THE HEAT CAPACITY OF SATURATED LIQUID ETHANE FROM THE BOILING POINT TO THE CRITICAL TEMPERATURE AND HEAT OF FUSION OF THE SOLID[1]

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The data presented in this paper are the results of further work on a series of investigations that are being carried out on the properties of ethane.[5] Measurements on the heat capacity of saturated liquid ethane have recently been made by A. Eucken and F. Hauck,[6] but their results are 10 and in some instances even 20% higher than ours; we shall discuss the relative merits of the data later.

The purpose of this investigation is to gain additional knowledge of the thermal properties of one of the constituents of natural gas from which helium is being extracted.

Preparation of Ethane.—The preparation of large quantities of pure ethane was difficult. At low temperatures 2.3 moles were necessary to fill the calorimeter, and altogether more than 12 moles of the substance were made.

Ethane was generated by electrolyzing a solution of potassium acetate as outlined by Murray.[7] The gas was passed successively and repeatedly through 30% solution of sodium hydroxide, fuming sulfuric acid, concentrated sulfuric acid, 30% solution of sodium hydroxide, potassium hydroxide sticks and phosphorus pentoxide. The liquefied gas was finally fractionated twice under stirring in a cryostat; the first and last portions were rejected. Before the final fractionation, several portions had been rejected during the process of chemical purification. From the heat effect associated with premelting and lowering of the melting point, the purity was estimated to be about 99 mole per cent. Two batches of ethane were initially prepared. The second batch showed signs of only slightly higher purity than the first one, even though considerably more care was used in its preparation. The fillings for the steel calorimeter were taken from the second batch and should have been of progressively greater purity as the amount of ethane in the calorimeter decreased.

Apparatus.—The apparatus for temperature control, similar to that used by Gibson and Giauque[8] is shown in Fig. 1.

The copper cylinder, B, weighing 3.8 kg., was suspended from the steel top of a vacuum-tight container, A, made from a solid brass cylinder. A lead gasket, D, was

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[5] Loomis and Walters, THIS JOURNAL, 48, 2051 (1926); Frank Porter, ibid., 48, 2055 (1926).

[6] A. Eucken and F. Hauck, Z. physik. Chem., 134, 161 (1928).

[7] Murray, J. Chem. Soc., 61, 10 (1892).

[8] G. E. Gibson and W. F. Giauque, THIS JOURNAL, 45, 93 (1923).

found quite satisfactory even at liquid–air temperatures, although it was necessary to tighten the nuts on the stud screws occasionally. The pressure was ordinarily less than 3×10^{-5} mm. of mercury. H and J were heating elements connected in series. The heater, J, was added to the apparatus after it was found that the temperature of the top lagged considerably behind the temperature of the body of the copper cylinder because of poor contact. One of the thermometer terminals is shown at G; F is a bakelite tube for thermocouple leads. The Wood's metal seal, E, insured good thermal contact with the steel tube leading to the calorimeter. The places marked TC indicated the positions of different thermocouples.

Two calorimeters as shown in Fig. 1 were used, a steel calorimeter, C, primarily for pressures above 1 atmosphere, and one made of copper, P, for low pressures.

The cylindrical steel calorimeter, C, had a wall thickness of 1.0 mm. The height was 14 cm., the diameter 3.8 cm. and the volume 123.3 cc. The bottom steel cap was screwed into the body of the calorimeter and the joint was made pressure tight by silver-soldering in a groove left for that purpose. A central heater tube, K, 10 cm. in length, made of a solid copper cylinder with twelve radial vanes cut out in a milling machine, was screwed and silver-soldered into the bottom cap. The heater, L, was wound around a thin copper tube closed on one end and in thermal contact with the central heater tube by means of Rose metal. A thermocouple well, M, of copper was extended from the top.

