The average value of the heat of fusion is 667.5 ± 3 cal. per mole of ethane. The melting point was found to be −183.65 ± 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

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE]

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]

RECEIVED OCTOBER 14, 1929 PUBLISHED FEBRUARY 6, 1930

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

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[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.)

[2] Physical Chemist, Helium Division, U. S. Bureau of Mines.

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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.

Joubert.[7] Their work involves several uncertainties due to lack of data, and confirmation was needed.

No heat capacity measurements of saturated liquid nitrogen or methane above 1 atmosphere were in existence, but several observers[8] have made determinations up to the boiling point. Their data have been incorporated for comparison.

Nitrogen and methane are two of the main constituents of helium-bearing natural gas, and it is of importance to know accurately their thermal behavior.

Preparation.—The purest commercial nitrogen available was used as crude material. The gas was passed successively through tightly packed copper leaf heated to about 350°, fused potassium hydroxide and phosphorus pentoxide. The liquefied gas was fractionated several times, the first and last portions being rejected each time.

Two different batches of methane were prepared. The Grignard method was used for the first. Dry methyl iodide in small quantities was added to fresh turnings from an ingot of magnesium in an excess of dry ether. The heat of reaction caused the ether to boil, and the vapors were condensed by means of a water-cooled reflux condenser placed vertically above the flask. A calcium chloride tube at the top of the condenser prevented the entrance of moisture. Water was then added to decompose the Grignard reagent, and the methane given off was passed successively through a condensation bulb to eliminate the ether, fuming sulfuric acid, concentrated sulfuric acid, 30% sodium hydroxide solution, potassium hydroxide sticks and phosphorus pentoxide. The liquefied gas was then fractionated several times, the first and last portions being rejected each time. The second batch was prepared by the method outlined by Gladstone and Tribe,[9] who prepared methane by the action of a copper–zinc couple on methyl iodide. The gas was purified in the same way as in the Grignard method. The melting point was determined to be $-182.9 \pm 0.1°$; a slight variation indicated some impurity. The value given in "International Critical Tables" is $-184°$.

Measurements.—The apparatus used has been described in detail in a previous paper.[10] The measurements were made in the steel calorimeter exclusively. The method outlined by Osborne and Van Dusen[11] was used

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[7] F. G. Keyes, L. B. Smith and D. B. Joubert, *J. Math. Phys. Mass. Inst. Tech.*, 1, 211 (1922).

[8] Klaus Clusius, *Z. physik Chem.*, 3B, 41 (1929). In this article Clusius criticizes the temperature scale used by W. F. Giauque and R. Wiebe in their work on the heat capacity of hydrogen chloride [This Journal, **50**, 109 (1928)]. The authors of the latter article wish to call attention again to the passage on page 111: "However, since the results deviate in only one direction, it is improbable that the difficulty can be due primarily to inaccurate temperature scale. Even an approximate knowledge of the extremes of the temperature range investigated would mean that if some results were too high, others would necessarily be made too low." In other words, if the extremes of the temperature range are known accurately and the size of the "degrees" is incorrect, it follows that some "degrees" must be too small and some too large and, therefore, some measurements too low and some too high.

[9] J. H. Gladstone and Alfred Tribe, *J. Chem. Soc.*, **45**, 154 (1884).

[10] R. Wiebe, K. H. Hubbard and M. J. Brevoort, This Journal, **52**, 611 (1930).

