rates for the process. Previously reported variations in the β melting points of the triglycerides have been observed by dielectric constant measurements. Tetradecyl palmitate resembles the monoglycerides in showing apparent freedom of rotation of the molecules around their long axes for some distance below the freezing point.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Thermodynamics of 1-Butyne from Calorimetric and Spectroscopic Data

BY J. G. ASTON, S. V. R. MASTRANGELO[1] AND G. W. MOESSEN

A study of the thermodynamic properties of 1-butyne and other compounds of the unsaturated type such as the butadienes, butenes, dialkylacetylenes, etc., is of particular interest because it yields additional information about the potential function hindering internal rotation. This paper presents the experimental data and potential barrier for one of these compounds, 1-butyne.

The Material.—We were kindly supplied with an A. P. I.-N. B. S. standard source; sample of 99.90 ± 0.07% purity (A. P. I. R. P. 45-O. S. U.) by Dr. F. D. Rossini. However, since this material was not too difficult to prepare, we prepared our own sample and purified it as a precaution against accidents to the standard sample in the many manipulations required. The sample of 1-butyne was prepared by the action of sodium acetylide on redistilled ethyl iodide.[2a,b] The acetylene was treated following the method of Hurd,[3] by passing tank acetylene through two traps immersed in a Dry Ice and acetone mixture and then condensed in an end trap maintained at liquid air temperatures. The glass apparatus was baked at 150° for three hours before use. A liter of liquid ammonia was condensed from a tank of anhydrous ammonia and placed in a three-necked, three-liter flask with a mercury seal stirrer and condenser refrigerated with solid carbon dioxide and attached to a liquid air trap. The flask was immersed in a bath of Dry Ice, acetone, carbon tetrachloride and chloroform freezing mixture. The temperature of this mixture reached −75°. The stirrer was started and 1.0 g. of hydrated ferric nitrate added to the liquid ammonia. Two grams of sodium was then added. When the blue color turned to gray, the rest of the 115 g. of sodium was added as rapidly as possible over a period of twenty minutes. The reaction was completed after half an hour as indicated by a large decrease in the rate of evolution of hydrogen gas. The solution was blue at this point. After an hour the solution turned gray. An excess of acetylene was then bubbled into the reaction mixture and after the addition, the solution stirred for two hours. Ethyl iodide was then added and shortly after, rapid refluxing was observed.

The reaction mixture was warmed up and the gases were passed through 4 l. of water in a 5-liter flask before condensing in three traps maintained at a temperature of −25 to −30° by careful addition of Dry Ice and finally through a mercury bubble counter to the atmosphere. Approximately 300 cc. of liquid was condensed in this way and purified by passing through 10% sulfuric acid, a tower of sodium hydroxide and finally through a tower of anhydrous calcium chloride. The yield of purified product was 54%.

The sample was finally purified through the laboratory low temperature column and a middle cut of about 50 cc. was used for this calorimetric study.

The Heat Capacity Measurements.—The apparatus and method used for these measurements has been described previously.[4a,b] Standard thermocouple S-7 was used as the primary temperature standard and standard thermocouple S-4 was used as a check. The two thermocouples deviated from one another by not more than 0.05°K. in the range from 10 to 20°K. For the range from 20 to 200°K. the deviations were less than 0.02°K. and at higher temperatures the deviations were somewhat less than 0.03°K.

The time of energy imput in the range from 30 to 275°K. was measured by means of the laboratory automatic timer, which was checked against Arlington time signals. During the second coverage, starting from 13°K., the current from a Type No. 816-B 60 cycle Vacuum-Tube Precision Fork generator (The General Radio Co., Cambridge, Mass.) was amplified to run an electric clock graduated in 0.1 sec. (Standard Electrical Time Co., Springdale,

TABLE I

THE MOLAL HEAT CAPACITY OF 1-BUTYNE

Mol. wt. 54.088; 0.47790 mole, 99.967 mole % pure; 0.0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules.