The steel calorimeter, C, was surrounded by a copper shell, O, 1.5 mm. thick, in order to equalize rapidly the outside temperature. The copper resistance thermometer, N, was wound on this copper sheet. The latter made contact only at the top
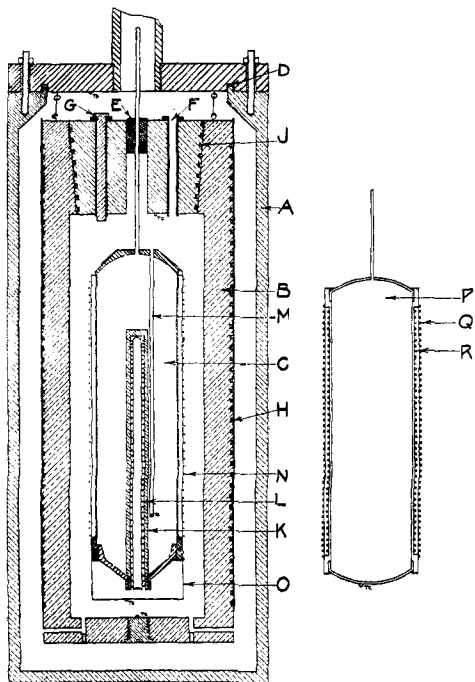

Fig. 1.—Apparatus for specific heat measurements.

and bottom of the cylindrical portion, which eliminated any strain in the thermometer due to differential expansion.

The copper calorimeter, P, had a wall thickness of 0.75 mm. The height was 13 cm. and the diameter 3.8 cm. Sixteen radial vanes of copper served to distribute the heat rapidly throughout the calorimeter. Ethane was introduced through a steel tube (O.D. 0.25 cm. and I.D. 0.19 cm.). Resistance thermometer Q and heater R were separate. The former was made of No. 40 B. and S. gage copper wire and had a resistance of 240 ohms at $0°$. The resistance thermometer was wound on the outer shell which was soldered to the calorimeter, while the heater, made of No. 32 B. and S. gage manganin wire, was wound around the body of the calorimeter. The resistance of the heater was 620 ohms at room temperature and remained very constant because of the small temperature coefficient of manganin wire. In using a copper resistance thermometer we

followed Onnes and Holst,[9] Meissner[10] and others.   The volume of the copper calorimeter was 144.8 cc.

The container was surrounded by a silvered pyrex Dewar flask 14 cm. in diameter. The storage cylinder used to keep and weigh the ethane under its saturation pressure was made of stainless steel (Allegheny metal, composition: C less than 0.2%; Cr, 17–20%; Ni, 7–10%; Fe, 70–76%).   The weight of the storage cylinder was 690 g. and its volume 360 cc.

Measurements.—Both energy and temperature measurements were made with a White double potentiometer, A, Fig. 2.   The electrical connections are shown in Fig. 2, and were essentially the same as those used by Gibson and Giauque.[8]   B indicates the resistance thermometer and C
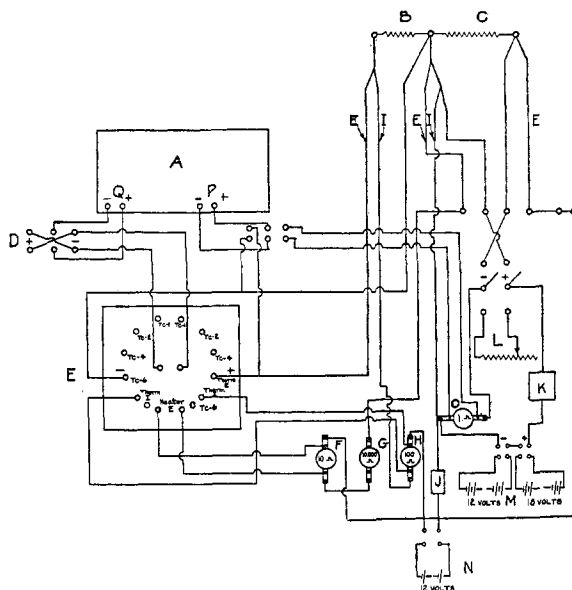

Fig. 2.—Electrical connections of apparatus.