[11] Nathan S. Osborne and Milton S. Van Dusen, Sci. Papers, Bureau of Standards, No. 313.

in making the necessary corrections in order to obtain the heat capacity of the saturated liquid. The gases were weighed in a steel cylinder at about 60 atmospheres' pressure. The average error is estimated to be about 1%; a few points are off slightly more, but all the rest fall well within this limit when a smooth curve is drawn through the results. The probable distribution of the percentage error is as follows

Weighing	0.1	Heat leak correction	0.1
Time measurement	0.1	Vapor space correction	0.1
Temperature interval	0.5	Heat cap. of empty calorimeter	0.1

The thermocouples were calibrated against the platinum resistance thermometer No. 2.[12]

TABLE I

NITROGEN

Fillings: I, 23.88 moles; II, 2.900; III, 2.611; IV, 2.297; V, 1.908. S_{SL}, heat capacity of the saturated liquid per mole. Molecular weight, 28.016. 15° gram calorie, 4.185 joules.

T, °K.	Heat cap. of empty calorimeter	C_{SL}, cal./deg.	Observer	Filling
63.95	...	13.34	Keesom and Onnes	...
64.6	...	13.15	Eucken	...
65.0	...	13.22	Eucken	...
66.9	...	13.54	Clusius	...
67.5	...	13.28	Eucken	...
68.2	...	13.25	Eucken	...
68.4	...	13.64	Clusius	...
69.15	...	13.40	Keesom and Onnes	...
69.73	...	13.28	Keesom and Onnes	...
70.2	...	13.63	Clusius	...
71.8	...	13.66	Clusius	...
72.7	...	13.33	Eucken	...
73.5	...	13.69	Clusius	...
75.46	...	13.74	Keesom and Onnes	...
76.49	...	12.96	Keesom and Onnes	...
79.17	18.09	13.76	Wiebe and Brevoort	I
82.64	19.08	13.95	Wiebe and Brevoort	I
89.50	20.95	14.16	Wiebe and Brevoort	II
95.39	22.54	14.50	Wiebe and Brevoort	II
95.46	22.36	14.71	Wiebe and Brevoort	III
99.55	23.60	15.04	Wiebe and Brevoort	III
103.31	24.53	15.63	Wiebe and Brevoort	IV
103.72	24.64	15.56	Wiebe and Brevoort	III
107.22	25.47	15.99	Wiebe and Brevoort	III
107.48	25.52	16.10	Wiebe and Brevoort	IV
111.57	26.46	17.30	Wiebe and Brevoort	IV
112.97	26.76	17.60	Wiebe and Brevoort	V
115.25	27.25	18.27	Wiebe and Brevoort	IV
116.99	27.62	18.72	Wiebe and Brevoort	V

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

TABLE II

METHANE

Fillings: I, 2.959 moles; II, 2.509; III, 1.789; IV, 1.148; V, 1.803. I, II, III and IV from first batch; V from second batch.

T, °K.	C_{SL}, cal./deg.	Observer	Filling
95.4	12.81	Clusius	
96.25	13.65	Eucken and Karwat	...
97.3	13.52	Eucken and Karwat	...
97.7	12.85	Clusius	...
97.73	12.94	Wiebe and Brevoort	I
98.9	12.90	Clusius	...
99.2	13.46	Eucken and Karwat	...
102.0	12.97	Clusius	...
102.27	13.09	Wiebe and Brevoort	I
103.2	13.43	Eucken and Karwat	...
103.9	13.43	Eucken and Karwat	...
105.3	13.01	Clusius	...
107.2	13.49	Eucken and Karwat	...
108.7	13.59	Eucken and Karwat	...
110.94	13.20	Wiebe and Brevoort	I
117.53	13.27	Wiebe and Brevoort	I
121.82	13.26	Wiebe and Brevoort	I
129.32	13.77	Wiebe and Brevoort	I
134.28	14.05	Wiebe and Brevoort	I
140.49	14.34	Wiebe and Brevoort	II
149.51	14.78	Wiebe and Brevoort	II
153.70	14.97	Wiebe and Brevoort	II
154.75	15.27	Wiebe and Brevoort	III
160.96	16.01	Wiebe and Brevoort	III
169.02	17.30	Wiebe and Brevoort	III
174.75	19.48	Wiebe and Brevoort	V
178.00	20.90	Wiebe and Brevoort	IV
180.86	22.18	Wiebe and Brevoort	V
182.82	23.92	Wiebe and Brevoort	IV
182.95	24.18	Wiebe and Brevoort	III
184.43	26.01	Wiebe and Brevoort	V
188.24	52.34	Wiebe and Brevoort	IV
191.03	Critical temperature		

