hood of the critical point, see Fig. 2. A consideration of these effects and a comparison of the work of Lamb and Roper with that of Aston and coworkers indicate clearly that the purity of the sample and not the experimental technique of measurement of pressures, temperatures, volumes, and masses is the limiting element in the accuracy of the final results in the type of experimental work considered here.

Summary

The vapor pressure and orthobaric liquid density of 1-butene has been measured in the range 30–125°. The pressures are represented fairly well by the equation

$$\log p(\text{atm.}) = 4.34677 - (1156.15/T), \; T = t°\text{C. (Int.)} + 273.16.$$

The combined measurements of Lamb and Roper and of the present investigation are represented quite well by the equation

$$\log p(\text{atm.}) = 5.196066 - 1298.722/T - 0.00124829T, \quad (T = t°\text{C.} + 273.16 \text{ and } -75° < t° < 125°)$$

The measured critical constants of 1-butene are: $t_c = 146.4 \pm 0.3$°C. (Int.), $p_c = 39.7 \pm 0.3$ normal atm., $v_c = 0.241$ liter per mole (4.30 ml. per g.), $d_c = 4.15$ moles per liter (0.233 g. per ml.), with an uncertainty of 5% in the critical volume and density.

Cambridge, Mass. Received July 6, 1949

[Contribution from the Naval Research Laboratory]

Some Physical Properties of Diborane, Pentaborane and Aluminum Borohydride

By S. H. Smith, Jr., and R. R. Miller

Various boron hydrides and borohydrides have been studied with regards to methods of synthesis, storage stability, methods of handling, etc. Pertinent physical properties of some of these compounds had been determined previously; *e. g.*, vapor pressure,[1] vapor density,[2] gaseous heat capacity,[3] liquid density,[4,5] melting point,[4] boiling point,[4] surface tension,[5] critical constants,[6] heat of formation[7] and heat of hydrolysis[8] of diborane; melting point,[9] boiling point[9] and vapor pressure[4,9] of dihydropentaborane; vapor pressure of decaborane[10]; heat of formation of B_2O_3[7,8,11]; vapor pressures, melting points, and boiling points of lithium borohydride, beryllium borohydride and aluminum borohydride.[12]

In this study the pressure–volume–temperature diagram of diborane (B_2H_6) has been obtained. An equation relating vapor pressure and temperature for diborane is presented. Density *versus* temperature has been measured for pentaborane (B_5H_9) and aluminum borohydride ($Al(BH_4)_3$), and equations for these relations are given. Viscosities and surface tensions of diborane, pentaborane and aluminum borohydride have been measured, and equations for the calculations of these values at any given temperature have been derived.

Pressure–Volume–Temperature for Diborane.—Measurements of diborane vapor pressure, liquid and gas (saturated) density and liquid compressibility were accomplished in the apparatus of Fig. 1. The system was assembled with no mercury in the capillary. With needle valve 1 closed, the capillary was evacuated and baked out. Then mercury was distilled from the storage bulb into the capillary until there was enough to bring the level slightly above valve 1 during subsequent measurements. (This would permit measurements under constant volume conditions by simply closing valve 1.) The mercury was adjusted to the proper position by letting atmospheric pressure into the vacuum line and reducing the pressure in the manifold through valve 2. Next the mercury was frozen in place with a liquid nitrogen bath, a known amount of diborane was condensed in the capillary over the mercury, and the capillary was sealed off near the top of the calibrated portion. (The method of using this calibration was to add the volumes of 1 cm. increments, since the diameter of the tube was non-uniform. The volume of the irregularly shaped seal was determined after the apparatus was dismantled.) The liquid nitrogen bath was then removed and a clear glass dewar was placed around the capillary. The dewar contained acetone and was cooled with Dry Ice to whatever temperature was desired. Temperatures were read to 0.1° by means of an iron–constantan thermocouple. Lengths were read with a cathetometer.

Diborane, Vapor Pressure.—To read vapor pressure, valve 2 was closed and the pressure in the manifold raised with nitrogen through valve 3

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[1] Stock and Kuss, *Ber.*, **56**, 789 (1923).

[2] Clarke, Ohio State University Research Foundation, "Literature Survey and Low Temperature Thermodynamics of the Boranes—Tentative Thermal Functions for Diborane."

[3] Stitt, *J. Chem. Phys.*, **8**, 981 (1940).

[4] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

[5] Laubengayer, Ferguson and Newkirk, This Journal, **63**, 559 (1941).