Temp., °K.	C_p, cal./deg./mole
Crystal:	
Series III	
13.30	0.736
16.72	1.363
19.29	1.961
21.69	2.473
24.74	3.199
28.43	4.048
33.46	5.169
37.25	5.941
Series IV	
14.65	0.988
19.16	1.921
24.83	3.210
32.18	4.924
39.34	6.320
45.16	7.452
50.56	8.330
Series I	
66.05	10.39
72.64	11.21
78.96	11.92
83.94	12.38
95.07	14.43
100.12	13.88
105.46	14.36
111.07	14.88
115.68	15.34
120.94	15.84
126.28	16.24
131.96	16.81
137.31	17.29
142.36	17.89
Series V	
61.25	9.742
66.04	10.374
71.14	11.005
76.75	11.659
83.04	12.281
89.73	12.906
Series VI	
31.35	4.698
36.54	5.790
41.74	6.807
46.45	7.673
51.10	8.401
55.94	9.088
60.73	9.678
65.50	10.349
70.20	10.900
Liquid:	
Series II	
149.88	27.31
155.93	27.31
163.01	27.33
169.47	27.42
176.03	27.55
181.83	27.66
187.38	27.74
192.85	27.80
198.67	27.96
204.10	28.17
209.72	28.28
215.61	28.43
220.93	28.51
262.28	28.71
232.47	28.97
239.03	29.32
246.11	29.76
253.38	30.23
260.15	30.42
265.53	30.89
270.58	31.08
275.09	31.14

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[1] Phillips Petroleum Fellow, 1946–1949.

[2] (a) Picon, *Compt. rend.*, **158**, 1184 (1914); (b) **156**, 1077 (1913).

[3] Hurd, THIS JOURNAL, **69**, 239 (1947).

[4] (a) Aston and Messerly, *ibid.*, **58**, 2354 (1936); (b) Messerly and Aston, *ibid.*, **62**, 886 (1940).

TABLE II

THE MOLAL HEAT CAPACITY OF 1-BUTYNE AT ROUNDED TEMPERATURES

Mol. wt., 54.088; 0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules

Temp., °K.	C_p, cal./deg./mole	Temp., °K.	C_p, cal./deg./mole
Crystal		Liquid	
14	0.865	150	27.30
16	1.223	155	27.33
18	1.644	160	27.36
20	2.105	165	27.40
25	3.259	170	27.45
30	4.418	175	27.53
32.5	4.965	180	27.61
35	5.490	185	27.67
40	6.455	190	27.77
45	7.432	195	27.88
50	8.254	200	28.00
55	8.940	205	28.13
60	9.610	210	28.26
65	10.254	215	28.39
70	10.880	220	28.51
75	11.483	225	28.67
80	12.012	230	28.87
85	12.480	235	29.12
90	12.945	240	29.40
95	13.410	245	29.68
100	13.875	250	29.97
105	14.341	255	30.25
110	14.809	260	30.52
115	15.267	265	30.79
120	15.720	270	31.07
125	16.173	275	31.34
130	16.625	280	31.65
135	17.075		
140	17.525		

Mass.). The heating switch and switch for the current operating the clock are incorporated into one unit such that the calorimeter heater and the clock are started or stopped simultaneously. One calorie was taken as equal to 4.1833 international joules. The experimental heat capacities are listed in Table I. The values obtained for the heat capacities at rounded temperatures are listed in Table II.

Corrections to the heat capacities for nonlinear drifts and incomplete thermal isolation at hydrogen temperatures were made using the method of Keesom and Kok[5a,b] as simplified by Aston and Szasz.[6] At higher temperatures, in the liquid region, corrections to the heat capacity for vaporization into the calorimeter free space and filling line were made using the modified Berthelot equation with T_c = 463.7°K. and liquid densities obtained by Morehouse and Maass,[7] and a value of P_c obtained as described at the foot of Table VIII.

Below 30°K., because of large heat leak and rapidly changing resistance thermometer derivatives, the accuracy of these heat capacities may be only ±5% at the lowest temperatures. Between 30 and 200° K. the accuracy is about 0.3% falling off to about 0.5% at higher temperatures due to radiation and increasing uncertainty in the vaporization corrections.

