determined for boron too low. In order to reduce these errors to the smallest possible value, the pH chosen should lie exactly in the middle of the two pK_a values, i.e., that of the boric acid and that of its polyol complex*. This would be 1/2(9.234 + 4.2) or a pH of 6.72.

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[31] Foote, F. J., *Ind. Eng. Chem., Anal. Ed.*, *4*, 39-42 (1932).

[32] Manov, G. G., DeLollis, N. J., and Acree, S. F., *J. Research Natl. Bur. Standards* *33*, 287-306 (1944).

*This fact can easily be shown as follows: if boric acid is represented as HA and the polyol complex as HB, the ionization equations can be written

$$HA \rightleftarrows H^+ + A^- \qquad K = \frac{[H^+][A^-]}{[HA]}$$

$$HB \leftrightarrows H^+ + B^- \qquad K = \frac{[H^+][B^-]}{HB} \quad .$$

Since the error in the boron determination will be numerically equal to the sum of the boric acid titrated before addition of mannitol and the polyol complex not titrated at the pH chosen, the total error will be equal to $[A^- + HB]$ at the desired pH.

Since from the above equation $[A^- + HB] = \frac{Ka[1-A^-]}{H^+} + \frac{[1-HB]H^+}{K_B}$,

$[A + HB]$ can be differentiated with respect to H^+ to get the pH of minimum error. Since A^- will be small with respect to 1 in the first titration and HB will be small with respect to 1 in the second,

$$[A^- + HB] = \frac{K_a \cdot K_B + [H^+]^2}{[H^+][K_B]} = \frac{K_a}{[H^+]} + \frac{[H^+]}{K_B} \; .$$

(Footnote cont. on bottom of next pg.)

The errors involved can now be calculated:

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad .$$

In adjusting the solution to pH 6.72,

$$\frac{[A^-]}{[HA]} = \frac{K_a(\text{boric acid})}{[H^+]} = \frac{5.84 \times 10^{-10}}{1.9 \times 10^{-7}} = 3.0 \times 10^{-3} = 0.30\%$$

of the boric acid is already neutralized.

After saturating the solution with mannitol and titrating back to pH 6.72,

$$\frac{[HA]}{[A]} = \frac{[H^+]}{K_a\ (\text{complex})} = \frac{1.9 \times 10^{-7}}{6 \times 10^{-5}} = 3.0 \times 10^{-3} = 0.30\%$$

of the boric acid - mannitol complex which is not neutralized.

Therefore the total amount of boron determined by this method will be 0.60% low. Another error which tends to counterbalance this one is the blank involved in the mannitol itself. Even C.P.-grade mannitol contains traces of acidic substances, and since 5-10 grams are required to saturate the 20-40 ml of solution used in the titrations, this blank should be determined. This latter error tends to counterbalance the first-mentioned error, and in a number of standards which were run they exactly balanced out.

The error involved in changing the number of moles of water per liter in a saturated mannitol solution and therefore also the ion product of the water is small and can be neglected. The cooling of the solution on dissolving the mannitol is considerable, and in careful work the solution should be restored to the original temperature. Carbon dioxide does not appear to affect the results, since the solution is acidic throughout most of the titration.

Footnote from page 39 (cont.)

$$\frac{d[A^- + HB]}{d[H^+]} = \frac{-K_a}{[H^+]^2} + \frac{1}{K_B} = 0 \quad .$$

Then $[H^+] = \sqrt{K_a K_B}$;

or

$$pH^+ = \frac{pK_a + pK_B}{2}$$

for the minimum error.

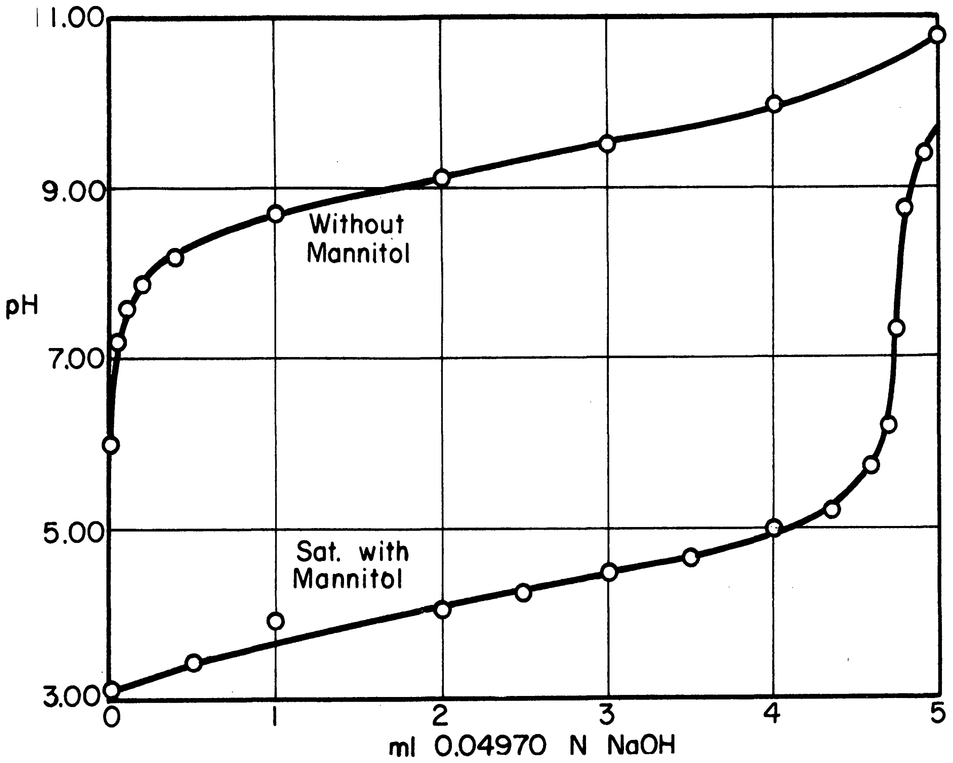

Fig. 9. Titration of 0.2355 meg. Boric Acid

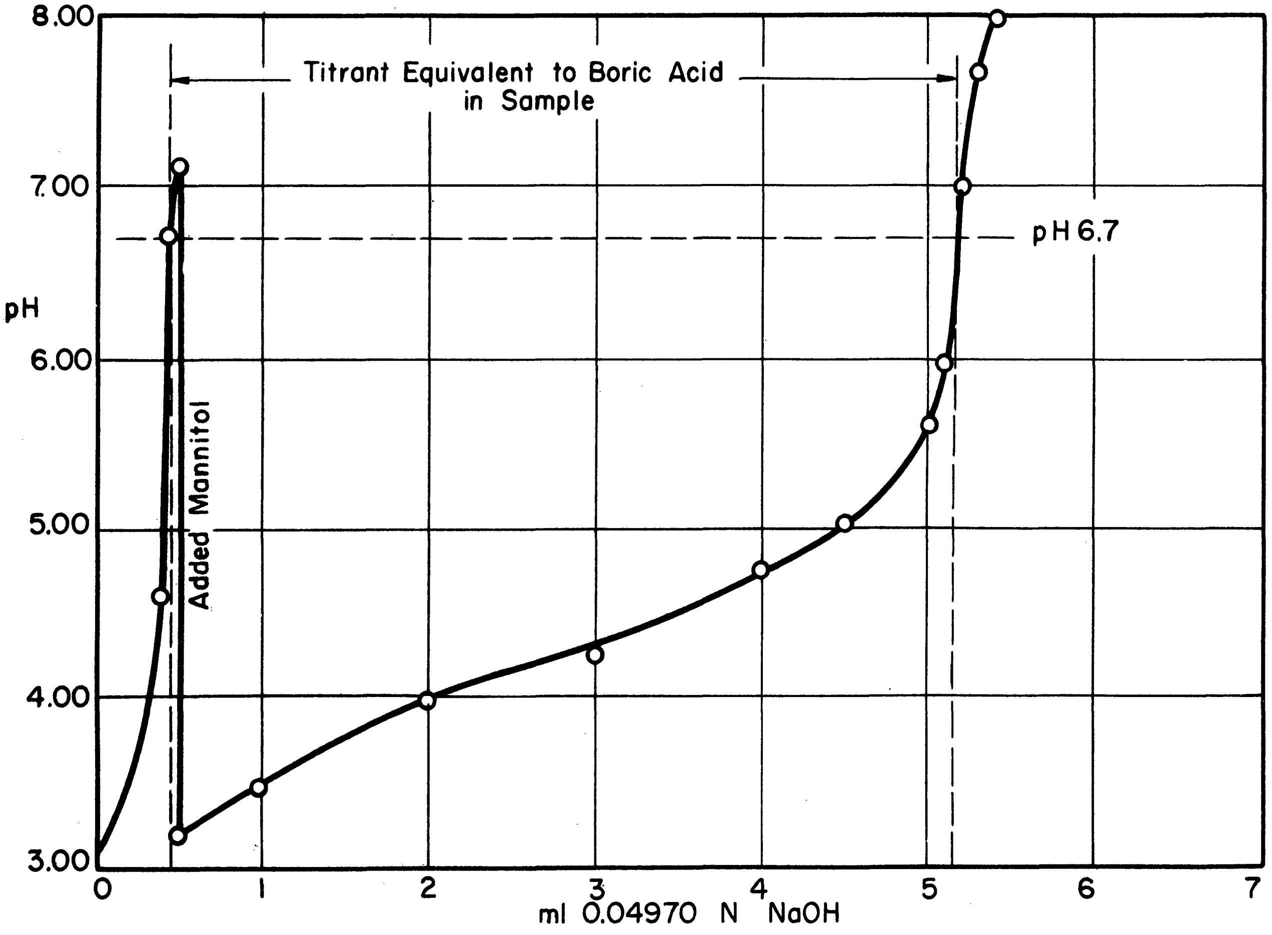

Fig. 10. Titration of 0.2355 meg. Boric Acid in Presence of 0.25 meg. NH_4Cl

The samples were prepared by hydrolyzing a weighed amount of the material with water or a dilute solution of H_2SO_4. A brief heating period with nitric acid was necessary for some samples to convert all the boron to boric acid. They were all diluted to about 30 ml in a 150-ml tall-form beaker and boron-free 1N NaOH was added dropwise until the pH was about 3.

The titrations were made using 0.05N NaOH from a 5-cc microburette. A Beckman Model G null-type battery-operated pH meter with a glass electrode and a calomel reference electrode was used to follow the pH of the solution during a titration. The data were recorded as pH vs ml of standard base. The standard base was added in small increments until the pH of the solution was about 7. The solution was then saturated with C.P. mannitol and the standard base was added in icrements until the pH was again about 7. The data were then plotted and the milliequivalents of base required to return the solution to a pH of 6.7 were determined. After the above corrections were applied, this figure represented the milliequivalents of boric acid in the sample.

The presence of buffering salts such as ammonium chloride tends to decrease the slope of the pH vs. ml titrant at the identical-pH point. When these salts are present in the same order of magnitude as the boric acid, the slopes of the curves in the region of pH 6.7 are still steep enough to determine the boron present with an accuracy of 1-4%. It was observed in all cases that the slopes of the curve before and after the addition of the mannitol are parallel in the region of pH 6.7; as is to be desired. A sample titration curve of boric acid in the presence of ammonium chloride is illustrated in Fig. 10.

IV. PHYSICOCHEMICAL STUDY OF $[BNH_6]_n$ AND THE CLASSICAL DIAMMONIATE OF DIBORANE

In the previous report[1] the compound $[BNH_6]_n$, obtained by loss of hydrogen from NH_4BH_4, was described. This compound had also been reported previously[33] by Aerojet Engineering Corporation. If n = 2, the compound should be identical to the diammoniate of diborane, however Aerojet reported that the compound failed to yield borazole on heating and hence was probably not the same as the diammoniate of diborane. Physical data reported previously from this laboratory indicate that the two compounds are the same; also the isolation in this laboratory of borazole by decomposition of the $[BNH_6]_n$ tends to indicate that the diammoniate of diborane can be produced from the decomposition of NH_4BH_4.

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[33] Armstrong, Aerojet Engineering Corp., Report No. 367, March 11, 1949.

