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

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

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

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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

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(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).

and density measurements were interspersed with those of heat capacity.

The general procedure was as follows: 1. Beginning with a few cubic centimeters of dead space in the top of the calorimeter, a series of vapor pressure points was taken until it was estimated that another 5° rise in temperature would completely fill the calorimeter with expanded liquid. 2. The temperature was then raised slowly and the tube heater run, at intervals of several seconds, until a sudden jump in pressure indicated that the liquid had just entered the inconel tube. Since the volume of the calorimeter was accurately known, this provided a measurement of density. 3. The calorimeter was then cooled to near the bottom of the particular temperature range under immediate investigation and a series of heat capacity runs was taken with temperature intervals of the order of 10°. During this series of runs the high pressure needle valve at the external end of the capillary tube was kept closed to minimize the correction due to vaporization. 4. When the temperature was nearly reached at which the calorimeter would be filled with liquid, the series of heat capacity runs was terminated and sufficient liquid vaporized from the calorimeter to provide dead space to permit a higher series of runs. The sequence of vapor pressures, densities and heat capacities was then repeated through the higher range of temperature.

All liquid vaporized from the calorimeter, either following a heat capacity series, or upon completion of the whole curve for gas density by making a suitable choice of critical series, was measured quantitatively in the 5-liter thermostated mercury buret described previously.[4] However, prior to each of these volume measurements the diborane vaporized from the calorimeter was condensed to a solid by means of liquid nitrogen, and evacuated for a few moments to remove hydrogen. Small amounts of decomposition, at the higher temperature, produced sufficient hydrogen to make this procedure significant although the purity of the residual liquid in the calorimeter was not much affected.

Methods of Data Treatment.—Corrections for the vaporization of diborane into the gas space, and for the energy absorbed by the gas were made by the method of Osborne and Van Dusen[6] with the aid of the following means of evaluating PVT data for gas and liquid. An estimate of the critical volume of diborane (170 cc.) was used as the basis for drawing a density *vs.* temperature plot in accordance with the law of the Rectilinear Diameter. Since the gas should follow van der Waals equation in the neighborhood of the critical point, and Berthelot's equation in the neighborhood of the boiling point, it is possible to trace out the whole curve for gas density by making a suitable choice of critical volume and assuming, for the intermediate temperature region, a compressibility curve that passes smoothly into the limiting values for the Berthelot and van der Waals regions. Since liquid densities are known for temperatures below the boiling point[7,8] and, from our own determinations, for several points between the boiling and critical points we are thus able to draw in the entire liquid curve, by use of the rectilinear diameter. This method, which depends upon an estimate of the critical volume, appears justified since its use resulted in a smooth heat capacity curve, while a variation of even 1 cc. in the choice of critical volume produced quite noticeable scattering of points.

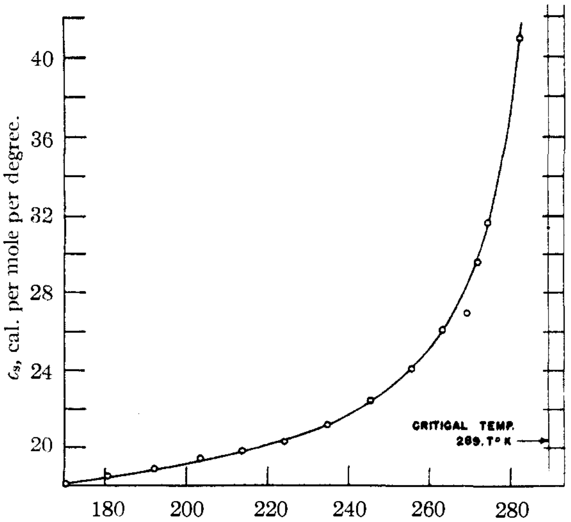

Fig. 1.—Heat capacity of saturated liquid diborane.

Values of dP/dT, also required in the Osborne and Van Dusen formula, were taken from our own vapor pressure formula (*cf. seq.*).

Aside from the correction for energy expended in heating the vapor, the calculation of heat capacity followed usual calorimetric procedure. Correction for the heat capacity of the empty calorimeter amounted to only 0.2 of 1% on the average.

