

ENGINEERING RESEARCH INSTITUTE
UNIVERSITY OF MICHIGAN
ANN ARBOR

FINAL REPORT

CHEMISTRY OF BORON HYDRIDES AND RELATED HYDRIDES

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Project M966

WRIGHT AIR DEVELOPMENT CENTER, U. S. AIR FORCE
CONTRACT AF 33(616)-8, E. O. R-464 Br-1

December, 1952

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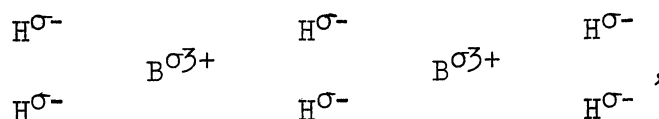
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FINAL REPORT

CHEMISTRY OF BORON HYDRIDES AND RELATED HYDRIDES

I. THE PROPOSED INVESTIGATION

The principal aims of the investigation covered by this report were: (1) an examination of several chemical reactions involving diborane and its derivatives, (2) the isolation and characterization of new or unusual products which might result from these chemical reactions, and (3) a discussion of the results of the above investigations in terms of the theories of the boron hydrides. In the latter connection, reactions suggested by models which attribute some negative or hydridic character to the diborane hydrogens were to receive special attention. The model to be tested can best be represented as a modification of a structure first suggested by Van Arkel and De Boer.



where σ is an arbitrary parameter between 0 and 1. The larger the value of σ , the more hydridic the diborane hydrogens would be. No effort has been made to establish or discuss molecular orbitals or other theoretical treatments for diborane, since these have been abundantly discussed in the literature. The primary purpose of this investigation was to check experimentally several reactions suggested by the assumption that diborane hydrogens may behave chemically in a manner somewhat analogous to the hydrogens of the typical alkali metal hydrides. The work has proceeded along several distinct lines, each of which is treated separately in the following report.

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

A. Background

Stock and Pohland¹ found that diborane will react with an excess of solid ammonia at -120°C . If the excess of ammonia is removed by sublimation at -80°C , a solid product of the formula $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$ results. The structural formula to be assigned to this compound has long been the subject of controversy. Stock and Wiberg² assumed that two of the hydrogens of diborane are acidic in character; this assumption leads to representation of the diammoniate as an ammonium salt, $[(\text{NH}_4)_2 \text{B}_2\text{H}_4]$.

Schlesinger and Burg³ questioned the formulation of Stock and Wiberg and proposed instead the formula $\text{NH}_4[\text{H}_3\text{B NH}_2\text{BH}_3]$. 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 $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$ in liquid ammonia at -77°C . Additional evidence bearing upon the question of acid hydrogens in diborane was presented by Burg.⁴ It has been shown that when the Brønsted-Lowry acid NH_4Cl is dissolved in liquid ammonia, a rapid interchange of the protons between the acid and the solvent molecule occurs.⁵ Burg conducted experiments with ND_3 and $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$ 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 experiments are convincing. It appeared, however, that an independent and more drastic method for evaluating acidic character would yield interesting results. The reaction between sodium and the diammoniate of diborane was selected as such a reaction, and deuterium has been used as a tracer to determine whether boron-hydrogen bonds, nitrogen-hydrogen bonds, or both are broken when sodium reacts with the diammoniate in liquid ammonia.

1 Stock, A., and Pohland, E., Ber. 58, 657 (1925).

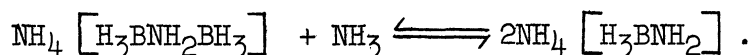
2 Stock, A., Hydrides of Boron and Silicon Cornell University Press, Ithaca, N. Y., 1933, p. 159.

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

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

5 Nyman, C. J., SiChang Fung, and Dodger, H. W., J. Am. Chem. Soc. 72, 1033 (1950).

The stoichiometry of this reaction also presents interesting points for investigation, since data of Burg³ have shown that the liberation of one hydrogen per $B_2H_6 \cdot 2NH_3$ can be expected only if the temperature of the system has not been allowed to rise above $-77^\circ C$. If at any time the temperature of the system has been allowed to rise to $-40^\circ C$, about 1.25 hydrogen atoms are liberated per molecule of B_2H_6 , even though the reaction itself is conducted at $-77^\circ C$. This fact has been interpreted in terms of the equilibrium



The recombination of $NH_4 [H_3BNH_2]$ to give the original $NH_4 [H_3BNH_2BH_3]$ would be indicated as a slow process by the fact that heating seems to have a more or less long-term effect on the stoichiometry of the reaction. The equilibrium shift proposed for higher temperatures should also be visible in the apparent molecular weight values obtained for the diammoniate in liquid ammonia near its boiling point. Rathjens and Pitzer⁶ observed that the molecular weight of the diammoniate corresponds to the formula $B_2H_6 \cdot 2NH_3$ at the freezing point of ammonia; however, the only data available near the boiling point of ammonia are the less precise tensiometric measurements of Stock,² which indicated no significant dissociation into $2NH_4 [BH_3NH_2]$. Such an observation is not consistent with the equilibrium system proposed by Burg and Schlesinger.

B. Statement of the Problem

The reactions which were studied are:

- 1) $B_2H_6 \cdot 2ND_3 + Na \xrightarrow[NH_3]{liq} H_2, D_2, \text{ or } HD + \text{solid residue.}$
- 2) $B_2D_6 \cdot 2NH_3 + Na \xrightarrow[NH_3]{liq} H_2, D_2, \text{ or } HD + \text{solid residue.}$
- 3) $B_2H_6 \cdot 2NH_3 + Na \xrightarrow[NH_3]{liq} H_2 + \text{solid residue.}$

The noncondensable gas evolved in each reaction was analyzed by the mass spectrometer to determine its isotopic composition. The data of Burg, the model of Schlesinger and Burg, and the polarized ionic model for diborane would suggest that Reaction 1 should liberate only D_2 , while Reactions 2 and 3 should liberate only H_2 . The results obtained up to the present time are not wholly consistent with these predictions, although the possibility of error in the contradictory case has not been entirely eliminated. A very careful reinvestigation of the problem is being conducted in order to obtain an unequivocal answer.

⁶ Rathjens, G. W., Jr., and Pitzer, K. S. J. Am. Chem. Soc. 71, 2783 (1949).

C. Experimental1. Materials

a. Magnesium Nitride. High-purity Mg_3N_2 was prepared by the reaction between highest-purity Dow magnesium and prepurified nitrogen. A special stainless-steel electrically heated tubular furnace served as a reaction vessel. The Mg_3N_2 was never exposed to moist air before use.

b. Deuteroammonia. High-purity ND_3 was prepared by allowing pure D_2O to distill onto the pure Mg_3N_2 . The ND_3 produced had a vapor pressure coincident with that of 99% deuterated ND_3 . When the ND_3 was allowed to react with metallic potassium in the presence of catalytic Fe_2O_3 , the resulting hydrogen gave a mass spectroscopic analysis corresponding to 90.40% D_2 , 7.93% HD, and 1.70% H_2 for a total of 94.4% deuterium.⁷

c. Ammonia. Ordinary tank NH_3 was distilled from sodium metal in the vacuum line before use.

d. Diborane. B_2H_6 was prepared by the reaction between BF_3 etherate and $LiAlH_4$ using conventional techniques. Satisfactory yields were obtained only when the impure brown commercial etherate was distilled before use. The vapor pressure of the B_2H_6 used was 226 mm at the temperature of a CS_2 slush bath, $-111.6^\circ C$.

e. Deuterodiborane. B_2D_6 was prepared by the reaction between BF_3 etherate and $LiAlD_4$ which was supplied by Metal Hydrides Corporation. The vapor pressures of the product were:

<u>Temp, °C</u>	<u>Pressure, mm Hg</u>
-127.5	72.8
-118	137.2
-112	246

The unexpected fact that B_2D_6 has a higher vapor pressure than B_2H_6 has been confirmed by both Burg⁸ and Schlesinger (private communication). Burg reports a value of 238 mm at $-112^\circ C$ for 98% B_2D_6 .

7 This value from the potassium reaction is probably lower than the actual percentage of D in the ND_3 . Since the sample was not exhaustively reacted with potassium, the preferential reactivity of H over D tends to make the evolved gas higher in protium content than the parent compound, and the residue of KND_2 should contain a higher percentage of its total hydrogen as deuterium.

8 Burg, A. B., J. Am. Chem. Soc. 74, 1340 (1952).

A criterion of isotopic purity is the analysis of the hydrogen evolved on slow hydrolysis of B_2D_6 . A sample of B_2D_6 (8.6 cc gas at S.T.P.) was condensed into a large excess of 83% H_2SO_4 at $-196^\circ C$ in an evacuated system. The temperature was allowed to rise to $25^\circ C$, and slow vapor-phase hydrolysis took place over a 4-1/2-day period. The hydrogen evolved was analyzed by the mass spectrometer, giving 84.9% HD, 6.7% D_2 , and 8.5% H_2 . This is in excellent agreement with the 85% HD, 7% D_2 , and 8% H_2 reported by Norton⁹ for pure B_2D_6 . The unusually close agreement is no doubt partly fortuitous.

f. Sodium. Small weighed samples of commercial metallic Na were sealed in thin-walled glass bulbs of about 4-5-mm diameter by well-known methods.¹⁰

2. Procedures

a. Preparation of the Diammoniate of Diborane and Its Isotopically Substituted Modifications. When diborane or deuterodiborane was allowed to react with an excess of solid ammonia or deuterioammonia at $-120^\circ C$, and the excess of ammonia was removed by sublimation at $-80^\circ C$, solid $B_2H_6 \cdot 2NH_3$ or its isotopically substituted modifications resulted.

b. The Reaction between Sodium and the Diammoniate of Diborane. A liquid ammonia solution of $B_2H_6 \cdot 2NH_3$ or of its isotopically substituted counterpart¹¹ was frozen with liquid nitrogen. A stream of dry nitrogen was passed through the reaction tube to prevent entrance of moisture when the tube was opened; then a sidearm was opened and a previously prepared glass bulb of sodium was crushed with a special tool and dropped onto the frozen solution. The sidearm was closed with a ground joint, the system re-evacuated, and the temperature of the solution fixed at $-78^\circ C$ with a dry-ice-acetone bath. As the ammonia melted and the sodium dissolved, hydrogen was liberated and continued to evolve at an appreciable rate for half an hour. Spattered sodium and mixed salts were washed down the walls of the reaction vessel by condensing rings of fresh ammonia on the walls from a side tube. As the rings melted, they carried spattered solids back into the reaction mixture. The volume of hydrogen evolved was measured by condensing the ammonia and measuring the H_2 pressure in the apparatus. Since the volume of the system had been determined previously, it was possible to calculate the number of moles of H_2 which had been liberated. Samples of H_2 for isotopic analysis were taken by allowing the gas to expand into evacuated sample tubes.

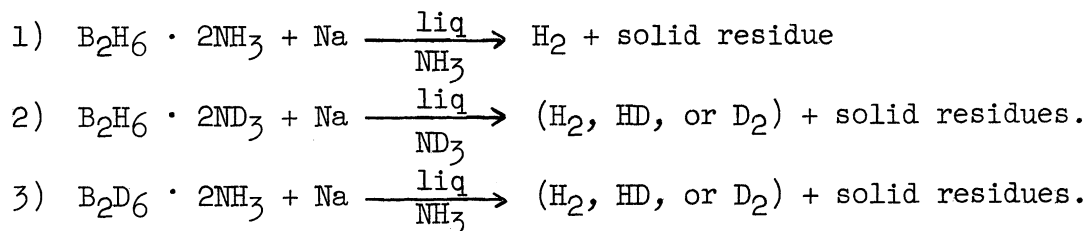
⁹ Norton, J. S., Science **111**, 202 (1950).

¹⁰ Sanderson, R. S., Vacuum Manipulation of Volatile Compounds, John Wiley and Sons New York, N. Y., 1948.

¹¹ When $B_2H_6 \cdot 2ND_3$ was used, the solvent ammonia was ND_3 , not NH_3 .

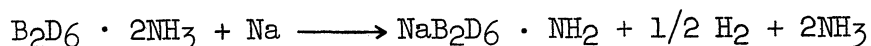
D. Results

Data for the following reactions are summarized in Table I.



Several points are worthy of specific comment. First, the amount of hydrogen evolved during the reaction was never equal to one equivalent of H_2 per mole of diborane. This result contrasts sharply with the earlier observation of Schlesinger and Burg,³ in which one equivalent of hydrogen per mole of diborane was consistently obtained above -77°C . The reason for the discrepancy is not apparent at this time. In the present work, the maximum number of equivalents of hydrogen per mole of diborane (0.64) was obtained when the temperature of the reaction medium rose from -81°C to -50°C (Run 2). In the two runs which were conducted at -81°C (Runs 1 and 5), the values obtained (0.573 and 0.589 equivalent of hydrogen per mole of diborane) show reasonably close agreement. Finally, in Runs 3 and 4, which were conducted at -79°C with deuterioammonia, the lower values (0.500 and 0.527 equivalents of hydrogen per mole of diborane¹²) suggest an isotope effect of some significance.

The second point of major interest relates to the isotopic composition of the evolved hydrogen. Data from Run 5, Table I, indicate that the hydrogen evolved from the reaction between $\text{B}_2\text{D}_6 \cdot 2\text{NH}_3$ and sodium was 99.5% H_2 and 0.5% HD. These values indicate the reaction shown below, in which only nitrogen-hydrogen bonds are broken by the sodium.



This result is the one to be expected in view of Burg's conclusion that only the hydrogen¹³ atoms attached to nitrogen will exhibit acidic character.

¹² The differences in Runs 3 and 4 (i.e. 0.500 equivalent as compared to 0.527 equivalent) are not completely unexpected, since conditions were not identical. In Run 3 a 2.6% excess of sodium was used and in Run 4 a 9.5% excess of diborane was employed. Because of the excess of diborane in Run 4, the hydrogen evolution was calculated as equivalents of hydrogen per equivalent of sodium, rather than as equivalents of hydrogen per mole of diborane.

¹³ In this discussion hydrogen refers to both isotopes of mass 1 and those of mass 2. Protium refers specifically to the isotope of mass 1 and deuterium to the isotope of mass 2.