Heat Capacity Data.—The following definitions are used in this article, subscripts L and V referring to the liquid and vapor state, respectively. C_S = heat capacity of the saturated state per mole; H = heat content per mole; S = entropy per mole and L = heat of vaporization per mole. Thermodynamics gives the following relations between these quantities

$$C_S = C_P - T\left(\frac{\partial v}{\partial T}\right)_P \frac{\mathrm{d}P}{\mathrm{d}T_{\mathrm{sat.}}} = C_P - \left(\frac{\partial v}{\partial T}\right)_P \frac{L}{\Delta v}$$

$$H = E + pv \qquad S_L = \int \frac{C_{SL}}{T}\,\mathrm{d}T \qquad S_V = S_L + L/T$$

The results are shown in Table I and II and are plotted in Figs. 1 and 2.

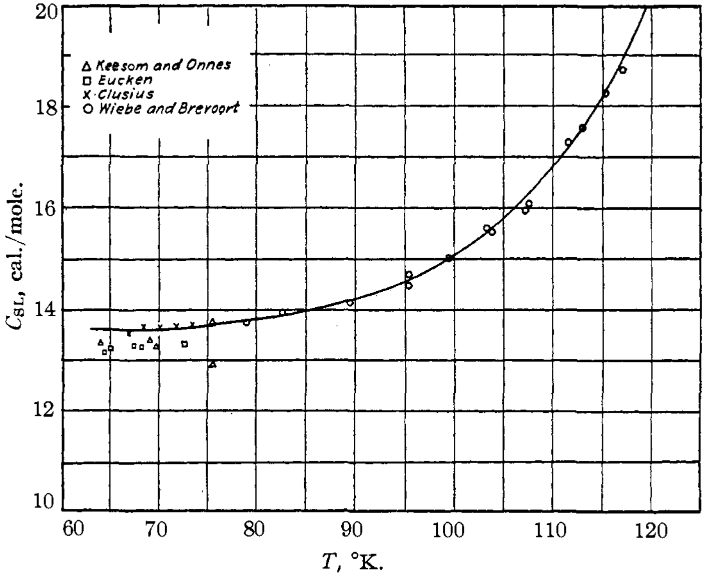

Fig. 1.—Heat capacity of saturated liquid nitrogen.

The measurements of previous investigators[8] have been included. Our extrapolated curve for nitrogen passes well through the values of Clusius and one point of Keesom and Onnes. The other points of the latter and

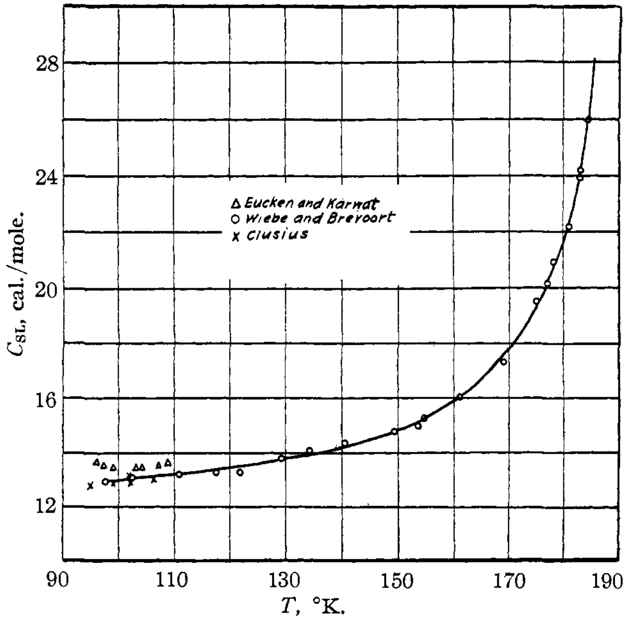

Fig. 2.—Heat capacity of saturated methane.

of Eucken are slightly lower. In case of methane, we also check the results of Clusius, while the determinations of Eucken and Karwat are too high.

