To avoid the complications associated with the pH concept at elevated temperatures, experiments were run using the same concentration of potassium hydroxide in the initial reaction medium at the different temperatures. They were regarded as being at the same "nominal pH." For example, at room temperature a 0.00012 N solution of potassium hydroxide had a pH of 9.6. If this solution was heated to 85°, the indicated pH-type reading was generally lower than 9.6. The "nominal pH 9.6" experiments were conducted at high temperatures by using a 0.00012 N potassium hydroxide as reaction medium and heating it to the desired temperature. A steady pH-type reading was then obtained, and this reading, whatever its value, was maintained throughout the subsequent titration.

Results at high temperature, pH, and salt content were probably influenced seriously by the limitations of the method which have been discussed. Actually, some non-linear titration curves were obtained and also OH/Ni equivalent ratios greater than unity. Although the latter is a possibility in the event of partial formation of a nickel-containing anion. This seems unlikely in view of the extremely low solubility of nickel hydroxide in strong alkali at room temperature.[9]

It is interesting to speculate how these metastable materials might form. Minute droplets of nickel salt solution striking the alkaline reaction medium might react at the surface to form a spherical shell coating of nickel hydroxide. Such a coating might impede the diffusion of the anions required to convert the unreacted nickel salt in the interior of the

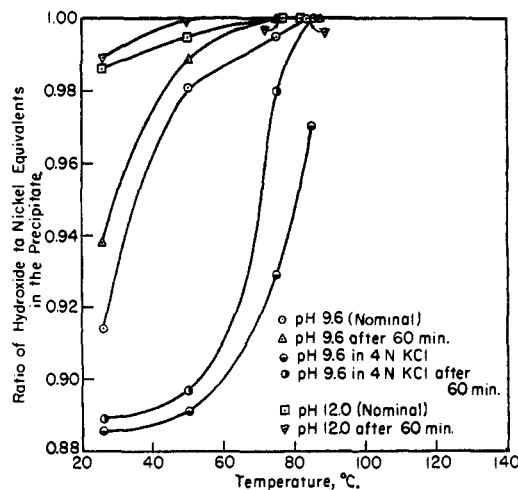(9) K. Gayer and A. B. Garrett, This Journal, 71, 2973 (1949).

Fig. 5.—The composition of basic nickel chlorides as a function of pH, temperature, time and concentration of chloride ion in the reaction medium.

particles to nickel hydroxide. Weak forces might also exist further stabilizing the interior of the "clump" of precipitate. These may be the forces which slowly develop the crystallinity observed by Feitknecht in precipitates stored in a medium containing a chemical deficiency of hydroxide ion.[3,5] Actually no simple picture gives an explanation of all of the experimental findings even in a qualitative way. A more comprehensive experimental application of this method with a more refined measuring apparatus would undoubtedly lead to a better understanding of these interesting basic salts.

Pittsburgh, Pa.

Condensed Gas Calorimetry. III. Heat Capacity, Heat of Fusion, Heat of Vaporization, Vapor Pressures and Entropy of Diborane between 13°K. and the Boiling Point (180.32°K.)[1]

By John T. Clarke, E. B. Rifkin and H. L. Johnston

Heat capacity measurements have been carried out on high purity diborane from 14–177 °K. Vapor pressures of the liquid were also measured for the temperature range 112–176 °K. The triple point was determined as 108.30 °K. and the normal boiling point 180.32 °K. Heats of fusion and of vaporization were determined as 1069.0 and 3412 cal., respectively. A less accurate value for the latter, 3422 cal./mole, was computed from the measured vapor pressures. Entropy and heat contents of the gas at the normal boiling points were found to be 49.43 ± 0.10 e.u. and 6520 cal./mole, respectively.

Introduction

Considerable interest, both practical and theoretical, has been evident recently in the physical and thermal properties of the hydrides of boron. The lack of adequate thermodynamic data on these compounds has hampered research and technical development. With these things in mind, the authors have undertaken a program of obtaining adequate thermodynamic data on several of the more important members of the boron hydride family.