TABLE I

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

Isotopic Run Composition of Diammoniate	Time and Temperature of Formation ^a	Equiv. Na Used	Equiv. B_2H_6 Used	Time and Temperature of Na Reaction	ml H_2 Evolved (S.T.P.)	Ratio: H Atoms B_2H_6 (Mol.)	Isotopic Analysis
1 $B_2H_6 \cdot 2NH_3$	14 hrs -150 to -100°C	.0023 (.04% excess)	.00232	105 mins -81°C	14.98	0.573	0.04% HD 99.96% H_2
2 $B_2H_6 \cdot 2NH_3$	5 hrs -133 to -109°C	.000522 (2.15% excess)	.000511	160 mins -80 to -50°C	3.66	0.64	0.02% HD 99.98% H_2
3 $B_2H_6 \cdot 2ND_3$	4.5 hrs -135 to -110°C	.000992 (2.59% excess)	.000967	100 mins -79°C	5.42	0.500	53.72% HD 3.19% H_2 43.09% D_2
4 $B_2H_6 \cdot 2ND_3$	4.75 hrs -129 to -95°C	.00157	.00172 (9.5% excess)	40 mins -79°C	9.27	0.527 ^b	41.31% HD 3.04% H_2 55.65% D_2
5 $B_2D_6 \cdot 2NH_3$	6.5 hrs -135 to -101°C	.00155	.00155	50 mins -81°C	10.24	0.589	0.50% HD 99.50% H_2

a All temperatures measured by copper-constantan thermocouple with error of $\pm 0.5^\circ C$.b Calculated on basis of .00157 equivalent Na because an excess B_2H_6 was used.

On the basis of the above data it is to be expected that the hydrogen obtained from the reaction between $B_2H_6 \cdot 2ND_3$ and sodium should be essentially pure D_2 . Data for Runs 3 and 4 in Table I indicate that this expectation is not realized. In Run 3 approximately 30% of the total evolved gas consisted of protium in the form of HD and H_2 , while in Run 4, with slightly different conditions, approximately 24% of the evolved gas was protium. The presence of protium in the evolved gas could result from an isotope effect of rather unexpected magnitude or, alternatively, from contamination of the deuterium with protium. Although many precautions were taken in obtaining the deuterium samples from runs 3 and 4, it seemed desirable to consider more carefully the possibility of protium contamination, and to do the experiments again under very stringent control. Accordingly, the entire apparatus has been redesigned and rebuilt and the experimental observations are being rechecked by an independent observer, using an improved technique. A discussion of the significance of the data from the tracer experiment will be withheld until the reality of the possible isotope effect is confirmed or discredited by forthcoming data.

E. The Reaction of Potassium with $B_2H_6 \cdot 2ND_3$ in Liquid Ammonia

The stoichiometry of the reaction between the diammoniate of diborane and a metal more reactive than sodium has not been reported. Since the reactivity of the metal might be a factor of major importance in determining the amount of hydrogen evolved from a given amount of the diammoniate of diborane, it seemed worthwhile to investigate the reaction involving potassium. Weighed crushable bulbs of potassium were prepared by standard techniques. The reaction between $B_2H_6 \cdot 2ND_3$ and potassium was effected in a manner exactly analogous to the procedure previously described for the reaction with sodium. Data on the stoichiometry are summarized in Table II. Unfortunately, the samples of hydrogen were accidentally contaminated with air before mass spectroscopic analysis could be conducted to determine the protium-deuterium ratio in the evolved gas.

TABLE II

REACTION BETWEEN POTASSIUM AND THE DIAMMONIATE OF DIBORANE

Equiv. K Used	ml B_2H_6 (S.T.P.)	Moles B_2H_6	ml H_2 Evolved	Equiv. H_2 per K
.000864	20.35	.000907 (5% excess)	6.50	0.671
.00102	23.8	.00106 (4% excess)	7.42	0.648

The numbers of moles of H_2 evolved for the reaction of K with each mole of $B_2H_6 \cdot 2ND_3$ were 0.671 and 0.648. The corresponding values for the reaction involving sodium were 0.500 and 0.527. These data indicate that under the conditions of this experiment the number of moles of H_2 evolved appears to be a function of the activity of the alkali metal employed.

III. METATHESIS REACTIONS IN LIQUID AMMONIA

A. Introduction and Background

In an attempt to synthesize heretofore unknown borohydrides and related compounds, metathesis reactions have been conducted in liquid ammonia. Ammonium borohydride has been synthesized and its decomposition products investigated. At the time that this work was undertaken we were unaware of a previous synthesis of ammonium borohydride by Armstrong *et al.* of Aerojet Engineering Corporation. The Aerojet work, which was reported in classified reports which were unavailable to us at the time, employed the metathetical reaction between sodium borohydride and ammonium sulfate in liquid ammonia. The resulting ammonium borohydride appeared to be contaminated with unreacted $NaBH_4$. The ammonium borohydride was unstable, decomposing with liberation of H_2 at temperatures above $-20^\circ C$.

B. Statement of the Problem

The problem to be investigated involved a study of the reaction between NH_4F and $NaBH_4$ in liquid ammonia. Since ammonium borohydride was expected as a product of the reaction, its physical and chemical properties, as well as the physical and chemical properties of its decomposition products, were to be investigated. Any compounds of potential interest to the Air Research and Development Command were to be reported with appropriate recommendations.

C. Experimental

1. Materials

a. Ammonium Fluoride. Reagent grade NH_4F from J. T. Baker Chemical Co. was dried over sulfuric acid before use.

b. Sodium Borohydride. Commercial $NaBH_4$ from Metal Hydrides was recrystallized once from liquid ammonia using a vacuum-line filtration

assembly. The resulting NaBH_4 was approximately 100% pure as indicated by measuring the hydrogen liberated on acid hydrolysis.

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

2. Apparatus and Procedure

The apparatus used is shown in Fig. 1. The reactor and filtration assembly were cooled by circulating alcohol through the cooling jacket. The alcohol was cooled to -46°C by pumping it through a copper coil immersed in a dry-ice trichlorethylene bath. Nonjacketed sections of the system were cooled by wrapping them in glass wool, and subsequently pouring liquid nitrogen over the glass wool. This type of operation could be performed just prior to filtration or solution-transfer operations.

The dry NH_4F , purified NaBH_4 , and a small magnetic stirrer were loaded into the dry reactor under nitrogen in a controlled-atmosphere gloved box. The reactor was then put in place on the filtration assembly, the system evacuated, and the cooling liquid passed through the jacket of the reactor. Ammonia was allowed to condense in the reactor and the reaction mixture was stirred continuously for four to six hours by means of the magnetic stirrer. The filter plate was then cooled by passing cold alcohol through its cooling jacket, and the nonjacketed tubes were cooled by pouring liquid nitrogen over the layer of glass wool which surrounded them. When the entire apparatus had been cooled to a temperature below -40°C , the precipitate was filtered off.

The actual filtration was effected by rotating the reactor through 180° and allowing the liquid to run down the cold gooseneck onto the jacketed filter plate. The filtrate was collected in a receiver cooled by liquid nitrogen. The precipitate on the filter plate was washed by distilling ammonia back through the porous filter, condensing it in the region above the plate, allowing the liquid to run down onto the precipitate, and then finally forcing the liquid back through the plate by cooling the receiver with liquid nitrogen.

Noncondensable gas was determined by measuring the pressure which remained after the solvent was frozen with liquid nitrogen. The volume of the system was previously calibrated using a weighed sample of carbon dioxide. The temperature of the noncondensable gas was assumed to be room temperature. From these data the number of moles of gas evolved could be calculated. The noncondensable gas was assumed to be hydrogen.

D. Results

If the reaction between NH_4F and NaBH_4 is carried out at -40°C or below and this temperature limit is carefully maintained during all filtration

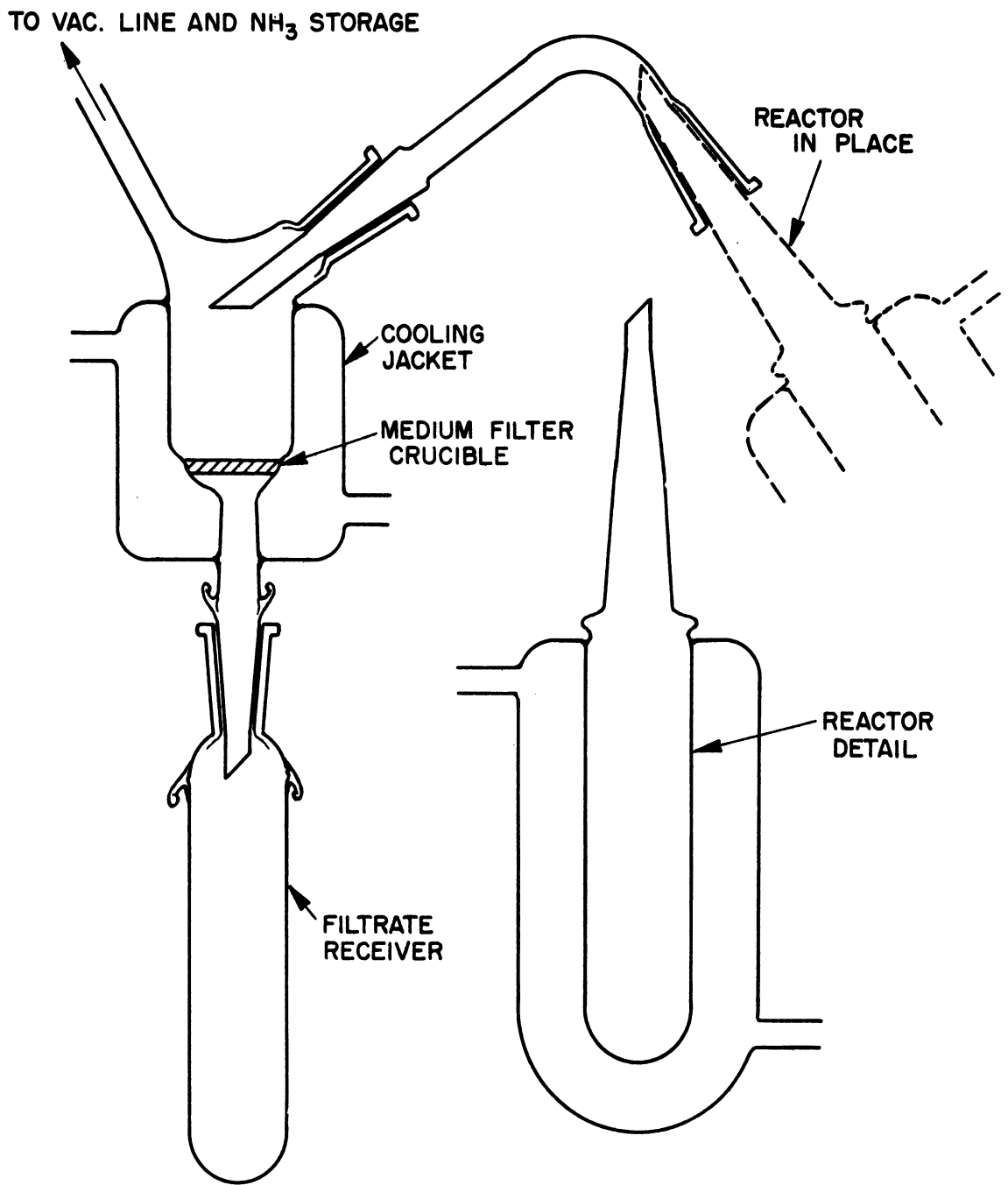
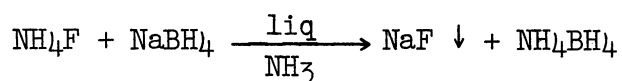


FIG. 1.
APPARATUS USED FOR METATHESIS REACTIONS IN LIQUID
AMMONIA.

and transfer operations, no hydrogen is evolved. The precipitate which remains on the filter plate was identified as NaF by fluorine analysis and by its x-ray diffraction pattern. The formation of this precipitate during the reaction is rather interesting. NaBH₄ is very soluble in liquid ammonia and NH₄F is relatively insoluble. The crystals of NH₄F gradually react and a semigelatinous precipitate of NaF could be observed.

If the ammonia was evaporated from the filtrate at -45°C, no hydrogen was evolved. The solid residue then evolved hydrogen as it was warmed to room temperature. The evolution of hydrogen from the solid is relatively slow and requires about two days to come to equilibrium. These facts, together with the quantitative stoichiometric data summarized in Table III, suggest two reactions. The first is the formation of ammonium borohydride at low temperatures (-40°C) by a simple metathesis reaction.



At higher temperatures the solid ammonium borohydride undergoes slow decomposition over a two-day period in accordance with the equation:

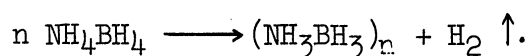


TABLE III

STOICHIOMETRY FOR THE PREPARATION OF AMMONIUM BOROHYDRIDE
AND ITS DECOMPOSITION PRODUCTS

Run	mmoles NH ₄ F	mmoles NaBH ₄	ml. NH ₃ Solvent	Temp Run	mm H ₂ Evolved	% NH ₃ in Residue	% ¹ Yield	% ² Purity
9	3.0	3.0	10	-43°	2.8	48.3%	93%	88%
10	3.0	3.0	10	-40°	2.5	42.7%	83	77
11	3.0	3.0	10	-50°	2.0	50.2	67	91
12	6.0	3.0	10	-48°	3.0		100	

- 1) % yield based on H₂ evolved as compared to theoretical yield from NaBH₄ used.
- 2) % purity based on total wt. of sample and wt. of NBH₆ as determined by Kjeldahl.

When stoichiometric quantities of NH_4F and NaBH_4 were used, the product always contained some 10 to 15% unconverted sodium borohydride. This is, in all probability, a mechanical problem which arises from the extremely low solubility of NH_4F at the temperature used, since the solid NH_4F crystals are coated with NaF as the reaction proceeds and the solubility of NH_4F at -45°C was found to be 14.2 mg./l NH_3 . A large excess of solid NH_4F should minimize contamination with NaBH_4 without introducing significant contamination by NH_4F , because the excess solid ammonium salt can be filtered off with the NaF . In Run 12 a 100% excess of NH_4F was used and complete conversion of the NaBH_4 to NH_4BH_4 was obtained.