The 1952 report indicated three methods of attacking the problem of the structure and chemistry of the diammoniate of diborane and BNH_6. The methods are (1) determination of molecular weights in liquid ammonia, (2) obtaining x-ray diffraction patterns of the solids, and (3) obtaining Raman spectra in liquid ammonia. In this report, no additional x-ray data are given, but some chemical evidence has been added.

X-ray photographs of the solid BNH_6 have shown no patterns. An attempt to prepare needle-like crystals of BNH_6 for examination by Professor W. N. Lipscomb of the University of Minnesota has not been successful up to the present time, although crystals were obtained much earlier. No new x-ray data are available. New molecular-weight data, Raman data, and chemical evidence are summarized below.

A. MOLECULAR-WEIGHT MEASUREMENTS

1. Experimental

The apparatus for determining the molecular weights was modified so that both mercury and mineral oil could be used as manometric fluids. The apparatus is shown in Fig. 11. The mineral oil was thoroughly tested for absorption of NH_3, and the density determined. At 25°C, $d = 0.8461$; therefore a factor of 15.996 is involved. The addition of the mineral-oil manometer permits determinations at lower concentrations.

Previous molecular-weight measurements on the diammoniate of diborane have been made by Stock and Pohland[2(a)] by vapor-pressure depression, and by Rathjens and Pitzer[16] by freezing-point depression. The work of Stock and Pohland showed a disturbing rise in molecular weight as infinite dilution was approached. Rathjens and Pitzer attempted to avoid any complications due to changes in the diammoniate by keeping the mixture at about -78°C*. However, an analyses of the data indicate that the rise in apparent molecular weight is found even at low temperatures.

Molecular-weight determinations of the diammoniate of diborane were made using a representative portion of a large sample of the diammoniate

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*Burg and Schlesinger[34] postulate that the diammoniate changes at -50°C according to the reaction

$$NH_4^+ \, BH_3NH_2BH_3^- + 2NH_3 \rightleftarrows 2NH_4^+ \, BH_3NH_2^- \ .$$

[34] Schlesinger, H. I., and Burg, Anton B., Chem. Rev. 31, 1-42 (1942)

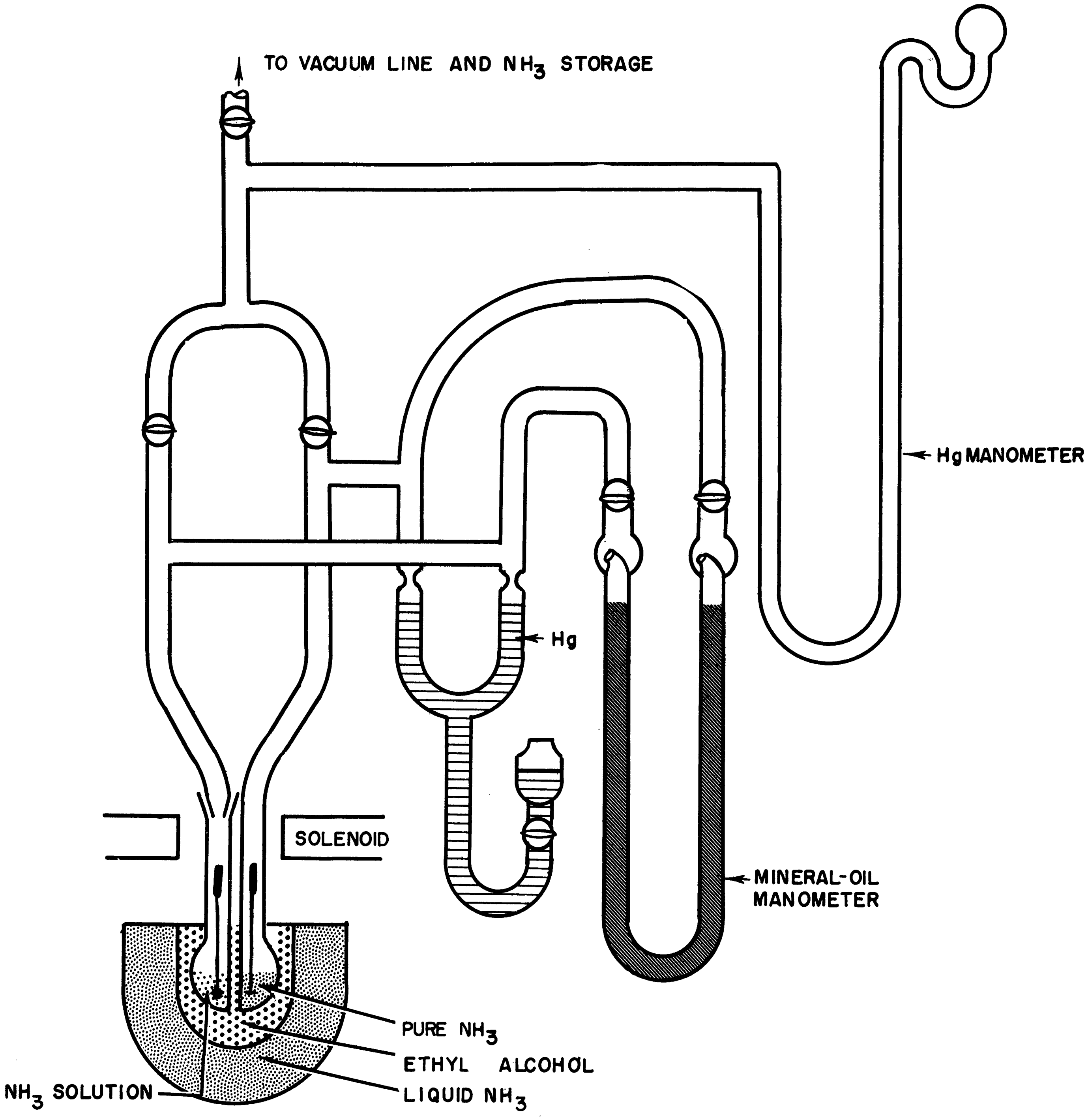

Fig. 11. Apparatus for Determining Molecular Weights in Liquid Ammonia by Vapor-Pressure Depression

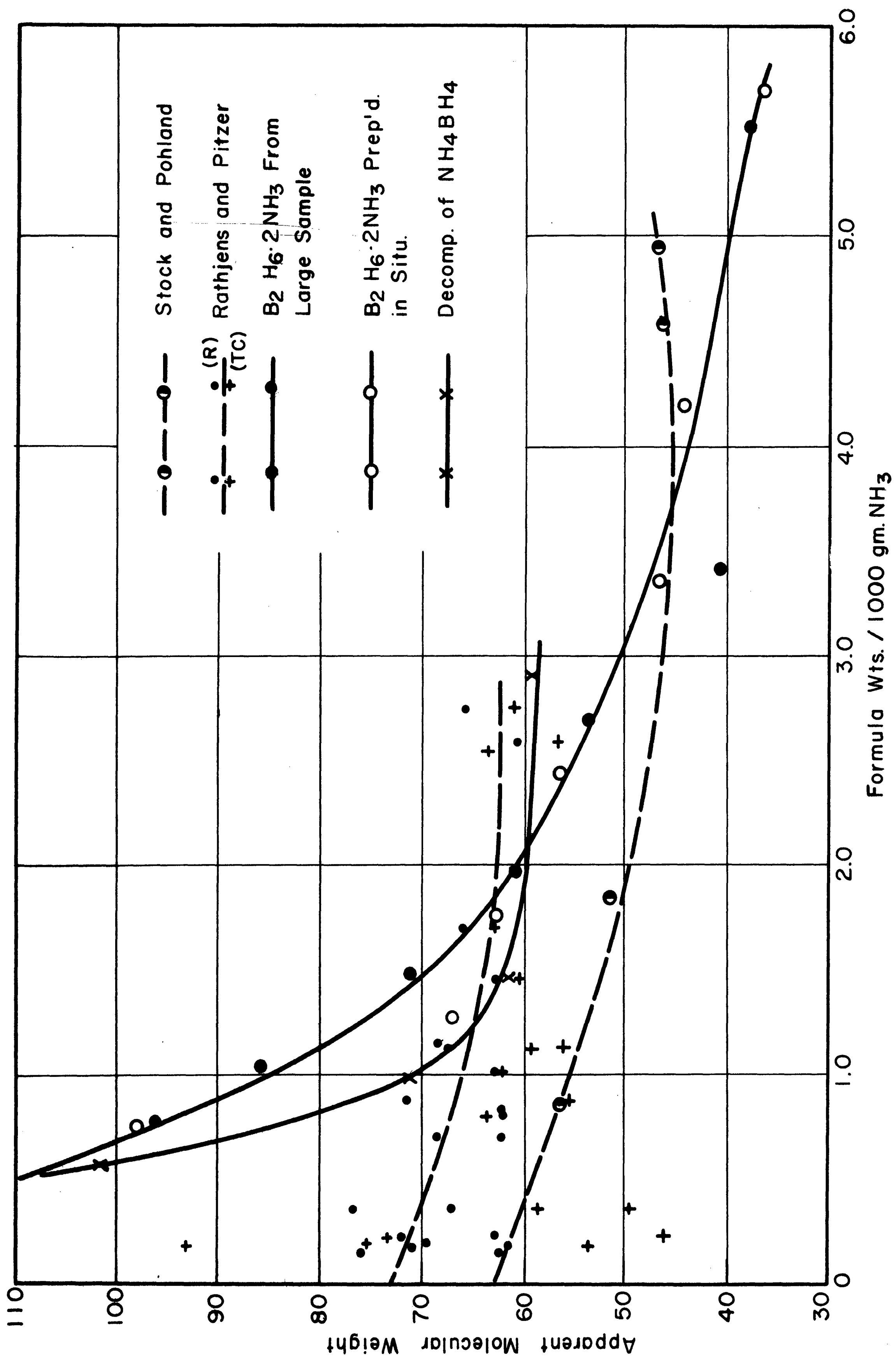

Fig. 12. Molecular Weight of Diammoniate of Diborane in Liquid Ammonia

and also a sample prepared in the molecular-weight apparatus. The latter method is essentially the same as was used by Stock and Pohland.

For comparison purposes, the decomposition product of ammonium borohydride, $(BNH_6)_n$, was also determined. The results are indicated in Fig. 12.

The experimental details were given in the 1952 report.

2. Results

Although quantitative agreement among the different sets of molecular-weight data is lacking, the general shape of the curves is similar. Only the gold-resistance thermometer data from the paper of Rathjens and Pitzer were plotted from their study, since the authors questioned the reliability of their copper-constantan thermocouple data. A comparison of the data obtained in this laboratory with the results of Stock and Pohland recalls the fact that discrepancies were noted in the standardization work on urea[1]. The results from this laboratory did, however, check with the early boiling-point-elevation studies done by Franklin and Kraus[35] on urea. In the work done in this laboratory, all the solvent ammonia was removed to check for the presence of the characteristic white solid prior to proceeding with the molecular-weight measurements. There is no indication that this was done in the work of Stock and Pohland. In view of the earlier observations on stoichiometry this may constitute a real difference.

In the work of Rathjens and Pitzer, the diborane was condensed on the solid ammonia and gradually warmed. The only indication of a reaction was found in the calorimetric data, and it is questionable whether this calorimetric quantity represents an actual heat of reaction or merely a heat of solution of diborane in liquid ammonia. At any rate, the excess ammonia was not sublimed off prior to making the freezing-point measurements. The wide scatter of their points raises real questions regarding the validity of precise conclusions.

The behavior of the decomposition product of ammonium borohydride, $(BNH_6)_n$, shows a marked similarity to the diammoniate of diborane, with the exception of one point. The rise in apparent molecular weight is as much a puzzle as it was when Stock and Pohland first observed it. It seems to indicate either a reversible polymerization at low concentrations or a solvation effect. The former is contrary to all experience. However, the data certainly do not indicate the presence of two ions, at high dilution nor the presence of monomeric BH_3 units at higher temperatures.

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[35] Franklin, E. C., and Kraus, C. A., Am. Chem. J. 20, 836-53 (1898).

B. RAMAN SPECTRA

1. Experimental

Raman-spectra work has been continued, but several modifications in the instrument have been made. The Raman instrument used was a Gaertner Raman Spectrograph, but the light source was changed to utilize a Toronto arc[36]. This cut down the background and pressure broadening considerably.