The Triple Point of 1-Butyne.—During measurement of the heat capacities, the glass vacuum filling line to the calorimeter suffered a break caused by vibration due to blasting on the college grounds. Since the sample became exposed to the atmosphere when its temperature was very low, a repurification was necessary. Purity data were obtained before the accident on the original sample and after the accident with the repurified sample. The purity was determined each time by observing the solid–liquid–vapor equilibrium temperature over a period of about seven hours with various fractions of material melted as estimated by the energy imput. The equilibrium temperatures of the sample were plotted against the reciprocal of the fraction melted. A straight line was obtained and extrapolated to zero reciprocal fraction melted to give the triple point, T_0. From these results and the heat of fusion data the mole fraction of impurity X was calculated using the equation (1)

$$\Delta T = (RT^2/\Delta H_f)\,X \qquad (1)$$

where ΔT is the lowering produced by a mole fraction X of impurity in the liquid phase, ΔH_f is the heat of fusion and T is the equilibrium temperature in the calorimeter. The purity was found to be 99.967 mole % for the original sample and 99.987 mole % for the repurified sample. The average triple point is 147.43 ± 0.05°K. The triple point data of 1-butyne are shown in Table III.

TABLE III

TRIPLE POINT OF 1-BUTYNE

Repurified sample, 0.47262 mole; 0°C. = 273.16°K.; original sample, 0.47790 mole

Melted, %	Recip. fractn. melted	T, °K.	Melted, %	Recip. fractn. melted	T, °K.
18.21	5.491	147.376	24.5	4.08	147.419
31.48	3.177	147.398	47.9	2.09	147.424
44.76	2.234	147.399	50.0^a	2.00	147.43
50.00^a	2.000	147.400^8	57.6	1.736	147.429
57.91	1.727	147.403	78.5	1.272	147.431
71.24	1.404	147.403^5	90.5	1.104	147.437
84.45	1.184	147.404	95.4	1.047	147.438
100.00^b	1.000	147.404^6	100.0^b	1.000	147.44
Triple point = 147.41°K.			Triple point = 147.45°K.		
Mole % impurity = 0.013% ± 0.005			Mole % impurity = 0.033% ± 0.01		

Triple point of 1-butyne = 147.43 ± 0.05°K.

[a] Interpolated. [b] Extrapolated.

The Vapor Pressures.—The results of vapor pressure measurements in the range 194–283°K., made as previously described,[2a,b] are given in Table IV. From 243.4 to 282.7°K. the data can be represented by equation (2).

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[5] (a) Keesom and Kok, Comm. Phys. Lab., University of Leiden, No. 219c (1932); (b) Keesom and Kok, *Proc. Acad. Amsterdam*, **35**, 294 (1932).

[6] Aston and Szasz, *J. Chem. Phys.*, **15**, 560 (1947).

[7] Morehouse and Maass, *Can. J. Research*, **5**, 306 (1931).

$$\log_{10} P_{\text{mm.}} = -1909.3940/T - 4.642748 \log_{10} T + 21.104226 - 4.672895 \times 10^{-4}\, T + 8.57412 \times 10^{-7}\, T^2 \quad (2)$$

and below 243.4° K. by equation (3)

$$\log_{10} P_{\text{mm.}} = -1909.3940/T - 4.642748 \log_{10} T + 21.040609 \quad (3)$$

These equations are given as a means of obtaining precise values of $\mathrm{d}P/\mathrm{d}T$ and the heats of vaporization from them. The normal boiling point obtained from equation (2) is 281.23 ± 0.05° K. (+8.07°). This is in fair agreement with the value of 8.5°, obtained by Hurd and Meinert[8] who also discuss boiling points obtained by other investigators. Table IV summarizes the vapor pressure data together with the calculated values obtained from equations (2) and (3) and the differences between the observed and the calculated pressures in terms of degrees.

TABLE IV

VAPOR PRESSURES OF 1-BUTYNE

0 °C. = 273.16 °K.; boiling point, 281.23 °K.; *g* for State College = 980.124 (I. C. T.)

T, °K.	*P* (obsd.), mm.	*P* (calcd.), mm.	*T* (obsd. − calcd.), °K.
194.402	3.92	3.92	0.000
204.249	9.24	9.26	−0.024
214.437	20.54	20.55	− .006
224.481	41.64	41.58	+ .021
231.935	67.08	67.04	+ .010
236.746	89.65	89.59	+ .011
243.399	131.04	131.07	− .005
249.303	179.82	179.76	+ .006
254.415	233.07	233.06	+ .001
258.723	287.38	287.39	− .001
262.916	349.64	349.67	− .002
267.322	426.39	426.38	+ .001
271.596	513.10	513.09	+ .001
275.885	613.55	613.63	− .003
279.321	704.87	704.88	.000
281.223	759.84	759.78	+ .002
282.713	805.16	805.08	+ .002

Vapor pressure determinations made after one-third of the sample had been distilled from the calorimeter indicated the presence of a volatile impurity which affected the pressures by an amount corresponding to 0.05° near the normal boiling point.