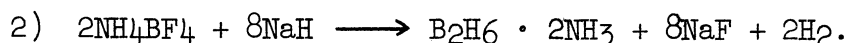
Acidic hydrolysis of the compound $(\text{BH}_3\text{NH}_3)_n$, which resulted from the thermal decomposition of NH_4BH_4 , gave 63% of the total hydrogen to be expected from complete hydrolysis. This observation is in agreement with observations of Stock on the hydrolysis of the diammoniate of diborane and with the observations of Aerojet on the hydrolysis of the BNH_6 which they obtained from NaBH_4 and $(\text{NH}_4)_2\text{SO}_4$ in liquid ammonia.

Hydrolysis was effected by adding dry oxalic acid to the solid BNH_6 in a tube. The tube was connected to the vacuum line and evacuated; then water was distilled onto the mixture. The pressure of the evolved hydrogen was measured after the excess water had been frozen down with liquid air. Since the volume of the system was known from previous calibration, the number of moles of hydrogen could be calculated.

The Kjeldahl determinations were by standard procedures, and the fluorine analyses were made by the method of Willard and Winter.¹⁴

E. The Reaction between NH_4BF_4 and NaH

The reaction between BF_3 and LiH in ether solution and an erroneous interpretation of some of our earlier data on reactions in liquid ammonia suggested that it might be worth while to investigate the reaction between NH_4BF_4 and an excess of NaH suspended in liquid ammonia. Two possible equations can be written for the reaction between these compounds:



Although the first reaction is the one to be expected from normal acid-base relationships, the possibility that the second reaction would take place seemed sufficiently attractive to warrant an experiment.

¹⁴ Willard, H. H., and Winter. O. B. Ind. and Eng. Chem. Anal. Ed. 5, 7-10 (1933).

The previously described apparatus of Fig. 1 was used. Ammonium fluoborate was prepared by modifying the method for KBF_4 given in Inorganic Synthesis, Vol. I, p. 24. Using DuPont commercial-grade NaH, 2 millimoles of NH_4BF_4 and 8 millimoles of NaH were placed in the reactor. When the reaction was carried out as described previously, H_2 was given off continuously. The solid products were analyzed by x-ray diffraction. The ammonia-insoluble portion was NaH, whereas the soluble portion contained NaBF_4 . Exactly 2 millimoles of H_2 were evolved. Reaction 1 is indicated by these data.

F. Solubilities in Liquid Ammonia

Reliable estimates of the solubility in liquid ammonia of salts such as NH_4F , NaH, and NaBH_4 could not be found in the literature. Since such data are germane to the previous metathesis study, these solubilities were estimated.

1. NaH

DuPont NaH was placed in the reactor of Fig. 1 and NH_3 was condensed into the system. The mixture was stirred for 1-1/2 hours at a temperature of -48°C . The suspended NaH was then filtered off and the filtrate was caught in a graduated receiver; the volume of the solution was recorded and then the ammonia was distilled off. The resulting trace of solid was hydrolyzed by the addition of water and the volume of the evolved hydrogen was measured. At -48°C less than 1 millimole of NaH dissolved in a liter of ammonia.

2. NaBH₄

NaBH_4 from Metal Hydrides was investigated in a manner exactly analogous to that used for NaH. The solubility of NaBH_4 in liquid ammonia is in excess of 100 grams/liter.

3. NH₄F

The literature gives data on the solubility of NH_4X in liquid ammonia when X is chloride, bromide, or iodide, but no data were found for NH_4F . There is a regular decrease in the solubility from iodide to chloride. The procedure used to measure the solubility of NH_4F was similar to that described above except that the fluoride in the residue was determined by the method of Willard and Winter.¹⁴ At -48°C , 14.2 milligrams or 0.38 millimole of NH_4F will dissolve in a liter of ammonia.

IV. A PHYSIOCHEMICAL STUDY OF NH_4BH_4 , $(\text{BH}_3\text{NH}_3)_n$,AND THE CLASSICAL DIAMMONIATE OF DIBORANEA. Introduction

From the philosophical standpoint, NH_4BH_4 in liquid ammonia was of some interest, since it represented a solution of borohydric acid in liquid ammonia. For this reason the extent of its dissociation into NH_4^+ and BH_4^- was a question worthy of investigation. In a more practical sense, the compound $(\text{BNH}_6)_n$ has an empirical formula which is identical with the diammoniate of diborane. If the two compounds are identical, the metathesis reaction would offer a new and simpler way to prepare the diammoniate of diborane. Data in the classified literature indicate that the two compounds are not the same; however, the evidence is far from conclusive and the resulting questions of structure have never been resolved. In an effort to obtain information pertinent to the above questions, the compounds NH_4BH_4 , $(\text{NH}_3\text{BH}_3)_n$, and $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$ have been investigated by (1) measuring their molecular weights in liquid ammonia, (2) obtaining x-ray diffraction pictures for the solids and (3) obtaining the Raman spectrum for NH_4BH_4 in liquid ammonia. The Raman spectra for $(\text{NH}_3\text{BH}_3)_n$ and the diammoniate of diborane in liquid ammonia are being obtained currently.

B. Molecular-Weight Measurements1. Experimental

Molecular weights were estimated by measuring the vapor pressure depression produced by dissolving the solid compounds in liquid ammonia. The apparatus used was a modified form of that used by Stock and Pohland¹ in their original investigation of the diammoniate. Details of the apparatus are shown in Fig. 2. One of the principal differences between this investigation and that of Stock was the use of an ethyl alcohol bath between the bulbs and the refrigerating liquid. Stock and Pohland apparently immersed the bulbs containing the pure ammonia and the liquid ammonia solution directly in the liquid ammonia refrigerant. In the current investigation such a procedure produced very erratic results, apparently because of uneven and erratic cooling resulting from the evaporation of ammonia at the glass-air-liquid interface. When the bulbs were surrounded by an ethyl alcohol bath, and then this bath was immersed in the liquid ammonia refrigerant (Fig. 2) reproducible vapor pressure depressions were obtained. Using this technique, the results with urea were significantly better than those reported by Stock in 1925. As shown in Fig. 3, the

FIG. 2.
APPARATUS FOR DETERMINING MOLECULAR WEIGHTS
IN LIQUID AMMONIA.

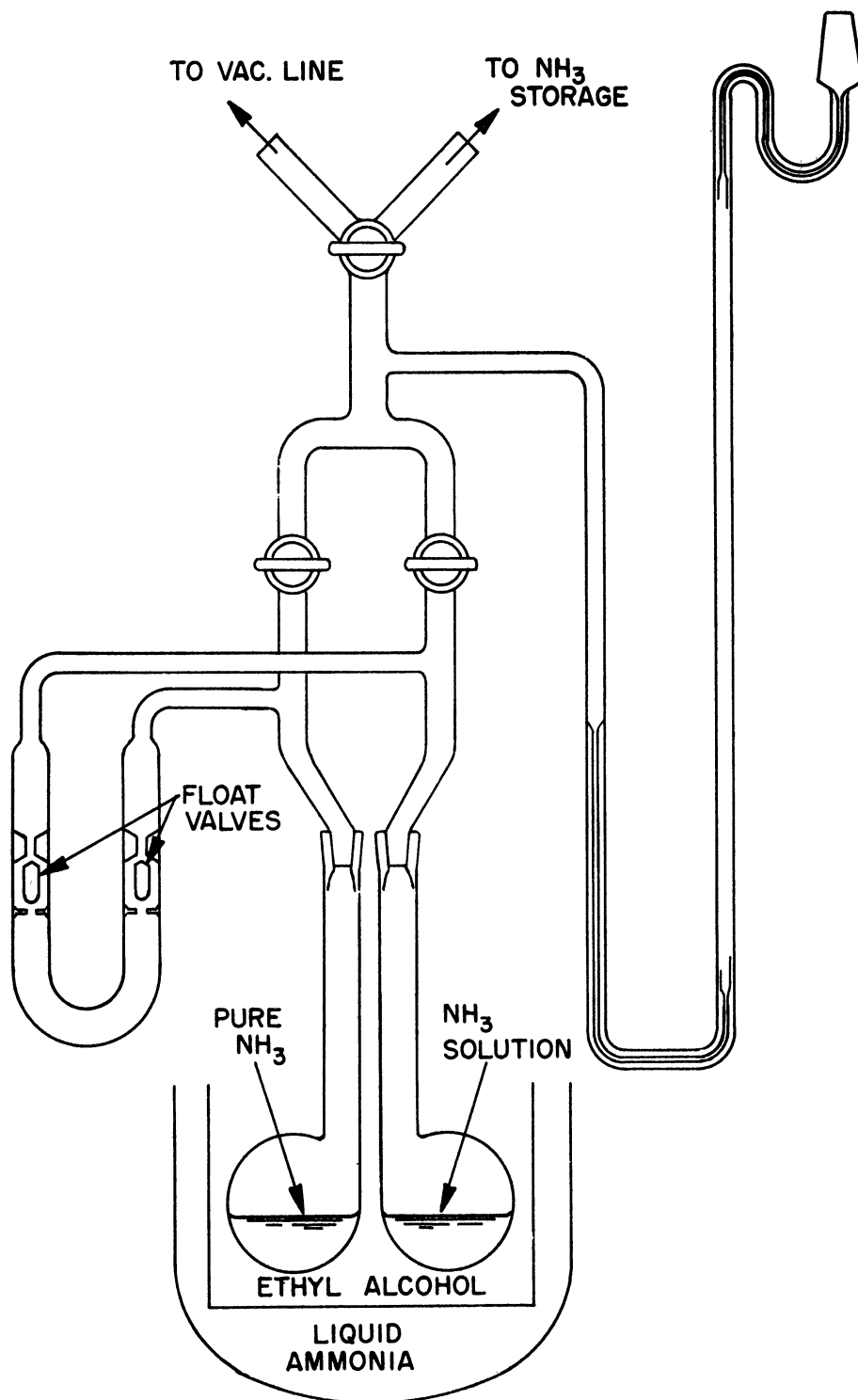
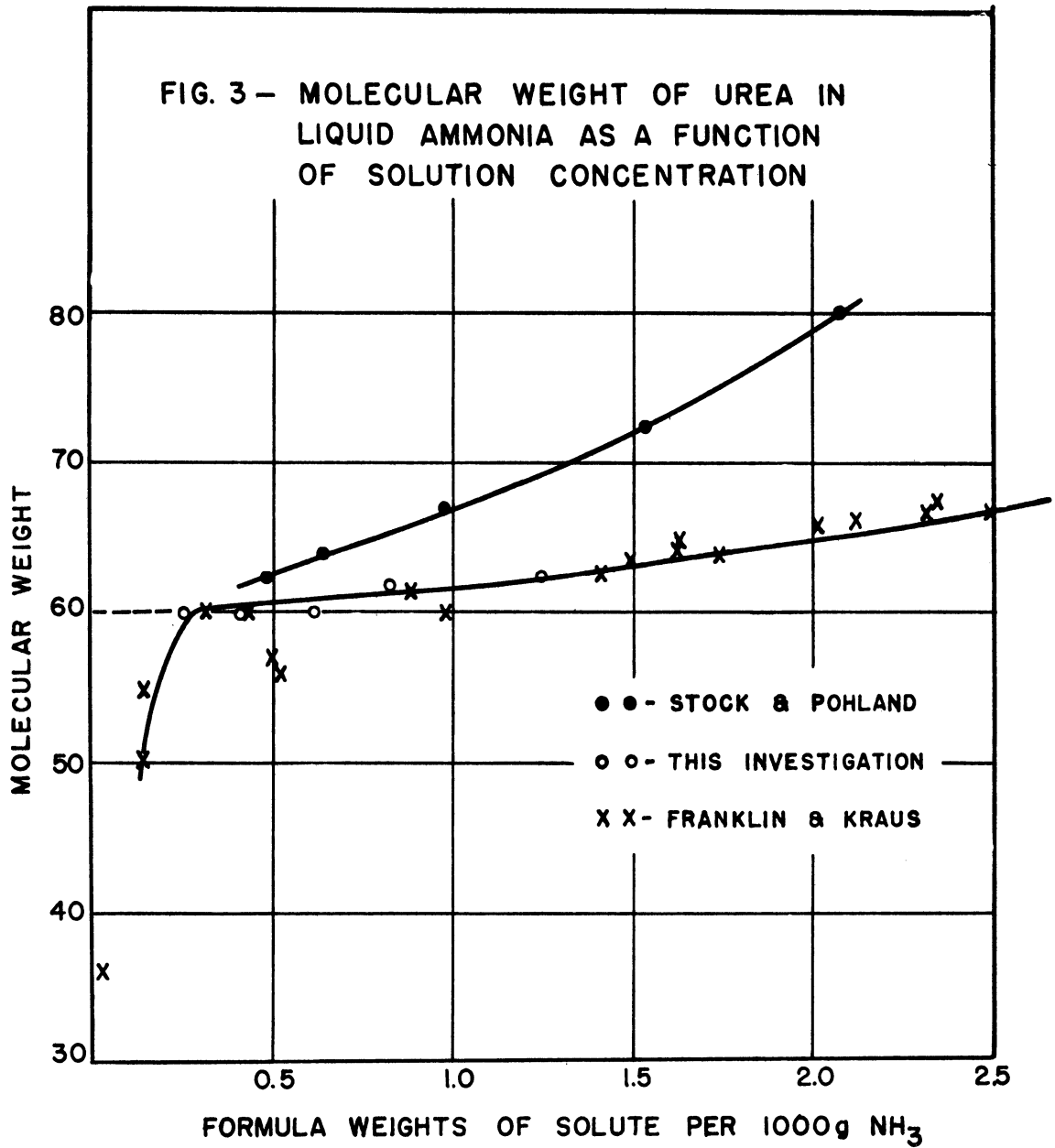


FIG. 3 - MOLECULAR WEIGHT OF UREA IN LIQUID AMMONIA AS A FUNCTION OF SOLUTION CONCENTRATION



tensiometric molecular-weight measurements of this investigation also check molecular-weight measurements on urea which were obtained by Franklin and Kraus¹⁵ using the boiling point elevation of liquid ammonia solutions.