Heat Content and Entropy.—Tables III and IV show the calculations made from the experimental data of the authors.

TABLE III

NITROGEN

Heat content/mole in cal.

T	$\int_{77.4}^{T} C_{SL} dT$	$\int v dp$	H_L	L	H_V
77.4	0.0	...	0.0	1335	1335
80	34.81	0.31	35.1	1314	1349
85	103.87	1.09	105.0	1265	1370
90	174.39	2.24	176.8	1213	1390
95	246.49	3.88	250.4	1161	1411
100	320.87	6.15	327.0	1102	1429
105	398.25	9.20	407.5	1028	1435
110	479.61	13.26	492.9	933	1426
115	566.45	18.60	585.1	806	1391
120	661.74	24.94	686.7	622	1308
125	...	...	870[a]	257	1137[a]
126	...	...	1005[a]	0	1005[a]

[a] Extrapolated values.

TABLE IV

METHANE

Heat content/mole in cal.

T	$\int_{100}^{T} C_{SL} dT$	$\int v dp$	H_L	L	H_V	H_{50}
100	0.0	0.00	0.0	2048	2048	1024
105	64.5	.20	65.7	2015	2081	1073
110	131.3	.48	131.8	1983	2115	1123
111.5	151.6	.59	152.2	1972	2124	1138
115	197.8	.89	198.7	1950	2149	1174
120	264.8	1.43	266.3	1917	2183	1224
125	332.5	2.16	334.7	1883	2218	1276
130	401.4	3.10	404.6	1847	2251	1327
135	470.9	4.30	475.2	1808	2283	1379
140	541.3	5.80	547.1	1767	2314	1430
145	612.9	7.65	620.2	1721	2341	1480
150	686.0	9.92	696.0	1670	2366	1531
155	761.3	12.67	774.0	1612	2386	1580
160	839.1	15.99	855.1	1546	2401	1628
165	920.3	19.95	940.2	1470	2410	1675
170	1006.1	24.65	1030.7	1382	2413	1722
175	1098.4	30.28	1128.7	1276	2405	1767
180	1201.6	37.00	1238.6	1141	2380	1809
185	1321.2	45.13	1366.3	939	2306	1836
191.03			1840[a]	0	1850[a]	1850[a]

[a] Extrapolated values.

The heats of vaporization for nitrogen were taken from a smooth curve drawn through the values given by Burnett[13] and Keesom and Houthoff.[14] Near the boiling point we inclined toward the values of the former, since the heat of vaporization at the boiling point has been determined experimentally,[15] while at higher temperatures the values of Keesom and Houthoff appeared to us more reasonable with regard to entropy and heat content especially at 125°K.

The densitites of the co-existing phases for nitrogen have been determined by Mathias, Kammerlingh Onnes and Crommelin.[16] The heats of vaporization and densities of the co-existing phases for methane were taken from the work of Keyes, Smith and Joubert.[7] Pickering[17] has summarized the critical constants of various gases obtained by different observers and selected the following values for nitrogen and methane.

	Nitrogen	Methane
T_c, °K.	126.0	190.6
P_c, atm.	33.5	45.7
d_c, g./cc.	0.3110	0.162

In Table V and Fig. 3, a comparison is made between the heat content values

TABLE V

NITROGEN

Heat Content in 15° cal./mole

Abbreviations: M. & S., Millar and Sullivan; B., Burnett; K. & M., Keesom and Houthoff; W. & B., Wiebe and Brevoort.