This paper deals with the simplest member of the series, diborane. With the exception of gaseous

heat capacities by Stitt[2] and the vapor pressure by Stock,[3] very few precise low temperature thermochemical data have been obtained on this compound.

There is, however, a considerable volume of literature dealing with proposed structures for diborane, based on interpolation of infrared and Raman spectra. From the entropy of diborane at its boiling point it is possible to make a check against proposed structures, based on various interpretations of spectroscopic data. Comparison of computed entropies with that obtained in this research,

(2) F. Stitt, J. Chem. Phys., 9, 780 (1941).
(3) A. Stock and E. Kuss, Ber., 56, 789 (1923).

favors the bridged structure suggested by Pitzer.[4]

In carrying out this work it was necessary to obtain an exact density of gaseous diborane at 2°[5] and develop a melting point calorimeter for determining its purity.[6] The condensed gas calorimeter used is that described by Johnston, Clarke, Rifkin and Kerr in their work with hydrogen[7] and with deuterium.[8]

Since diborane decomposes at an appreciable rate at 25° the constant temperature bath used for metering the amount of diborane withdrawn from the calorimeter and described previously,[7] was maintained at $2 \pm 0.01^\circ$. This was accomplished by immersing the expansion coils of a Freon refrigerating unit in the bath and vigorously circulating the water from the bath past the coils. The rate of cooling supplied by the refrigerating unit was kept approximately constant and greater than the heat leak into the bath, so that temperature control was accomplished by a mercury regulator that controlled a 500-watt heater through a thyratron circuit.

Since the density of diborane was not known at 2° this was determined by weighing calibrated bulbs which had been immersed in the constant temperature bath and filled to a measured pressure with diborane. The imperfection was represented by the equation

$$n = \frac{PV}{RT + BP}$$

where B was found to have the value -227 ml. as reported in the paper by Carr, Clarke and Johnston.[5] This equation was used in determining the number of moles in each filling of the 5-liter bulb.

Temperature Scale.—The standard thermocouple, used to calibrate the gold resistance thermometer, was the same one used in the earlier work on hydrogen,[7] and on deuterium.[8] Our temperature scale up to $90^\circ K$., based on calibration against vapor pressures of hydrogen, neon and oxygen, is the same as employed with deuterium.[8] Above 90° the calibration consists of an intercomparison with a thermocouple that was previously calibrated at the National Bureau of Standards.

The heat capacities themselves were actually based on temperature rises observed on the sensitive gold resistance thermometer. Actually there was a primary calibration of the gold resistance thermometer in the temperature ranges 14 to $26^\circ K$. and 55 to $90^\circ K$. since readings were taken directly on the thermometer during vapor pressure calibrations of the standard thermocouple. The resistance thermometer proved highly reproducible and three determinations at the triple point of hydrogen over a period of three months agreed to within 0.002°. The calibration of the resistance thermometer did not change within a period of 15 months as evidenced by its comparison with the thermocouple. During this time hydrogen, deuterium, neon, oxygen, diborane and pentaborane were introduced into the calorimeter.

Source and Purity of Diborane.—The diborane used in this research was obtained from Dr. R. R. Miller of the Naval Research Laboratory in Washington, D. C. Mass spectrometer analysis indicated that ethane was the greatest impurity although B_4H_{10} was also present. Since the diborane had to be condensed into the calorimeter at low tem-