the heater of the calorimeter.   A constant thermometer current was obtained by discharging six lead storage cells, N, continuously through a 50,-000-ohm resistance, J, in series with the thermometer.   The potential drop across the 100-ohm standard resistance, H, gives the value of the thermometer current, amounting to about 0.00024 ampere.   The e.m.f. of the thermometer was measured directly across its terminals.   In order to obtain the heat input, the potential drops across F and O were read; the former gave the current directly while the latter was a known fraction of the total drop.   The parallel lead correction and also the correction for heat generated in the lead wires between the calorimeter and copper cylinder were made; the latter was in most cases negligible.   Energy was

[9] Onnes and Holst, *Comm. Phys. Lab. Univ. Leiden*, No. 142A (1914).
[10] Meissner, *Ver. deut. phys. Ges.*, **16**, 262 (1914).

obtained from a set of lead storage batteries, M. The rheostat, L, was used to stabilize the heating current; the ammeter, K, gave its approximate value. E was a mercury master switch, D a mercury reversing switch for thermocouples, and Q and P the two independent circuits of the White double potentiometer. An attempt was made to heat the copper cylinder simultaneously with the calorimeter, but for the runs with the copper calorimeter, this had to be abandoned, since a decided temperature lag was noticed in the cover of the copper cylinder. For the runs with the steel calorimeter an extra heating element was wound around the cover, and the two thermocouples, one near the bottom of the cylinder, and the other at the bottom of the cover, registered a simultaneous rise. Since the rates of heating of the calorimeter and cylinder were not always identical, the heat leak correction for the steel calorimeter was made graphically by plotting the temperatures of the copper block and the outside of the steel calorimeter against time and obtaining the area between the two curves by means of a planimeter; from the area and the rates of heating before and after each run, the heat leak was calculated.

An additional correction discussed by Giauque and Wiebe[11] was not necessary in case of the steel calorimeter, since the temperature difference between calorimeter and copper cylinder remained very nearly the same at all times and a check made by means of the thermocouple inside the well showed no discrepancies in the two temperature rises. The check runs at lower temperatures made with the steel calorimeter did not indicate any discrepancies with respect to the runs made with the copper calorimeter, beyond the experimental error.

For the lowest temperatures liquid nitrogen boiling under reduced pressure was used; otherwise liquid nitrogen, air, oxygen or ethyl bromide cooled by means of liquid nitrogen served as the bath liquid in the Dewar.

The average run lasted ten minutes.

All standard resistances, the standard cell of the potentiometers and the stop-watch were checked by the U. S. Bureau of Standards before and after the measurements.

The stop-watch showed a discrepancy of less than 0.02% for a ten-minute interval between the two calibrations, and we place our accuracy of time measurement at 0.05%. For the heat capacity measurements on the empty calorimeter, hydrogen was introduced in order to speed up the attainment of equilibrium; a small correction was applied to take into account the heat capacity of this gas.

Each batch was weighed when put in and when taken out of the calorimeter. The discrepancy between the two weighings was less than 0.005%.

Temperature Scale.—The thermocouples used were calibrated at approximately ten-degree intervals against platinum resistance thermom-

11 W. F. Giauque and R. Wiebe, THIS JOURNAL, 50, 109 (1928).

eter No. 2^{12} of the laboratory. The calibration was made in a cryostat described by Walters and Loomis.[13] In their work the boiling point of liquid oxygen was assumed to be $-183.00°$, while according to the recent international agreement[14] the boiling point has been fixed at $-182.97°$. We have applied the necessary correction to the melting-point temperature only, since in specific heat determinations we are concerned with temperature differences primarily. The absolute temperature is probably correct to $0.07°$ except below $-185°$, where it may or may not be better than $0.10°$. The ice point of the resistance thermometer was found to check the original value within the accuracy of the instrument. The copper resistance thermometers were calibrated in place by means of the thermocouples attached to the calorimeter. The calibration was checked repeatedly.