T, °K.	H_L, M. & S.	H_L, B.	H_L, K. & H.	H_L, W. & B.	H_V, M. & S.	H_V, B.	H_V, K. & H.	H_V, W. & B.	H_{50}, W. & B.
77.4	0.0	0.0	0.0	0.0	1335	1336	1317	1336	668
80	39	34.5	33.3	35.1	1352	1348	1329	1349	692
85	115	102.0	97.2	105.0	1381	1368	1350	1370	734
90	189	170.6	160.8	176.8	1402	1383	1370	1390	783
95	257	239.2	225.3	250.4	1412	1394	1387	1411	830
100	326	310.0	295.9	327.0	1412	1398	1399	1429	878
105	393	383.5	376.5	407.5	1402	1394	1406	1435	922
110	460	461.3	471.8	492.9	1379	1379	1404	1426	959
115	534	547.2	586.7	585.1	1338	1350	1387	1391	988
120	625	650.5	732.3	686.7	1269	1294	1345	1308	998
125	781	823.6	962.1	870[a]	1112	1154	1214	1137[a]	...
126	952	990.4	1106	1005[a]	952	990.4	1106	1005[a]	1000[a]

[a] Extrapolated values.

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[13] E. S. Burnett, unpublished report to the U. S. Bureau of Mines; see Millar and Sullivan, Ref. 6.

[14] Professor Keesom has kindly sent us his values for comparison, see Ref. 5.

[15] Heinrich Alt, *Ann. Physik,* [4] 19, 639 (1906); L. I. Dana, *Proc. Am. Acad. Arts Sci.,* **60,** 241 (1926).

[16] E. Mathias, H. Kammerlingh Onnes and C. A. Crommelin, *Comm. Phys. Lab., Univ. Leiden,* No. 145c (1914).

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

obtained by Millar and Sullivan,[6] Burnett,[13] Keesom and Houthoff[4] and the authors for nitrogen.

Burnett had obtained his values from two empirical equations expressing the heat content along the 50% quality line

$$H_{50} = 1090 - 1.5486\ (T_c - T)^{1.375}$$

and the heat of vaporization

$$L = H_V - H_L = 331\ (T_c - T)^{0.375} - 0.404\ (T_c - T)^{1.375}$$

The former was arrived at by adjusting values derived from Keyes' equation of state in the neighborhood of the critical point to conform to the known behavior of other gases and thus obtaining values for the change in heat content between different P–T points in the superheat field and the

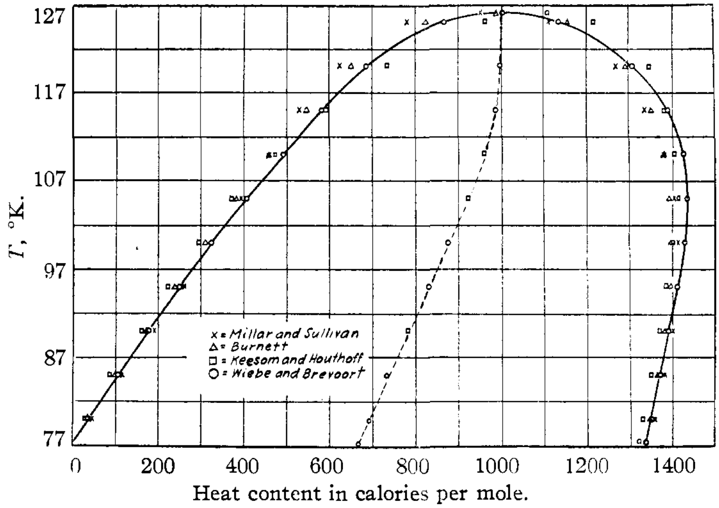

Fig. 3.—Mollier diagram for nitrogen.