[6] Newkirk, *ibid.*, **70**, 1978 (1948).

[7] Prosen, Johnson and Yenchius, Nat. Bur. Stand. (U. S.) Technical Report on Project NA-onr-8-47 dated 9/30/48.

[8] Roth and Borger, *Ber.*, **70**, 48, 971 (1937).

[9] Burg and Schlesinger, This Journal, **55**, 4009 (1933).

[10] Stock and Pohland, *Ber.*, **62**, 90 (1929).

[11] Todd and Miller, This Journal, **68**, 530 (1946).

[12] Schlesinger, Sanderson, Burg and Brown, *ibid.*, **62**, 3421 ff. (1940).

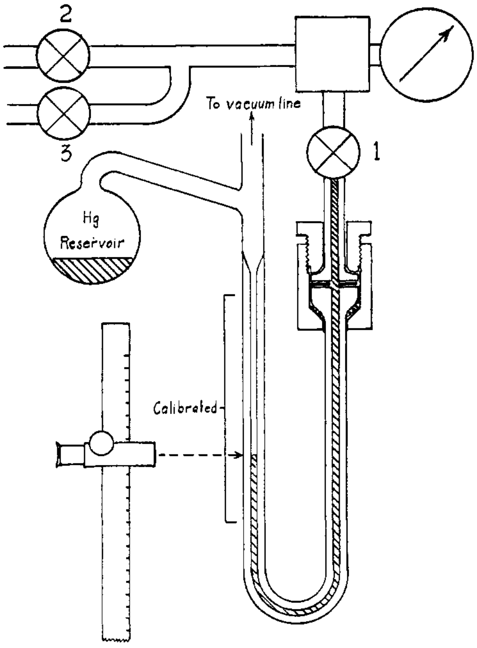

Fig. 1.—Pressure–volume–temperature apparatus.

to a point known to be higher than the diborane vapor pressure at that temperature. Then valve 3 was closed and valve 1 opened. Nitrogen was bled off through valve 2 until the diborane existed in both the liquid and vapor phase. The vapor pressure was then indicated on the pressure gage (previously calibrated on a dead-weight apparatus), after a small correction for the mercury column in the capillary was made.

Making use of all values available from the above measurements and from the measurements of Stock and Kuss[1] the equation of the best line through these points was determined: $\log p = 7.185 - 782.8/T$ wherein p is pressure in mm. and T is °A. (°C. + 273.2).

Experimental and calculated values for diborane vapor pressure are listed in Table I.

TABLE I

VAPOR PRESSURE OF DIBORANE (ACCURACY ± 2%)

Sample 1			Sample 2		
Temp., °A.	Pressure, mm. Exp.	Pressure, mm. Calcd.	Temp., °A.	Pressure, mm. Exp.	Pressure, mm. Calcd.
243.1	8890	9200	235.4	7240	7240
249.9	10800	11300	240.3	8430	8430
256.1	13400	13400	246.1	10200	10100
268.1	19000	18400	251.2	11700	11700
275.8	21700	22200	255.3	12800	13100
277.3	22400	23000	260.8	15000	15200
277.8	22700	23200	265.7	17000	17300
284.0	26300	26800	270.7	19000	19600
287.1	28100	28700	278.9	23700	23800
288.9	30200	29800	285.2	27500	27500
$(=t_c)$[a]	$(=p_c)$		288.2	29300	29400
195.2[b]	1550	1500	290.0	30400	30500
219.6[c]	3980	4140	$(=t_c)$[a]	$(=p_c)$	

[a] By disappearing meniscus method. [b] Average of several readings in Dry Ice-baths. [c] Reading taken in unsaturated gas density apparatus.

Diborane, Liquid Density.—In measuring liquid density, the procedure was to increase the nitrogen pressure in the manifold through valve 3, leaving valve 1 open, until the pressure was slightly above the vapor pressure at the existing bath temperature. This caused the diborane sample to go completely to the liquid phase. The volume was then ascertained by reading the mercury meniscus with a cathetometer and referring to the calibration of the capillary. Values of results obtained by this method are presented in Table II and plotted in Fig. 2.