Heat Capacity Data

The results are given in Table I and Fig. 3. The data of Eucken and Hauck lie on a straight line and, therefore, approach our data at low and high

TABLE I

HEAT CAPACITY DATA

Mol. wt., 30.0462. 15° gram calorie, 4.185 joules. Fillings: I, 2.597 moles; II, 2.542; III, 2.050; IV, 1.782; V, 1.540; VI, 1.294. I and II, copper calorimeter; III, IV, V and VI, steel calorimeter. C_{SV}, heat capacity of saturated vapor per mole; C_{SL}, heat capacity of saturated liquid per mole.

T, °K.	Heat cap. of empty cal., cal./deg.	C_{SL}, cal./deg.	$-C_{SV}$, cal./deg.	Filling
67.46	9.81	11.18	..	I
70.64	10.43	11.71	..	II
71.59	10.67	11.99	..	I
73.41	11.06	12.26	..	II
75.67	11.49	12.85	..	I
89.52	Melting point	...	..	...
96.77	14.88	16.35	..	II
96.82	14.88	16.42	..	I
98.06	23.24	16.37	..	III
101.54	15.41	16.41	..	I
107.08	25.43	16.39	..	III
108.65	16.20	16.37	..	II
115.74	16.95	16.40	..	II
116.19	27.46	16.35	..	III
122.70	17.57	16.51	..	II
123.60	17.65	16.52	..	I
128.08	18.03	16.61	..	I
128.49	18.06	16.60	..	II
132.65	18.37	16.68	..	II
138.00	18.78	16.69	..	II
138.18	18.79	16.72	..	I

[12] Loomis and Walters, THIS JOURNAL, **47**, 2851 (1925).

[13] Walters and Loomis, *ibid.*, **47**, 2302 (1925).

[14] F. Henning and J. Otto, Z. *Instrumentenk.*, **48**, 372 (1928).

TABLE I   (Concluded)

T, °K.	Heat cap. of empty cal., cal./deg.	C_{SL}, cal./deg.	$-C_{\mathrm{SV}}$, cal./deg.	Filling
138.31	31.41	16.68	..	III
142.43	19.07	16.74	..	I
143.36	19.14	16.73	..	II
151.75	19.74	16.71	..	II
152.60	19.72	16.75	..	I
154.99	33.60	16.78	..	III
156.98	19.96	16.78	..	I
157.42	19.98	16.74	...	II
160.10	20.16	16.98	..	I
162.65	20.25	17.00	..	II
164.49	34.57	17.13	..	III
165.93	20.40	17.03	..	I
168.09	20.49	17.10	..	II
170.18	20.57	17.14	..	I
172.05	20.64	17.14	..	II
172.69	35.44	17.23	..	III
178.17	20.81	17.39	..	II
181.50	36.29	17.45	..	III
182.03	20.90	17.51	..	II
184.46	Boiling point	...	..	...
190.00	37.04	17.56	5.82	III
199.86	37.82	17.76	5.47	III
208.88	38.48	18.07	5.21	III
212.80	38.74	18.14	5.23	IV
220.48	39.44	18.58	5.07	IV
228.76	39.74	19.25	4.88	IV
236.21	40.18	19.66	5.12	IV
244.61	40.62	20.05	5.80	IV
252.53	41.08	20.81	6.45	IV
258.22	41.34	21.12	7.51	V
265.25	41.66	22.05	8.71	V
273.06	41.96	23.43	10.78	V
278.07	42.12	24.20	13.15	V
284.07	42.31	26.06	16.44	VI
291.27	42.50	29.30	24.51	VI
294.85	42.58	32.43	30.47	VI
305.2	Critical point	..	..	...

temperatures. It will be seen from Table II and Fig. 3 that the discrepancies between the values reported by Eucken and Hauck[6] and the values presented here are outside any experimental inaccuracy or impurity. As a matter of fact, it is not thought that their ethane was of higher purity than ours if we take into account the purity of some of the other substances they used and the difficulty of purification. The points in our favor are improved calorimetric design and from 20 to 30 times larger amounts. Since other measurements have been made with the same apparatus and values of other observers have been checked, it is believed that the measurements pre-