perature through a long narrow tube it was important to know that the diborane was sufficiently pure before placing it in the calorimeter so that it would not plug the tube. The diborane as obtained from the cylinder was put through a two-stage distillation and condensed into a small melting point calorimeter which showed that the diborane had a purity of 99.94%. This melting point calorimeter[9] was developed by Clarke, Johnston and DeSorbo[6] specifically for this purpose. Diborane treated in this manner was used in series I. A glass purification train consisting of two 300-ml. condensing traps connected through two bubble traps was constructed. In operation diborane was condensed into the first condensing trap with liquid nitrogen: this was allowed to warm and enough diborane condensed into the first bubble trap to cover the inlet tube: the second bubbler was treated similarly and the liquid nitrogen level in an unsilvered dewar adjusted (somewhat below the bottom of bubbler) to keep the liquid diborane one-half inch above the bottom of the inlet tube. The purified diborane was then condensed in the second condensing bulb. In Series II and III the diborane was purified through the bubblers in addition to a one-plate separation: premelting data showed it to have a purity of 99.99 + mole per cent. Between runs the diborane was stored in stainless steel cylinders at Dry Ice temperature. It was found that it could be stored for months at this temperature without the formation of hydrogen. Premelting data showed a purity of 99.992 for series II and 99.994 mole per cent. for series III.

Heat Capacity of Solid Diborane.—The heat capacity of solid diborane was determined from 14 to $108^\circ K$. in series I and series II. The treatment of the diborane in these two series is given in the section on source and purity of diborane. Two high temperature points were determined in series III. A summary of the results is given in Table I. The experimental heat capacity values have an average deviation of 0.021 cal./deg./mole in the range 14 to $50^\circ K$. and 0.028 cal./deg./mole in the range 50 to $108^\circ K$. from a smooth curve through the points. The uncertainty of the smooth curve is considerably less than this. For temperatures below $21^\circ K$. the experimental points lie on the straight line $C_v = 1.486 \times 10^{-4}T^3$ which corresponds to a Debye characteristic temperature of $146^\circ K$. In determining the entropy at the melting point the values at low temperatures were calculated from this equation and at higher temperatures were taken from the smoothed curve at even degrees.

Heat Capacity of Liquid Diborane.—Three series of runs were made with liquid diborane as continuations of series I, II and III with solid diborane. These runs were carried out in a manner similar to that for the heat capacities of the solid, with the exception that the blocks were kept warmer than the calorimeter throughout the heating period. In making these calculations it was necessary to allow for the amount of vaporization occurring during the

(9) Two small melting point calorimeters were developed, but the one used on diborane consisted of a 100 ohm coiled helix (No. 40 platinum-rhodium) resistance thermometer mounted on a mica cross. This was placed at the bottom of a 12-mm. tube into which the diborane could be condensed. The tube was surrounded by a double walled radiation shield in a glass vacuum jacket which could be immersed in liquid nitrogen. In operation a known amount of diborane was condensed into the calorimeter cooled below the melting point and drift rates determined using a G2 Mueller Bridge. Known amounts of electrical energy were added in periods of 1 to 2 minutes and drift rates run for about 10 minutes. From the data the melting point as a function of the fraction melted could be determined and the purity by cryoscopic calculations. Since ethane was the most abundant impurity and because of the fact that it has physical properties similar to diborane and is the most likely impurity to form mixed crystals with diborane, known amounts were added to diborane to test the behavior. Normal melting point lowering was obtained.

(4) K. S. Pitzer, THIS JOURNAL, 67, 1126 (1945).

(5) E. M. Carr, J. T. Clarke and H. L. Johnston, ibid., 71, 740 (1949).

(6) J. T. Clarke, H. L. Johnston and W. DeSorbo, Anal. Chem. (to be published).

(7) H. L. Johnston, J. T. Clarke, E. B. Rifkin and E. C. Kerr, THIS JOURNAL, 72, 3933 (1950).

(8) E. C. Kerr, E. B. Rifkin, H. L. Johnston and J. T. Clarke, ibid., 73, 282 (1951).