TABLE II

DIBORANE LIQUID DENSITY (ACCURACY ± 3%)

Sample 1		Sample 2	
Temp., °A.	Density, g./cc.	Temp., °A.	Density, g./cc.
243.6	0.333	235.4	0.341
249.9	.316	240.3	.334
255.9	.307	246.1	.325
268.1	.285	251.2	.316
275.9	.259	255.3	.309
277.8	.253	260.8	.294
284.1	.231	265.8	.284
287.1	.212	270.7	.274
288.4	.154	278.9	.256
		285.2	.228
		288.2	.210

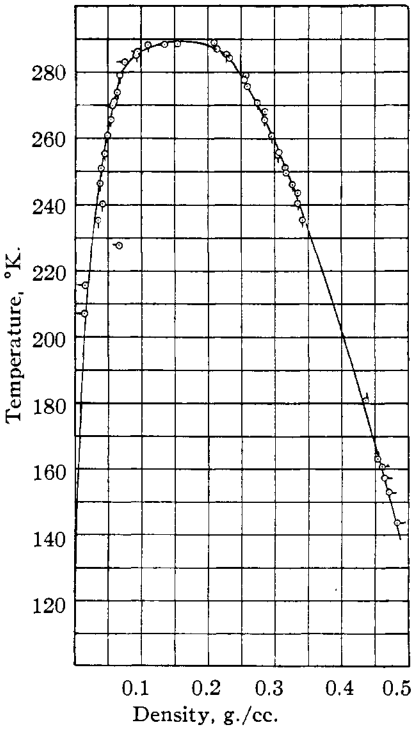

Fig. 2.—Liquid and vapor densities of diborane: ⊙, sample 1; ♀, sample 2; -⊙, constant volume measurements; ⊙̍, Stock; ⊙-, Laubengayer.

Diborane, Saturated Gas Density.—Saturated as densities were measured at the same time vapor pressures were measured. Both the mercury and diborane menisci were read by a cathetometer. Since diborane was either evaporating or condensing, it was necessary to read one meniscus, then the other, and then the first again at equally spaced intervals (a few seconds). The average of the first and third readings was assumed to be the level prevailing when the second reading was taken. Now, since the liquid density had already been measured, and the total amount of diborane in the tube was known, the gas density could be calculated.

The constant volume condition previously mentioned could, as an alternative, be used to eliminate the movement of the menisci; also with this constant volume condition established, one could make measurements below the f. p. of mercury. Several points were taken this way, and they agreed well with values taken when valve 1 was open (see Fig. 2).

Table III

Diborane Saturated Gas Density (Accuracy ± 3%)

Temp., °A.	235.4	240.3	246.2	251.3	255.3	260.8
Density, g./cc.	0.0348	0.0407	0.0382	0.0393	0.0470	0.0492
Temp., °A.	265.8	270.7	274.0	278.9	285.2	288.2[a]
Density, g./cc.	0.0541	0.0588	0.0625	0.0581	0.0927	0.1100
Temp., °A.	286.2[a]	283.0[a]	269.9[a]	227.9[a]	215.5[a]	207.0[a]
Density, g./cc.	0.0950	0.0759	0.0567	0.0673	0.0145	0.0151

[a] Constant volume measurements.

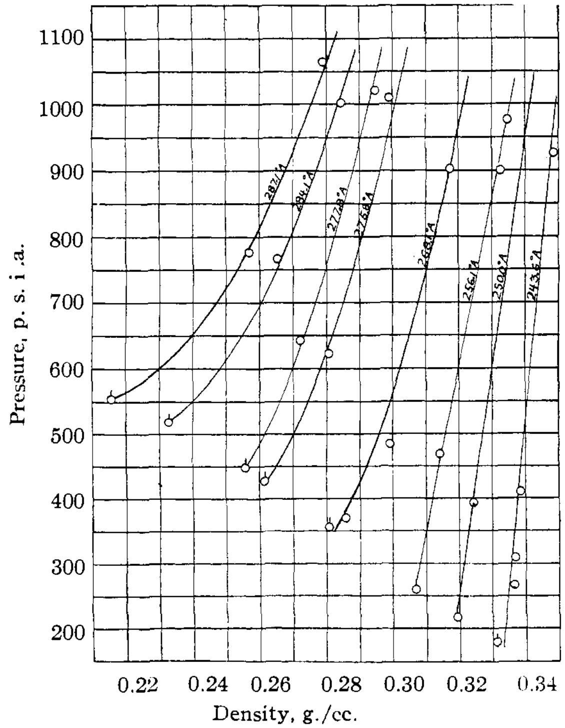

Fig. 3.—Diborane liquid compressibility isotherms: O, experimental; ȯ, from liquid density curve.

