yields were 22 and 24%, respectively, based on $(CNCl)_3$. Pure $C_3N_3F_2Cl$ boiled at 113–114°, froze at 22–23°, gave positive tests for both fluorine and chlorine, and was very sensitive to hydrolysis.

Anal. Calcd. for $C_3N_3F_2Cl$: Cl, 23.4; mol. wt., 152. Found: Cl, 23.3; mol. wt. (Victor Meyer), 149, 149.

Preparation of Cyanuric Fluorochloride (II).—Commercial $(CNCl)_3$ (60 g.), SbF_3 (20 g.) and $SbCl_5$ (10 g.) were placed in a round-bottom flask equipped with a total reflux, partial take-off head with a thermometer inserted in a well at the top. The flask was then heated with a Glass-col mantle and all of the liquid product distilled over as rapidly as possible under anhydrous conditions keeping the reflux temperature below 190°. Approximately 15 cc. of a mixture of solid and liquid was obtained. This product was combined with 25 cc. of similar material obtained earlier and the mixture rectified through an 18″ heated column packed with glass helices. There was obtained: forerun, b.p. 114–152° (5 cc.); a colorless liquid central cut, b.p. 152° (25 cc.); and residue, b.p. 153–190° (10 cc.). The central cut was rectified carefully through a 12″ Podbielniak column, and finally there was obtained: forerun, b.p. 114–115° (3 cc.); $C_3N_3FCl_2$(II), b.p. 155° (16 cc.); and high boiling residue (6 cc.). The yield of II was about 20% based on $(CNCl)_3$ used. Pure $C_3N_3FCl_2$ boiled at 155°, froze at 2°, gave positive tests for both fluorine and chlorine and was sensitive to hydrolysis.

Anal. Calcd. for $C_3N_3FCl_2$: F, 11.3; mol. wt., 168. Found: F, 11.2; mol. wt. (Victor Meyer), 166, 171.5.

DURHAM, NORTH CAROLINA

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SAINT LOUIS UNIVERSITY, AND THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

Etherates of Lithium Borohydride. II. The System Lithium Borohydride–Diethyl Ether

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Pressure–composition isotherms at 25.0, 0.0, −35.3, −45.2, and −63.5° for the system lithium borohydride-diethyl ether indicate that two solid diethyl etherates, $LiBH_4 \cdot (C_2H_5)_2O$ (I) and $(LiBH_4)_2 \cdot (C_2H_5)_2O$ (II), exist. Values for the heats, free energies and entropies of dissociation of these compounds per mole of diethyl ether evolved at 25° are ΔH_d = (I) 13.36 and (II) 11.90 kcal.; ΔF_d = (I) 1.26 and (II) 1.67 kcal.; and ΔS_d = (I) 40.6 and (II) 34.3 e.u. The standard heats and free energies of formation and absolute entropies at 25° are ΔH_f^0 = (I) −118.6 and (II) −164.3 kcal./mole; ΔF_f^0 = (I) −60.3 and (II) −91.2 kcal./mole; and S^0 = (I) 63.4 and (II) 84.7 e.u. Approximate values for the heats of solution of lithium borohydride (III) and its diethyl etherates in diethyl ether at 25° are (III) −3.8, (I) +2.1 and (II) −2.9 kcal./mole. Solubility data for lithium borohydride in diethyl ether over the temperature range −112 to 25.0° are presented. The state of aggregation of the solute in lithium borohydride–diethyl ether solutions at room temperature is about 2 to 3 times its formula weight, as evidenced by deviations from Raoult's law.

Results and Discussion

Pressure–composition isotherms for the system lithium borohydride–diethyl ether are presented in Fig. 1. These isotherms give clear evidence for the existence of two solid etherates. Abrupt pressure changes occur at lithium borohydride mole fractions (n_2) 0.500 and 0.667, denoting phase transformations between the diethyl etherate of lithium borohydride, $LiBH_4 \cdot (C_2H_5)_2O$, previously described by Schlesinger and his co-workers[3]; and the hitherto unreported hemi-(diethyl etherate), $(LiBH_4)_2 \cdot (C_2H_5)_2O$; and lithium borohydride. Representative data for isotherms at 25.0, 0.0, −35.3, −45.2 and −63.5° are listed in Table I. Also included is a partial isotherm at 15.0° in the region of the saturated solution from which the solubility of lithium borohydride may be calculated.