TABLE I

HEAT CAPACITY OF SOLID DIBORANE

Temp., °K.	Heat capacity, cal./mole	Temp., °K.	Heat capacity, cal./mole
Series I		Series II	
82.68	10.831	13.83	0.407
89.56	11.736	15.77	0.582
95.68	12.352	18.24	0.897
101.80	13.051	20.54	1.302
14.41	0.436	22.75	1.680
17.17	0.757	25.09	2.204
18.83	0.996	29.24	3.065
20.91	1.292	34.37	4.022
23.18	1.825	41.98	5.483
25.27	2.189	55.098	7.322
27.22	2.601	65.615	8.869
29.90	3.154	77.550	10.224
32.94	3.790	92.367	11.964
35.93	4.342	104.558	13.482
39.52	4.990	Series III	
43.86	5.829		
48.69	6.484	96.71	12.542
53.866	7.276	102.58	13.203
59.929	8.058		
66.978	9.039		
74.888	9.919		
82.789	10.907		
89.544	11.688		
96.473	12.472		

TABLE II

HEAT CAPACITY OF LIQUID DIBORANE

Temp., °K.	Heat capacity, cal./mole/deg.	Temp., °K.	Heat capacity, cal./mole/deg.
Series I		Series III	
115.27	18.08	112.86	18.18
123.93	18.02	118.75	18.08
132.93	17.97	126.23	18.01
142.45	17.98	146.62	18.09
Series II		158.61	18.19
		165.42	18.20
114.00	18.18	176.72	18.38
138.32	18.01		
152.08	18.02		
166.23	18.21		
170.95	18.21		

temperature of the calorimeter bulb in order that no condensation would occur during the measurement. The constant volume manometer previously described,[7,8] was used for the measurements and meniscus corrections were made according to Cawood and Patterson.[12]

TABLE III

VAPOR PRESSURES OF DIBORANE

Temp., °K.	P, cm.	Temp., °K.	P, cm.
111.78	0.116	154.15	13.101
116.20	0.231	173.15	49.061
123.50	0.611	175.65	56.967
140.49	3.923		

run and, to a much lesser extent, the heat capacity of the gas in the calorimeter. The amount of vapor in the calorimeter was determinined by knowing experimentally when the calorimeter was full and considering the decrease in liquid volume with temperature from the density data of liquid diborane as determined by Laubengayer.[10] The correction for the gaseous heat capacity was made using the data of Stitt.[2] Correction was made for gas imperfection using B values which were determined for diborane at 275°K. by Carr, Clarke and Johnston,[5] and estimated for diborane from the values given for ethane and ethylene by Eucken[11] for 180°K. and lower: this amounts to less than 0.01% in the heat capacity for the runs reported. The heat capacities were corrected for vaporization during the run using the calorimetric heat of vaporization. This, in turn, was corrected for temperature using liquid heat capacities determined in this research and gaseous heat capacities determined by Stitt.[2] The total vaporization correction amounted to a maximum of about 0.4%. The data are summarized in Table II. The experimental values agree with the smoothed curve with an average deviation of 0.025 cal./mole or 0.14%. When these data are plotted they exhibit a flat minimum at about 140°K. The appearance of such a minimum is typical of liquids that exhibit partial association. We conclude therefore that diborane exhibits some association (probably to B_4H_{12}) in the liquid range.

Vapor Pressure of Diborane.—The vapor pressure of diborane was determined between the liquid heat capacity runs of series II. The blocks and tube were kept one or more degrees above the

In carrying out the measurements drift rates were taken simultaneously on the resistance thermometer and the manometer. The pressure readings were compared with a standard meter bar located between the arms of the manometer in the insulated case. The results obtained are given in Table III, and a graph of $\log_{10} P_{(mm.)}$ vs. $1/T$ is given in Fig. 1.
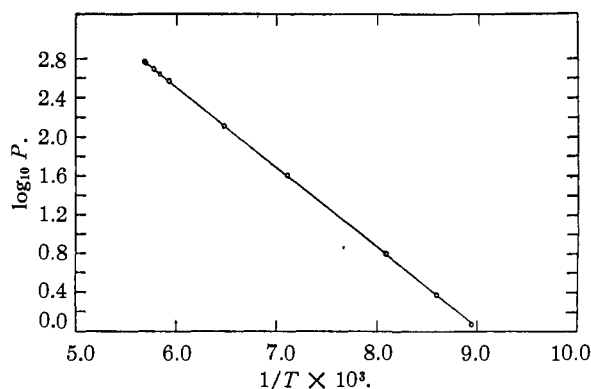

Fig. 1.—Vapor pressure of diborane.