Diborane, Liquid Compressibility.—The compressibility of liquid diborane was measured at the time liquid density was measured. Since the maximum safe pressure for the apparatus was considered to be about 1200 p. s. i., the range for compressibility was rather limited (see Fig. 3).

Table IV

Diborane Compressibility (Accuracy ± 3%)

Temp., °A.	Pressure, p. s. i. a.	Density, g./cc.	Temp., °A.	Pressure, p. s. i. a.	Density, g./cc.
243.6	268	0.337	275.8	622	0.281
	309	.337		1010	.299
	410	.338	277.8	642	.272
	927	.348		1022	.295
250.0	393	.324	284.1	767	.266
	900	.332		1002	.284
256.1	469	.314	287.1	777	.257
	977	.334		1065	.279
268.1	370	.286			
	484	.299			
	902	.317			

Method of Terminating Test.—With the completion of the measurements discussed up to this point, the apparatus of Fig. 1 had served its purpose, and only the problem of checking the amount and purity of the diborane in the apparatus remained. This was done as follows: The bend of the capillary was embedded in powdered Dry Ice—freezing the mercury into a plug—the capillary cut a few inches below the metal to glass coupling, and this cut end sealed to an analytical apparatus. After the analytical apparatus and connection thereto had been evacuated and closed off from the pump, the mercury in the capillary was allowed to melt and free the diborane by virtue of its own pressure into the analytical system. There its volume was measured, and it was hydrolyzed to determine its purity. As a check the resulting boric acid solution was titrated. The purity was found to be the same as on a sample taken before the measurements. The purity had been expected to remain high, since only about three days elapsed during the measurements on a given sample.

Mention should be made of the fact that the final volume of diborane was about 14% less than the original volume measured into the tube for sample 2. This quite appreciable discrepancy was attributed to loss during the sealing of the capillary; this was not detected since the line was being pumped during the seal-off. Consequently, the final volume was used in calculations.

Diborane, Unsaturated Gas Density.—Density of unsaturated diborane vapor *versus* temperature was measured in the apparatus of Fig. 4. The fundamental idea involved was the expansion of a sample of gas at high pressure in a small bomb (100 ml.) into a volume large enough (11,000 ml.) to drop the pressure to less than atmospheric, where Boyle's law could be assumed to apply and the weight of gas calculated. Both the volume of the bomb and the aforementioned large volume (bomb + gage + lines + glass bulb) were calibrated.

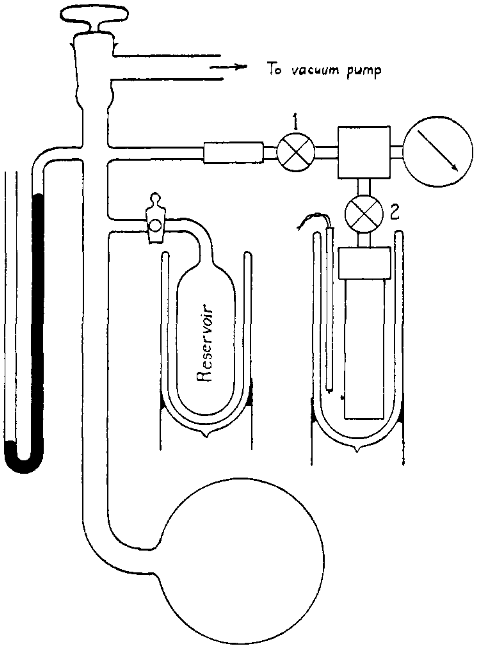

Fig. 4.—Unsaturated vapor density apparatus.

In practice the diborane sample was condensed at liquid nitrogen temperature in the bomb, which had been previously evacuated along with the whole system. Valve 1 was then closed and the temperature of the bomb adjusted to that desired as measured by an iron–constantan thermocouple. Excess sample was then bled off to a reservoir (−196°) on the vacuum system until the desired pressure was reached. Then the pressure and bath temperature were read and valve 2 closed. The diborane remaining in the space between valves 1 and 2 was bled off through valve 1 to the previously mentioned reservoir, the stopcock to the reservoir closed, and the whole calibrated volume evacuated up to valve 2. Then, with the line to the pump closed, valve 2 was cracked, allowing diborane to expand throughout the large volume. With the bomb-bath removed, the whole system was allowed to come to temperature equilibrium in an air-bath and the temperature and pressure measured. Fluctuations in the volume of the mercury manometer were ignored, since they were beneath the accuracy of the calibration (see Fig. 5).