The absence of a discontinuity of the phase diagrams at $n_2 = 0.33$ shows unambiguously that a bis-(diethyl etherate) of lithium borohydride does not exist even at temperatures as low as −63.5°.[4] This places the lithium borohydride–diethyl ether system in marked contrast to the lithium borohydride–dimethyl ether system, in which a stable bis-(etherate) is readily formed.[5] On the other hand, the two systems are similar in that no etherates lower than an hemi-(etherate) were found.

Heats of dissociation of the two diethyl etherates of lithium borohydride were determined from the dissociation pressures of the respective etherates at various temperatures, Table II. That the data are well represented by a simple linear equation (Table III and II) indicates that the heats of dissociation for the processes

$$2LiBH_4 \cdot (C_2H_5)_2O(s) = (LiBH_4)_2 \cdot (C_2H_5)_2O(s) + (C_2H_5)_2O(g) \quad (1)$$

and

$$(LiBH_4)_2 \cdot (C_2H_5)_2O(s) = 2LiBH_4(s) + (C_2H_5)_2O(g) \quad (2)$$

are constant in the temperature range considered. Extrapolation of the dissociation pressure–temperature data to lower temperatures show an intersection at −40° and 0.17 mm.; below −40° only lithium borohydride diethyl etherate is stable.

Values for the various thermodynamic quantities associated with the dissociation processes described by equations 1 and 2 at 25° are summarized in Table III. The data in Table III may be combined with the thermodynamic properties of lithium borohydride and diethyl ether to allow cal-

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(1) Taken in part from a thesis presented to the Graduate School of Saint Louis University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1957.

(2) Taken in part from a thesis presented to the Graduate School of Saint Louis University in partial fulfillment of the requirements for the degree of Master of Science, February, 1955.

(3) H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp, THIS JOURNAL, **75**, 199 (1953).

(4) E. Wiberg, H. Nöth and R. Uson, *Z. Naturforsch.*, **11b**, 490 (1956), report failure to isolate lithium borohydride bis-(diethyl etherate) at temperatures down to −80°.

(5) G. W. Schaeffer, T. L. Kolski and D. L. Ekstedt, THIS JOURNAL, **79**, 5912 (1957).

Table I

Data for Pressure--Composition Isotherms at Various Temperatures for the System Lithium Borohydride-Diethyl Ether

−63.5°		−45.2°		−35.3°		0.0°		15.0°		25.0°	
Comp., n_2	Press., mm.	Comp., n_2	Press., mm.	Comp., n_2	Press., mm.	Comp., n_2	Press., mm.	Comp., n_2	Press., mm.	Comp., n_2	Press., mm.
0.000	3.1[a]	0.000	13.1[a]	0.000	26.5[a]	0.000	185.3[a]	0.000	360.7[a]	0.000	537.0[a]
.0445	3.0	.0445	12.8	.0445	24.4	.0386	183.3[b]	.0388	352.9[b]	.0548	521.0[b]
.136	3.0	.136	12.7	.136	24.4	.0447	182.6	.0543	350.3[b]	.0794	516.8[b]
.233	3.0	.233	12.7	.234	24.4	.240	182.6	.0783	346.9[b]	.149	508.2[b]
.337	3.0	.338	12.9	.339	24.3	.447	182.2	.0997	344.4[b]	.319	510.1
.418	2.9	.420	12.8	.422	24.4	.491	181.3	.146	347.6	.404	509.1
.457	3.0	.459	12.8	.480	24.3	.500	149.2	.194	347.8	.455	508.8
.509	0.1	.499	4.1	.499	14.0	.500	94.2	.253	347.6	.490	505.8
.586	.1	.509	0.2	.504	0.6	.500	28.9			.499	317.4
.627	.1	.586	.2	.586	.4	.505	11.5			.500	221.5
.706	.1	.627	.2	.627	.4	.660	11.4			.500	132.9
.753	.1	.706	.2	.706	.3	.675	7.5			.528	90.4
		.753	.2	.753	.3	.850	7.5			.657	90.0
						.964	7.3			.669	77.3
										.672	45.6
										.871	45.8
										.990	44.8

[a] "International Critical Tables" Vol. V, McGraw--Hill Book Co., Inc., New York, N. Y., 1933. [b] No solid phase present.

culation of the standard heats of formation, free energies of formation and absolute entropies at 25° for the two diethyl etherates of lithium borohydride. These values[6] are listed in Table IV.