Samples were purified using liquid ammonia as a solvent and were loaded into the Raman sample tube using the apparatus shown schematically in Fig. 13. The joints in the apparatus were designed so that it could be folded around and fitted into a large unsilvered Dewar. The sample was loaded into A and dry nitrogen was passed through the apparatus. The whole apparatus was then placed in the Dewar, cooled with a Dry-Ice - isopropyl alcohol bath. The stopcock could be closed by using a metal rod. Dry ammonia was admitted through blow-off 2 and the ammonia condensed in A. If agitation was required to effect solution, dry nitrogen could be admitted through blow-off 2. Filtration was accomplished by admitting dry nitrogen through blow-off 1 and reducing the pressure on blow-off 2. When the solution reaches the level of the stopcock, the latter was opened and pressure was reduced from blow-off 3. After filtration through the two filters in A and B, the solution was forced from C to the Raman tube by increasing the pressure on blow-off 3 and decreasing the pressure on blow-off 4.

2. Results

The quality of many of the Raman spectra of liquid ammonia solutions obtained up to the present time has suffered because of a troublesome background scattering which has obscured weaker lines completely and in some cases has even partially hidden some of the stronger frequencies. The origin of this background apparently is not due to suspended solid material and its elimination has proved very difficult. Nevertheless fairly satisfactory spectra have been obtained for the borohydride ion in liquid-ammonia solutions of $NaBH_4$. This information has been used to confirm spectroscopically the presence of the borohydride ion in solutions of NH_4BH_4 prepared by the metathesis of NH_4F and $NaBH_4$.

To date, six frequencies have been observed which can be assigned to the borhydride ion. These are listed below.

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[36] Welsh, H. L., Crawford, M. F., Thomas, T. R., and Love, G. R., *Can. Jour. Phys.* 30, 577-596 (1952).

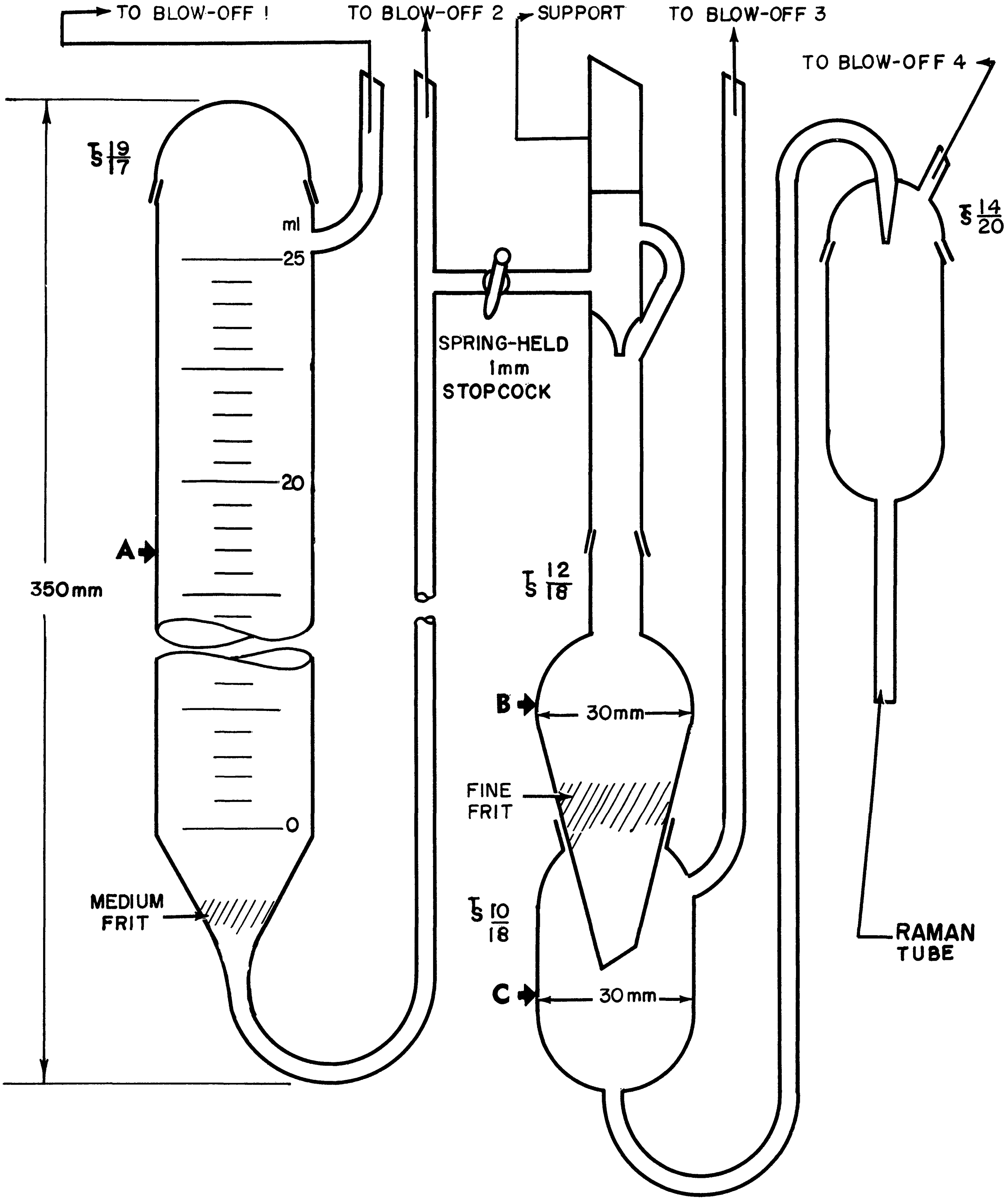

Fig. 13. Apparatus for Purification and Loading Samples in Raman Tube

Observed Borohydride Ion Frequencies

Frequency, cm^{-1}	Intensity
1137	vvw
1214	w
2156	w
2223	w
2264	ms
2398	w

For a pentatomic ion with tetrahedral symmetry, only four fundamental frequencies are to be expected. With the exception of the relatively strong frequency at 2264 cm^{-1}, which is undoubtedly the symmetrical B-H breathing frequency, the assignment of fundamentals is not obvious. Moreover, a fairly strong frequency has been reported at 1080 cm^{-1} in the infrared spectrum of crystalline $NaBH_4$. In liquid-ammonia solution, unfortunately, a strong band due to the solvent occurs at precisely this position and consequently it will be necessary to use one of the methyl amines as a solvent in order to examine this region.

Several attempts have been made to obtain the spectrum of the diborane diammoniate but with rather indifferent success (at best) due to the presence of the previously mentioned background. Weak bands have been observed in the region around 2200-2400 cm^{-1}, which is the same region in which the characteristic band of the borohydride ion appears. However, a band usually appears in this portion of the spectrum whenever the molecule contains a $-BH_3$ group (not for a $-BH_2$ group, incidentally), and in any case the quality of the spectra was such as to make it unwise to try to draw any definite conclusions. The general band contour did not appear to resemble strongly that of the borohydride ion.

Further work is being aimed at eliminating the background trouble and obtaining satisfactory spectra of the diammoniate and also of $(BNH_6)_n$. If a satisfactory assignment of fundamentals can be made, force constants will be calculated for the borohydride ion.

Raman-spectra data obtained to date are shown in Table VII.

TABLE VII

RAMAN SPECTRA OF BORON COMPOUNDS
Wave-Number Shift in Cm^{-1}

$NaBH_4$	$B_2H_6 \cdot 2NH_3$		Assignment
	-1-	-2-	
1086.7			B-H Deformation
	1244	1243	
	1486		
1531			
1623			
2159			
		2234	
2270	2272	2268	B-H Stretch
		2325	
2395		2405	
2504			
2602	2599	2597	Hg 2602
3232	3220	3213	NH_3-3212
3297	3298	3293	NH_3-3300
3380	3388	3376	NH_3-3380

C. CHEMICAL COMPARISON OF $(BNH_6)_n$ AND THE DIAMMONIATE OF DIBORANE

1. Experimental

The preparation of borazole from the decomposition product of ammonium borohydride is described below along with several other characteristic chemical properties of the decomposition product.

a. Preparation of Borazole from BNH_6. A sample (25.6 mg) of BNH_6 (99.6% pure by analysis) prepared from the decomposition of ammonium borohydride was heated for 2-1/2 hours at 180°C in a tube equipped with a manometer. Hydrogen (1.53 mM) was evolved and a volatile product (0.04 mM) was also obtained. On careful fractionation of the volatile material, 0.035 mM of pure borazole was obtained. The borazole was identified by vapor-pressure measurements and by molecular weight. The micro apparatus used for these determinations is shown in Figs. 14 and 15. A molecular weight of 77 was obtained (theoretical for $B_3N_3H_6$ is 80.4), which is as good as can be expected considering that the determination was made on only 1.22 mg.

The data indicate about 15% yield of borazole from BNH_6, and this compares favorably with the reported yields of 20% from diammoniate of diborane[37]. The residue from the pyrolysis was insoluble in liquid ammonia and could be BNH_4.

b. Hydrolysis of BNH_6 and the Diammoniate of Diborane. Aerojet reported that only two-thirds of the hydrogen could be obtained by hydrolysis of $[BNH_6]_n$ with 3N HCl[38]. Similar results have been obtained in this laboratory using 20% H_2SO_4 as the hydrolyzing medium and temperatures up to 45°C. The diammoniate of diborane behaves in a similar fashion. Complete hydrolysis of the diammoniate of diborane has been reported as a result of treatment with acid above 100°C in a sealed tube[39]. It is probably significant that boron analysis on incompletely hydrolyzed samples gave low results, yet, after boiling the sample with concentrated nitric acid, theoretical percentages of boron were obtained

TABLE VIII

HYDROLYSIS OF BNH_6 AND DIAMMONIATE OF DIBORANE

$(BNH_6)_n$		$B_2H_6 \cdot 2NH_3$	
Sample	Percent of Theoretical Value	Sample	Percent of Theoretical Value
I-125	61.7	II-11	67.3
III-18	65.7	II-51	62.0
		III-36	73.6

[37] Stock, Alfred, and Pohland, Erich, Ber. 59B, 2215 (1926).

[38] Schlechter, W. H., Adams, R. M., and Jackson, C. B., "Boron Hydrides and Related Compounds", Callery Chemical Co., Navy Bureau of Aeronautics Contract NO a(s) 10992, March, 1951, p. 88.

[39] Schaeffer, George, St. Louis University, Personal conversation, Feb. 26, 1954.