TABLE VI

NITROGEN

T, °K.	T_L, cal./deg./mole	L/T	S_V, cal./deg./mole
77.4	0.0	17.25	17.25
80	0.451	16.42	16.87
85	1.295	14.88	16.17
90	2.098	13.48	15.58
95	2.877	12.22	15.10
100	3.635	11.02	14.66
105	4.393	9.79	14.18
110	5.142	8.48	13.62
115	5.925	7.01	12.94
120	6.727	5.18	11.91
125	8.28	2.06	10.34
126	9.32	0.00	9.32

corresponding points on the saturation curve. By combining the two equations of Burnett, we obtain

$$H_V = [1090 - 1.5486\,(T_c - T)^{1.375}] + [165.5\,(T_c - T)^{.375} - 0.202\,(T_c - T)^{1.375}]$$
$$H_L = [1090 - 1.5486\,(T_c - T)^{1.375}] - [165.5\,(T_c - T)^{.375} - 0.202\,(T_c - T)^{1.375}]$$

Burnett chose 70°K. as his reference zero, and we subtracted H_L 77.4 − H_L 70 from his values. We have given two values for the heat content at the critical point; one was obtained by completing the dome plotted from the H_L and the H_V values against temperature, while the other and probably more correct value was found by extrapolating the heat content of the 50% quality line.

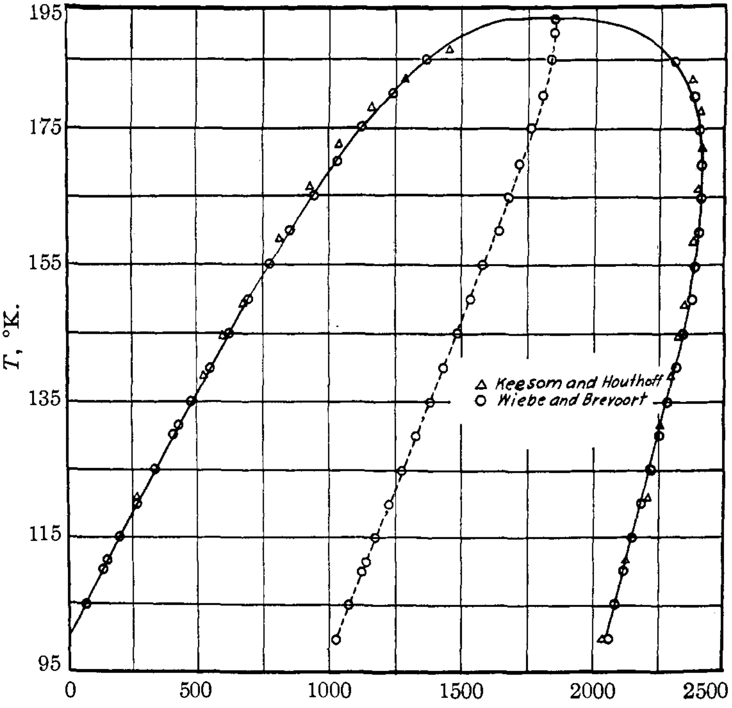

Fig. 4.—Mollier diagram for methane.

Figure 4 shows a comparison between the heat content values of Keesom and Houthoff and those calculated from our experimental data. The agreement is good except in the neighborhood of the critical point, where their values deviate slightly.

Tables VI and VII give the entropy values calculated from our experimental values and Table VIII and Fig. 5 give a comparison between the values of Millar and Sullivan, Keesom and Houthoff, Rodebush, Andrews and Taylor and the authors for nitrogen.