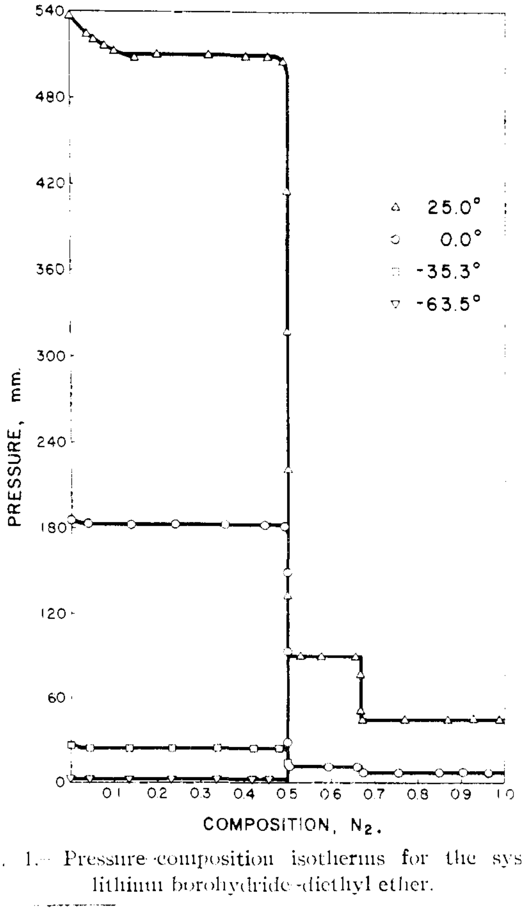

Fig. 1.—Pressure-composition isotherms for the system lithium borohydride-diethyl ether.

Table II

Dissociation Pressures of the Diethyl Etherates of Lithium Borohydride

A. $LiBH_4 \cdot (C_2H_5)_2O$			B. $(LiBH_4)_2 \cdot (C_2H_5)_2O$		
Temp., °C.	Pressure, mm.		Temp., °C.	Pressure, mm.	
	Obsd.	Calcd.		Obsd.	Calcd.
−36.6	0.33	0.25	−25.7	0.83	0.75
−19.3	1.89	1.77	−12.7	2.54	2.49
0.0	11.53	11.50	0.0	7.20	7.25
19.8	60.6	60.6	14.8	22.7	22.4
32.0	151.6	151.60	25.3	46.5	46.5
			35.1	88.7	87.4
			45.0	160.6	161.1
			54.9	284.2	284.2

Table III

Thermodynamics of Dissociation at 25° for the Diethyl Etherates of Lithium Borohydride

$$\text{Log } P_{\text{mm}} = A - \frac{B}{T}$$

Process	A	B	ΔH, kcal.	ΔF, kcal.	ΔS, e.u.
$2LiBH_4 \cdot (C_2H_5)_2O$ to $(LiBH_4)_2 \cdot (C_2H_5)_2O$ (eq. 1)	11.7447	2918.9	13.36 13.8[a]	1.26	40.6
$(LiBH_4)_2 \cdot (C_2H_5)_2O$ to $2LiBH_4$ (eq. 2)	10.3818	2601.2	11.90 11.4[a]	1.67	34.3
$LiBH_4 \cdot (C_2H_5)_2O$ to $LiBH_4$			12.63 12.6[a]	1.46	37.4

[a] Determined by the heat of solution method.

Table IV

Standard Heats of Formation, Free Energies of Formation and Absolute Entropies of the Diethyl Etherates of Lithium Borohydride at 25°

Compound	$\Delta H f^0$, kcal./mole	$\Delta F f^0$, kcal./mole	S^0 e.u.
$LiBH_4 \cdot (C_2H_5)_2O(s)$	−118.6	−60.3	63.4
$(LiBH_4)_2 \cdot (C_2H_5)_2O(s)$	−164.3	−91.2	84.7
$LiBH_4(c)$	−46.36[a]	30.74[a]	18.13[a]
$(C_2H_5)_2O(l)$	−66.4[b]	28.3[b]	60.5[c]

[a] "Thermodynamic Properties of Boron Compounds at 25°," National Bureau of Standards, Washington 25, D. C., April 1954. [b] G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," Chemical Catalog Co., New York, N. Y., 1932, pp. 167–168. [c] G. S. Parks, K. K. Kelly and H. M. Huffman, This Journal, 51, 1969 (1929).