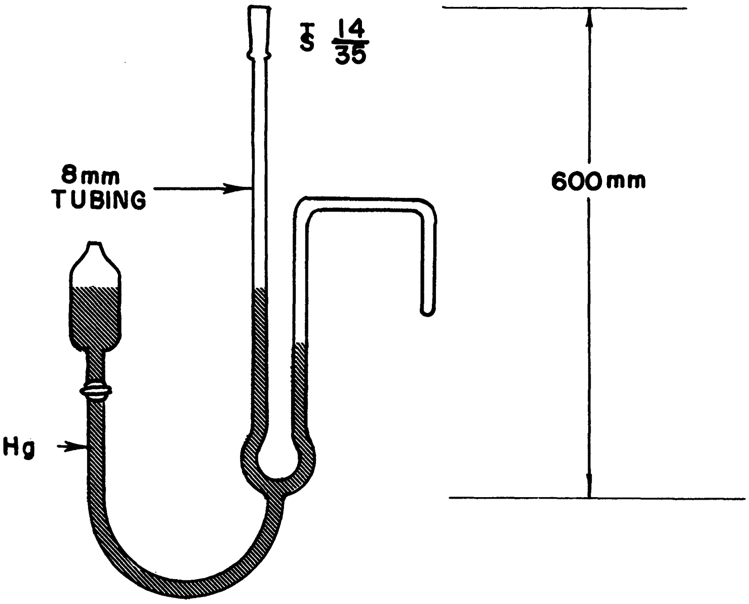

Fig. 14. Apparatus for Determination of Vapor Pressure on Micro Samples

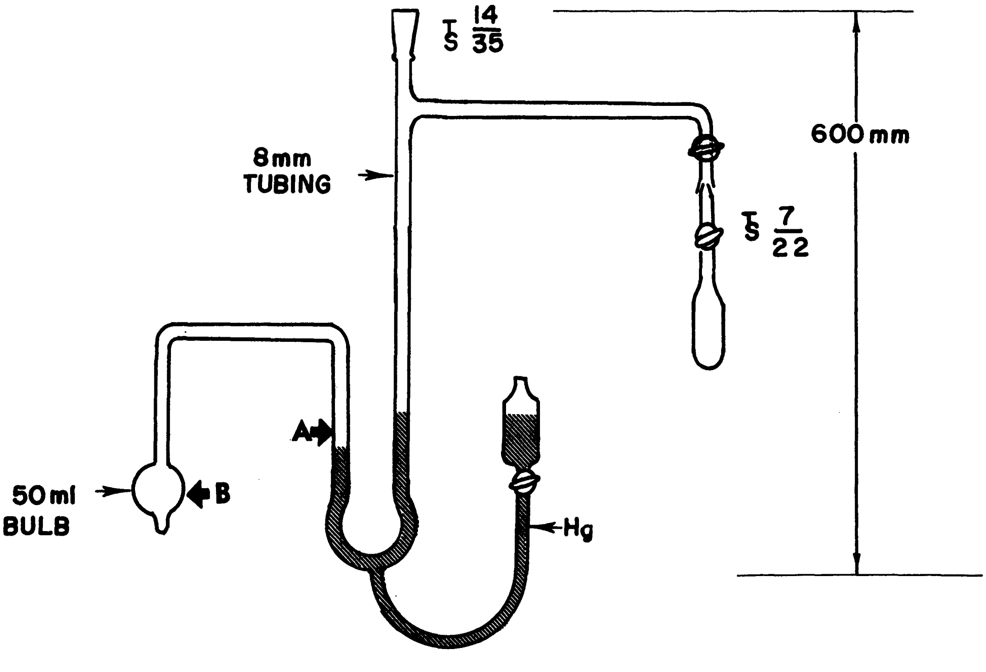

Fig. 15. Apparatus for Determination of Molecular Weight by Vapor Density on Micro Samples

c. Chemical Reactions of $(BNH_6)_n$ and the Diammoniate of Diborane. Stock[2(b)] has pointed out that the diammoniate of diborane in aqueous solutions gives reactions characteristic of OBH_3^-. These same reactions are observed with $(BNH_6)_n$:

(1) $Ni^{++} \dashrightarrow Ni_2B$

(2) $Ag^+ \dashrightarrow Ag^\circ$

(3) $Hg^{++} \dashrightarrow Hg^\circ$

(4) $Cu^{++} \dashrightarrow CuH$

V. THE REACTION BETWEEN SUBSTITUTED HYDROXYLAMINES AND DIBORANE

A. BACKGROUND

In the previous report[1] it was shown that diborane reacts slowly with a stirred ether suspension of hydroxylamine at -112°C without liberation of appreciable amounts of H_2. The stoichiometry of the reaction under these conditions may be represented by the equation

$$nB_2H_6 + 2nNH_2OH \rightleftarrows 2[H_3BNH_2OH]_n$$

Slight reversibility of the reaction was indicated by the fact that prolonged and strenuous condensation procedures at the end of the reaction at -112°C permitted removal of some of the diborane which had previously undergone combination with hydroxylamine.

If the compound H_3BNH_2OH is allowed to warm up, hydrogen is liberated through the reaction between the acidic hydroxyl hydrogen of the hydroxylamine and the hydridic hydrogen of the diborane.

B. STATEMENT OF THE PROBLEM

A logical extension of the hydroxylamine reaction involves the use of alkyl substituted hydroxylamines and alkyl substituted diboranes. The recent work has been devoted to a study of the reaction between diborane and o-methyl hydroxylamine.

C. EXPERIMENTAL

1. The Decomposition of the Solid Residue Obtained from the Reaction between B_2H_6 and NH_2OH

After the compound $[H_3BNH_2OH]_x$ lost hydrogen to give a solid polymer it was removed from the vacuum line and stored in a screw-top bottle. The percentage of nitrogen in the solid decreased slowly with time, and the ultimate white solid obtained was $[NH_4]HB_4O_7$.

	% N	% B	B/N Ratio
Stored 3 months	19.08	-	-
Stored about 1 year	8.06	24.28	3.90
Theoretical for $NH_4H\ [B_4O_7]$	8.04	24.84	4.0

2. The Reaction between B_2H_6 and CH_3ONH_2

a. Reagents. (1) Methoxyamine: Methoxyammonium chloride, kindly furnished to us by Dr. P. A. S. Smith, was neutralized by a 50% solution of KOH. The reaction was carried out in a 60-ml pear-shaped flask fitted with a Claisen-type micro distilling head and condenser. The free base was distilled from the aqueous solution into a flask cooled in an ice-water bath. The fraction distilling at 46 to 50°C was collected. It was dried over solid potassium hydroxide and then transferred to the weighing tube, which contained about 1 gram of anhydrous barium oxide.

(2) Diborane: B_2H_6 was prepared by the reaction between $LiAlH_4$ and excess BF_3 etherate in ether solution[7]. The vapor pressure of the product, purified by low-temperature trap-to-trap distillation, was 225 mm at -111.6°C.

(3) Ether: Reagent-grade commercial ether was distilled from sodium in the vacuum line.

b. Apparatus and Procedure. The reaction system, previously described[1], consisted of a 20-mm pyrex tube containing a magnetic stirrer and attached to a conventional high-vacuum manifold through a jacketed packed distilling column. The procedure used was similar to that previously described for the hydroxylamine reaction except for the method used to introduce the amine. Methoxyamine, being a liquid, was easily* distilled into the reaction tube from a small weighing tube which was attached to the manifold through a standard taper joint. A small amount of anhydrous barium oxide was used as a dessicant in the weighing tube. After the tube was attached to the manifold, the methoxyamine was frozen and the air was pumped out. Dissolved and entrapped air was removed by melting the amine and then freezing and pumping.

To carry out the reaction with diborane, dry ether was condensed in the tube. Then an excess of diborane was distilled in by cooling the tube with liquid nitrogen. After the transfer was complete the temperature of the system was raised to -112°C, where reaction took place. After several hours, the excess diborane was distilled out of the system and the amount reacting was computed.

In order to estimate the completeness of separation of the excess diborane from the reaction mixture, a sample consisting of 5.729 mm of diborane was mixed with 5.6 ml of ether in the reaction cell. The system was stirred for several hours; then the B_2H_6 was distilled from the system for 20 minutes (reaction cell at -112°C, receiver at -196°C). After the B_2H_6 was purified by distillation in the vacuum line, 5.655 mmoles were recovered. This represents a loss of about 1.3% of the original sample or about 0.064 mmoles of diborane in 5 cc of ether.

D. EXPERIMENTAL RESULTS AND DISCUSSION OF THE DIBORANE-METHOXYAMINE REACTION

In all cases two molecules of methoxyamine will react with one molecule of diborane to give a solid addition compound,

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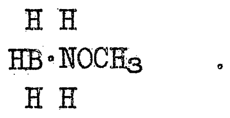
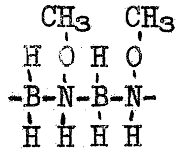
*The distillation procedure was somewhat different in the first run, which gave the volatile liquid product. Here the methoxyamine was in a glass-stoppered vial inside the tube which was attached to the line. After the outer tube was evacuated, the glass stopper of the inner vial was popped out by heating the methoxyamine. Because there were small amounts of air in the system the liquid then distilled slowly and the methoxyamine was warmed to facilitate transfer. After this experience the process was modified as described.



$$\begin{array}{l}\ \ \mathrm{H\ H} \\ \mathrm{HB\cdot NOCH_3} \\ \ \ \mathrm{H\ H}\end{array} .$$

This solid can be crystallized from ether below 0°C but is quite soluble above this temperature. Molecular-weight measurements, by vapor-pressure depression of the ether, indicate that the solid is monomeric in solution. This solid will lose hydrogen, the exact temperature of the loss being greatly influenced by the presence of foreign impurities and other factors which are still incompletely defined. Loss of hydrogen converts the solid into a very viscous liquid of low vapor pressure, probably a polymer of the type



$$\begin{array}{cccc} & \mathrm{CH_3} & & \mathrm{CH_3} \\ \mathrm{H} & \mathrm{O} & \mathrm{H} & \mathrm{O} \\ -\mathrm{B}- & \mathrm{N}- & \mathrm{B}- & \mathrm{N}- \\ \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} \end{array}$$

or a more strongly cross-linked analogue. In two cases where loss of hydrogen had been slow up to room temperature, the solid was heated. The solid melted and loss of hydrogen became quite rapid, finally at a temperature of 90°C (two runs) the system exploded violently. The explosion had many of the characteristics of a detonation and did not appear to be simply a result of rapid hydrogen evolution.

Since the eight individual runs on this system differ in several interesting details and since several incompletely identified products have been obtained in small amounts, it seems advisable to describe the results of one or two characteristic runs in some detail. In the first run hydrogen was evolved at low temperatures (below 0°C) and a liquid product was obtained which underwent disproportionation. This run is described below.

A sample of methoxyamine, prepared as previously described and weighing 0.7495 g. (15.9 mmoles), was distilled into the reaction tube (see footnote on p. 55). Then 8 ml of ether were distilled in to serve as solvent, and 10.43 mmoles of diborane were added. The temperature of the solution was held at -112°C for 13 hours and the solution was stirred constantly. About 0.48 mmole of H_2 was evolved during this period. After excess diborane had been distilled out of the system, it was found that 7.94 mmoles had reacted with 15.9 mmoles of methoxyamine. The temperature of the system was then allowed to rise in intervals as shown in Table IX below. Hydrogen, identified in each case by a molecular weight determination, was evolved as indicated in the table.