TABLE II

HEAT CAPACITY DATA

T, °K.	C_{SL}, Eucken and Hauck	C_{SL}, Wiebe, Hubbard and Brevoort	T, °K.	C_{SL}, Eucken and Hauck	C_{SL}, Wiebe, Hubbard and Brevoort
100	18.0	16.37	210	22.55	18.14
110	18.05	16.38	220	23.0	18.56
120	18.9	16.44	230	23.3	19.19
130	19.3	16.54	240	23.7	19.71
140	19.7	16.68	250	24.1	20.54
150	20.1	16.83	260	24.5	21.60
160	20.60	17.00	270	25.0	22.96
170	21.0	17.22	280	..	24.86
180	21.4	17.38	290	..	28.56
190	21.8	17.58	295	..	32.54
200	22.2	17.80			

sented here are the more reliable. The accuracy is estimated to be 0.5% for the liquid below the boiling point and 1% at higher temperatures. The few measurements of solid ethane are probably not more accurate than to within 1 to 2%.
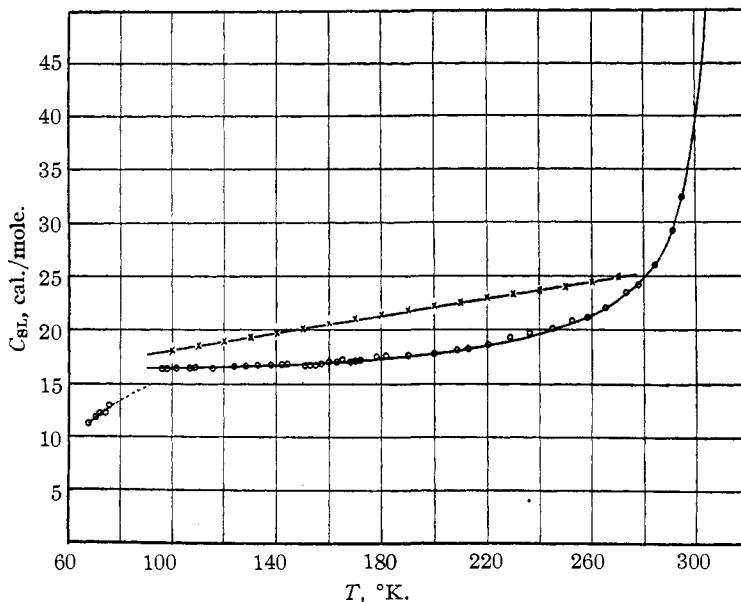

Fig. 3.—Heat capacity in calories per mole of saturated liquid ethane.

The method outlined by Osborne and Van Dusen[15] was used to calculate the heat capacity of the saturated liquid. The heats of vaporization

[15] N. S. Osborne and M. S. Van Dusen, Sci. Papers, Bureau of Standards, No. 313 (1917).

were taken from Porter[5] and from Dana and co-workers.[16] The liquid and vapor densities have been measured by Porter,[5] Kuenen[17] and Maass and McIntosh[18] and Maass and Wright.[19]

The critical data have been summarized by Pickering,[20] who selected the following values for ethane: T_c, 305.2°K.; P_c, 48.8 atm.; d_c, 0.21 g./cc. The following data are given as a typical example for the calculation of the heat capacity.

Sample Calculation.—Potentiometer reading across F, Fig. 2, is 0.0265856 volt.

$$I_{av.} = \frac{0.0807261 + 0.0807088}{2} = 0.0807175 \text{ amp.}$$

Time, 601.8 sec.

Energy added to calorimeter plus that lost in parallel resistance and lead wires

$$\frac{10014}{10} \times 0.0265856 \times 0.0807175 \times 601.8 \times 0.23895 = 309.017 \text{ cal.}$$

Energy lost in parallel resistance

$$\frac{10014}{10^2} \times (0.0265856)^2 \times 601.8 \times 0.23895 = 10.178 \text{ cal.}$$

Lead wire correction, 0.084 cal.