TABLE V

DIBORANE—UNSATURATED VAPOR DENSITY (ACCURACY ± 1%)

Temp., °C.	Pressure, p. s. i. a.	Density, g./cc.	Temp., °A.	Pressure, p. s. i. a.	Density, g./cc.
243.6	173	0.0392	277.8	420	0.0604
	131	.0148		298	.0345
	85	.00873		153	.0138
	172	.0332		118	.0106
250.0	183	.0214	284.1	490	.0731
	125	.0133		462	.0639
	71	.00669		393	.0470
	178	.0220		296	.0311
	208	.0397		152	.0139
	57	.00522			
256.1	243	.0359	287.1	435	.0538
	198	.0232		382	.0435
	131	.0136		250	.0246
	68	.00610		152	.0137
	64	.00583		113	.00977
268.1	324	.0427	292.5	418	.0548
	276	.0326		300	.0303
	181	.0187		785[a]	.243
	109	.00943		695[a]	.212
				620[a]	.154
				570[a]	.0856
				447[a]	.0516
				218[a]	.0184

[a] New sample.

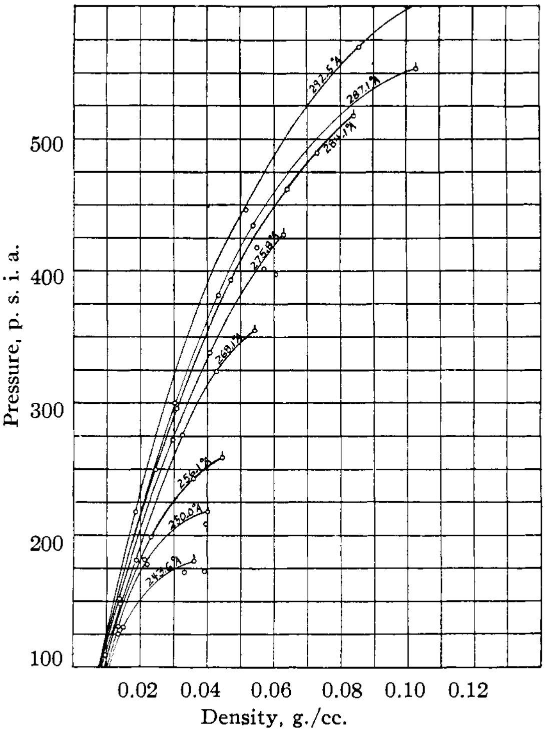

Fig. 5.—Diborane unsaturated vapor density isotherms: O, experimental; ὁ, from saturated gas density curve.

To test whether Boyle's law was obeyed up to atmospheric pressure, a given amount of diborane was measured in four different volumes and the

TABLE VI

P, mm.	V, cc.	T', °A.	PVT/T', units
653.6	136	299.8	1.000
248.6	359	300.0	1.002
236.1	377	300.1	1.000
183.7	484	300.3	0.998

constancy of the product PV noted. As shown in Table VI, it appeared constant within experimental error.

All the data on the pressure–volume–temperature relationships of diborane are plotted as a family of isotherms in Fig. 6.

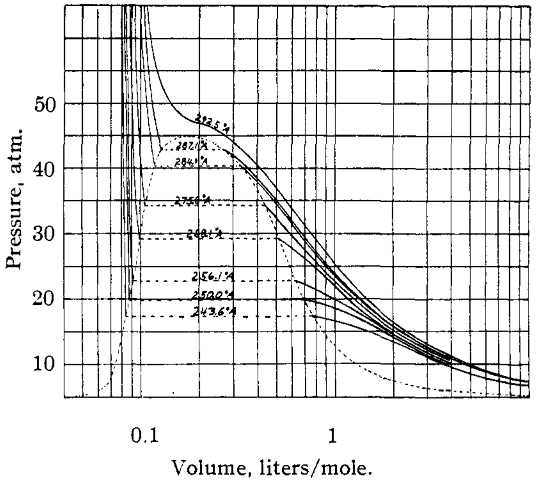

Fig. 6.—Diborane pressure–volume–temperature diagram.