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(6) In these computations the heat of vaporization of diethyl ether was taken as 6.7 kcal./mole. "International Critical Tables" Vol. V, McGraw-Hill Book Co., Inc., New York, N. Y., 1933, p. 138, gives a value of 6.38 kcal./mole, while D. R. Stull, *Ind. Eng. Chem.*, **39**, 522 (1947), gives vapor pressure data from which the value 6.92 kcal./mole is calculated.

Approximate values for the heats of solution of lithium borohydride, lithium borohydride diethyl etherate and lithium borohydride hemi-(diethyl etherate) in diethyl ether at 25° were determined calorimetrically with sample sizes taken to give final concentrations of 0.1–0.2% by weight. These heats of solution: $LiBH_4$, −3.8 kcal./mole; $LiBH_4 \cdot (C_2H_5)_2O$, +2.1 kcal./mole; and $(LiBH_4)_2 \cdot (C_2H_5)_2O$, −2.9 kcal./mole, may be used to derive values for heats of dissociation of the diethyl etherates of lithium borohydride

$$2LiBH_4 \cdot (C_2H_5)_2O(s) + X(C_2H_5)_2O(l) = 0.15\%\ \text{soln.} \quad \Delta H = +4.2\ \text{kcal.} \quad (3)$$

$$(LiBH_4)_2 \cdot (C_2H_5)_2O(s) + (X + 1)(C_2H_5)_2O(l) = 0.15\%\ \text{soln.} \quad \Delta H = -2.9\ \text{kcal.} \quad (4)$$

$$\frac{(C_2H_5)_2O(l) = (C_2H_5)_2O(g) \quad \Delta H = +6.7\ \text{kcal.}}{2LiBH_4 \cdot (C_2H_5)_2O(s) = (LiBH_4)_2 \cdot (C_2H_5)_2O(s) + (C_2H_5)_2O(g) \quad \Delta H = 13.8\ \text{kcal.}} \quad (5)$$

and

$$(LiBH_4)_2 \cdot (C_2H_5)_2O(s) + X(C_2H_5)_2O(l) = 0.15\%\ \text{soln.} \quad \Delta H = -2.9\ \text{kcal.} \quad (4)$$

$$2LiBH_4(s) + (X + 1)(C_2H_5)_2O(l) = 0.15\%\ \text{soln.} \quad \Delta H = -7.6\ \text{kcal.} \quad (6)$$

$$\frac{(C_2H_5)_2O(l) = (C_2H_5)_2O(g) \quad \Delta H = +6.7\ \text{kcal.}}{(LiBH_4)_2 \cdot (C_2H_5)_2O(s) = 2LiBH_4(s) + (C_2H_5)_2O(g) \quad \Delta H = 11.4\ \text{kcal.}} \quad (7)$$

The heats of dissociation thus obtained compare well with the values determined manometrically, in view of the unelaborate calorimetric techniques employed.

The solubility of lithium borohydride in diethyl ether may be estimated from the isotherms at 25.0, 0.0° and the partial isotherm at 15.0° by determining the point at which the vapor pressure curve for the unsaturated solution intersects the plateau representing the vapor pressure of saturated solution. To supplement these data, direct solubility measurements have been made between the temperatures −112 and 0.0°. The accumulated data are summarized in Table V.

TABLE V

SOLUBILITY OF LITHIUM BOROHYDRIDES IN DIETHYL ETHER AT VARIOUS TEMPERATURES

Temp., °C.	Solubility, g./100 g. solvent	Temp., °C.	Solubility, g./100 g. solvent
25.0	$4.28^{a,c,e}$	− 34	0.56^{b}
15.0	$2.32^{a,d}$	− 45	$.46^{b}$
5.3	1.52^{b}	− 63	$.41^{b}$
0.0	$1.28^{a,b}$	− 78	$.28^{b}$
−23	0.73^{b}	−112	$.20^{b}$

[a] Calculated from vapor pressure data. [b] Direct solubility measurements. [c] J. R. Elliott, W. L. Roth, G. F. Roedel and E. M. Boldebuck, THIS JOURNAL, 74, 5211 (1952), report a solubility of 3.0 g./100 g. solvent at 25°. [d] Schlesinger, *et al.* (ref. 3), report a solubility of 2.5 g./100 g. solvent at 19°. [e] Metal Hydrides, Inc., Technical Bulletin 402-C gives a solubility of *ca.* 4 g./100 solvent at room temperature.