Compounds which were not damaged by air were weighed directly into the appropriate molecular-weight bulb; the bulb was connected to the apparatus and the system was evacuated. A previously measured quantity of liquid ammonia was distilled in on top of the compound; then the solution was stirred by means of the magnetically operated stirring rod until solution was complete. The constant-temperature bath was put in place around the bulbs, and the difference in vapor pressure between the solution and the pure solvent was obtained using a Stock valve as a differential manometer. Variation in the concentration of the solution was easily achieved by distilling known quantities of ammonia into or out of the bulb containing the solution.

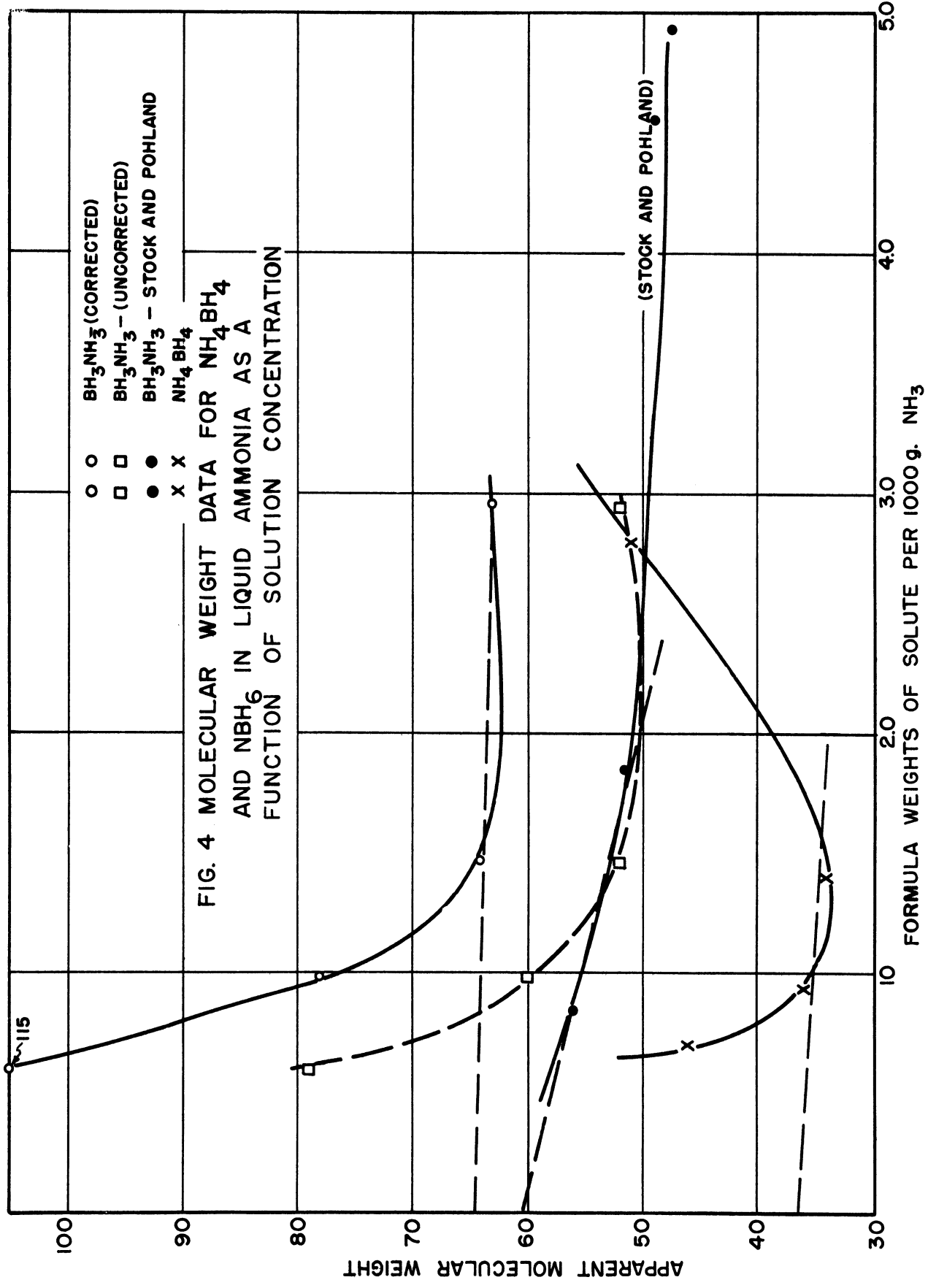
Since NH_4BH_4 and $(\text{NBH}_6)_n$ are both damaged by exposure to air and moisture, these materials were made in liquid ammonia solution and filtered directly into the molecular-weight bulb. After the measurements on vapor pressure depression were completed, the volume of solvent ammonia was determined by distilling the solvent into a calibrated tube. The total weight of solid was obtained by weighing the molecular-weight tube with and without the solid. Purity of the sample was determined by analyzing the solid for ammonia by the Kjeldahl procedure.

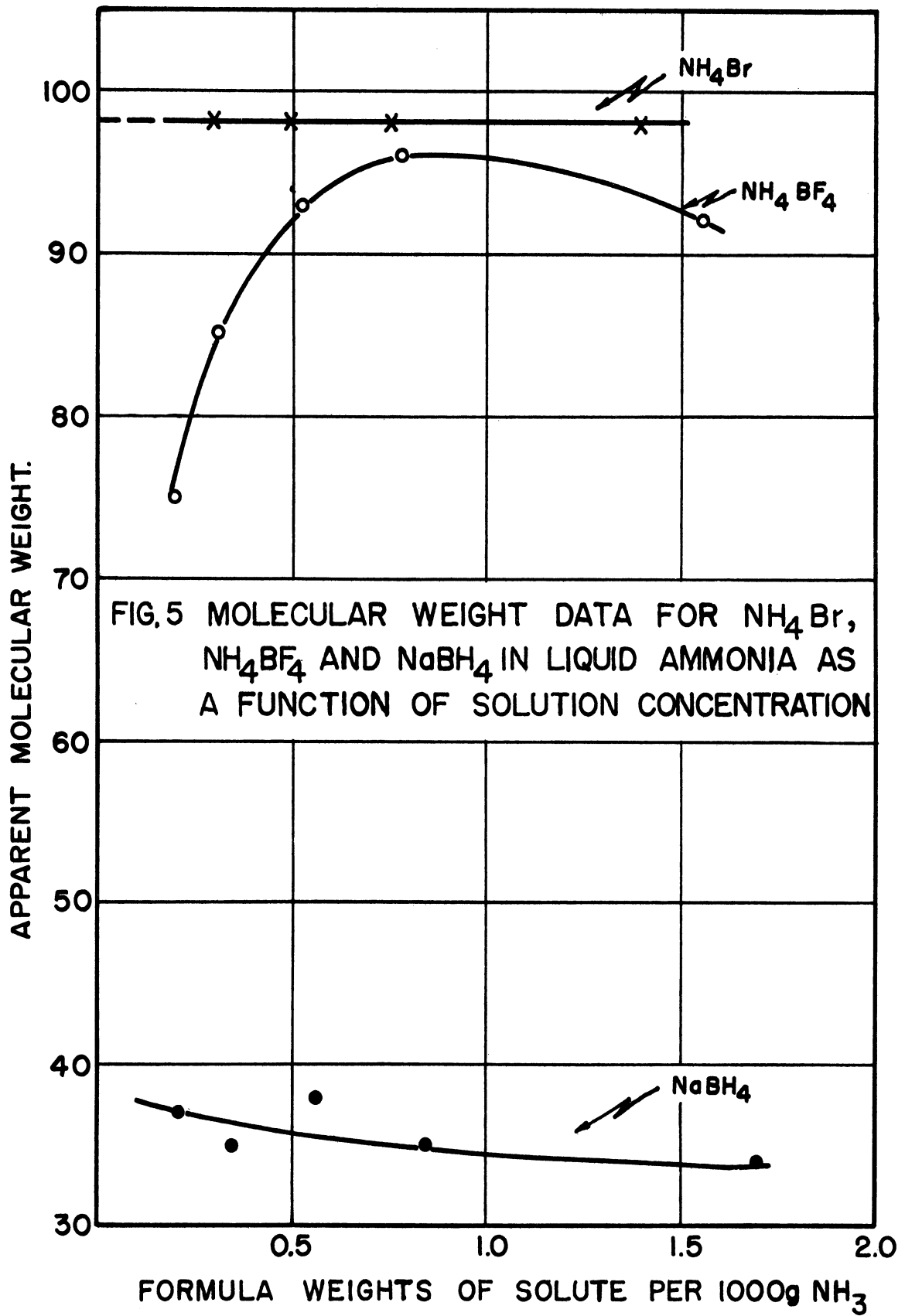
2. Results

Data for samples of NH_4BH_4 and NBH_6 are summarized in Fig. 4. The solids in this run were contaminated with about 13% NaBH_4 . The molecular-weight values shown in the figure have been corrected for the 13% NaBH_4 by using later data on the molecular weight of NaBH_4 in liquid ammonia as the basis for the corrections. The strange variation of molecular weight with concentration and the unexpected rise in molecular weight as the solutions became more dilute prevent an unequivocal interpretation of the results. An investigation of the behavior of better known compounds in liquid ammonia then seemed pertinent. NH_4BF_4 , NaBH_4 , and NH_4Br were selected as appropriate comparison compounds. These data are plotted in Fig. 5.

It is interesting to note that NH_4Br and NaBH_4 gave constant values of molecular weight and showed little evidence of dissociation in liquid ammonia solution, whereas NH_4BF_4 showed an initial rise in molecular weight followed by a marked decrease at high dilution. This decrease can be interpreted as indicating dissociation of the NH_4BF_4 at low concentration of the fluoborate and is the expected behavior for acid dissociation in a solvent. On the basis of these data, one is led to conclude that NH_4BF_4 is a significantly stronger

¹⁵ Franklin, E. C. and Kraus, C. A., Am. Chem. J. 20, 836-53 (1898).





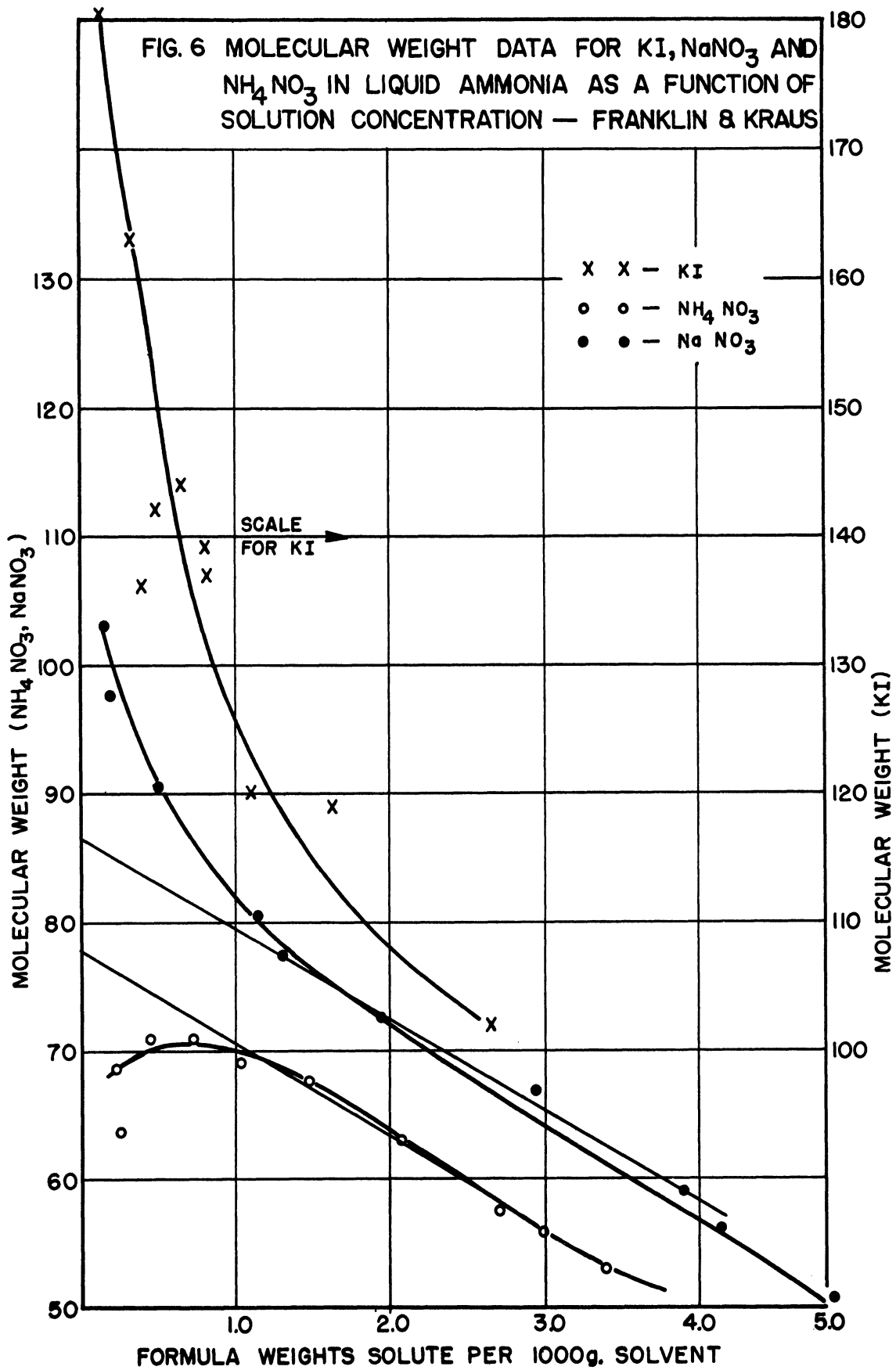
acid in liquid ammonia than is NH_4Br . None of these compounds gave the rise in molecular weight at high dilution which was observed with NH_4BH_4 and $(\text{NBH}_6)_n$.