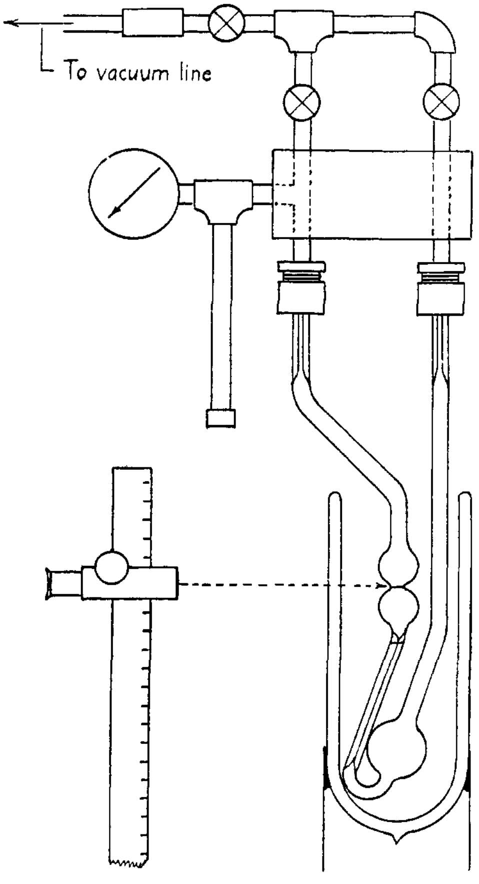

Fig. 7.—Viscosity apparatus.

Viscosity.—Viscosities of diborane, pentaborane and aluminum borohydride have been measured in an Ostwald viscometer fashioned out of quartz (see Fig. 7). The low expansion coefficient of quartz was needed since the instrument was calibrated with water and then used as low as −130°. The calibration data gave the equation $\eta = 16.4734(10^{-6})dht - 2591.8(10^{-6})dh/t$, in which η is viscosity in poises, d density in g./cc., h mean liquid head in cm. and t time of flow in seconds. The ultimate accuracy of any viscosity calculated from this calibration is ±2%.

Diborane Viscosity.—The viscosity of diborane was measured through two temperature ranges as widely separated as was conveniently possible so that extrapolation up to the critical temperature could be accomplished. The upper temperature limit was imposed by the ability of the viscometer to withstand pressure. It was

TABLE VII

VISCOSITY OF DIBORANE

Temp., °A.	T, sec.	d, g./cc.	h, cm.	η, millipoises
145.6	37.2	0.4783	9.42	2.45
148.6	36.0	.4747	9.34	2.31
152.7	34.0	.4698	9.24	2.10
164.0	30.7	.4552	9.24	1.77
195.7	23.9	.4100	9.06	1.06
197.6	23.7	.4073	9.06	1.04
198.8	23.7	.4055	9.08	1.04
198.9	23.8	.4052	9.08	1.04
198.9	23.5	.4052	9.08	1.02
202.3	23.1	.4001	9.08	0.975
203.9	23.2	.3976	9.08	0.976

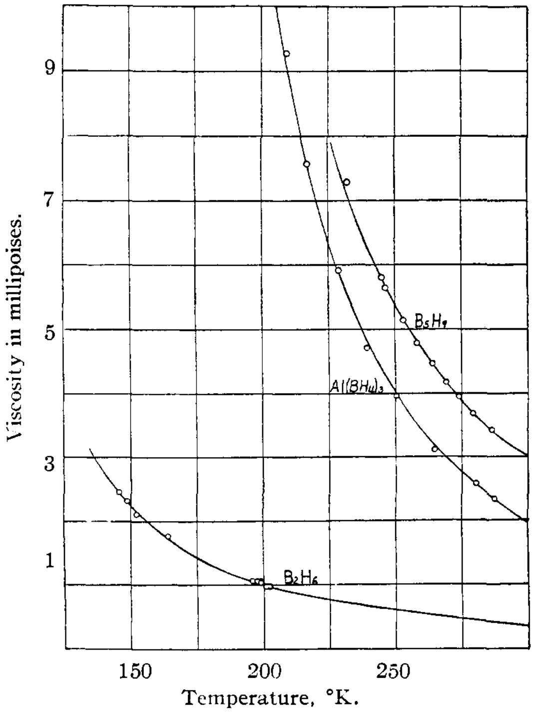

Fig. 8.—Liquid viscosity.

hydrostatically tested to 70 p. s. i. before measurements were begun. The vapor pressure at the highest temperature at which a measurement was made (−69.3°) still left a factor of safety of two. The lower temperature limit was the freezing point of diborane (−165.5°). The data taken and the values calculated (accuracy ±2.5%) with the calibration formula are in Table VII and also plotted on Fig. 8.

Pentaborane Density.—Before the absolute viscosity of pentaborane could be measured, it was necessary to determine accurately the density *versus* temperature. This was done in a quartz dilatometer. Quartz was again used because of its low expansion coefficient. The apparatus was charged with 22.5 (±0.1) g. of pentaborane and the data in Table VIII taken (accuracy ±0.5%).