Energy supplied to calorimeter = 309.017 − 10.178 − 0.084 = 298.755 cal.

Initial resistance 225.9667 ohms.   Final resistance 230.4005 ohms

Rate of warming in ohms per minute

Before starting run...0.00103
After close of run when equilibrium was attained...................0.00127
Equilibrium period, 10 minutes

Resistance interval correction calculated graphically from initial and final rates, initial and final temperature differences between calorimeter and surroundings, and special rate determinations

Correction for period during the run, ohms...................	0.0193
Correction for equilibrium period, ohms.....................	0.0127
	0.0320
Initial temperature, °C....................................	−30.551
Final temperature, °C.....................................	−26.602
Uncorrected temperature rise, °C...........................	3.949
Temperature interval correction...........................	− .028
Corrected temperature rise................................	3.921

[16] L. I. Dana, A. C. Jenkins, J. N. Burdick and R. C. Timm, *Refrig. Eng.*, **12**, 387 (1926).

[17] Kuenen, *Phil. Mag.*, **40**, 173 (1895).

[18] Maass and McIntosh, THIS JOURNAL, **36**, 737 (1914).

[19] Maass and Wright, *ibid.*, **43**, 1098 (1921).

[20] S. F. Pickering, *J. Phys. Chem.*, **28**, 97 (1924).

Total heat input per degree, 298.755/3.921 = 76.215..........   76.215 cal.
Heat capacity of empty calorimeter.........................   40.650 cal.

Difference...   35.565 cal.

Weight of ethane, g....................................   53.534
Moles of ethane.......................................   1.7817
Heat capacity of ethane 35.565/1.7817.....................   19.96 cal.
Correction for vapor present.............................   0.09 cal.

Corrected heat capacity per mole of ethane..................   20.05 cal.
Average temperature....................................   244.61 °K.

The heat capacities of the saturated vapor and liquid C_{SV} and C_{SL} are defined as follows

$$C_S = C_P - T\left(\frac{\partial v}{\partial T}\right)_P \frac{dP}{dT_{sat.}}$$

TABLE III
ENTROPY AND HEAT CONTENT DATA

$$S_L = \int_{184.46}^{T} dQ/T\, dT =$$

$$\int_{184.46}^{T} C_{SL}/T\, dT = \text{entropy of liquid}$$

$$S_V = S_L + L/T = \text{entropy of vapor}$$

T, °K.	S_L cal./deg. per mole	L/T	S_V cal./deg./ mole
184.46	0.0000	18.03	18.03
185	.0510	17.96	18.01
190	.5181	17.33	17.85
195	.9747	16.71	17.69
200	1.424	16.13	17.55
205	1.862	15.57	17.43
210	2.297	14.99	17.29
215	2.726	14.44	17.17
220	3.149	13.92	17.07
225	3.570	13.37	16.94
230	3.988	12.85	16.84
235	4.403	12.33	16.73
240	4.817	11.79	16.61
245	5.230	11.28	16.51
250	5.644	10.74	16.39
255	6.052	10.19	16.24
260	6.462	9.64	16.10
265	6.876	9.08	15.95
270	7.293	8.48	15.77
275	7.720	7.85	15.57
280	8.156	7.19	15.35
285	8.607	6.48	15.08
290	9.082	5.65	14.73
295	9.601	4.68	14.29
300	10.200	3.41	13.61
305.2	11.95	0.00	11.95

TABLE IV
ENTROPY AND HEAT CONTENT DATA

T, °K.	H_L, heat content of liquid, cal./mole	L, heat of vapor, cal. per mole	H_V, heat content of vapor, cal./mole
184.46	0.0	3325	3325
190	97.7	3292	3390
195	186.3	3258	3444
200	275.7	3226	3502
205	365.9	3187	3553
210	457.1	3149	3605
215	549.3	3106	3655
220	642.6	3060	3703
225	737.3	3007	3744
230	833.4	2954	3788
235	931.3	2894	3825
240	1031.0	2830	3861
245	1133	2760	3893
250	1239	2684	3923
255	1344	2600	3944
260	1455	2507	3962
265	1568	2398	3966
270	1685	2290	3975
275	1806	2151	3957
280	1933	2014	3947
285	2067	1840	3907
290	2211	1638	3849
295	2370	1381	3751
300	2540[a]	1026	3566[a]
305.2	3050[a]	0	3050[a]

[a] Extrapolated values.