Table VII

Methane

Entropy in cal./deg./mole

T, °K.	S_L, entropy of satd. liquid	L/T, entropy of vaporization	S_V, entropy of satd. vapor
100	0.000	20.48	20.48
105	.641	19.19	19.84
110	1.246	18.03	19.27
111.5	1.431	17.68	19.11
115	1.844	16.96	18.80
120	2.406	15.98	18.38
125	2.962	15.06	18.02
130	3.509	14.21	17.72
135	4.042	13.39	17.44
140	4.563	12.62	17.18
145	5.072	11.87	16.94
150	5.569	11.13	16.70
155	6.051	10.39	16.45
160	6.549	9.66	16.21
165	7.052	8.91	15.96
170	7.568	8.13	15.70
175	8.103	7.29	15.40
180	8.680	6.34	15.02
185	9.327	5.08	14.40
191.03	11.92	0	11.92

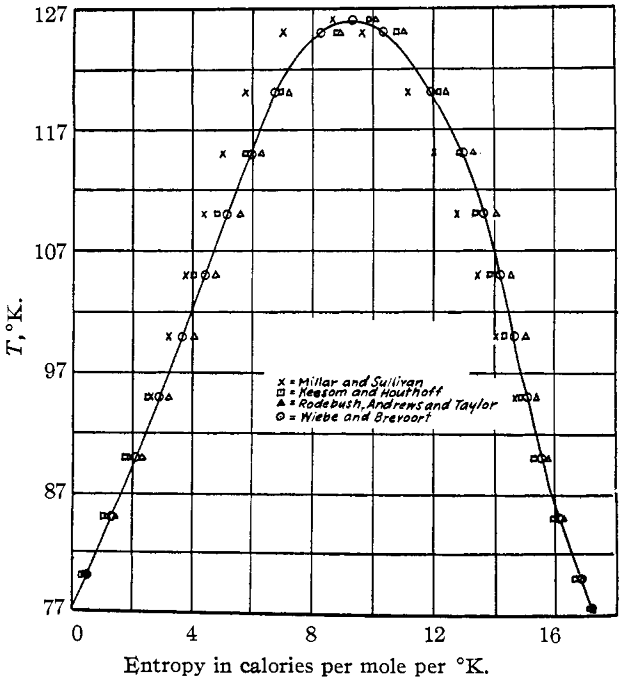

Fig. 5.—Temperature–entropy diagram for nitrogen.

TABLE VIII

NITROGEN

T, °K.	S_L, M. & S.	S_L, K. & H.	S_L, R., A. & T.	S_L, W. & B.	S_V, M. & S.	S_V, K. & H.	S_V, R., A. & T.	S_V, W. & B.
77.4	0.0	0.0	0.0	0.000	17.25	17.17	17.25	17.25
80	0.42	0.36	0.48	0.451	16.83	16.70	16.90	16.87
85	1.18	1.04	1.39	1.295	16.08	15.94	16.27	16.17
90	1.90	1.77	2.28	2.098	15.38	15.33	15.76	15.58
95	2.56	2.52	3.16	2.877	14.72	14.79	15.38	15.10
100	3.21	3.22	4.01	3.635	14.07	14.32	15.03	14.66
105	3.81	4.01	4.75	4.393	13.43	13.84	14.54	14.18
110	4.39	4.82	5.56	5.142	12.74	13.36	14.04	13.62
115	5.01	5.77	6.27	5.925	11.99	12.86	13.28	12.94
120	5.78	6.92	7.15	6.727	11.14	12.16	12.33	11.91
125	7.22	8.84	8.89	8.28	9.64	10.85	10.95	10.34
126	8.67	9.90	10.01	9.32	8.67	9.90	10.01	9.32

Entropies of the vapor by Rodebush, Andrews and Taylor were calculated by adding our entropies of vaporization to their liquid entropies taken from a smooth curve through their data.