Data from the literature, discovered after the accumulation of the above evidence, made an interesting supplement to the current investigation. In 1898 Franklin and Kraus¹⁵ measured the boiling points for various solutions of electrolytes and nonelectrolytes in liquid ammonia. From their data, molecular-weight values of each substance can be calculated by using a boiling point constant of 0.318 for liquid ammonia. This constant differs somewhat from the presently accepted value of 0.34,¹⁶ but the value 0.318 is the empirical constant obtained from their data using several known compounds, and thus includes all of their systematic errors. Molecular-weight values for a number of different compounds at different solution concentrations have been calculated from their data. These data are summarized in Figs. 3 and 6. The close agreement between the best data of Franklin and Kraus and the data of the present investigation for urea is significant, (Fig. 3). It is also interesting to note that the salts NaNO_3 and KI show behavior analogous to that of $(\text{BNH}_6)_n$, while NH_4NO_3 behaves as an acid in a manner analogous to NH_4BF_4 , (Fig. 6).

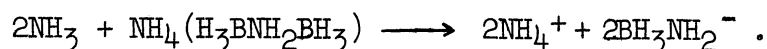
The rapid rise in apparent molecular weight for NH_4BH_4 and $(\text{NBH}_6)_n$ in solutions of high dilution is an interesting and somewhat disturbing result of the current study. The fact that NaNO_3 and KI showed the same behavior in an earlier and independent investigation raises fundamental questions concerning the nature of the liquid ammonia solutions. Franklin and Kraus gave no explanation for the phenomenon and to the best of the author's knowledge the anomaly has not been considered since. The unusual rise in molecular weight with dilution was indicated in Stock's molecular-weight measurements on the diammoniate of diborane. His standard urea, showed exactly the opposite behavior with dilution. To obtain the dimeric formula for $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$ the molecular weight curve was extrapolated to infinite dilution from a concentration of .415 molal (i.e. .415 formula weights $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3/1000$ g. solvent) (Fig. 4). A reasonable formula weight for monomeric NaNO_3 can be obtained by making such an extrapolation of the curve of Franklin and Kraus and neglecting the experimental points at high dilution (Fig. 6). The curve of KI does not show an unambiguous extrapolation because of a lack of data at higher concentrations. Even in the case of urea, the experimental points of Franklin and Kraus at very high dilution must be neglected in order to obtain the known molecular weight of 60 (Fig. 3).

Data currently being taken in this laboratory indicate that the diammoniate of diborane undergoes a sharp rise in apparent molecular weight as the solution concentration decreases beyond Stock's minimum concentration of 0.415 molal. In view of the above facts it is likely that Stock's molecular-weight value, which indicates a dimeric formula for the diammoniate of diborane,

¹⁶ Moeller, T., Inorganic Chemistry John Wiley and Sons Inc. New York, 1952, p. 341.



is too uncertain to offer evidence for or against the proposal that the diammoniate is in equilibrium with borine amine at the boiling point of liquid ammonia; i.e.,



The dimeric formula does, however, seem most reasonable in view of all current data.

A consideration of the molecular-weight data for NH_4BH_4 and $(\text{NH}_3\text{BH}_3)_n$ can now be made in the light of the above evidence for known and previously accepted compounds. As seen in Fig. 4, a reasonable extrapolation for NH_4BH_4 indicates a molecular weight of 34, which corresponds to a monomeric undissociated solute comparable to NaBH_4 . An extrapolation for NBH_6 indicates a molecular weight of 65, corresponding to the dimeric formula $(\text{NH}_3\text{BH}_3)_2$. Insofar as the present data permit a conclusion, one is led to favor the assumption that the product obtained from NH_4F and NaBH_4 under the conditions previously described is the same as the diammoniate of diborane. This investigation does, however, raise interesting questions concerning the nature of liquid ammonia solutions, particularly at high dilution. An area for further research is indicated.

C. X-Ray Diffraction Studies

An attempt has been made to obtain x-ray diffraction patterns for the solid $(\text{NH}_3\text{BH}_3)_n$ and the classical diammoniate of diborane. The instability of NH_4BH_4 at room temperature has prevented an examination of this solid in currently available equipment.

For a direct comparison between $(\text{NBH}_6)_n$ and $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$, it was necessary to synthesize an authentic sample of the diammoniate of diborane. Since relatively large quantities of material were needed, the synthesis was attempted on a scale greater than any heretofore recorded.

1. Attempts at Large-Scale Synthesis of the Diammoniate of Diborane

The procedure outlined by Schlesinger and Burg³ for the synthesis of the diammoniate of diborane was followed except that the scale of the reaction was increased by a factor of 8. Thus 400 cc (S.T.P.) of B_2H_6 (0.01647 mole) were used in the reaction. Approximately 0.0132 mole of diborane was absorbed (80% of total) to give a theoretical yield of 0.81 g $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$. Actually, only about 0.5 g was obtained and significant amounts of hydrogen and a more volatile product of boron (probably $\text{B}_2\text{H}_5\text{NH}_2$) were found. The

formation of $B_2H_5 \cdot NH_2$ from diborane and the diammoniate is to be expected. Analysis of the sample of the diammoniate indicated 54.15% ammonia as against a theoretical value of 55.15%. The low value could indicate slight contamination of the product with aminodiborane. A portion of this diammoniate of diborane was recrystallized from liquid ammonia. Only a trace of ammonia is required to keep the diammoniate in solution; consequently, as the last of the ammonia evaporated at $-45^\circ C$, it appeared as though there was no solid left. When the $-45^\circ C$ bath was removed and the remaining ammonia was condensed into another trap at $-196^\circ C$, solid material immediately appeared on the walls of the crystallization tube and needle-like crystals appeared in this solid. In order to remove the last traces of free ammonia the system was evacuated. The needles disappeared in a decrepitation process, leaving a white solid residue. This residue was analyzed and also used in the x-ray work described below.

A second attempt to prepare 1 g. of the diammoniate of diborane in a single lot yielded a product so badly contaminated with aminodiborane that no effort was made to recover any of the desired product. In all subsequent operations small lots of about 0.1 g. of the diammoniate have been made to minimize contamination with the aminodiborane and produce a more reliable sample.

2. Preparing X-Ray Diffraction Pictures

X-ray powder patterns were obtained as standards for use in the identification of solid products obtained from the metathesis reactions. Patterns for NaF, NH_4F , H_3BO_3 , $NaBF_4$, NH_4BF_4 , NaH, and $NaBH_4$ were obtained using a Phillips powder camera of 180-mm circumference with Cu-K α radiation and exposure times of up to 10 hours. The NaF, NH_4F , H_3BO_3 , NH_4BF_4 , and $NaBF_4$ samples were mounted by mixing the compounds with Duco cement, rolling each mixture into a thin fiber, and mounting the fiber in the x-ray camera. NaH, $NaBH_4$, the diammoniate of diborane, and the new compound $(NH_3BH_3)_2$ reacted with the solvent in the Duco cement, so it was necessary to use thin glass capillaries to hold the powder in these cases. Unfortunately, no definite lines were recognizable in the photographs for the diammoniate of diborane and the new compound $(BH_3NH_3)_2$. This is interpreted as indicating an amorphous structure for both of the solids used.

D. Studies of the Raman Spectra

Since previously described x-ray and molecular-weight data failed to yield an unambiguous answer to the question concerning the relationship between the diammoniate of diborane and the new compound of the same empirical formula, a Raman spectral study of the two compounds has been undertaken with the aid of Dr. R. C. Taylor. A comparison of the two spectra should provide an unequivocal method for deciding whether the two compounds are identical or

TABLE IV

RAMAN SPECTRA OF BORON COMPOUNDS

Wave Number Shift in cm^{-1}

NH_4BH_4	NaBH_4	NH_4BF_4	Assignment
		340	BF_4^- - 353*
		523	BF_4^- - 524*
		767	BF_4^- - 769*
		944	
984			Hg - 986
		1077	
	1081		
		1112	
		1469	
		1542	
	1630		
		1643	
	2152		
	2219		
2266	2262		BH_4^-
2602	2602	2602	Hg - 2602
2783		2790	Hg - 2783 to 2790
		3047	Hg - 3045
3209	3211	3224	NH_3 - 3212
3295	3292	3304	NH_3 - 3300
3372	3375	3395	NH_3 - 3380

* Confirmed: Gowbeam and Bess, Z. anorg. allgen. Chem. 268, 221 (1952) for NH_4BF_4 in aqueous HF - NH_4BF_4 solution.

not. In addition, if frequencies can be properly assigned, structural information can be obtained.

The Raman instrument used was a Gaertner Raman Spectrograph and the sample tube was cooled by a cold air stream. The air was cooled by passing it through a copper coil immersed in a bath composed of dry ice and isopropyl alcohol. By this arrangement the Raman tube could be maintained at about -40°C . Liquid ammonia solutions to be studied were filtered directly into the sample tube by using it as a receiver on the apparatus shown in Fig. 1. Exposure times varied from 1/2 to 6 hours.

The plates were measured with a comparator and a Leeds and Northrup Knorr-Albens recording microphotometer.

Raman data for NH_4BH_4 are summarized in Table IV. Comparative data to aid in the assignment of frequencies are also recorded for NaBH_4 and NH_4BF_4 . It appears from this table that the 2260-cm^{-1} shift is due to the BH_4^- . In addition, the intensity of the 3212-cm^{-1} shift for ammonia was decreased by the presence of the solute in every case.

Data for $(\text{NH}_3\text{BH}_3)_2$ and the diammoniate are not yet available.²

V. THE REACTION BETWEEN HYDROXYLAMINE AND DIBORANE

A. Background

In a strictly formalistic view, a large number of nitrogen-containing compounds can be considered as substitution derivatives of ammonia. For example, replacing a hydrogen atom of an ammonia molecule by groups such as $-\text{CH}_3$, $-\text{OH}$, or $-\text{NH}_2$ gives rise successively to methylamine, hydroxylamine, or hydrazine. Additional replacements of hydrogen atoms by alkyl groups give rise to molecules such as dimethyl- and trimethylamine.

The accepted structure of the well-known trimethylamine borine is $\text{H}_3\text{B:N}(\text{CH}_3)_3$, and the compound is well characterized. The related compounds with dimethylamine and methylamine have been reported, but are much less definitely characterized. Additional work on them is being done in other laboratories.

The reaction between hydrazine and diborane has been studied recently by Emeleus and Stone¹⁷ and by Schlesinger.¹⁸

¹⁷ Emeleus, H. J., and Stone., F. G. A., J. Chem. Soc. 1951, 840-1.

¹⁸ Schlesinger, H. J., private communication.

Emeleus and Stone failed to obtain a stoichiometric compound when they conducted the reaction between anhydrous hydrazine and diborane in the absence of a solvent. On the other hand, Schlesinger found that hydrazine and diborane react in a 1:1 mole ratio in the presence of diethyl ether.

The corresponding reaction of hydroxylamine with diborane has never been studied. The contrast between the effects on the basic strength of the ammonia nitrogen produced by substitution of the $-NH_2$, $-CH_3$, and $-OH$ groups seemed to offer an interesting area for investigation. In addition, the possibility of forming unusual polymers or heterocyclic rings containing boron, nitrogen, and oxygen by thermal decomposition of a diborane-hydroxylamine addition compound made the study attractive from the more practical point of view. A polymer with great heat stability might result from the complete pyrolysis of the addition compound.

B. Statement of the Problem

The problem to be investigated involved a study of the reaction between hydroxylamine and diborane under different sets of experimental conditions. The chemical and physical properties of all compounds formed were to be studied and compounds which might be of practical use to the Air Research and Development Command were to be reported with appropriate recommendations.¹⁹

C. Experimental

1. Reagents

a. Hydroxylamine. The free hydroxylamine base was prepared by the reaction of sodium butoxide with hydroxylammonium chloride suspended in butanol.²⁰ This preparation required very thorough elimination of all sources of water; the salt was dried at $110^\circ C$ before use. Hydroxylamine undergoes rapid decomposition at temperatures above $15^\circ C$, yielding ammonia, nitrogen, nitrous oxide, and water. It dissolves in water, and cannot easily be dehydrated. For these reasons it was found advisable to store the free base at $-10^\circ C$ under anhydrous butanol. Samples were removed immediately before use, filtered, washed with cold anhydrous ether, and weighed as described in a later section.

¹⁹ The original contract called for a study of the reaction of hydrazine as well as hydroxylamine with diborane. The investigation with hydrazine was dropped when the reports of Schlesinger's work were sent to us.

²⁰ Charles D. Hurd, Inorganic Syntheses, Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 87.

b. Diborane. Diborane was prepared as previously described by the reaction of lithium aluminum hydride and boron trifluoride etherate in ether solution. The ether was separated from the diborane by low-temperature fractional condensation. The high degree of purity of the diborane produced by this method was indicated by a vapor pressure of 225 mm Hg at -111.8°C .

c. Ether. Reagent-grade commercial ether was distilled from sodium in the vacuum line.

2. Apparatus and Procedure

a. Weighing and Handling Hydroxylamine. The instability of hydroxylamine at room temperature, especially in the presence of the moisture and carbon dioxide of the air, makes it necessary to confine the material in a closed container at a low temperature as much as possible, and to complete all transfers and manipulations rapidly. In order to fulfill these requirements, the weighing unit pictured in Fig. 7 was developed. The use of the small Dewar flask made it possible to keep the hydroxylamine cold during the weighing process and prevented the condensation of moisture on the container. A tight seal around the weighing bottle was necessary to prevent evaporation of water and to permit inverting the unit in order to dump the hydroxylamine into the reaction cell after weighing.

The plate-like hydroxylamine crystals were removed from the cold butanol mother liquor by suction filtration, washed with cold ether, and transferred to the weighing bottle. After weighing, the crystals were dumped into the reaction tube, which was immediately cooled with ice water, attached to the vacuum line, and evacuated. The special weighing bottle was then tared.