TABLE VIII

DENSITY OF PENTABORANE

Temp., °A.	226.9	227.0	235.2	235.4	246.1
Density, (g./cc.)	0.681	0.681	0.675	0.675	0.666
Temp., °A.	253.0	263.2	274.6	283.5	289.3
Density, (g./cc.)	0.660	0.652	0.642	0.635	0.630

The equation of the line determined by these points is: $d = 0.8674 - 0.00082T$—d is g./cc., and T is A.

Pentaborane Viscosity.—The viscosity of pentaborane was measured through a range of temperatures from −28 to 40°. It was found necessary, however, to discard all values taken above 20° since polymerization or some other phenomenon occurred above this temperature to increase the viscosity quite markedly. The data presented in Table IX are plotted in Fig. 8 (accuracy is ±2.5%).

TABLE IX

VISCOSITY OF PENTABORANE

Temp., °A.	*T*, sec.	*d*, g./cc.	*h*, cm.	η, millipoises
232.2	76.1	0.6766	8.84	7.82
245.0	62.8	.6662	8.80	5.29
246.5	61.1	.6651	8.80	5.64
253.2	56.6	.6598	8.78	5.14
258.4	53.4	.6554	8.78	4.78
264.1	50.5	.6509	8.76	4.45
269.0	48.0	.6468	8.76	4.17
274.1	46.1	.5426	8.73	3.94
279.6	43.7	.6382	8.72	3.68
286.4	41.5	.6326	8.70	3.42

Aluminum Borohydride Density.—It was necessary for aluminum borohydride as for pentaborane to determine the density *versus* temperature before absolute viscosity could be measured. The same dilatometer was used again. It was charged with 20.8 (±0.1) g. of material and the data in Table X taken (accuracy ± 0.5%).

TABLE X

DENSITY OF ALUMINUM BOROHYDRIDE

Temp., °A.	209.2	209.7	223.0	235.9	245.6	259.7	259.9
Density, g./cc.	0.622	0.622	0.611	0.600	0.592	0.581	0.581
Temp., °A.	241.5	266.3	266.5	274.1	274.5	208.6	
Density, g./cc.	0.595	0.576	0.576	0.569	0.569	0.618	

The equation of the line determined by these points is: $+d = 0.7866 - 0.000793T$—d is g./cc., and T is A.[13]

Aluminum Borohydride Viscosity.—Values for the viscosity of aluminum borohydride were determined experimentally from −63.9 to 32.5° with accuracy of ±2.5%. The data are given in Table XI and plotted on Fig. 8.

TABLE XI

VISCOSITY OF ALUMINUM BOROHYDRIDE

Temp., °A.	*T*, sec.	*d*, g./cc.	*h*, cm.	η, millipoises
209.3	100.7	0.6203	9.16	9.28
217.3	83.9	.6141	9.13	7.58
228.9	66.5	.6048	9.12	5.91
239.6	55.5	.5966	9.06	4.69
250.3	48.1	.5881	9.04	3.93
261.7	42.9	.5806	9.04	3.39
265.0	40.3	.5765	9.02	3.12
280.5	35.3	.5642	9.00	2.58
287.4	33.1	.5588	8.97	2.34
305.6	29.5	.5445	8.92	1.93

Equations for Viscosity.—In determining the equations by which one could calculate the viscosity at a given temperature, the Andrade formula was used.[14] His formula is $\eta V^{1/3} = Ae^{c/VT}$ in which η is viscosity in poises, V specific volume in cc./g., A a constant, c a constant and T temperature in °A. With the constants evaluated for each liquid and $1/d$ substituted for V the following formulas result

$$\eta_{\mathrm{B_2H_6}} = 36.86(10^{-5})d^{1/3}e^{651.8/dT}$$
$$\eta_{\mathrm{B_5H_9}} = 41.15(10^{-5})d^{1/3}e^{1024d/T}$$
$$\eta_{\mathrm{Al(BH_4)_3}} = 23(10^{-5})d^{1/3}e^{1291d/T}$$

The curves in Fig. 8 are calculated by these formulas rather than being drawn through the experimental points. No experimental point deviates more than 3% from these curves.