Experimental Heat Capacities.—Experimental results are given in Table I and illustrated in Fig. 1, which shows the rapid rise in heat capacity near the critical point. The data represent saturation heat capacities, C_s, rather than constant pressure heat capacities, C_p. Their difference is given by the relationship[6]

$$C_s = C_p - P(\partial V/\partial P)_T(dP/dT) \qquad (1)$$

Both of the parenthetical terms are larger near the critical point, which accounts for the steep rise in C_s shown in the figure. However, the difference term rapidly approaches zero as the temperature is lowered to the boiling point so that calorimetric measurements which are, in reality, measurements of C_s may be equated to C_p.

Because of the lack of accurate compressibility data on liquid diborane we have felt it worthwhile, in the present instance to convert the C_s values measured directly to C_p values.

Error Limits.—A maximum uncertainty of 0.01° in the 10 degree ΔT's of the heat capacity runs limits the heat capacity error from this source to about 0.1 of 1%. An additional error limit of 0.1 of 1% may also be set for the uncertainty from heat leak corrections since the heat leak to the calorimeter was normally about 1% of the energy input and was uncertain to no more than 10% of itself.

The major sources of error lie in the corrections for energy expended in vaporizing liquid into the dead space and in heating the vapor phase. The method of making this correction was discussed above, and its magnitude is shown in the final column of Table I. Noting that this correction amounts to no more than 0.15 of 1% of the total energy below 200°K., but reaches nearly 30% near the critical point, and recognizing that the liquid volume in the calorimeter, as arrived at by the Rectilinear Diameter method may be uncertain to as much as 2% near the critical region, we estimate that error contribution from this source cannot exceed 0.1 of 1% below 200° but may attain 5% at 288°K.

TABLE I

HEAT CAPACITY IN CAL./DEG./MOLE OF SATURATED LIQUID DIBORANE

T_{av}	C_s	Vap., cor.
170.09	18.08	−0.03
180.86	18.51	− .03
192.00	18.94	± .00
203.36	19.35	+ .08
213.63	19.76	− .18
224.11	20.33	− .09
234.87	21.23	+ .18
245.64	22.52	.59
255.64	24.09	.82
263.14	26.06	1.61
269.14	27.03	2.71
271.95	29.55	2.70
274.58	31.7	2.7
282.31	40.9	9.2

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(6) N. S. Osborne and M. S. Van Dusen, *Bull. of Bur. Stand.*, **14**, 397 (1918).

(7) A. W. Laubengayer, R. P. Ferguson and A. E. Newkir, THIS JOURNAL, **63**, 559 (1941).

(8) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

Vapor Pressures between the Normal Boiling and Critical Points.—Vapor pressures were measured in the calorimeter by means of the calibrated Bourdon gages. To avoid errors that might arise from condensation of vapor, both blocks and the inconel tube were maintained at a temperature slightly higher than that of the calorimeter.

The principal source of error arose from the slow decomposition of diborane to yield hydrogen and higher boranes. The effect of such decomposition is to give apparent vapor pressures higher than the true values. To avoid appreciable error from this cause it was our custom to limit all vapor pressure determinations to a period that lay within 20 minutes of the time when a considerable amount of material was vaporized from the calorimeter, thus sweeping out any accumulated hydrogen. This, of course, limited the length of temperature equilibration periods during vapor pressure measurements, and so introduced a small inaccuracy from this source. However, we were able to get good reproducibility when measurements were duplicated within the 20-minute period, whereas results were high and non-reproducible often when the calorimeter was allowed to stand unpumped for more than an hour.

To indicate the degree of decomposition to which we refer, we should add that the total amount of decomposition, over the period of several days in which these calorimetric and vapor pressure measurements were carried out, amounted to no more than 0.001 to 0.002 mole of B_2H_6, as estimated from the quantity of hydrogen removed. Thus, the decomposition resulted in negligible error in the determinations of heat capacity.

Vapor pressure results are shown in Table II. When these were combined with our vapor pressure measurements below the normal boiling point[4] we were able to represent the entire range of vapor pressures by the single equation

$$\log_{10} P_{\text{mm}} = 8.1251 - 870.68/T - 0.002339\ T \tag{2}$$

This equation reproduces experimental values below 230°K. to within 1% and, between 230 and 288°K., to within 2 or 3%.

Equation (2) yields, for the normal boiling point, the value 180.6 ± 0.2°K.