In order to determine the degree of accuracy that can be attained by handling the hydroxylamine in this manner, a weighed sample of the free base was dissolved in an excess of standard acid and the excess acid was titrated with standard base; a second weighed sample was dissolved in water and titrated directly with standard acid. The course of each titration was followed by measuring the pH of the solution with a Beckman pH meter. The pH of a hydroxylammonium chloride solution of approximately the same concentration as the titrated solutions was measured with the same meter to aid in determining the end points of the titrations. The pH of a solution containing approximately 10 mmoles of hydroxylammonium chloride per 100 ml was 3.49. This solution was then diluted with an equal volume of water; the pH of the latter solution was 3.63, indicating a reasonably high buffering capacity of the hydroxylammonium chloride solution. Data are presented in Table V and Fig. 8. Results of these determinations indicate that the weight of the hydroxylamine sample, as determined by the method described above, is about 8% high.

b. Toepler-Pump System. A Toepler pump and gas buret system was constructed as shown in Fig. 9. By means of this system a noncondensable gas

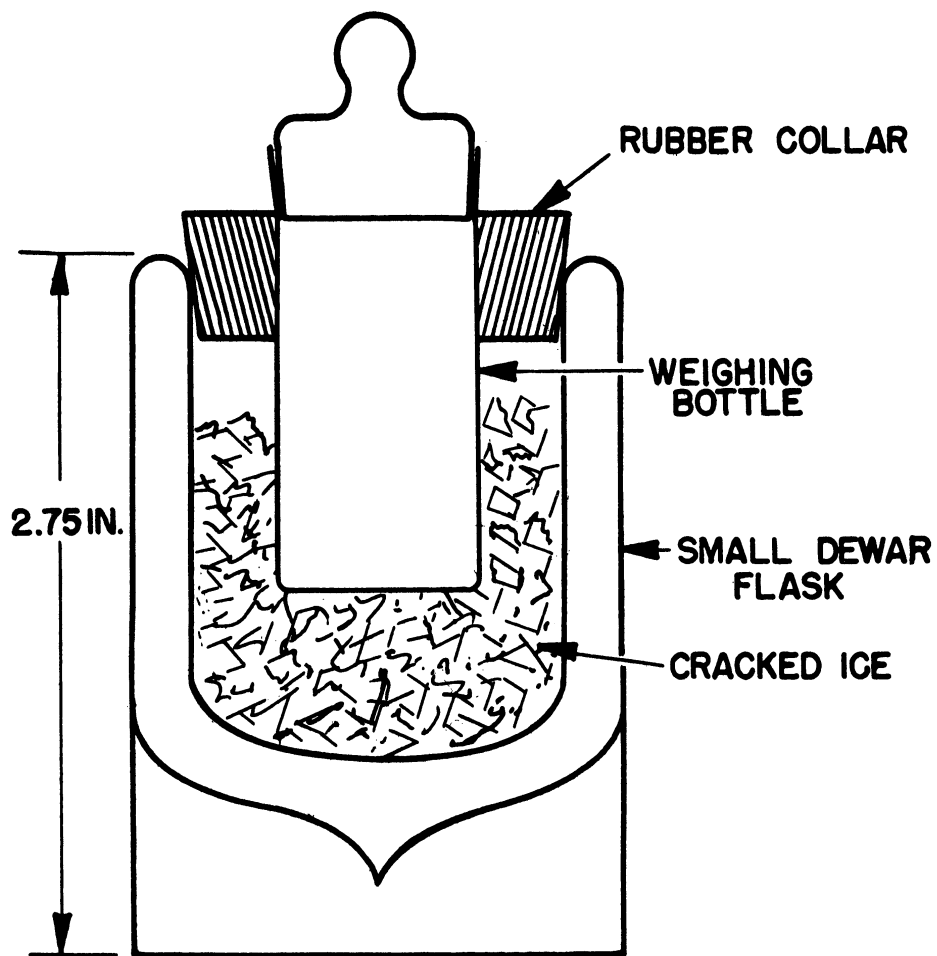
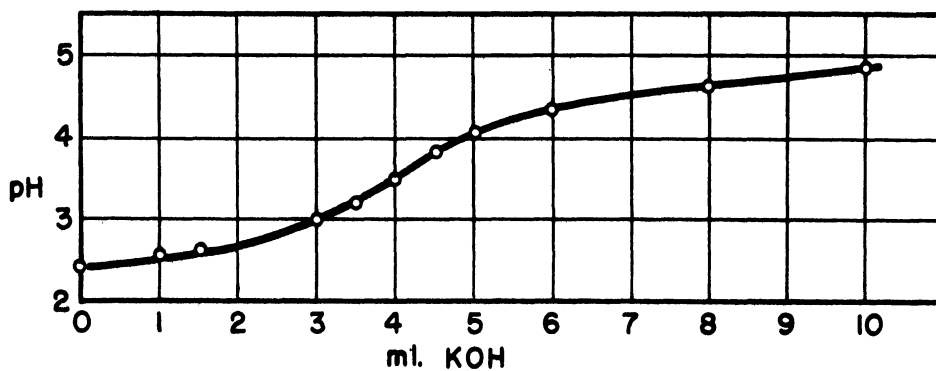
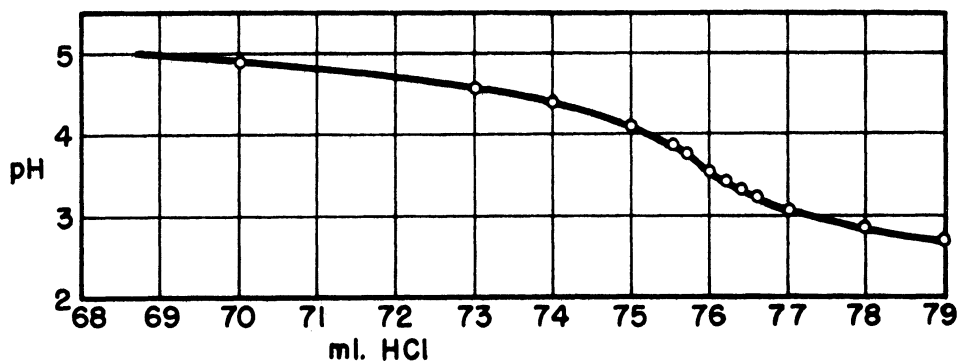


FIG. 7. SPECIAL WEIGHING UNIT FOR HYDROXYLAMINE



A. TITRATION OF EXCESS HCl WITH KOH. 0.2535g NH_2OH DISSOLVED IN 75 ml. 0.09863N HCl. EXCESS HCl BACK TITRATED WITH 0.08084N KOH.



B. TITRATION OF NH_2OH WITH HCl. 0.2653g NH_2OH DISSOLVED IN 60 ml. H_2O AND TITRATED WITH 0.09863N HCl.

FIG. 8. TITRATION CURVES FOR HYDROXYLAMINE.

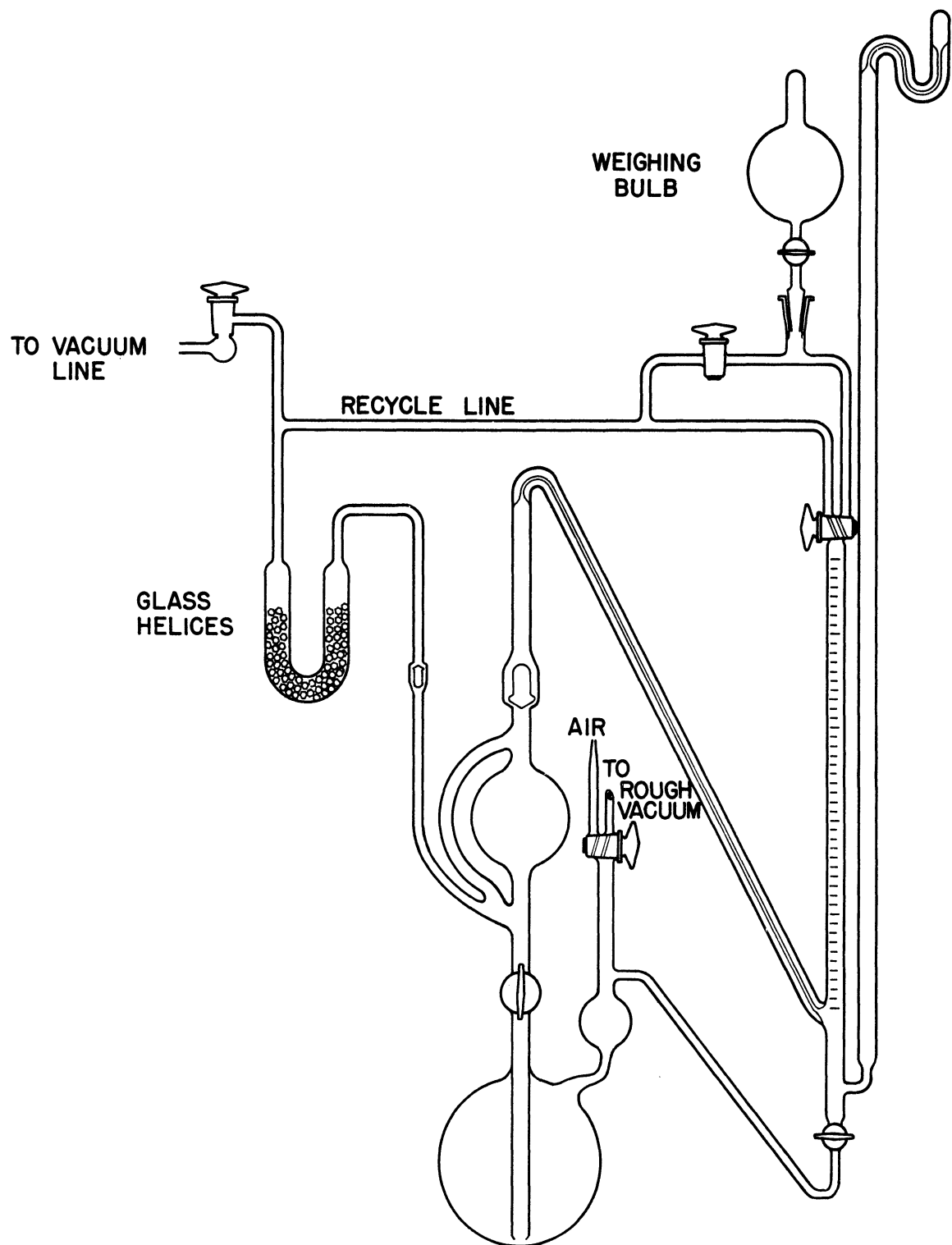


FIG. 9. TOEPLER PUMP AND BURET SYSTEM

TABLE V

TITRATION OF WEIGHED SAMPLE OF HYDROXYLAMINE

A. 0.2535 g. NH_2OH (7.68 mmoles)
dissolved in 75 ml 0.09863 N
HCl and titrated with 0.08084
N KOH

B. 0.2653 g. NH_2OH (8.05 mmoles)
dissolved in 60 ml H_2O and
titrated with 0.09863 N HCl

V_{KOH} (ml)	pH	V_{HCl}	pH
0	2.40	0	8.38
1.0	2.54	5.0	7.04
1.5	2.60	10.0	6.73
3.0	3.00	15.0	6.53
3.5	3.20	20.0	6.38
4.0	3.51	30.0	6.14
4.5	3.85	40.0	5.93
5.0	4.07	50.0	5.68
6.0	4.37	60.0	5.40
8.0	4.68	65.0	5.20
10.0	4.88	70.0	4.90
12.5	5.03	75.0	4.09
		75.5	3.85
		75.7	3.73
		76.0	3.52
		76.2	3.42
		76.4	3.30
		76.6	3.20
		77.0	3.05
		78.0	2.82
		79.0	2.66
		80.0	2.45

could be removed from other parts of the vacuum line and measured. A cold trap, packed with glass helices, was provided to permit the removal of traces of entrained condensable gases. A gas-weighing bulb was attached through a standard taper joint; this made it possible to identify the gas by weighing a measured quantity and calculating the molecular weight.

c. The Reaction. The reaction system is shown in Fig. 10. The reaction tube was attached to the vacuum-jacketed condenser at point A, and the condenser was attached to the manifold at point B. All ground joints and stopcocks in the system were lubricated with Dow Corning high-vacuum grease, which is more resistant to attack by ether than other lubricants tested.

In a typical experiment, a weighed sample was placed in the reaction tube, which was then attached to the condenser, cooled with ice water, and evacuated. Approximately 6 ml of ether were distilled into the cell and frozen by surrounding the tube with liquid nitrogen. A slight excess of diborane, assuming that two moles of hydroxylamine react with one mole of diborane, was measured and distilled into the reaction tube. The reaction mixture was maintained at the desired temperature by surrounding the tube with the appropriate slush bath, and the mixture was stirred constantly for several hours. The tube and its contents were then frozen with liquid nitrogen and the hydrogen evolved during the reaction was pumped off by means of the Toepler pump and measured in the gas buret. The unreacted diborane was then distilled out of the tube, separated from traces of ether by fractional condensation, and measured. Hydrogen evolved during the reaction was identified by weighing a measured quantity of the gas in a bulb and calculating the molecular weight.

In order to determine the completeness of separation of the excess diborane from the reaction mixture, a sample of diborane was mixed with ether in the reaction cell, stirred for several hours, and then distilled out and measured. A 5.6 ml sample of ether was distilled into the cell. To this was added 5.729 mmoles of diborane, and the mixture was stirred for 18 hours. When this solution was frozen, no noncondensable gas remained. The diborane was then distilled out of the cell for 20 minutes, purified by fractional condensation until its vapor pressure at -111.8°C was 225 mm, and measured. The quantity removed was 5.655 mmoles. This represents a loss of about 1.3 per cent of the original sample.

D. Results

Diborane reacts with hydroxylamine in the presence of ether, with the evolution of hydrogen at temperatures above -112°C , to form a white solid compound which is relatively stable at room temperature, but evolves additional hydrogen when heated.