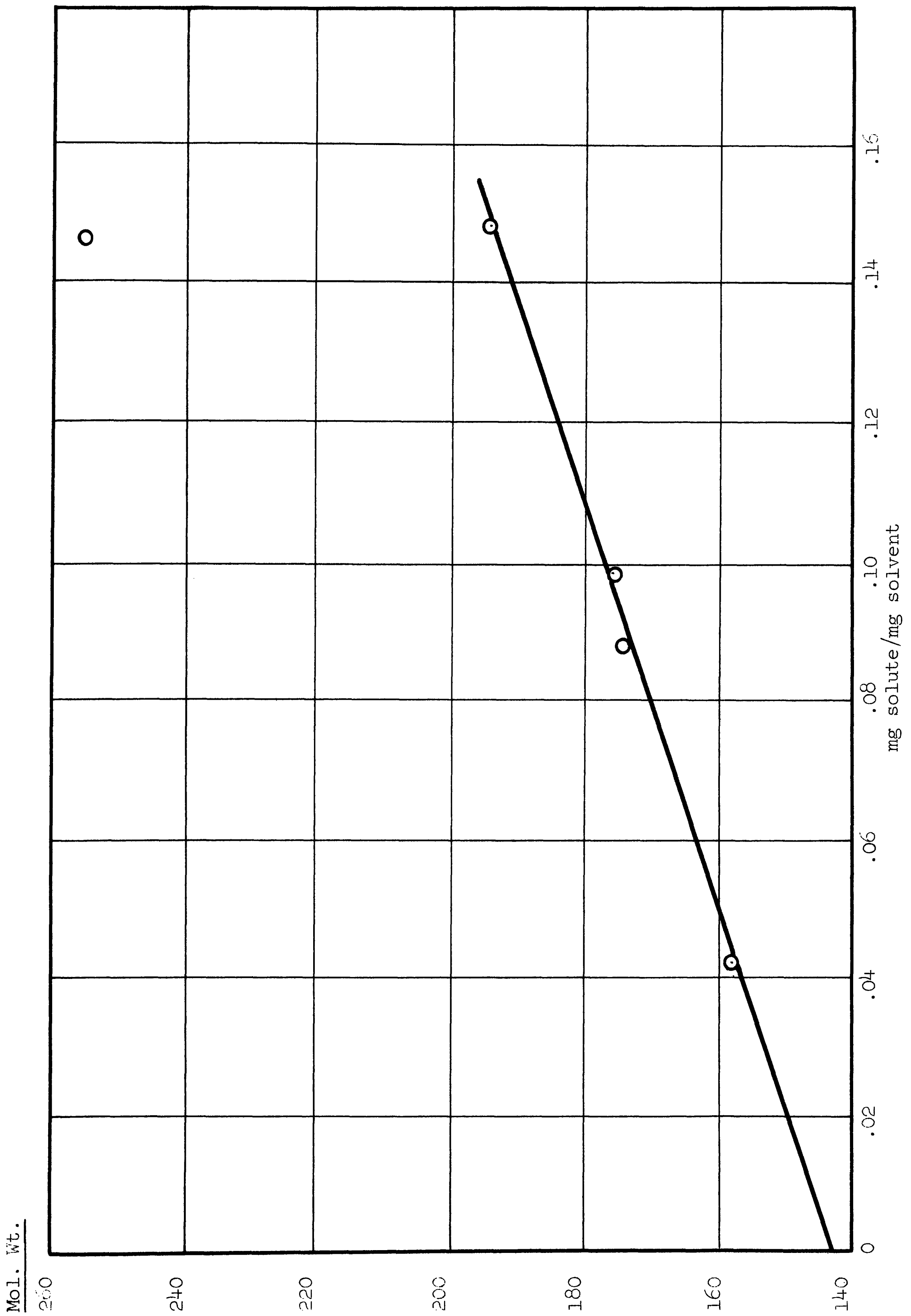


Fig. 16. Molecular Weight of Solid Disproportionation Product

TABLE IX

HYDROGEN EVOLVED IN REACTION OF DIBORANE WITH METHOXYAMINE, LIQUID PRODUCT

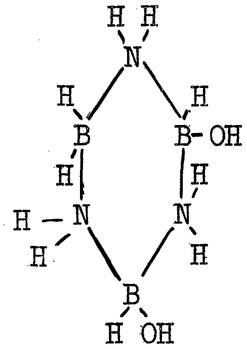
Run 1

t, °C	H_2 evolved mmoles	Total H_2, mmoles	$\frac{H_2}{B_2H_6}$	$\frac{H_2}{CH_3OH_2}$
-112	0.48	0.48	0.06	0.03
- 78	0.16	0.64	0.08	0.04
- 64	0.07	0.71	0.09	0.045
- 46	0.08	0.79	0.10	0.05
- 23	0.32	1.11	0.14	0.07
0	4.33	5.44	0.69	0.34
14	1.15	6.69	0.84	0.42
26	4.46	11.15	1.40	0.70

During the time that the reaction temperature was rising to -23°C, there was a large amount of a white precipitate in the reaction tube. This must have been a new compound, since methoxyamine melts at -86°C and diborane is a gas at this temperature. When the temperature was raised to 0°C the precipitate dissolved completely within 2 hours and the hydrogen evolution became noticeably more rapid. After gas evolution at 0°C became very slow the temperature of the system was raised to room temperature and H_2 was collected until the rate of its evolution became very slow. Higher temperatures were impractical because of potential damage to the stopcock grease by ether; therefore the system was cooled to -46°C and ether was distilled off.

During the time of hydrogen evolution a precipitate began to appear in the tube at about 14°C. This precipitate and a relatively nonviscous liquid remained in the reaction tube after the ether was removed. The liquid (about 0.5 ml and 0°C) had a vapor pressure of 29 mm at 0°C and a molecular weight by vapor density of 62.5 ± 1. On standing at about 14°C some of the liquid underwent decomposition to give in one case 0.296 mmoles of B_2H_6 and 53 mg of a white solid. Since the solid dissolved in liquid ammonia, its molecular weight could be estimated by vapor-pressure depression. Values obtained at different solution concentrations are shown in Fig. 16. The value at infinite dilution is 144. After 3 days of standing in liquid ammonia a trace of precipitate was detected in the tube to prevent any further possible reaction between solvent and solute, the ammonia was distilled off and the entire sample was hydrolyzed with dilute H_2SO_4. Boron and nitrogen analyses were run on the solution using methods previously described (see p.38).

Results are: %B = 27.6, %N = 35.70, % active H = 3.4, mol wt. = 144. A test for carbon made on the residue obtained by evaporating off the sulfuric acid indicated none present; the titration curve on the hydrolysate indicated that the nitrogen was present as an ammonium salt. A structure consistent with these facts is:



	Theor. %	Obs. %
N	35.7	35.4
B	27.4	27.6
Active H	3.40	3.37
Mol wt	117.5	144*

However, it should be clearly recognized that the results are not conclusive and must be reproduced before acceptance. Unfortunately, all attempts to reproduce the details of the above run have been unsuccessful. The reaction has always taken a different course, as described later, and the nonviscous liquid which disproportionates has never been obtained as an important product of later runs.

A small amount of the original nonviscous liquid remained after much of it had undergone disproportionation as described above. This residue was analyzed for B, N, and active H. Results are not particularly precise because of the very small amounts of B and N present, but the approximate B/N/H ratios are probably of significance. Diethyl ether was isolated from the system after hydrolysis, indicating that the original liquid had not been freed from ether by distillation. Data are summarized in Table X.

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*Some association of compound in liquid NH_3 probable.

TABLE X

ANALYSIS OF NONVISCOUS LIQUID RESIDUE

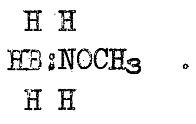
Mol wt of original liquid by vapor density = 63.5±1
V. P. of nonviscous liquid at 0°C = 31.9 mm; of orig. liquid = 28 mm

27.18 mg liquid + 1 drop conc - H_2SO_4 + 5 drops H_2O
yielded:

0.15 mmoles diethyl ether
0.256 mmoles boron
0.113 mmoles nitrogen
0.555 mmoles active hydrogen

An approximate ratio of 1/2/5 for N/B/H is indicated. It may be pertinent that structures of the aminodiborane type are known to disproportionate to give B_2H_6 and solid B-N polymers.

In all later attempts to reproduce the results previously described, the reaction invariably took a different course. Hydrogen evolution always began at a significantly higher temperature and the resulting product, obtained after loss of H_2, was always a thick viscous liquid of very low vapor pressure, a solid, or a mixture of liquid and solid. In one case (run No. 4, Table XI) when very pure methoxyamine which had been used for vapor-pressure measurements was used, less than 10% of the theoretical amount of hydrogen had been evolved after the homogeneous ether solution had stood at 24°C for more than 5 days. When the ether was removed from this system, the resulting material was a white crystalline solid rather than the liquids of earlier runs. An estimate of the molecular weight of this saturated solid by vapor-pressure depression of the ether solution gave a value of 65, which suggests that it was the saturated monomer



$$\begin{array}{c} \text{H}\ \text{H} \\ \text{HB:NOCH}_3 \\ \text{H}\ \text{H} \end{array} .$$

The solid was soluble in ether above 0°C but crystallized out quite rapidly at temperatures below 0°C; it melted somewhat above room temperature and began to lose H_2. At 70°C H_2 loss was quite rapid. When about 25% of the theoretical amount of hydrogen required for formation of the unsaturated compound had been evolved, the system was cooled down with liquid air and hydrogen was removed. On warming to room temperature the material was still a solid, but a small amount of a second unidentified solid could be sublimed

TABLE XI

SUMMARY OF REACTIONS BETWEEN DIBORANE AND METHOXYAMINE

Run No.	B_2H_6 Used, mmoles	Methoxyamine, mmoles	$\frac{MeONH_2}{B_2H_6}$	Temp. of Comb., °C	Solvent		Total H_2 per CH_3ONH_2 at 0°C	Appearance of Residue at 25°C after Removal of Solvent	Remarks
					Kind	Vol., ml			
1 (see text)	7.94	15.9 warmed up to distill into tube	2.0	-112	diethyl ether	8	0.34	Small amount solid and nonviscous liquid. Vapor pressure = 28 mm at 0°C	Liquid product disproportionates to give B_2H_6 and solid.
2	3.88	7.12	1.84	-186 to -64	none	-	0.15	White solid which changed to viscous liquid as H_2 was lost. Liquid heated slowly to 215°C without explosion.	Excess B_2H_6 present during warm-up of product to 25°C. Vapor pressure of viscous liquid negligible at 0°C.
3	3.410	6.45	1.89	-112	diethyl ether	4.1	0.18	Solid and viscous liquid and small amount volatile solids.	Solid soluble in ether above 0°C, crystallizes below 0°C.
4	3.73	7.10 (very pure)	1.91	-112	diethyl ether	5.5	0.024	Solid; soluble in ether above 0°C. Melts just above room temp.	Product loses H_2 on melting. Molten mass blew up at 90°C.
5*	7.13	13.32	1.87	-112	diethyl ether	8	0.152	Viscous liquid and solid.	Methyl borate isolated as one of products.
6	5.98	9.904	1.66	-112	diethyl ether	7.3	.203	Viscous liquid.	Platined asbestos added. 120 mg decomposed $NeONH_2$, small amount of liquid similar to that in Run 1 obtained, disproportioned to solid and diborane.
7	6.77	12.52	1.85	- 78.5	diethylene glycol dimethyl ether	10	.08	Solvent not removed. Products all soluble in solvent.	Solvent first dried with diborane. On hydrolysis with H_2O and KOH, ammonia and methanol isolated.
8	2.39	3.46	1.45	-112	diethyl ether	5	.18	Viscous liquid	KOH added as catalyst. Hydrolysed with methanol. Volatile solid obtained not characterized as yet.
9	7.04	13.43	1.91	- 78	diethyl ether	5	.45	Viscous liquid	KOH added as catalyst. $MeONH_2$ dried over BaO for one week instead of one day.

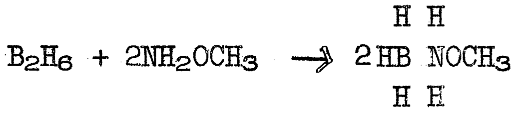
* There was a different observer for Runs 5-9.

from the system (v.p. = 22 mm at 0°C; mol wt. by vapor density = about 59.5±1). The bulk of the solid again melted just above room temperature when heat was applied. H_2 evolution was again noted from the molten material. At 90°C the material exploded with a rather sharp detonation. At the time that the explosion occurred, hydrogen evolution indicated that somewhat more than half of the addition product had been converted to the unsaturated form. The explosion is good evidence that the methoxygroup had not migrated from the nitrogen to the boron earlier.

Other runs have given results intermediate between the above two extremes. Removal of ether after loss of some hydrogen left a solid, a viscous liquid of very low vapor pressure, and in some cases traces of volatile solids. Currently efforts are being made to define more precisely the experimental conditions required for the decomposition of the addition product in different ways. A summary of several runs on this system is given in Table XI. Details on the first four of these runs are available in the dissertation of Dr. D. H. Campbell[40].

E. SUMMARY OF THE DIBORANE-METHOXYAMINE REACTION

It has been shown that diborane and very pure methoxyamine react at -112°C in accordance with the equation:



$$B_2H_6 + 2NH_2OCH_3 \longrightarrow 2\,H\overset{H}{\underset{H}{B}}\,\overset{H}{\underset{H}{N}}OCH_3$$

The resulting product is a white solid, monomeric in ether, and may be crystallized from ether below 0°C. It is stable at room temperature in vacuum, but the solid melts somewhat above room temperature and evolves H_2. At 90°C the product explodes violently. It is interesting to note that the methoxyamine addition compound seems to be more stable than the hydroxylamine adduct, since the prolonged condensation procedures removed some of the B_2H_6 from hydroxylamine at -112°C but did not remove it from methoxyamine. This behavior is contrary to that expected from the relative base strengths of the two amines since, as is shown later, hydroxylamine is the stronger base by a factor of 10.

In other cases in which the methoxyamine is somewhat less pure, the adduct loses hydrogen below room temperature to form a viscous thick liquid of low vapor pressure, together with traces of volatile solids which are still being studied.

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[40] Campbell, D. H. Doctoral Dissertation, Univ. of Mich. 1953.

In one case hydrogen was evolved at low temperature and the principal product was a volatile liquid which disproportionated to give B_2H_6 and a solid product containing boron and nitrogen in a 1-to-1 ratio. This run has not been reproducible up to the present time. The system is still being studied in an effort to define all experimental variables more precisely.