TABLE II

VAPOR PRESSURE OF LIQUID DIBORANE

Temp., °K.	Pressure, mm.	Temp., °K.	Pressure, mm.
169.81	406.8	218.59	4205
180.33	756.7	229.81	6150
199.89	2017	233.31	6894
202.86	2307	239.82	8430
208.83	2927	249.85	11170
209.64	3028	287.11	27200
210.40	3098	288.43	27460

Entropy and Heat Content Values.—Values of molal entropy were obtained by adding values of the integral $\int C_s \mathrm{d} \ln T$ between limits of180.68° K. and T°K. to 30.57,[3] the entropy at the normal boiling point. Molal heat contents were obtained by adding the two integrals $\int C_s\,\mathrm{d}T$ and $\int V\mathrm{d}P$, for the same limits, to 3115,[3] the heat content at the normal boiling point. Entropy and enthalpy values so obtained are those for the liquid under its saturated vapor pressure. These values are listed in Table III. Contributions to enthalpy from the $V\mathrm{d}P$ integral, for whose evaluation we employed our vapor pressures and densities, ranged from 1.0 cal./mole at 190° to about 81 cal. at 290°K.

Third Law Entropy of Diborane and the Structure of the Molecule.—Lack of adequate data of state for diborane vapor precludes the accurate calculation of the entropy of diborane in the ideal gaseous state at the critical point where, otherwise, the calculation would be relatively simple. However, the calculation should be reasonably reliable up to 230°K. where the pressure of the vapor amounts to about 8 atmospheres and should not deviate seriously from Berthelot's equation. Accordingly we have made a calculation for this temperature. Steps in the calculation are indicated in Table IV.

TABLE III

VALUES OF MOLAL ENTROPY AND MOLAL HEAT CONTENT FOR LIQUID DIBORANE UNDER ITS SATURATED VAPOR PRESSURE

Temp., °K.	$S - S_0$, cal./mole/deg.	$H - H_0$, cal./mol.
180.68	30.57	3115
190	31.58	3290
200	32.56	3482
210	33.50	3678
220	34.43	3880
230	35.33	4089
240	36.24	4313
250	37.15	4538
260	38.10	4788
270	39.10	5066
275	39.66	5223
280	40.29	5403
285	41.02	5623
289.7 (extrap.)	41.85	5861

TABLE IV

EVALUATION OF THE ENTROPY OF DIBORANE IN THE IDEAL GASEOUS STATE AT 230°K. AND 1 ATMOSPHERE

a, Entropy of the saturated liquid at the boiling point	30.56 e.u.
b, ($S_{230} - S_{180.68}$) saturated liquid	4.76
c, Entropy of vaporization at 230°K. 2897/230	12.60
d, $S_{1\text{ atm.}} - S_{230^\circ}$ vapor pressure	3.91
e, Correction for non-ideality	0.10
Entropy of ideal gas at 230°K. and 1 atm.	51.93 e.u.

Steps (d) and (e) were carried out by Berthelot's equation; while the value chosen for ΔH of vaporization in step (c) was arrived at by adding to the normal boiling point, heat of vaporization, 3412 cal.,[3] the integral $\int (C_g - C_s)\mathrm{d}T$ between the limits of 180.68 and 230°K. C_s values for use in this integral were taken from our Table II while C_g values were taken from the statistical computations of Webb, Neu and Pitzer,[9] without correction for the small influence of pressure on the gaseous C_p's.

Table V compares the Third Law entropies for diborane in the ideal gaseous state, with the values scaled from Table V of Webb, Neu and Pitzer,[9] at the respective temperatures of 180.68 and 230°K.

TABLE V

COMPARISON OF THIRD LAW ENTROPIES WITH THOSE COMPUTED STATISTICALLY BY WEBB, NEU AND PITZER

Temp., °K.	Third law	Statistical
180.68	49.46	49.91
230.00	51.93	52.51

The statistical calculations[9] were made on the basis of a bridge structure for B_2H_6 and on the assignment of a 369 wave number frequency as the lowest fundamental.

The discrepancies, which amount to approximately a half entropy unit in each instance, are outside the limits of accuracy of either the calorimetric data or the statistical computations but may arise from one of the following causes: (1) an undetected and not apparent source of random entropy in the solid lattice; (2) an incorrect selection of structure for the molecule (not likely) in the statistical calculations; or (3) an incorrect assignment of fundamental frequencies—more particularly in the low frequency assignment.[10] We do not see a means of distinguishing between these at the present time.

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[9] A. N. Webb, J. T. Neu and K. S. Pitzer, *J. Chem. Phys.*, **17**, 1007 (1949).