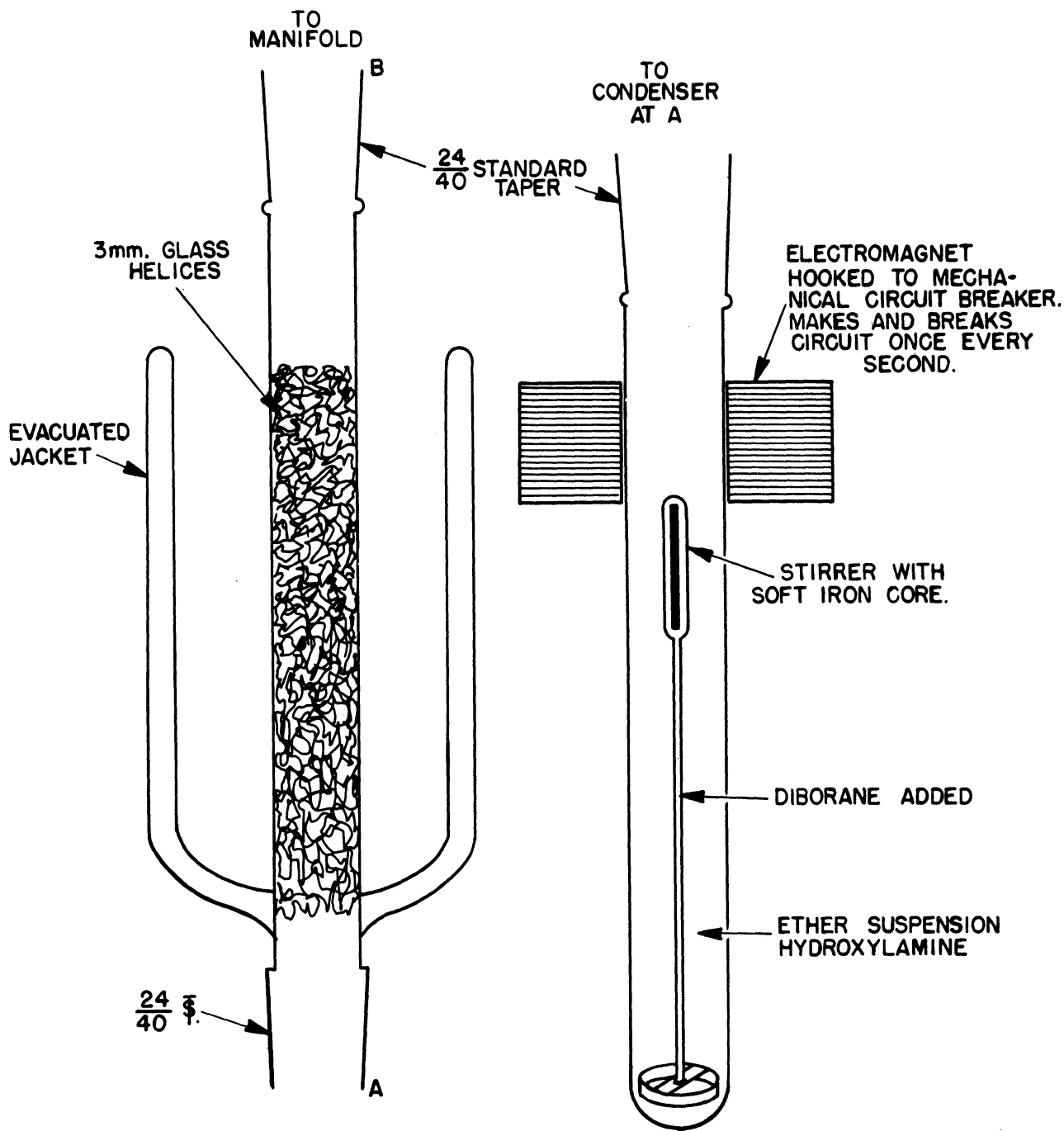


FIG. 10. REACTION TUBE AND CONDENSER

In Run 1, a crudely weighed sample of hydroxylamine, estimated to be about 20 mmoles was placed in the reaction tube, which was then attached to the vacuum line, cooled, and evacuated. A 20.7-mmoles sample of diborane was condensed into the cell and vapor-pressure measurements were made as the temperature of the system was allowed to rise slowly. These vapor-pressure data, covering the temperature range from -145° to -96°C , are presented in Table VI. The curve obtained by plotting these values approximates the accepted vapor-pressure curve for diborane. There was no visible evidence of reaction between diborane and hydroxylamine under these conditions (no solvent present).

TABLE VI

VAPOR PRESSURE OF DIBORANE OVER HYDROXYLAMINE

t($^{\circ}\text{C}$)	P(mm Hg)	t($^{\circ}\text{C}$)	P(mm Hg)	t($^{\circ}\text{C}$)	P(mm Hg)
-145.0	5	-135.7	29.2	-107.3	ca. 360
-142.0	8	-134.2	34.6	-103.7	ca. 411
-140.5	10.1	-131.5	44.6	-101.3	ca. 468
-139.5	11.8	-125.7	80.8	-99.3	ca. 534
-137.0	21.3	-121.3	117.2	-96.0	ca. 660
-136.5	25.4	-118.3	144.0		

Part of the diborane was then removed from the reaction tube, leaving only the amount estimated to give a pressure of approximately $1/2$ atmosphere at room temperature. It was planned to allow the temperature to rise slowly to 0°C . However, after the liquid nitrogen was removed and before the cold bath was in place, the temperature increased to some value above -100°C and an explosive reaction occurred. A white solid compound was formed.

In order to moderate the reaction rate, ethyl ether was used as a reaction medium in Run 2 and subsequent experiments. In Run 2, diborane was condensed into the reaction cell containing hydroxylamine and ether, and the system was permitted to warm slowly from liquid-nitrogen temperature to -78°C and to remain at this temperature until the pressure attained a constant value. When the cell and contents were then frozen with liquid nitrogen, a residual pressure was observed, indicating the formation of a noncondensable gas in the reaction. This gas was pumped off, measured, and weighed. The molecular weight of the gas, calculated from the quantity (1.82 mmoles) and weight (3.8 mg.), was 2.1, indicating that the gas evolved was hydrogen. The hydroxylamine sample

was not weighed, but was estimated to be approximately 0.4 g. (ca. 12 mmoles). The total diborane consumed was 6.99 mmoles, and the hydrogen evolved was 5.15 mmoles.

In Run 3, a sample of hydroxylamine weighing 0.428 g. was used. Assuming that the weight was 8% high, the sample contained ca. 12 mmoles of hydroxylamine. Ether and diborane were condensed into the cell as before. The temperature was maintained at -78°C by the use of a slush bath of solid CO_2 in isopropanol. The reaction was allowed to proceed over a period of four days, with the diborane being added in three separate portions during that time. The reaction was assumed to be complete when the pressure attained an essentially constant value. The evolved hydrogen and the excess diborane were then removed and measured, and the ether was removed. The temperature was not permitted to rise above -78°C until dry nitrogen had been admitted to the reaction tube. The net amount of diborane consumed was 5.75 mmoles, and the quantity of hydrogen evolved was 7.57 mmoles. (The gas was identified as hydrogen by M.Wt. = 2.04.)

Run 4 was conducted in the same manner as Run 3, except that the temperature of the reactants was allowed to rise gradually to 0°C during the reaction. A sample of hydroxylamine weighing 0.437 g. (ca. 12 mmoles) was used, and 5.69 mmoles of diborane were consumed. During the reaction, 9.1 mmoles of hydrogen were evolved. The tube and contents were permitted to warm to room temperature after the hydrogen, ether, and excess diborane had been removed and the system was still under vacuum. During this temperature rise the solid product spontaneously lost an additional 9.3 mmoles of hydrogen. (The gas was identified as hydrogen by M. Wt. = 2.8.)

A hydroxylamine sample of approximately 5.3 mmoles was used in Run 5. To this there was added 5.6 ml of ether and 4.38 mmoles of diborane. In this experiment the progress of the reaction as a function of temperature was studied. Slush baths of CS_2 (-111.8°C), CO_2 -isopropanol (-78°C), CHCl_3 (-64°C), $\text{C}_6\text{H}_5\text{Cl}$ (-46°C), CCl_4 (-23°C), ice-water (0°C), and water at room temperature (27°C), were used in that order. The reaction was allowed to continue until the pressure remained essentially constant at each temperature, and the hydrogen was removed and measured before the mixture was permitted to warm to the next higher temperature. The unreacted diborane was removed and measured after the reaction at -78°C ; 2.99 mmoles of diborane were consumed. Results of the experiment are given in Table VII. The gas evolved was identified, as usual, by a molecular-weight determination. The molecular weight obtained for the gas evolved at -78°C was 2.7. It was assumed that the high value was due to contamination by ether which was entrained. In order to minimize this error, the cold trap adjacent to the Toepler pump was packed with 3-mm glass helices. The gas was then recycled through this trap, which was cooled with liquid nitrogen, and again measured and weighed. The molecular weight was then 1.95, which is considered to represent the molecular weight of hydrogen, within the limits of error of the method and system.

TABLE VII

THE REACTION BETWEEN DIBORANE AND HYDROXYLAMINE, RUN 5

Temperature (°C)	H ₂ Evolved (mmoles)	Total H ₂ (mmoles)	H ₂ B ₂ H ₆	H ₂ NH ₂ OH
-112	0.082	0.082	0.027	0.015
-78	2.234	2.316	0.774	0.44
-64	0.228	2.544	0.851	0.48
-46	0.990	3.534	1.182	0.67
-23	0.203	3.737	1.249	0.71
0	0.279	4.016	1.343	0.76
+27	1.287	5.303	1.773	1.0

a Ratio of B₂H₆ to NH₂OH present during this period was 4.38/5.3. Excess diborane was then removed.

b Ratio of B₂H₆ to NH₂OH present during this period was 2.99/5.3.

In Run 6, a sample of hydroxylamine weighing 0.372 g. was used. Taking the estimated error of 8% into consideration, this represents approximately 10.4 mmoles. The rate of the reaction at -112°C was studied in this experiment. The unreacted diborane was removed and measured after the reaction had proceeded for a measured time; then the excess diborane was returned to the cell and the reaction was allowed to continue at the same temperature. By repeating this process, the progress of the reaction with time could be followed. The data are presented in Table VIII and plotted in Fig. 11.

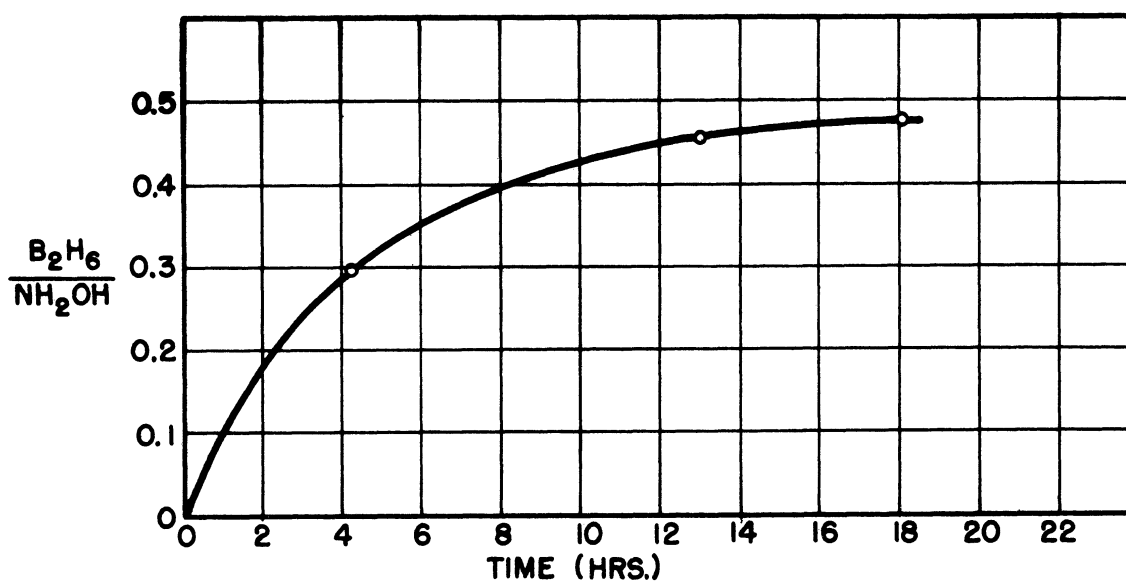


FIG. 11. REACTION OF DIBORANE WITH HYDROXYLAMINE AT -112°C.

TABLE VIII

THE REACTION OF DIBORANE WITH HYDROXYLAMINE AT -112°C NH_2OH : 10.4 mmoles

Time ^a (hrs.)	B_2H_6 Combines (mmoles)	Mole Ratio $\text{B}_2\text{H}_6/\text{NH}_2\text{OH}$
4.2	3.08	0.296 ^b
13	4.72	0.454 ^b
18	4.92	0.473 ^b
36.8	4.51	0.433 ^c
	4.24	0.408 ^d
	4.03	0.388 ^d

a Times recorded are number of hours reaction proceeded in the presence of excess diborane, and do not include distillation time.

b Removable B_2H_6 distilled out for 20 minutes. (See Section C,2,c.)

c B_2H_6 removed by distillation for one hour.

d Distillation continued for 2.5 hours after previous measurement.

Only 0.661 mmole of hydrogen was evolved during the reaction at -112°C , although the mole ratio of diborane to hydroxylamine approached 1:2, as indicated in Fig. 11.

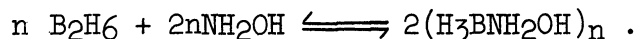
After this part of the experiment was completed, sufficient diborane was added to the reaction mixture to increase the total quantity to 5.01 mmoles. The mole ratio of diborane to hydroxylamine was then approximately 1:2.

When the reaction temperature reached -78°C , hydrogen was evolved much more rapidly until the total hydrogen evolved increased to approximately 6 mmoles. Some additional hydrogen was evolved after long stirring at -78°C , but not a significant amount. (The gas was identified as hydrogen by M.Wt. = 2.31.)

The solid product of these experiments dissolves in water, methanol, and ethanol, with the evolution of hydrogen. It is not appreciably soluble in anhydrous ether, benzene, toluene, 1,4-dioxane, or liquid ammonia. When the compound is heated it liberates more hydrogen. A sample weighing 47.8 mg. liberated 0.938 mmole of hydrogen (identified by M.Wt. = 1.8) when it was heated to 250°C for two hours. (This is approximately equivalent to the loss of the 9.3 mmoles of hydrogen by the reaction product in Run 4.) The solid compound remaining after the release of this additional hydrogen dissolves with difficulty in water, but dissolves readily in dilute acid or base. It is insoluble in ether, benzene, toluene, and 1,4-dioxane.

E. Discussion

The data from Run 6, given in Table VIII and shown in Fig. 11, indicate that diborane reacts slowly with a stirred ether suspension of hydroxylamine at -112°C without the liberation of appreciable amounts of hydrogen. The stoichiometry of the reaction at -112°C may be represented by the equation



The slow reversibility of the reaction is suggested by the fact that prolonged and strenuous condensation procedures at the end of the reaction at -112°C permitted the removal of some of the diborane which had previously undergone combination with hydroxylamine. In view of the relatively weak basic strength of the hydroxylamine, this reversibility is not surprising.