Surface Tension.—Since the bore of the capillary on the quartz viscometer was accurately known, it was a simple matter to measure the capillary rise of liquid in the viscometer at various temperatures at the same time viscosity data were being taken. Hence, surface tensions of the three liquids under discussion were measured. The classical formula was used, namely, $\gamma = {}^1/_2\, hdgr$, in which γ is surface tension in dynes/cm., h capillary rise in cm., d density of liquid in g./cc., g gravitational constant (980.66 dynes) and r radius of capillary in cm.

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[13] The above data agree within 2% with some rough data taken by Schlesinger in connection with other work on a Navy contract.

[14] E. N. Andrade, *Phil. Mag.*, Ser. 7, **17** (698) Part II.

Only two points were taken for diborane since the viscosity measurements were made in two rather narrow temperature ranges. At −69.7° the capillary rise was 1.65 cm. making γ = 10.9 dynes/cm.; at −121.6° the rise was 2.38 cm. making γ = 18.6 dynes/cm.; (accuracy ±3%). These values agree well with those of Laubengayer, Ferguson and Newkirk.[5]

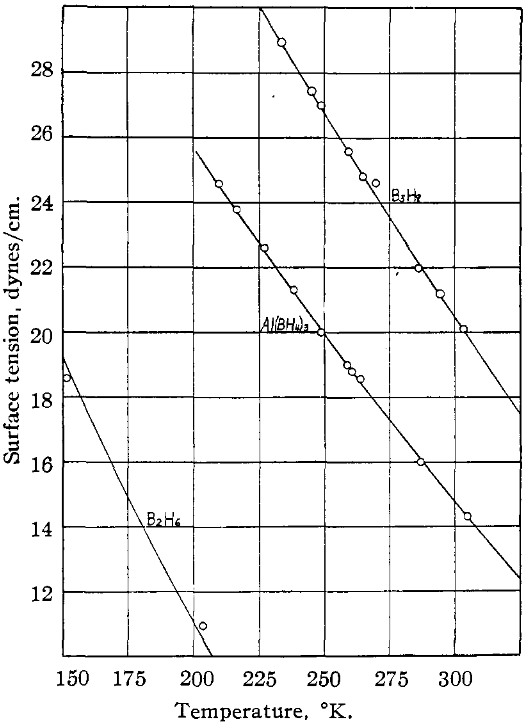

Fig. 9.—Surface tensions.

Data were taken for the surface tension of pentaborane from −28.1 to 30.1° with an accuracy of ±3% (see Fig. 9).

Table XII

Surface Tension of Pentaborane

Temp., °A.	Capillary rise, cm.	γ, dynes/cm.
233.9	2.59	28.9
245.1	2.49	27.4
249.0	2.46	27.0
259.3	2.37	25.6
264.7	2.31	24.8
269.5	2.29	24.5
286.2	2.10	22.0
294.4	2.05	21.2
303.3	1.97	20.1

Data were taken for the surface tension of aluminum borohydride from −63.6 to 31.9° with an accuracy of ±3% (see Fig. 9).

Table XIII

Surface Tension of Aluminum Borohydride

Temp., °A.	Capillary rise, cm.	γ, dynes/cm.
209.6	2.40	24.6
216.2	2.34	23.8
227.4	2.26	22.6
238.3	2.16	21.3
248.9	2.05	20.0
258.7	1.98	19.0
260.3	1.96	18.8
263.7	1.95	18.6
286.8	1.76	16.0
305.1	1.59	14.3

If one plots $\gamma(MV)^{2/3}$ against T a straight line results (Eötvös). This was done for each of the materials under discussion and the best line through the points was determined by the method of least squares. The resulting equations relate surface tension to temperature (provided the density is known as with the viscosity equations).

$$\gamma_{B_2H_6} = (65.7 - 0.227T)d^{2/3}$$
$$\gamma_{B_5H_9} = (71.1 - 0.143T)d^{2/3}$$
$$\gamma_{Al(BH_4)_3} = (61.0 - 0.130T)d^{2/3}$$

γ is in dynes/cm., T in °A. and d in g./cc. The curves plotted on Fig. 9 are calculated by the above formulas. None of the experimental points, excepting those for diborane, deviates more than 1.5% from these curves.

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Summary

The pressure–volume–temperature diagram of diborane, the density of aluminum borohydride and pentaborane, and the viscosities and surface tensions of diborane, pentaborane and aluminum borohydride have been determined. Convenient equations for calculation of these physical properties at given temperatures have been derived. The most obvious omission is an equation of state for diborane, but an attempt to derive fitting constants for the Beattie–Bridgeman equation failed initially, and no further work has been done on this.

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