VI. THE PROPERTIES OF THE SUBSTITUTED HYDROXYLAMINES - THE VAPOR PRESSURE AND MELTING POINT OF METHOXYAMINE AND THE pK_B VALUES FOR HYDROXYLAMINE, METHOXYAMINE, AND N-METHYL HYDROXYLAMINE

The above physical and chemical properties of the substituted hydroxylamines were not found in the literature. Since these data were pertinent to the present research, the values have been determined and are herewith reported.

A. THE VAPOR PRESSURE AND MELTING POINT OF METHOXYAMINE

1. Experimental

a. The Vapor Pressure. A sample of methoxyamine was prepared as described earlier and distilled into the vacuum line, where final purification was effected. A three-trap procedure was employed. The first trap was held at -63°C, the second trap was held at -78°C, and the third was cooled with liquid nitrogen (-196°C). The methoxyamine that collected in the second trap was used.

As a test for purity of the sample, two small portions were distilled from it at -63°C, and vapor-pressure measurements at 0°C were made. The values obtained from three measurements on each of these small portions were:

	Sample 1	Sample 2
	85.15 mm	85.30 mm
	85.35 mm	85.20 mm
	85.20 mm	85.20 mm
Ave.	85.23 mm	85.23 mm

The constancy of vapor pressure during distillation was taken as an indication of purity.

A sample of the pure compound was then distilled into the evacuated bulb of an apparatus similar to that shown in Fig. 15 except that the bulb B had a volume of only 2 cc. The U tube A served as a differential manometer and the pressure was read by means of a precision cathetometer. The temperature of the liquid in the bulb was obtained by immersing the bulb in a suitable bulb contained in a Dewar. Temperature in the range 0 to 20°C was read using a large thermometer previously calibrated by the Bureau of Standards. Lower temperatures were obtained using pure two-phase slush baths of chloroform (-63.5°C), chlorobenzene (-45.3°C), carbon tetrachloride (-22.8°C), and water. A calibrated thermocouple attached to a Leeds and Northrup Portable Potentiometer was used to determine intermediate temperatures of a one-phase bath consisting of a mixture of 1 liter of commercial-grade methyl pentanes and 20 ml of 99 mole % isopentane. The vapor pressure of the methoxyamine is given by the expression

$$\log_{10} P = \frac{-2023.14}{T} + 9.7375 - 5.4714 \times 10^{-6}T^2 ,$$

where P = vapor pressure in mm and
T = the absolute temperature.

Experimental values and values calculated from the above relationship are compared in Table XII.

b. Melting Point of Methoxyamine. The melting point of the purified methoxyamine sample was determined on the vacuum line using an apparatus similar to that described by Stock[41]. A value of -86.4 ± 0.5°C was obtained on four trials with the same sample.

2. Discussion of the Vapor-Pressure Data

From the vapor-pressure curve for o-methyl hydroxylamine the heat of vaporization of the free liquid base can be estimated. Since the apparatus used in these experiments was not well adapted to use above room temperature, the value of Trouton's constant obtained from the extrapolated curve is of limited accuracy. Further the Hildebrand-Trouton constant [i.e., the entropy of vaporization at a constant vapor phase concentration of 0.00507 mole per liter - Hildebrand, J. H., J. Am. Chem. Soc. 37, 970 (1915)] is of more fundamental significance. The Hildebrand-Trouton constant for a group of amines is compared with the value of $\Delta H_{vap}/T$ at 200 mm pressure for the same series in Table XIII. It will be noticed that all of the amines except

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[41] Stock, A., Ber. 50, 156 (1917).

TABLE XII

THE VAPOR PRESSURE OF METHOXYAMINE

t, C°	T, K°	Obs. Pressure, mm	Pressure* Calculated, mm	ΔP, Calc-Obs., mm
-63.5	209.66	0.75	0.70	- .05
-52.8	220.36	1.75	1.95	+ .2
-45.3	227.86	3.55	3.75	+ .2
-28.0	245.16	14.05	14.34	+ .3
-22.8	250.36	20.50	20.59	+ .1
-20.4	252.76	24.2	24.19	.0
-17.7	255.66	29.0	29.09	+ .1
-13.3	259.86	38.2	38.2	.0
-10.35	262.81	45.6	45.9	+ .3
- 6.8	266.36	56.4	56.7	+ .3
0	273.16	83.9	83.7	- .2
6.4	279.56	118.6	118.3	- .3
10.80	283.96	148.5	148.5	.0
12.58	285.74	162.9	162.3	- .6
14.40	287.56	177.3	177.6	+ .3
16.00	289.16	192.1	192.0	-0.1
17.70	290.86	208.4	208.4	.0
19.08	292.24	222.8	222.5	-0.3
20.05	293.21	233.6	232.9	-0.7
21.10	294.26	243.9	244.5	+0.6

* Calculated values obtained from empirical equation:

$$\mathrm{Log}_{16}\, P = \frac{-2023.14}{T} + 9.7375 - 5.4714 \times 10^{-6}\, T^2$$

TABLE XIII

A COMPARISON OF THE "TROUTON CONSTANT" AT A PRESSURE OF 200 MM WITH THE HILDEBRAND-TROUTON CONSTANT AT A UNIFORM VAPOR CONCENTRATION OF .00507 MOLE/LITER FOR A SERIES OF AMINES

	Trouton Constant			Hildebrand-Trouton Constant				
Compound	$\Delta H_{vap.}$ 200 mm [cal/mole]	T° A	$\frac{\Delta H_{vap.}}{T}$	Temp for vap. conc. of .00507 mole/liter	P for vap. conc. (mm)	$\Delta H_{vap.}$ at this temp cal/mole	$\frac{\Delta H}{T}$	Ref.
NH_3	5,860	216	27.1	200	63	6,041	30.2	a
CH_3NH_2	6,770	240	28.2	224	72	6,860	30.5	b
$(CH_3)_2NH$	7,100	252	28.2	236	76	7,330	31.1	c
$(CH_3)_3N$	6,090	245	24.8	227	72	6,150	27.0	c
N_2H_4	10,230	351	29.1	337	107	10,280	30.5	d
NH_2OH	16,600	361	46.0	352	106	17,266	49.0	a
NH_2OCH_3	8,400	290	29.0	273	84	8,483	31.0	e
H_2O	10,070	340	29.6	325	105	10,202	31.3	a
CCl_4(Ref.)	7,680	311	24.7	294	48	7,938	27.0	a

a Stull, D. R., Ind. Eng. Chem. 39, 540 (1947).
b Aston, et. al., J. Am. Chem. Soc. 59, 1743 (1937).
c Jordan, T. E., "Vapor Pressures of Orig. Compds." Interscience Publishers, New York (1954) p 176 and 178.
d Audrieth, L. F., and Ogg, B. A., "Hydrazine" John Wiley and Sons, New York p 74 (1951).
e This investigation.

the trimethyl derivatives show a comparable degree of association in the liqui phase prior to vaporization, a fact which may be ascribed to hydrogen bonding. This is indicated by the Hildebrand-Trouton constant but not by the "Trouton constant" at a constant pressure of 200 mm.

The literature value of 49.0 for the Hildebrand-Trouton constant of hydroxylamine deserves further consideration. In comparison to the corresponding constants for the closely related water, hydrazine ammonia, and methoxyamine, this value is unusually high. In view of the instability of the free hydroxylamine above 10°C, it is almost certain that the high value indicates some decomposition of the sample during the vapor pressure measurement, a fact which would complicate any efforts to refine the vapor pressure curve.

B. THE BASIC STRENGTH OF HYDROXYLAMINE AND ITS METHYL DERIVATIVES

The pK_B values for NH_2OH, NH_2OCH_3, and CH_3NHOH have been determined.

1. Experimental

a. Hydroxylamine. Commercial reagent-grade hydroxylamine was recrystallized once from water, dried at 110°C and then converted to the free base by reaction with sodium butoxide in cold butanol[42]. The free base was stored at -10°C under anhydrous butanol before use. Crystals of the free base were filtered from the alcohol, washed with cold ether, transferred to a closed titration vessel, and titrated with standard HCl at 25°C. The pH was followed by means of a carefully standardized Beckman Model G pH meter with a combination glass-calomel electrode system. The reverse titration of recrystallized hydroxylamine hydrochloride salt with NaOH was also conducted using a 0.0023 M solution of hydroxylamine hydrochloride and 0.0497 M NaOH. Separate titrations were also made in which the salt concentration was systematically varied by addition of KCl. Apparent pK_a values for the hydroxylammonium ions versus total salt concentration are shown in Table XIV. Extrapolation of the data to infinite dilution gives a pK_B value of 8.03 (see Fig. 17) for NH_2OH.

The glass electrode was used because of its rapidity and because of errors arising from the reducing action of hydroxylamine on noble-metal salts of the usual reference electrode[43]. In order to estimate the magnitude of the systematic errors arising from the glass electrode system, the

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[42] Booth, H. S., Inorganic Syntheses, Vol. I McGraw-Hill Book Co. Inc., New York, 1939, p. 87.

[43] Yost, D. M., and Russell, H., Jr., Systematic Inorganic Chemistry, Prentice Hall, Inc. New York, 1944.

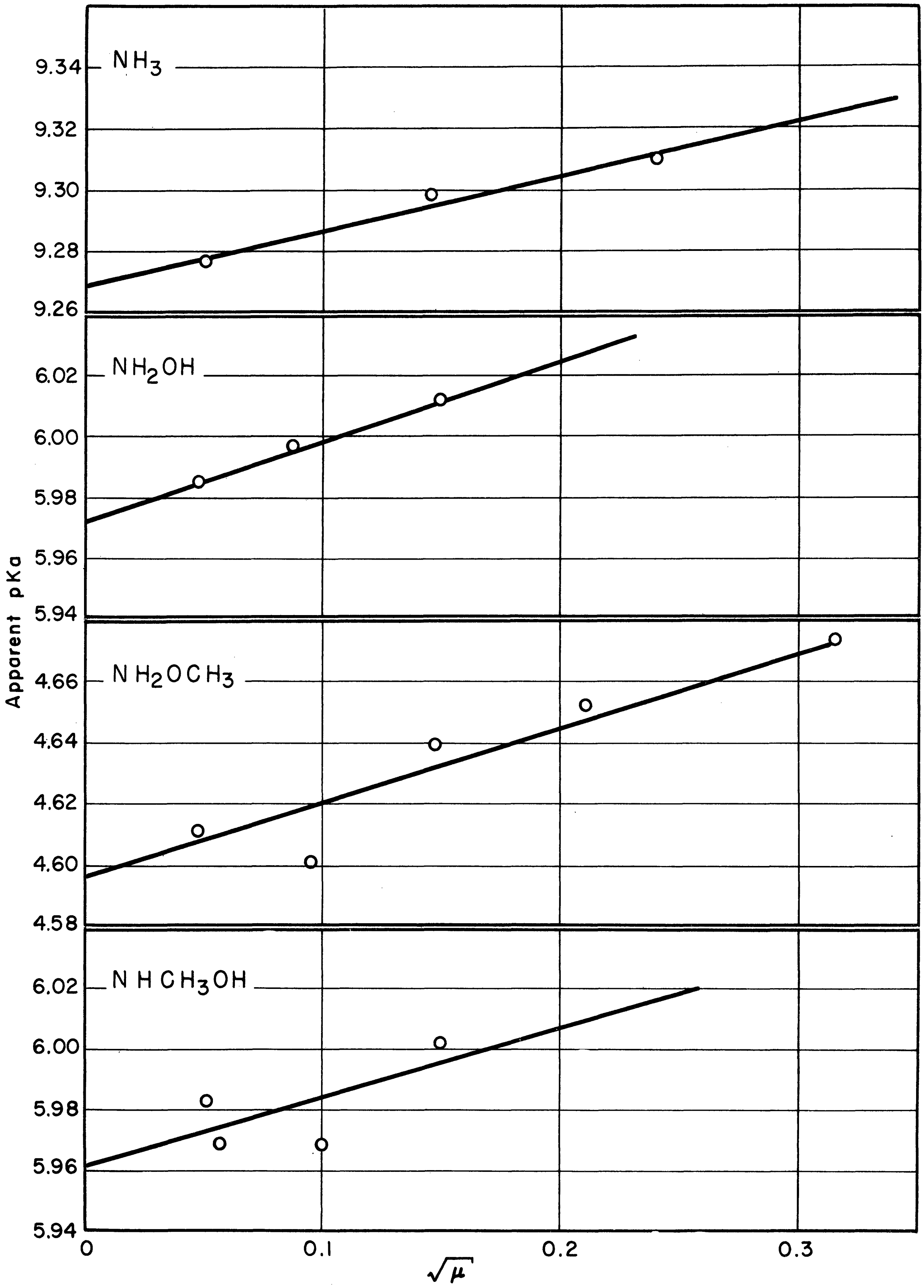

Fig. 17. pK_a Values for Several Ammonium-Type Salts as a Function of Ionic Strength

constants for NH_4OH were determined by an identical procedure. Data shown in Table XIV give a pK_B of 4.73 for NH_4OH. The precision value of Bates and Pinching[44] is 4.7551, indicating a systematic error of approximately 0.02 pK unit in the measurements on NH_3.

b. o-Methyl Hydroxylamine or Methoxyamine. In a one-piece micro distillation apparatus were placed 2 grams of o-methyl hydroxylamine hydrochloride from Eastman Kodak along with 10 cc of 50% KOH solution. The free base was distilled from the system and the sample boiling at 45-50°C was collected in 2 cc of concentrated HCl in the receiving flask. The flask was cooled in an ice bath and the excess solvent was removed from the crystals of o-methylhydroxylamine hydrochloride. The crystals were dried at 105°C for 2 hours and then transferred to a dessicator over P_2O_5. A 0.0022 M stock solution of o-methylhydroxylamine hydrochloride was prepared and 100-cc aliquots of this solution were titrated with 0.0497 M NaOH, which was discharged from a 5-cc burette into a vessel thermostated at 25± .05°C. The pK_a values were calculated over the middle third of the titration curve, as was done for the hydroxylamine.