[10] Only the 369 cm.$^{-1}$ assignment makes any significant vibrational contribution at these temperatures. Preliminary statistical calculations carried out some time ago in this Laboratory,[11] based on a low fundamental assignment of 412 wave numbers (a frequency assigned as an overtone by Bell and Longuet-Higgins[12]) gave somewhat better agreement with the Third Law entropies. Discrepancies were: 0.24 e.u. at 180.68° and 0.06 e.u. at 230°K.

[11] C. W. Beckett, J. T. Clarke and H. L. Johnston, Technical Report to the Office of Naval Research (1948).

[12] R. P. Bell and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (*London*), **A183**, 357 (1945).

COLUMBUS, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Polarographic Current–Time Relation during Individual Drop Life

BY JAMES J. LINGANE

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An improved technique of measuring the current–time curve during an individual drop life is described. Current–time curves at various mercury pressures and correspondingly various drop times have provided evidence that a major cause of divergence of the observed curves from those predicted by either the original or modified Ilkovic equation is the variation of the rate of mercury flow during the drop life. The back pressure due to the interfacial tension is much larger at the beginning than at the end of the drop life and correspondingly the instantaneous area (and hence current) is smaller at the beginning of the drop life than it would be if the mercury flow rate were constant. This effect becomes more pronounced the smaller the total applied pressure. When the difference between the total applied pressure and the back pressure is very small, the current–time curve shows a measurable pause at zero current immediately after the drop falls. Apparently after a drop falls the mercury thread retracts into the capillary lumen and the pause at zero current corresponds to the time required for it to re-emerge. At very small net driving pressures the curves also show a distinct inflection as soon as the new drop begins to form. This inflection probably reflects the non-spherical and varying geometry of the very young mercury surface. At short drop times the current–time curve goes through a flat maximum, because the stirring produced by the rapid dropping movement disturbs the diffusion layer and enhances the current. With an electrode whose characteristics correspond to those normally employed, and a drop time in the neighborhood of 3.0 to 3.5 sec., the observed current–time curve does approximate quite closely during the last three-fourths of the drop life to that predicted from the modified Ilkovic equation.

The original Ilkovic equation[1,2] for the instantaneous diffusion current during the life of an individual mercury drop is

$$i_t = 709\, nD^{1/2}Cm^{2/3}t^{1/6} \text{ (microamp.)} \qquad (1)$$

If the rate of flow of mercury, m, is constant, this predicts that the current–time curve should be a sixth-order parabola, $i_t = kt^{1/6}$.

Steghart[3] and McKenzie[4] were the first to report that oscilloscopically observed current–time curves deviated considerably from the above relation; in particular the current during the very early life of the drop was much too small. This was confirmed by Taylor, Smith and Cooter[5] in the case of cadmium ion in 0.1 M potassium chloride. From attempts to fit their data to an equation of the form $i_t = kt^y$, Taylor, Smith and Cooter concluded that no single value of y applied over the entire drop life; from 0.1, 0.5, 1 and 2 sec. to the end of the drop life (*ca.* 3.5 sec.) the observed values of y were *seriatim* 0.31, 0.249, 0.227 and 0.186, instead of the 0.167 predicted by eq. 1. Kambara, Suzuki and Tachi[6] also reported that the value of y during the later life of the drop is between $^1/_4$ and $^1/_5$, but they do not provide sufficient experimental information to permit one to judge the precision of their measurements. From a very well executed study, using cupric ion in dilute sulfuric acid, MacDonald and Wetmore[7] also concluded that the current–time curve does not follow a simple parabola but that the average value of y is close to 0.21.

On the other hand Airey and Smales[8] reported that the relation $i_t = kt^{1/6}$ was obeyed to ±2.5% from 0.75 sec. to the end of the life of a 3.9 sec.

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[1] D. Ilkovic, *Collection Czechoslov. Chem. Communs.*, **6**, 498 (1934); *J. chim. phys.*, **35**, 129 (1938).

[2] I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1952, p. 34 *et seq.*

[3] F. L. Steghart, *Chemistry and Industry*, 157 (1948).

[4] H. A. McKenzie, THIS JOURNAL, **70**, 3147 (1948).

[5] J. K. Taylor, R. E. Smith and I. L. Cooter, *J. Research Natl. Bur. Standards*, **42**, 387 (1949).

[6] T. Kambara, M. Suzuki and I. Tachi, *Bull. Chem. Soc. Japan*, **23**, 220 (1950).

[7] J. J. MacDonald and F. E. W. Wetmore, *Trans. Faraday Soc.*, **47**, 533 (1951).

[8] L. Airey and A. A. Smales, *Analyst*, **75**, 287 (1950).