Since C_{SL} was measured, C_{SV} was calculated from the Clausius relation

$$C_{SV} - C_{SL} = \frac{dL}{dT} - \frac{L}{T}$$

where L is the heat of vaporization. In order to calculate the temperature coefficient of the heat of vaporization, the following equation was found satisfactory

$$L = 483.2 \, (T_c - T)^{1/2} - 16.45 \, (T_c - T)$$

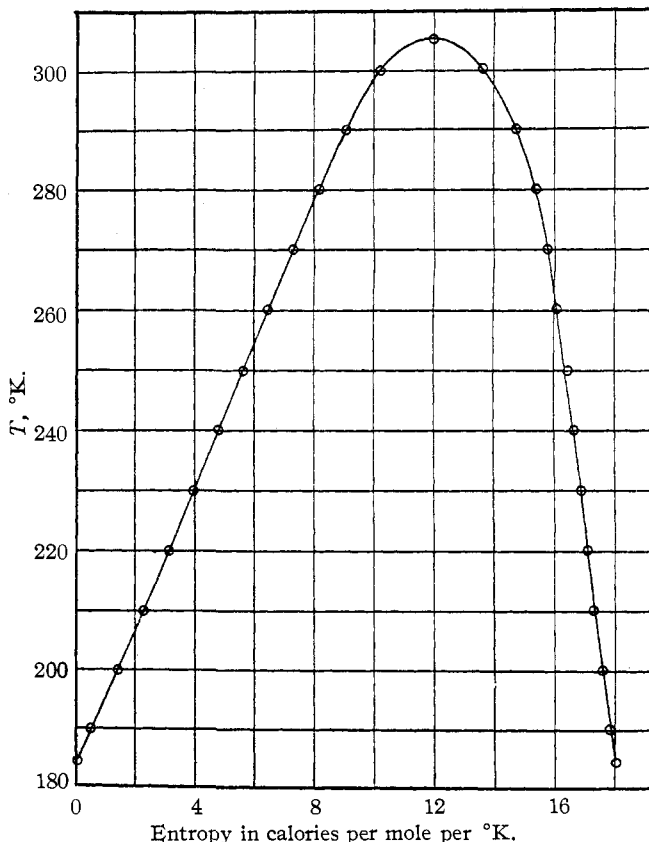The entropy and heat content of the saturated liquid and vapor are given in Tables III and IV and Figs. 4 and 5. The normal boiling point of

Fig. 4.—Temperature–entropy diagram for ethane.

ethane, 184.47°K., was taken as zero for both the entropy and heat content. The heat content is defined by the equation

$$H = E + pv$$

where E is the internal energy of the system.

As will be seen in the Table, C_{SV} is negative. A general rule for ascertaining whether a substance has positive or negative values of C_{SV} cannot