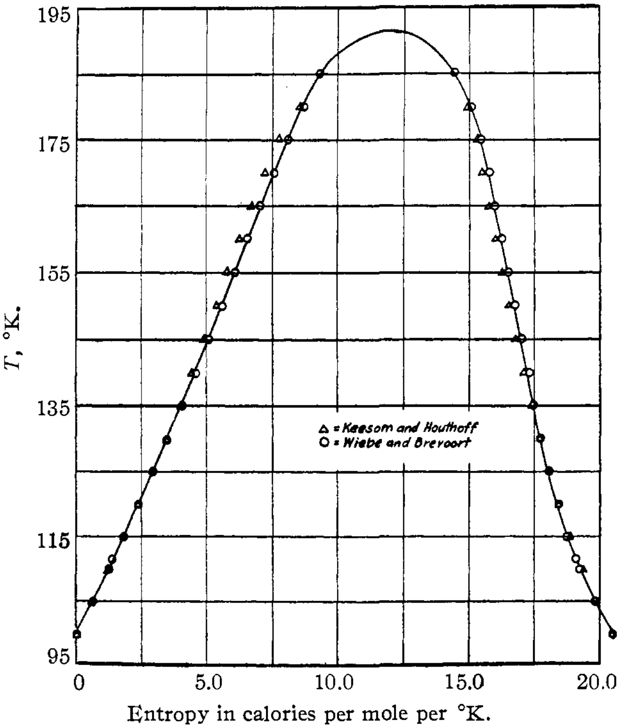

Fig. 6.—Temperature–entropy diagram for methane.

The results of Rodebush, Andrews and Taylor seem to indicate that their vapor was contaminated with liquid spray, which made their percentages too high. A more efficient baffle system would probably reduce or even eliminate the danger of contamination.[18] The entropy values of Keesom and Houthoff and the authors are shown in Fig. 6.

The authors wish to express their appreciation to Mr. G. St. J. Perrott, Superintendent of the Pittsburgh Experiment Station, U. S. Bureau of Mines, and to Dr. David F. Smith of the physical chemistry section for permitting the work of this investigation to be carried out at the Pittsburgh Station.

Summary

The specific heats of saturated liquid nitrogen and methane from the boiling point to the critical temperature have been measured.

The entropy and heat content of the saturated state have been calculated.

AMARILLO, TEXAS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF UTAH]

THE COMPOSITION OF CONSTANT BOILING HYDROCHLORIC ACID AT PRESSURES OF 50 TO 1220 MILLIMETERS[1]

BY WALTER D. BONNER AND ALBERT C. TITUS

RECEIVED OCTOBER 15, 1929 PUBLISHED FEBRUARY 6, 1930

Since Hulett and Bonner[2] published their paper on the preparation of standard hydrochloric acid solutions from constant boiling hydrochloric acid, their acidimetric standard has been checked by others, and its use has become fairly common.[3]

However, the only precise determinations of the compositions of these acids so far published are those made near sea level, and those made at the rather low barometric pressures near 640 mm.[4] The experiments of Roscoe and Dittmar, published 70 years ago,[5] remain the only work covering a considerable range of pressures. We have, therefore, determined the compositions and densities of various hydrochloric acids of constant boiling point between the pressures of 50 and 1220 mm. The procedure used was much that of Foulk and Hollingsworth[4] except that the pressure control apparatus was filled with mercury rather than with water. The compositions were determined gravimetrically, by means of silver chloride. The silver nitrate used was very carefully purified. The

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[18] This was suggested to the authors by Mr. E. S. Burnett.

[1] Arranged from the Master's Thesis of Albert C. Titus, University of Utah.

[2] Hulett and Bonner, THIS JOURNAL, **31**, 390 (1909).

[3] See Morey, *ibid.*, **34**, 1027 (1912); Hendrixson, *ibid.*, **37**, 2352 (1915); Popoff, "Quantitative Analysis," P. Blakiston's Sons, Philadelphia, **1927**, 2d ed., p. 98.

[4] Foulk and Hollingsworth, THIS JOURNAL, **45**, 1220 (1923); Bonner and Branting, *ibid.*, **48**, 3093 (1926).

[5] Roscoe and Dittmar, *Ann.*, **112**, 343 (1859); *J. Chem. Soc.*, **12**, 128 (1860); Roscoe, *Ann.*, **116**, 213 (1860).