As before, the concentration of salt in the system was increased by addition of KCl, then the pK_a values were plotted against total salt concentration and the result extrapolated to infinite dilution (see Fig. 17). The pK_B values were obtained from the pK_a values. A pK_B value of 9.39 ± .03 was obtained in this manner for CH_3ONH_2.

c. N-methyl Hydroxylamine. A sample of the N-methyl hydroxylamine hycrochloride salt obtained from Professor P. A. S. Smith was purified by recrystallization from water. Since the long white needles melt below 110°C the moist crystals were dried above P_2O_5 in a vacuum dessicator. To obtain positive identification of the sample, an aliquot of the crystals was analyzed. Results show:

	Obs.	Calc. for H MeNOH·HCl
% C	14.62	14.38
% H	7.21	7.20

An additional check on the authenticity of the sample was obtained by weighing a sample (21.61 mg) of the dry crystals out on a microbalance and titrating this weighed sample in 100 cc of CO_2-free water with standard 0.04970 M NaOH. Using the molecular weight of N-methyl hydroxylamine hydrochloride and the weight of the sample one predicts 0.259 millimoles. The titration also indicates 0.259 millimoles. The pK_B values were calculated from the above and other titrations in a manner exactly analogous to the procedure used for the o-methyl hydroxylamine (see Fig. 17). A pK_B value of 8.03 ± .03 was obtained which is identical within the limits of experimental error, to the value obtained for the unsubstituted hydroxylamine.

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[44] Bates, R. G., and Pinching, G. D., Res. Paper 1982, J. Research Natl. Bur. Standards, 42, 419-30 (1949).

TABLE XIV

pK_a VALUES FOR NH_3, NH_2OH, NH_2OCH_3 AND NCH_3HOH AT DIFFERENT TOTAL SALT CONCENTRATIONS

Lowest salt concentrations due only to hydrochloride salt of base; higher values obtained by adding KCl as inert electrolyte. T = 25°C; pH meter checked against K acid phthalate buffer and borax buffer

Molarity of Salt or Ionic Strength for MX	Average Apparent pK_a	$\sqrt{\mu}$	Extrapolated Value of pK_B at Infinite Dilution	Molarity of Salt or Ionic Strength for MX	Average Apparent pK_a	$\sqrt{\mu}$	Extrapolated Value of pK_B at Infinite Dilution
	NH_3				NH_2OH		
.058	9.310	.241		.0226	6.012	.150	
.0213	9.298	.146		.0075	5.997	.087	
.0025	9.277	.050		.0023	5.985	.048	
Extrapolate 0.000	9.27	0.00	4.73	Extrapolate 0.00	5.97	0.00	8.03
	NH_2OCH_3				$NHCH_3OH$		
.1000	4.674	.316		.0226	6.002	.150	
.044	4.652	.210		.0100	5.968	.100	
.022	4.639	.148		.00337	5.969	.058	
.00905	4.601	.095		.0026	5.983	.051	
.00216	4.611	.047		Extrapolate 0.000	5.96	0.00	8.04
Extrapolate 0.000	4.60	0.00	9.40				

2. Discussion of the Basic Strength of Hydroxylamine and its Methyl Derivatives

The basic ionization constant usually given for hydroxylamine[45,46] is the early value of Winkelbleck[47], 6.6 x 10^{-9}, corresponding to a pK_B of 8.18. A second pK_B of 7.38 has been reported in more recent years[48]. Winkelbleck's early value was based on conductivity measurements and was of comparatively low precision. The value 8.02 ± .03 obtained in this investigation represents a refinement of the earlier value. The pK_B of 7.38 appears to be erroneous.

If the inductive effects of an alkyl group, usually assumed to be active in the methylamines, were active in the alkyl derivatives of hydroxylamine, it would be expected that the N-methyl hydroxylamine would be significantly stronger as a base than the hydroxylamine. It is, then, rather surprising that the N-methyl derivative and the unsubstituted hydroxylamine have the same pK_B within the precision of the measurements. This situation implies that the electron-donor powers of the methyl group are trivial in comparison to the electron-withdrawing powers of the hydroxyl group.

On the basis of an inductive effect alone it would also be expected that the o-methyl hydroxylamine would be slightly stronger than hydroxylamine. The pK_B value for the o-methyl derivative of 9.39 ± .03 indicates that the reverse is true and confirms implications of earlier chemical data that the o-substituted hydroxylamine derivatives are, in general, weaker bases than hydroxylamine.

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[45] Yost, D. M., and Russell, H. R., Systematic Inorganic Chemistry, Prentice-Hall, Inc., New York, 1944, p 98.

[46] Latimer, W., Oxidation Potentials, Prentice Hall, Inc., New York, 1938, p 89.

[47] Winkelbleck, K., Z. Phys. Chem., 36, 574, (1901)

[48] Ishikawa, and Aoki , Bull. Inst. Phys. and Chem. Research 19, 136 (1940).

VII. HYDRIDES AS REDUCING AGENTS FOR THE REDUCTION OF THE CHLOROPHOSPHINES; ALUMINUM HYDRIDE AS A LEWIS ACID

A. BACKGROUND

In connection with certain physical and chemical investigations in this laboratory on the phosphorus bases, it became necessary to synthesize several of the alkyl phosphines. Since existing methods of synthesis for these compounds are rather poor at best, it seemed worth while to investigate new approaches such as the reduction of the known chlorophosphines with selected hydrides. The use of reagents such as $LiAlH_4$ and the possible role of AlH_3 as a Lewis acid in the presence of phosphines suggested that the work could be properly included in the current hydride program.

Aside from some early investigations of Thenard, the first worker in the field of phosphine synthesis was A. W. van Hofmann[49]. He used the reaction between PCl_3 and dialkyl zinc as a route to the trialkyl phosphines and also used the sealed-tube reaction between phosphonium iodide and alkyl iodides or alcohols in the presence of ZnO as a route to the primary and secondary phosphines, these bases supposedly forming a hydroiodide double salt with the zinc iodide. The primary phosphine is liberated by treatment with water, while alkali is necessary to break up the secondary phosphonium iodide - zinc iodide double salt. Davidson and Brown[50] applied high-vacuum techniques to the isolation of the primary and secondary phosphines. Because of very low yields the inconvenience and hazard of sealed-tube reactions, and theinconvenience associated with the production of large quantities of phosphonium iodide, the Hofmann procedure is rapidly becoming obsolete. The use of the Grignard reagent and PCl_3 now provides a convenient route to the trialkyl phosphines. However, it has not been possible to add only one or two alkyl groups to PCl_3 by means of the Grignard reagent[51].

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[49] (a) Cahouns, A., and Hofmann, A. W., Ann. 104, 1 (1857).

(b) Hofmann, A. W., Ber. 4, 205, 372, 430, 605 (1871) 6, 292 (1873).

[50] Davidson, N., and Brown, H. C., J. Am. Chem. Soc. 64, 718 (1942)

[51] Yoke, J. T., III, Ph.D. Thesis, Univ. of Mich., 1953, p 15

The replacement of one hydrogen in phosphine by an active alkali metal such as sodium or potassium gives a dihydrogen phosphide which will react with alkyl halides to produce the corresponding primary phosphine. The monoalkali dihydrogen phosphides are made by the action of phosphine on a solution of the alkali metal in liquid ammonia. The above technique was applied in this laboratory to the synthesis of methyl phosphine, but the procedure was somewhat less successful when applied to the ethyl phosphine.

An easy route to PCl_2Et by means of the reaction between PCl_3 and commercially available $Pb(Et)_4$[52] suggested that reduction of $PEtCl_2$ with appropriate hydrides might give a convenient synthesis of $PEtH_2$. The reaction between PCl_3 and $LiAlH_4$ to give up to 70% yields of PH_3 had already been carried out in this laboratory.

B. EXPERIMENTAL

1. Reagents

The Mg, C_2H_5Br, PCl_3, and $AlCl_3$ were analytical-grade reagents which were used without further purification. $LiAlH_4$ and LiH were the commercial products obtained from Metal Hydrides, Inc. Tetrahydrofuran, obtained from Eastman Kodak, was distilled from mineral oil through a Snyder column, dried over Na, and refractionated; b.p. = 63.0-63.3°C uncorrected. Tetraethyl lead, practical grade from Eastman Kodak, was distilled under reduced pressure, b.p. 64-70°C. Tetra n-propyl lead, a research sample kindly given us by the Ethyl Corporation, was used without further purification.

2. Preparation of Ethyldichlorophosphine

C_2H_5MgBr was prepared from 12.1 gm (0.5 mole) of Mg and 54.5 mg, (0.5 mole) of C_2H_5Br in 100 cc ether. This was added dropwise in a nitrogen atmosphere to 68.7 gm, (0.5 mole) of PCl_3 in 100 cc of ether at 0°C with stirring. No $C_2H_5P(OH)_2$ (or $C_2H_5PO(OH)_2$) could be isolated by ether extraction of the hydrolyzed reaction mixture; hence it was concluded that no $C_2H_5PCl_2$ was formed.

Next 50. gm (0.15 mole) of $Pb(C_2H_5)_4$ and 68.7 gm, (0.5 mole) of PCl_3 were refluxed for 30 hours in a nitrogen atmosphere. It was found desirable not to pass a stream of N_2 through the apparatus during the reflux period,

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[52] Kharasch, M. S., Jensen, E. V., and Weinhouse, S., J. Org. Chem. 14 429 (1949).

contrary to the directions of Kharasch, et al[52]. After 30 hours the volatile material was distilled in N_2 and fractionated through a Widmer Column; much PCl_3 was recovered, indicating that the reaction was not complete at this time under the conditions used, although Kharasch[52] reported that this reaction went nearly to completion under these conditions. $C_2H_5PCl_2$, b.p. 111-112°C uncorrected, density 1.19 gm/cc was collected; yield was 26.8 gm or 45.5%.

3. Preparation of n-Propyldichlorophosphine

In the same way 9.5 gm (0.025 mole) of $(n\text{-}C_3H_7)_4Pb$ and 6.55 cc (0.075 mole) of PCl_3 were refluxed in a nitrogen atmosphere for 36 hours, and the volatile material fractionated in a high-vacuum line. Yield of $n\text{-}C_3H_7P\ Cl_2$ was 6.6 gn, 60.9%.