The results may be expressed by the equation

$$\log_{10} P_{(mm.)} = 8.1110 - 870.95/T - 2.221 \times 10^{-3} T \quad (1)$$

which represents the data with an average deviation of about 0.6% below 10 mm. pressure and 1% above 10 mm. pressure. The boiling point, calculated from equation (1), is 180.32°K. The data of Stock and Kuss,[3] which deviate from this equation by 3 mm. on the average, are scattered so as to give

(10) A. W. Laubengayer, R. P. Ferguson and A. E. Newkirk, THIS JOURNAL, 63, 559 (1941).

(11) A. Eucken and A. Parts, Z. physik. Chem., B20, 184 (1933).

(12) W. Cawood and H. S. Patterson, Trans. Faraday Soc., 29, 514 (1933).

TABLE IV

HEAT OF FUSION OF DIBORANE

Series	Temp. interval, °K.	Total elec. energy, cal.	Energy to heat solid and liquid, cal.	Heat leak from blocks, cal.	Pre-melting, cal.	Total energy to melt solid	Diborane, moles	Heat of fusion, cal./mole
III (1)	107.35–111.38	2103.9	−160.6	1.4	2.7	1947.4	1.8176	1071.4
III (2)	107.82–110.85	2060.5	−125.2	0.7	5.4	1941.4	1.8176	1068.1
I	106.85–110.66	1951.1	−143.9	−0.1	3.4	1810.5	1.6955	1067.8
II	108.08–111.40	2074.6	−140.4	1.7	15.6	1951.5	1.8317	1065.4[a]
							Av.	1069.1
							Av. dev.	1.5

[a] This value was not used in obtaining the average, since the premelting correction which may be off by 30% is large.

values both above and below those yielded by our equation.

By use of Berthelot's equation to correct for gas imperfection one obtains

$$\Delta H = RT^2 \frac{d \ln P}{dT}\left[1 + \frac{9PT_c}{128P_cT}\left(1 - \frac{6T_c^2}{T^2}\right) - \frac{PV_{liq}}{RT}\right] \quad (2)$$

The values of Newkirk[13] were used for the critical constants and a liquid volume of 64 cc. at the boiling point from the density of Laubengayer.[10] This gives a value for the heat of vaporization, $\Delta H = 3431$ cal./mole.

Kelley,[14] who used the data of Stock and Kuss[3] to calculate the heat of vaporization of diborane, computed 3685 cal./mole.

Melting Point of Diborane.—The melting point of diborane was determined in series II with diborane which had just been purified by a one-plate separation and then by passage through the system of bubblers. The melting point was determined for $N = 0.084$, 0.445 and 0.748, respectively, for an over-all time of 4.5 hr. In this period the resistance thermometer changed by only $0.01°$ which is well within the accuracy of our knowledge of the absolute temperature. The melting point was $108.30°K.$ according to the resistance thermometer and $108.31°K.$ according to the standard thermocouple.

Heat of Fusion of Diborane.—Heats of fusion were measured in the usual manner starting approximately 1° below the melting point and ending approximately 3° above the melting points. The energy necessary to warm the solid to the melting point and heat the liquid above the melting point was determined from the heat capacity runs in the series considered. The heat leak from the block to the calorimeter was determined by measuring the area of the block temperature minus the the temperature of the surface of the calorimeter against the time of heating: this was converted to calories using the heat transfer coefficient interpolated from drift rates on heat capacity runs above and below the melting temperature. The abnormally high values of B_n during premelting were not used.