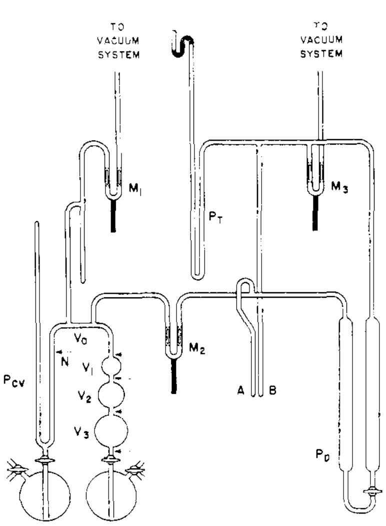
Solutions of lithium borohydride in diethyl ether exhibit vapor pressures considerably greater than would be predicted for ideal solutions. Assuming that the predominant species in solution consists of one to one complex, calculations show that at 25.0° the state of aggregation of the solute ranges from 1.8 times the formula weight at lithium borohydride diethyl etherate mole fraction 0.041 to 3.3 times the formula weight at mole fraction 0.175. Similarly at 15.0° the extent of aggregation increases from 1.9 at mole fraction 0.040 to 2.4 at mole fraction 0.111.

Experimental

Materials.—Lithium borohydride was purified in the same manner as previously described.[5] Anhydrous analytical reagent grade diethyl ether was thoroughly dried over lithium borohydride and fractionated in the high vacuum system, after which it exhibited vapor tensions of 13.1 mm. at −45.2° (lit. 13.1 mm.) and 186.6 mm. at 0.0° (lit. 185.3 mm.).

Determination of the Isotherms.—The apparatus and experimental techniques used for obtaining isotherms were identical with those described in a previous paper.[5] At all times during the measurement of diethyl ether quantities, the pressure of the sample was maintained at less than one-half its saturation pressure at room temperature in order to minimize deviations from ideal gas behavior. Because its vapor will slowly erode stopcock greases, diethyl ether was not allowed to remain in the gas measuring system for extended periods.

Determination of Dissociation Pressures at Various Temperatures.—An apparatus such as that depicted in Fig. 2 was employed to determine precise values of dissociation pressures of the diethyl etherates of lithium borohydride at various temperatures. This assembly is essentially similar to that used in the isotherm determinations but has the advantages of being grease-free, giving pressure data of higher accuracy and having a greater pressure range of applicability. In the figure, a gas volume measuring system, which embodies a constant volume manometer (P_{CV}) containing a glass needle (N) as a reference point, is bounded by mercury float valves M_1 and M_2. The total volume of this system could be varied over a large range by running mercury up in the vertically placed calibrated bulbs (V_1, V_2 and V_3) to the desired reference mark.



ARROWS INDICATE REFERENCE MARKS.

Fig. 2.—Apparatus for determination of dissociation pressures.

The pressure over the sample contained in Tube A was measured with a differential manometer (P_D) which was constructed of 20 mm. diameter tubing so that mercury meniscus errors would be reduced to a minimum. The range of pressures which could be measured with this system was greatly increased by inclusion of the tube B, into which a pure substance exerting a known vapor pressure at a given temperature could be introduced. The extra manometer (P_T) attached to tube B could serve as a vapor pressure thermometer if another means of temperature measurement were inconvenient or unavailable.