4. Reduction of PCl_3 with $LiAlH_4$

In a flask fitted with a dropping funnel and a glass-helices-packed column were placed 1.0 gm (0.026 mole) of $LiAlH_4$ and 75 cc of ether. This column led to a train consisting of a similarly packed U trap, then a U trap with two stopcocks, and an exit tube dipping under mercury. A stream of nitrogen was passed through the apparatus. Slush baths at -75°C were placed around the flask, the packed column, and the packed U trap, and the final U trap was immersed in liquid nitrogen. A solution of 1.06 cc (0.0122 mole) of PCl_3 in 25 cc of ether was added dropwise with magnetic stirring. After addition was complete, the cooling bath was removed from the reaction flask. The highly volatile PH_3 formed, passed through the train, and condensed in the final trap, while most of the ether was separated by the packed column and U trap. The stopcocks on the final U trap were then closed, it was attached to the vacuum line by a standard taper joint, and the PH_3 was distilled into the line and fractionated at -126°C (methylcyclohexane bath) until its vapor pressure corresponded to the literature values for PH_3. Yields ranged from 55 to 70% of theory. M. W.: found, 35; theory, 34.

5. Reduction of PCl_3 by LiH

Three runs were made using the same apparatus as above but without the packed U trap in the train. The packed column was cooled with dry ice and the U trap with liquid nitrogen. In two runs the reaction flask was not cooled. In one of these a trace of $LiAlH_4$ was added as a catalyst. In the third run the reaction flask was cooled to about -60°C. The results of all three runs were substantially the same.

A solution of 1.15 cc (0.0132 mole) of PCl_3 in 20 cc of tetrahydrofuran was added dropwise to 0.315 gm (0.0396 mole) of 200-mesh LiH suspended in 75 cc of tetrahydrofuran under a nitrogen stream. Vigorous agitation of the suspension was achieved by means of a magnetic stirrer. The PH_3 formed condensed in the U trap and was transferred to the vacuum line and purified, as above. Yield was 0.000744 mole, 5.6% of theory based on $3LiH + PCl_3 \rightarrow PH_3 + 3LiCl$. A large amount of red phosphorus was formed in the reaction flask; this was filtered on a ground-glass crucible, dried, and weighed. Yield was 0.293 gm, 71.6% of theory based on $3LiH + PCl_3 \rightarrow P + 3/2H_2 + 3LiCl$.

6. Reduction of Ethyldichlorophosphine with $LiAlH_4$

A special apparatus was constructed (Fig. 18) and was attached to the vacuum line. It included a Toëpler pump and gas burette to measure the noncondensable gas, which (it had been observed in preliminary runs) is given off in this reaction.

Ethyldichlorophosphine, 4.695 gm (0.0358 mole), was transferred to the vacuum line and distilled into the reaction flask along with 25 cc of tetrahydrofuran which had been distilled in vacuo from $LiAlH_4$. A chloroform slush bath (-63°C) was placed in the cold finger and the packed column was cooled with powdered dry ice. The reaction flask was kept at a low temperature by the refluxing of the solvent from the cold finger in the evacuated system.

$LiAlH_4$, 7.0 gm (very large excess), was stirred with 75 cc of tetrahydrofuran. Since all the (impure) hydride does not dissolve, the mixture was centrifuged and the supernatent liquid transferred with a hypodermic syringe to the dropping funnel. The solution was then added dropwise with magnetic stirring to the reaction flask. As the pressure built up, the stopcock leading to the Toëpler pump was occasionally opened and the noncondensable gas pumped into the gas burette. The packed U trap before the Toëpler pump was immersed in liquid nitrogen. After the addition was complete, 0.0370 mole of noncondensable gas had been formed; it was shown to be hydrogen by a molecular-weight determination (M. W. found, 2.2). Ratio $H_2/C_2H_5PCl_2 = 1.03$.

Only a very small amount of $C_2H_5PH_2$ could be obtained at this point by fractional vacuum distillation from the reaction flask. However, when the solvent was all distilled from the reaction flask and the nonvolatile solid reaction residue hydrolyzed with a 20% solution of water in tetraethylene glycol diethyl ether (used because of its very low volatility), much more $C_2H_5PH_2$ was formed and could be purified by fractional vacuum distillation. Yield was 0.0173 mole, 48.8% of theory. M. W.: found, 62.5, theory, 62.1.

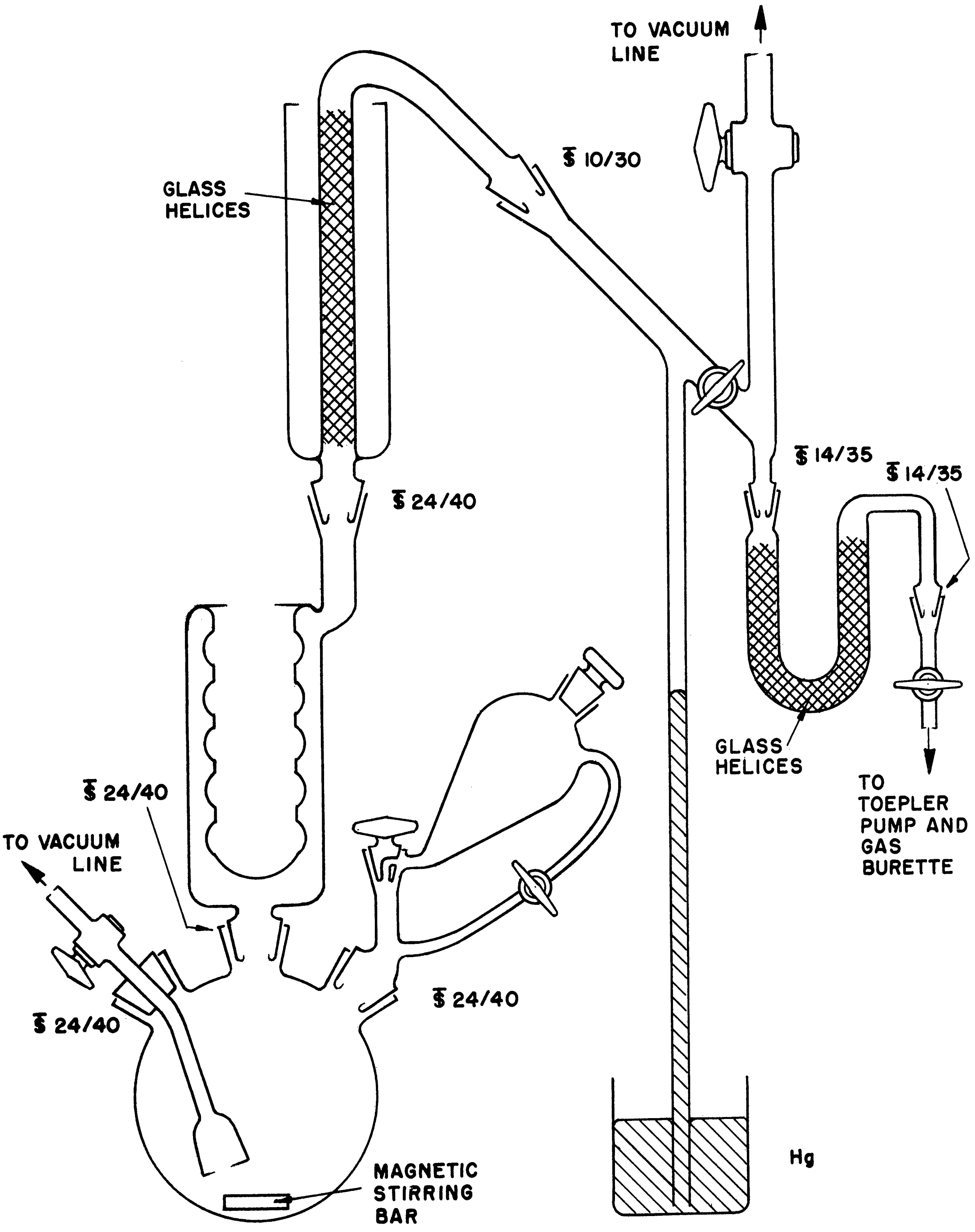

Fig. 18. Apparatus for Reduction of Phosphorous Hallides with Lithium Aluminum Hydride

A small amount of PH_3 (identified by vapor pressure and molecular weight) was also formed. This is attributed to the disproportionation of ethylphosphine discussed above. Considerable amounts of tetrahydrofuran were also liberated from the nonvolatile reaction residue on hydrolysis.

7. Aluminum Hydride and Ethylphosphine

A solution of AlH_3 in ether was prepared following the method of Wiberg, Graf, and Uson[53], by mixing standard solutions of $AlCl_3$ and $LiAlH_4$ in the stoiciometric amounts, in a special apparatus (Fig. 18). The solution was immediately frozen in liquid nitrogen, an excess of $C_2H_5PH_2$ was distilled into the flask, and the liquid-nitrogen bath was removed. The reaction flask was kept at a low temperature by the refluxing of the solvent from the dry-ice-cooled cold finger in the evacuated system. Later it was allowed to warm up to room temperature. There was no formation of a noncondensable gas and the $C_2H_5PH_2$ was subsequently recovered, indicating that there was no reaction between the hydrogen bound to phosphorus in $C_2H_5PH_2$ and the hydrogen in AlH_3. Moreover, no stable addition compound was formed under the conditions of this experiment.

C. DISCUSSION

The reduction of PCl_3 with $LiAlH_4$ at -60°C in the presence of diethyl ether produces good yields of PH_3 which can be readily distilled from the reaction system. It is interesting to note that this vigorous reaction will not occur, even at room temperature, in the absence of a solvent. Ethyldichlorophosphine, like PCl_3, can also be reduced by $LiAlH_4$ in ether solution; but the resulting $C_2H_5PH_2$, unlike PH_3, remains in the reaction vessel at the temperature of the reduction process. $LiAlH_4$ reacts with $C_2H_5PH_2$, splitting out hydrogen to yield the new solid component $Li\,Al(C_2H_5PH)_4$. Ethyl phosphine can be obtained by hydrolysis of the solid. Since liquid ethylphosphine undergoes spontaneous disproportionation to yield triethylphosphine and phosphine, the above solid offers a convenient way to store and handle the ethylphosphine.

The disporportionation of liquid primary ethyl phosphine according to the equation:

$$3RPH_2 \longrightarrow 2PH_3 + PR_3$$

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[53] Wiberg, E., Graf, H., and Uson, R., Z. anorg. u. allgem, Chem. 272, 221 (1953).

was found to be catalyzed by ethyl iodide, presumably according to a mechanism such as:

$$RPH_2 + RI \rightarrow R_2PH_2I$$

$$R_2PH_2I + RI \rightarrow R_3PHI + HI$$

$$R_3PHI \rightarrow R_3P + HI$$

$$R_2PH_2I + HI \rightarrow 2RI + PH_3.$$

The disproportionation of a highly purified sample is slow, but occurs even at -78°C and even when no alkyl iodide has been used in the synthesis. Thus it was observed even when $C_2H_5PH_2$ was prepared from $C_2H_5PCl_2$ and $LiAlH_4$. When alkyl iodide has been used in the synthesis, as in the case of the reaction between ethyl iodide and sodium dihydrogen phosphide, the disproportionation is so important that the yield is largely dependent on the time required for the isolation and purification of the product. When the volatile distillate from the reaction (impure ethyl phosphine) was allowed to stand in a trap at 0°C, the vapor pressure of the system rose steadily due to evolution of phosphines. As the volatile material was transferred from trap to trap it left a nonvolatile white solid behind. This white solid reacted vigorously with water, giving off the foul smell characteristic of alkylphosphines. On treatment of this solid with silver iodide - potassium iodide solution, the silver iodide complex of triethylphosphine was obtained, thus confirming the formation of the tertiary phosphine. The disproportionation of methylphosphine, prepared from $NaPH_2$ and CH_3I, was also observed.

The vapor pressure of $C_2H_5PH_2$, not previously reported, is approximated by the equation $\log P = -1381/T + 7.61$. Experimental values are tabulated below:

TABLE XV

T, °C	P, mm	T, °C	P, mm
-83.6	2.3	-22.9	130.9
-63.5	10.4	0.0	363.4
-45.2	35.7	16.9	690.2
-36	62.9	20	760

It was significant that aluminum hydride frozen out of diethyl ether would not add to ethylphosphine at room temperature, yet $AlCl_3$ formed the addition compound readily. Aluminum hydride as an adduct is being explored in more detail.