The fraction of diborane initially melted was calculated from the initial temperature and the purity as determined by the premelting data.[15]

The results are summarized in Table IV and give

(13) A. E. Newkirk, THIS JOURNAL, 70, 1978 (1948).

(14) K. K. Kelley, U. S. Bureau of Mines, Bull. No. 383 (1935).

(15) H. L. Johnston and W. F. Giauque, THIS JOURNAL, 51, 3194 (1929).

an average value of 1069 cal./mole with an average deviation of 1.5 cal./mole. The value reported is estimated to be accurate to 0.20%.

Heat of Vaporization of Diborane.—The heat of vaporization of diborane was determined in Series I and Series II. The procedure used was similar to that of Giauque and Johnston[16] and consisted of vaporizing the diborane at a constant pressure of approximately one atmosphere into a calibrated 5-liter bulb. The total electrical energy input was corrected for amount of heat to change the temperature of the liquid from the initial state to the final state. Correction was made for the amount of diborane vaporized by calculating the change in the number of moles of gas initially and finally present in the calorimeter. In series II the calorimeter was full at a temperature slightly below the boiling point so it was possible to calculate the empty space in the calorimeter from a linear extrapolation of the liquid density data of Laubengayer.[10]

The blocks and tubes were kept warmer than the calorimeter and the heat leak corrected by determining the temperature difference between the calorimeter surface and the blocks during the heating period and using the heat transfer coefficient obtained in the heat capacity runs. The results are summarized in Table V. The average of these values is 3412 cal./mole with an average deviation of 3.0 cal./mole. The over-all uncertainty is probably 5 cal./mole. As discussed under vapor pressure the heat of vaporization determined from the vapor pressure equation using Berthelot's equation for gas imperfection was 343 cal./mole. This value agrees satisfactorily with the calorimetric value of 3412 cal./mole.

TABLE V

HEAT OF VAPORIZATION OF DIBORANE

Series	Vaporized, moles	Heat of vaporization, cal./mole
I (1)	0.14579	3424
I (2)	.21484	3425
III (1)	.14300	3421
III (2)	.18523	3420
III (3)	.12570	3422
	Av.	3422

Entropy and Heat Content of Gaseous Diborane at the Boiling Point (180.32°K.).—The entropy of gaseous diborane at the boiling point was determined from the heat capacity, heat of fusion and heat of vaporization reported in this work.

(16) W. F. Giauque and H. L. Johnston, ibid., 51, 2300 (1929).

TABLE VI

ENTROPY OF DIBORANE

Calculation of the entropy of diborane gas		Estd. uncertainty
0 to 12°K., extrapolation	0.085	0.002
12 to 108.30°K. graphical	11.351	.048
Fusion 1069.1/108.30 °K.	9.872	.020
108.30 to 180.32 °K., graphical	9.240	.010
Vaporization 3412/180.32°K.	18.888	.020
Total entropy of gas at the boiling point	49.43	±0.10

Using Berthelot's equation and the critical constants of Newkirk one obtains a correction of +0.14 e.u. in going to the ideal gas at one atmosphere. This gives a value of 49.57 for entropy of ideal diborane at one atmosphere and a temperature of 180.32°K.

The heat content of diborane referred to the solid at 0°K. has been determined for the gas at the boiling point (180.32°K.) by graphically integrating the area of the smoothed heat capacity values for liquid and solid diborane and adding the heat of fusion and vaporization. This gives a value of 6520.2 cal. for the gas at 1 atmosphere and 180.32°K. The results are summarized in Table VII.

TABLE VII

HEAT CONTENT OF DIBORANE

0 to 12°K., extrapolation	0.77
12 to 108.30°K., graphical	733.83
Heat of fusion	1069.0
108.30 to 180.32°K., graphical	1304.6
Heat of vaporization	3412.0
Heat content of gas at 180.32°K.	6520.2° cal./mole

Discussion.—A discussion of these data, as it relates to the structure of diborane and a comparison with the statistically calculated entropy, will appear in the following paper of this series.