If the compound $(\text{H}_3\text{BNH}_2\text{OH})_n$ is allowed to warm up, hydrogen is liberated, probably through the reaction between the acidic hydroxyl hydrogen of the hydroxylamine and the hydridic hydrogen of the diborane. Either intramolecular or intermolecular elimination of hydrogen could occur. The latter process would give rise to a polymeric structure or a heterocyclic compound, while the former process would result in an unsaturated compound which might or might not undergo an addition reaction to form either a heterocyclic or a polymeric compound. The low solubility and the nonvolatile nature of the solid product obtained suggest that a polymeric compound has been formed. Molecular-weight measurements have been prevented thus far by the lack of a suitable solvent for the solid.

Further discussion and characterization of the products will be reserved until additional experiments are completed.

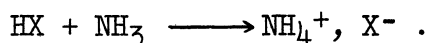
VI. CONDUCTIVITY MEASUREMENTS IN LIQUID DIBORANE

A. Background

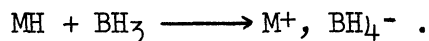
Measurements of conductivities and solubilities in several solvents of low dielectric constant have been recorded. Liquid hydrogen sulfide, ether, and benzene have been studied to some extent, while ammonia solutions have been investigated rather extensively. Ammonia, with a dielectric constant of 28, might be classed as a liquid with properties between those of water and the nonpolar liquids mentioned above. It is interesting to note that, even in

ammonia, ionic solids form large numbers of ion pairs in solution. Examples of this are found in the earlier section on molecular weights in liquid ammonia.

Although the dielectric constant of liquid diborane is not recorded, it is probable that the value is low, being near that of liquid hydrogen sulfide, or perhaps even the hydrocarbons. In spite of this, the existence of the borohydrides suggests an interesting formal analogy which made it seem worthwhile to investigate conductivities in liquid diborane. Ammonia, as a basic solvent, is capable of dissolving acidic substances by means of the interaction



On the other hand, diborane, as an acidic solvent, might dissolve basic substances of low lattice energy as represented by the equation:



The following exploratory studies were used to test this hypothesis.

B. Experimental

1. Reagents

a. Ammonia. Commercial-grade ammonia, supplied by the Matheson Co., Inc., Joliet, Ill., was purified by distillation from sodium in the vacuum apparatus.

b. Diborane. Diborane was prepared as previously described by the reaction of lithium aluminum hydride and boron trifluoride etherate in ether (vapor pressure = 225 mm at -111.8°C).

c. Potassium Chloride. Reagent-grade potassium chloride, further purified by recrystallization and ignition, was obtained from Dr. Robert C. Taylor of this laboratory.

d. Potassium Fluoride and Potassium Cyanide. Baker and Adamson reagent-grade potassium fluoride and potassium cyanide were used without further purification.

e. Sodium Borohydride, Lithium Borohydride, and Lithium Aluminum Hydride. Sodium borohydride, lithium borohydride, and lithium aluminum hydride furnished by Metal Hydrides, Inc., Beverly, Mass., were used without further purification.

2. Apparatus and Procedure

a. Measuring Volume of Solvent. A 12-ml graduated centrifuge tube was sealed to the vacuum manifold, and the solvent was distilled into this tube for volume measurements. The temperature was controlled by the use of the appropriate slush bath, which was removed briefly for volume observations.

b. Weighing Solutes. Potassium chloride samples were weighed by difference in a Kimble micro weighing tube, using a semimicro analytical balance. The weighing tube was then inserted into the conductivity cell and the sample was dumped directly into the bottom of the cell. In this way no particles of the sample could be left adhering to the wall of the upper part of the cell. Samples of the other compounds were not weighed, since only qualitative tests were performed on them.

c. Conductivity Cell. A conductivity cell was constructed as shown in Fig. 12. The problem was to provide a cell capable of maintaining a high vacuum and withstanding extreme temperature changes as well as fulfilling the electrical requirements. In view of the fact that the work was exploratory in nature, and only semiquantitative results were expected, it was considered advisable to compromise on the electrical requirements where necessary. For this reason the leads to the electrodes were placed inside the cell as shown, in spite of the fact that this is not the best design for avoiding undesirable capacitance effects. These leads were enclosed in the glass tubes as far as possible.

The most serious difficulty to be overcome was the construction of satisfactory metal-to-glass seals. For this purpose the platinum tube seals described by Hnizda and Kraus²¹ were used. These were not always satisfactory, however, and many seals were made before a cell was obtained which proved to be dependable.²²

d. Measurement of Resistance. A direct-reading alternating-current bridge, employing a Wagner earthing device to reduce errors caused by capacitance couplings, was furnished by Dr. Robert C. Taylor and was used throughout these experiments. This bridge is useful for measuring resistances up to approximately 100,000 ohms, but does not measure accurately resistances of the order of a million ohms or higher.

e. Determination of Cell Constant. A comparison cell having a cell constant of 1.5141 was used in the determination of the constant of the cell

21 Hnizda, Vincent F., and Kraus, Charles A., J. Am. Chem. Soc., 71, 1565 (1949).

22 We wish to express our appreciation to Dr. Hnizda of the Ethyl Corporation for his assistance in the ultimate production of a successful seal.

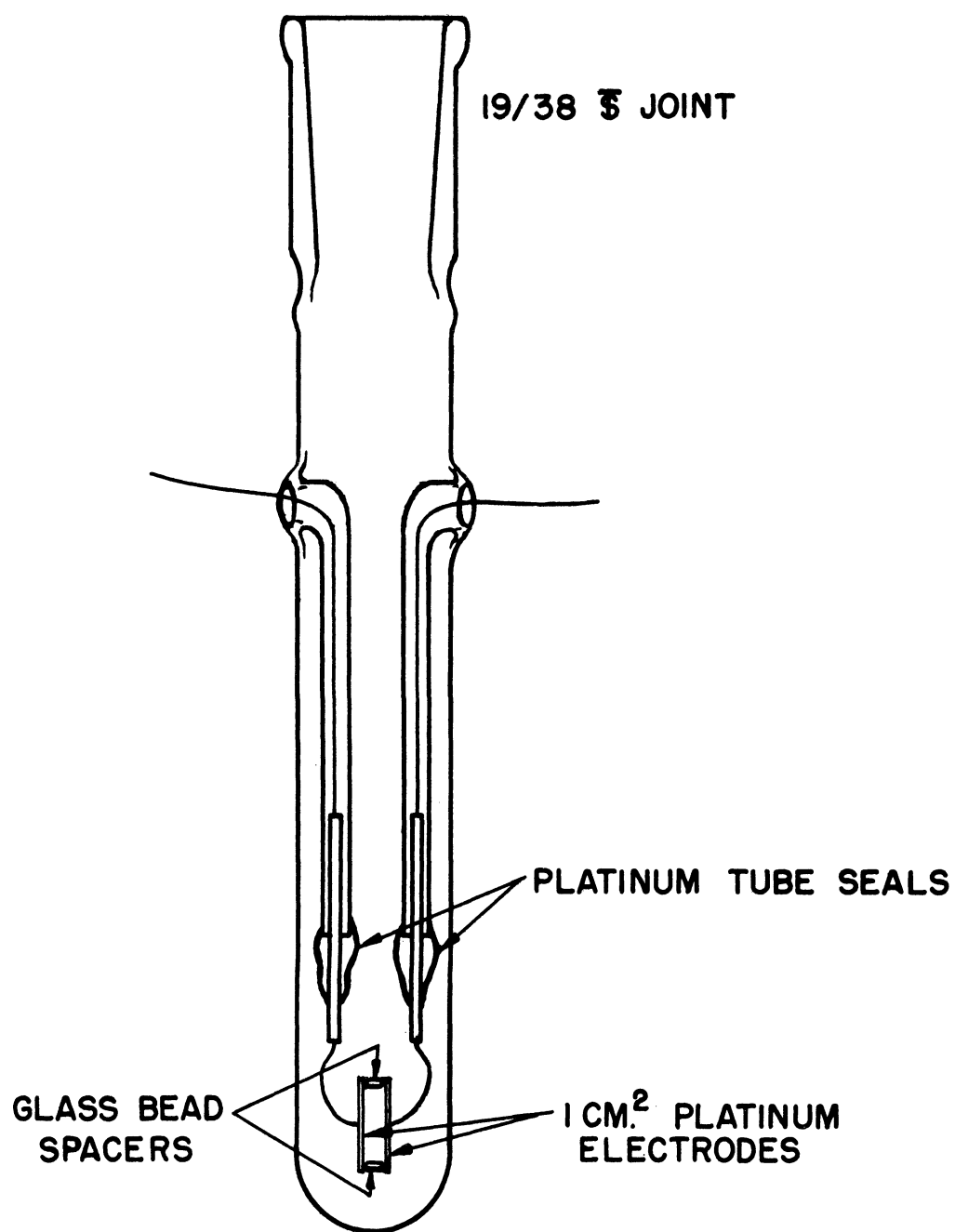


FIG. 12. CONDUCTIVITY CELL (ACTUAL SIZE)

described above. It was found that the resistance of a solution of approximately 0.002 N KCl could be measured in both cells, and such a solution was used in the determination of the cell constant. This determination had to be repeated each time the cell was repaired after a failure of a metal-to-glass seal. Data for the final determination are given in Table IX.

TABLE IX

RESISTANCES OF ca. 0.002 N KCl SOLUTION

IN COMPARISON CELL (R_c) AND EXPERIMENTAL CELL (R_e)

$$J_c = 1.5141$$

R_c (ohms)	R_e (ohms)
7972.3	1011.4
7972.7	1011.7
7970.5	1010.1

$$J_e = 1.5141 \times 1011.1/7971.4 = 0.19204$$

f. Determination of Accuracy of Experimental Method. In order to determine the accuracy of the method under conditions similar to those used later with diborane, a series of measurements was made on potassium chloride solutions in liquid ammonia. Data obtained in this series of measurements are presented in Table X.

C. Results

An attempt was made to measure the resistance of pure diborane, but an accurate measurement was not possible because of the extremely high resistance. The resistance was estimated to be about 10 megohms. Since the cell constant was 0.1920, the specific conductance of pure diborane must be of the order of 10^{-8} mho.

Samples of potassium fluoride, sodium borohydride, lithium borohydride, lithium aluminum hydride, and potassium cyanide were placed in the cell in successive experiments and stirred with liquid diborane by means of a small magnetic stirrer. Attempts to measure the resistance in each case led to results similar to those obtained with diborane alone. An accurate

TABLE X

CONDUCTIVITY OF POTASSIUM CHLORIDE IN LIQUID AMMONIA

KCl: 0.48 ± 0.01 mg. $J = 0.1847$

Conc. ^a ($\times 10^2$)	t ($^{\circ}$)	R _t ^o (Ohms)	R ₋₃₄ ^o ^b (Ohms)	L ($\times 10^4$)	Λ Calcd.	Λ Accepted ^c
115	-35.5	777.0	765.4	2.413	209.8	212
115	-35.7	750.0	737.2	2.505	217.8	212
115	-36.0	749.6	734.6	2.514	218.5	212
77.6	-35.2	1014	1002	1.843	237.5	232
77.6	-35.2	1017	1005	1.837	236.8	232
77.6	-35.7	1028	1011	1.826	235.4	232
66.1	-36.4	1174	1146	1.611	243.9	241
66.1	-36.7	1173	1141	1.618	244.9	241
66.1	-36.3	1166	1139	1.622	245.4	241

KCl: 1.00 ± 0.01 mg. $J = 0.1685$

225.4	-35.5	446.0	439.3	3.836	170.2	179
225.4	-36.0	446.3	437.4	3.852	170.9	179
225.4	-36.0	446.5	437.6	3.851	170.8	179
186.3	-37.0	511.7	496.3	3.395	182.2	188
186.3	-36.8	512.0	497.9	3.384	181.7	188
186.3	-37.2	512.1	495.5	3.401	182.5	188
152.4	-35.5	594.4	585.5	2.878	188.8	198
152.4	-35.5	594.6	585.7	2.877	188.8	198

a Concentration expressed as moles of solute per liter of solvent.

b The temperature coefficient of 1% per $^{\circ}$ C, given by Hnizda and Kraus¹ was used in calculating resistances at -34° C.c Accepted values of equivalent conductances at these concentrations were determined by interpolation of data given by Hnizda and Kraus.¹

determination of the resistance could not be made in any case, but there was no indication that the resistance was lowered by the presence of any of these compounds with the diborane. There was no visible evidence of solubility of any of these compounds in diborane; for example, no residue was deposited on the walls of the tube when the diborane was removed from the cell by evaporation.

D. Conclusions

In this investigation it has been shown that the method used for determining the conductances of solutions of salts in liquid ammonia is capable of yielding results that are satisfactory for rapid estimations. An inspection of the data contained in Table X shows that the errors in the calculated values of the equivalent conductances of the solutions range from approximately 1.5% to about 5%. This indicates that the method is suitable for the exploratory experiments that were attempted in this study.

The results indicate that ordinary salts have no tendency to dissolve in liquid diborane, and that even the salt-like metal borohydrides do not dissolve.

An analysis of the solution process indicates that the driving force for the dissolving of a metal fluoride or hydride would, in all probability, arise largely from the solvation of the anion. The interaction between the basic anion and the acidic borine group of the solvent would give a reaction which might, in a formal sense, be compared to the interaction between the proton and the basic ammonia molecule. A high lattice energy of the solute and the low dielectric constant of diborane would retard the solution process. Apparently the lattice energies of sodium and lithium borohydrides and the other salts tested were too high to permit solution in diborane. There is, of course, the possibility that other borohydrides, such as those of beryllium or aluminum, might be soluble in diborane, but these solutions would probably be poor conductors. Since the determination of the conductances of these poor conductors would require the use of very highly refined bridge equipment which is not currently available, it was decided to stop work on the problem, at least for the present.

The solubilities of several tetraalkyl ammonium salts in solvents of low dielectric constant, such as liquid hydrogen sulfide, have been reported. Since these salts would have relatively low lattice energies, the solubilities of such compounds in liquid diborane might be measurable. Qualitative tests are contemplated.