Temperature control of the sample tube within less than 0.1 degree was achieved and sufficient time was allowed for complete equilibrium to be established. Readings were taken at intervals of several hours until no perceptible change in pressure occurred with time. From 36 hr. (higher temperatures) to 72 hr. (lower temperatures) were required for each pressure determination. For temperatures above 0°, a small constant temperature water-bath was raised into position about the sample tube. For lower temperatures, since the usual low temperature slush baths were quite inadequate for the purpose, it was necessary to employ a cryostat with an automatic coolant feed. The cryostat was patterned closely after the one described in detail by Scott.[7] The thermoregulator used in the present work consisted of a sulfur dioxide vapor pressure thermometer which was constructed with two metal contacts, one situated at the bottom of the sulfur dioxide-supported mercury column, the other at the top; these contacts communicated with a relay which, through a set of adjusted resistances, sent a slight additional amount of current through the heating coil of the cryostat when the control circuit was open. The bath temperature was initially set by running the proper amount of mercury up into the vapor pressure thermometer so that the control circuit would just be closed at the pressure of sulfur dioxide corresponding to the desired temperature. Thus the device served the dual function of temperature indicator and temperature controller. An automatic means of feeding liquid nitrogen into the outer jacket of the cryostat was arranged with a reservoir of sufficient capacity so that a constant temperature could be maintained in the cryostat for as long as 18 hr. without supervision.[8]

Determination of Heats of Solution.—Utilizing a simple calorimeter constructed from a 300-ml. Dewar flask,[8] the heat effect observed when a sample was dissolved was compared with the observed heat effect of a known amount of electrical current passing through a heating coil.

1. **Lithium Borohydride.**—The heat effect was measured for the solution of 200–250 mg. samples of purified lithium borohydride[5] in 150 ml. of diethyl ether at 25°. Four runs gave the following results.

ΔH, kcal./mole	Final concn. of $LiBH_4$, g./100 g. solvent
−3.64	0.236
−3.71	.217
−3.95	.200
−3.79	.206
av. −3.77	

2. **Lithium Borohydride Diethyl Etherate.**—A slight excess of diethyl ether was condensed on a sample of purified lithium borohydride. The excess was removed slowly to a point well above the dissociation pressure of the diethyl etherate. After allowing three days for equilibration, the pressure of the system remained about 40 mm. above the dissociation pressure of lithium borohydride diethyl etherate but considerably below the pressure of the saturated solution at room temperature. This material was taken for use in the heat of the solution measurements without further adjustment of ether content. Quantities of 425–990 mg. were dissolved in 150 ml. of diethyl ether at 25°. Four runs gave these results

ΔH, kcal./mole	Final concn. of $LiBH_4$, g./100 g. solvent
+2.28	0.090
+1.95	.180
+2.09	.210
+1.92	.138
av. +2.06	

Because lithium borohydride diethyl etherate has a large dissociation pressure (90.4 mm. at 25°), it would be expected that loss of diethyl ether would occur unless the sample remained confined in a closed system. That some diethyl ether was indeed being lost between the charging of the sample tubes in the dry-box and the introduction of the samples into the calorimeter is indicated by the percentage of lithium borohydride in the samples (theoretically 22.72%) as shown by analysis at the beginning (22.8%), during (23.3%) and immediately after (24.2%) the calorimetric runs.

3. **Lithium Borohydride Hemi-(diethyl etherate).**—A slightly greater than stoichiometric amount of diethyl ether (24.27 mmoles) was condensed on 1.0437 g. (47.89 mmoles) of purified lithium borohydride. The small excess of 0.32 mmole of diethyl ether was allowed for loss in handling. Analysis showed that the percentage of lithium borohydride in the samples (theoretically 37.03%) increased only slightly (from 37.0 to 37.1%) during the calorimetric runs. The results of four determinations were

ΔH, kcal./mole	Final concn. of $LiBH_4$, g./100 g. solvent
−2.89	0.136
−2.96	.171
−2.91	.136
−2.76	.140
av. −2.88	

Determination of Low Temperature Solubilities.—Purified lithium borohydride and insufficient diethyl ether to effect complete solution at the temperature concerned were equilibrated in a closed system. Samples of the solution were weighed and analyzed for lithium borohydride content by titrimetric determination of boric acid (as the mannitol complex) formed on acid hydrolysis.[9]

Acknowledgment.—The assistance of D. L. Ekstedt in the assembly of the cryostat is gratefully acknowledged. This research was supported in part by The Olin Mathieson Chemical Corporation and the Bureau of Aeronautics through Contract NOa(s)52-1023, Subcontract 3181-14.

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(7) R. B. Scott, *J. Research Natl. Bur. Standards*, **25**, 459 (1940).

(8) This device is described in the Ph.D. thesis of T. L. Kolski, Saint Louis University, June, 1957.

(9) For more complete experimental details, the M.S. thesis of Lillian E. Roth, Saint Louis University, February, 1955, should be consulted.