COLUMBUS 10, OHIO

Condensed Gas Calorimetry. IV. The Heat Capacity and Vapor Pressure of Saturated Liquid Diborane above the Boiling Point[1,2]

BY ELLIS B. RIFKIN, E. C. KERR AND HERRICK L. JOHNSTON

RECEIVED JUNE 9, 1952

Heat capacities of liquid diborane have been measured along the saturated vapor pressure curve, over the temperature range 170 to 282°K. Vapor pressures were also measured over the range 170 to 288°K. The latter fit the equation (2) to within 1% below 230°K. and to within 2–3% up to 288°K. The special high pressure calorimeter is described. Entropies were also calculated by use of the Third Law, and compared with statistical entropies based on an assumed structure of the molecule and on Webb, Neu and Pitzer's assignment of fundamental frequencies. Possible explanations have been given for the half-unit discrepancy.

Introduction

The purpose of the present investigation was to extend the measurement of Clarke, Rifkin and Johnston[3] to the critical point of diborane.

Apparatus.—Because of the pressure attained in the calorimeter (~ 35 atmospheres) it was necessary to employ a modified form of the condensed gas calorimeter[4] used in the earlier work.

The principal modification was the copper calorimeter itself. The calorimeter, 5.40 cm. in diameter by 10 cm. long, has a 2.5-mm. wall thickness. The upper surface and the wall were machined from a single piece of un-annealed copper. The bottom, which was also machined from a single piece of copper, contains a re-entrant well 5 cm. deep by 13 mm. inside diameter, which serves as a well for insertion of a cylindrical copper jacketed platinum resistance therometer designed in this Laboratory. The copper bottom of the calorimeter is joined to the calorimeter body by a threaded joint covered with silver solder. The resistance thermometer is held firmly in place by a set screw which projects diagonally into the well. Good thermal contact is assured by use of stopcock grease.

A standard thermocouple, held in a narrow well drilled upward into the wall of the re-entrant thermometer well, by means of cerrobend alloy, serves as a primary temperature standard. This was calibrated in terms of the laboratory helium thermometer scale.[5]

The helium-filled platinum resistance thermometer also served as a heater during periods of energy input to the calorimeter. In order to facilitate circulation of liquid, and so ensure heat transfer in the body of the liquid, a cylindrical copper baffle of 0.01-inch copper was mounted around the re-entrant well, on the inside of the calorimeter in such a way as to maintain a liquid layer of about 6 mm. thickness in contact with the plug.

Both the outside of the calorimeter and the inside of the lower block were gold plated to reduce heat transfer by radiation. The capillary tube leading to the calorimeter was 2.4 mm. o.d. inconel with 0.5 mm. wall, which was silver soldered into a boss that was machined at the center of the upper surface of the calorimeter. The inconel tube terminated in a Teflon packed steel needle valve (manufactured by American Instrument Company) through which the diborane was admitted to the calorimeter. The calorimeter and inconel tube were pressure tested with nitrogen to 80 atmospheres prior to use.

Three Bourdon gages, each covering a different range of pressure, were used to measure vapor pressures of diborane. These gages were calibrated at close intervals against a precision dead weight gage from the high pressure division of this Laboratory.

Procedure.—All measurements on diborane were made in a single series of runs although they appear, effectively, as five consecutive series since it was necessary to make four withdrawals of material from the calorimeter in the course of measuring fourteen heat capacity points. This was due to thermal expansion of the liquid. Series of vapor pressure

(1) This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

(2) This paper likewise contains a description of the Ohio State Calorimeter for measurement of saturated heat capacities above boiling point temperatures.

(3) J. T. Clarke, E. B. Rifkin and H. L. Johnston, THIS JOURNAL, 75, 781 (1953).

(4) H. L. Johnston, J. T. Clarke, E. B. Rifkin and E. C. Kerr, ibid., 72, 3933 (1950).

(5) T. Rubin, H. L. Johnston and H. Altman, ibid., 73, 3401 (1951).