be given, but approximate calculations by van der Waals[21] show that in the case of mono-, di- and triatomic substances a positive value of C_{SV} is entirely excluded, while substances with more than three atoms may have positive values over part of the range before and after which they are negative. Ether is an example showing positive values for the heat capacity of the saturated vapor.
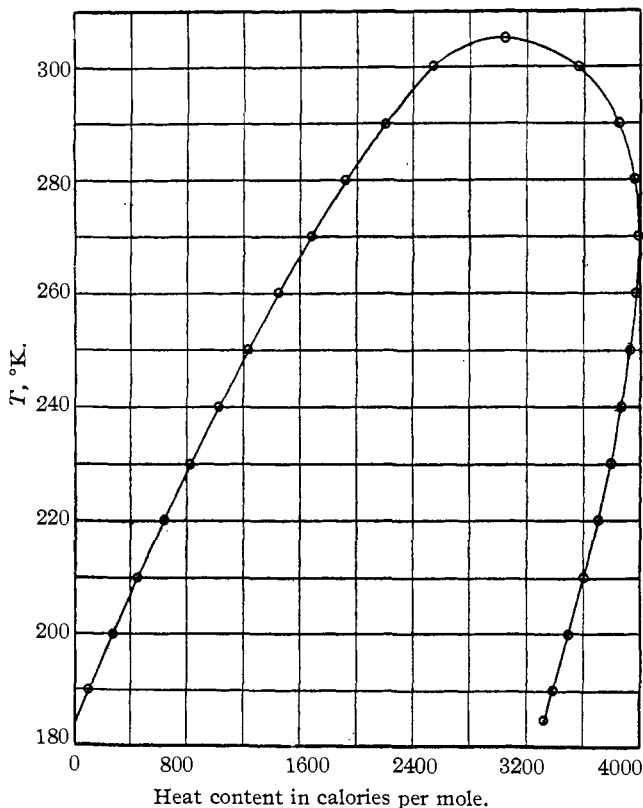

Fig. 5.—Mollier diagram for ethane.

Heat of Fusion and Melting Point.—The amount of heat consumed in premelting below the initial temperature of the run was determined graphically in each case and added as a correction to the heat of fusion. Table V gives the results of six determinations.

TABLE V

HEATS OF FUSION

Initial T, °K.	86.97	87.84	88.52	87.47	86.68	86.41
Final T, °K.	90.37	91.63	92.02	90.37	91.10	90.79
Heat of fusion, cal./mole	665.2	666.6	665.3	669.1	669.8	668.7

[21] Van der Waals–Kohnstamm, "Lehrbuch der Thermodynamik," Vol. I, p. 70.

The average value of the heat of fusion is 667.5 $\pm$ 3 cal. per mole of ethane. The melting point was found to be $-183.65 \pm 0.10°$C. Ladenburg and Krügel[22] give $-172.1°$ and Lebeau[23] remarks that ethane is still liquid at $-195°$.

We wish to express appreciation to Dr. C. W. Kanolt, formerly in charge of the Cryogenic Laboratory, Bureau of Mines, for the interest he has shown in our work, and to thank Messrs. Rowe and Schmidt of the instrument shop of the Pittsburgh Station for their excellent construction of the apparatus used in this study.

Summary

One low-pressure and one high-pressure calorimeter for determinations of heat capacities of liquids below room temperatures under their saturation pressure have been described.

Measurements of the heat capacity of saturated liquid ethane and the heat of fusion are presented.

Calculations of the entropy and heat content of the saturated liquid and vapor have been made.

AMARILLO, TEXAS

THE HEAT CAPACITY OF SATURATED LIQUID NITROGEN AND METHANE FROM THE BOILING POINT TO THE CRITICAL TEMPERATURE[1]

BY R. WIEBE[2] AND M. J. BREVOORT[3]

Three papers have recently been published on the thermodynamic properties of nitrogen.[4,5,6] Since large discrepancies exist between the results of the different workers, it was thought desirable to obtain accurate experimental values in order to decide the question.

Keesom and Houthoff[5] have recently prepared temperature–entropy and Mollier charts of methane utilizing the results of Keyes, Smith and

[22] A. Ladenburg and C. Krügel, Ber., **33**, 637 (1900).

[23] Lebeau, Compt. rend., **140**, 1456 (1905).

[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

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[4] Worth H. Rodebush, John W. Andrews and John B. Taylor, THIS JOURNAL, **47**, 313 (1925).

[5] W. H. Keesom and D. J. Houthoff, Comm. Phys. Lab. Univ. Leiden, Suppl. No. 65.

[6] Russell W. Millar and John D. Sullivan, U. S. Bureau of Mines, Technical Paper 424.