The Heat of Fusion.—The data for the heat of fusion were taken in the usual manner.[2a,b] The results are given in Table V. The premelting corrections were obtained from the purity data and equation (1).

TABLE V

HEAT OF FUSION OF 1-BUTYNE

Mol. wt., 54.088; m. p. 147.43 °K.

Temp. interval, °K.	Cor. heat input, cal./mole	$-\int C_p\,\mathrm{d}T$, cal./mole	Premelting, cal./mole	Moles of samples in calorimeter	Δ*H* fusion, cal./mole
144.902–147.510	1512.79	77.63	5.68	0.47790	1440.84
145.173–150.728	1641.09	202.55	2.43	.47262	1440.97
144.958–149.158	1584.04	144.98	2.21	.47262	1441.27
				Average	1441.03 ± 0.2

The Heat of Vaporization—The heat of vaporization at several different temperatures was measured in the usual manner.[9] These values can be represented to within 0.12% by equation (4) obtained by least squaring the data.

$$\Delta H = 10{,}440.3 - 16.2845T \quad (4)$$

Δ*H* is obtained in calories per mole. The molal heat of vaporization at the normal boiling point from this equation is 5860.6. The heat of vaporization data and the heats of vaporization calculated by means of equation (4) are summarized in Table VI.

The Vapor Density.—The vapor density data, determined in the usual manner,[8] are summarized in Table VII.

The molecular weight calculated by the method of limiting density is 54.084. The formula weight of pure 1-butyne is 54.088 using the 1948 table of atomic weights. The mean value of the second virial coefficient is 0.748 liter/mole at 298.16°K.

The Second Virial Coefficients from Heats of Vaporization.—The second virial coefficients *B* can be obtained as a function of temperature from the heat of vaporization and vapor pressure data. The method has been previously described.[10] The heats of vaporization were obtained from equation (4). The experimental error in the second virial coefficients obtained in this way is about ±10%, corresponding to about

TABLE VI

THE HEAT OF VAPORIZATION OF 1-BUTYNE

Mol. wt. 54.088; 0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules

Moles vaporized	Mean temp. of vapn., °K.	Total cor. heat input, cal./mole	$\int C_p\,\mathrm{d}T$, cal./mole	Δ*H* at mean temp. of vapn. to real gas state Obsd.	Calcd.[a]
0.065667	262.53	6145.0	+21.5	6166.5	6165.1
.040264	262.71	6238.7	−77.0	6161.7	6162.2
.074321	276.95	5947.0	−19.0	5928.0	5930.3
.073462	281.31	5934.9	−71.2	5863.7	5859.3
.076115	281.46	5841.0	+ 8.6	5849.6	5856.9
.076804	282.52	5820.9	+23.3	5844.2	5839.6

[a] Calculated from $\Delta H = 10{,}440.3 - 16.2845T$.

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[8] Hurd and Meinert, THIS JOURNAL, **53**, 289 (1931).

[9] Aston, Sagenkahn, Szasz, Moessen and Zuhr, *ibid.*, **66**, 1171 (1944).

[10] Aston, Fink, Bestul, Pace and Szasz, *ibid.*, **68**, 52 (1946).

Table VII

The Vapor Density of 1-Butyne at 298.16°K.

Pressure, atm.	Density, g./cc.	P/d obsd.	P/d calcd.[a]	B, liter/mole
1.04166	0.00238036	43.760	43.756	−0.739
0.81617	.00185205	44.069	44.066	− .751
.57984	.00130560	44.412	44.412	− .751
.57016	.00128327	44.430	44.425	− .747
.34903	.00078005	44.744	44.739	− .748
.28843	.00064353	44.822	44.825	− .765
.22000	.00048966	44.931	44.923	− .738
			45.235[b]	

[a] Calcd. from $P/d = 45.235 - 1.420\,P$. [b] Extrapolated to $P = 0$.

±0.3% error distributed between the heat of vaporization and $\mathrm{d}P/\mathrm{d}T$. The largest deviation of the experimental virial coefficients from those calculated by an equation, linear in T, obtained by least squares is only 7%. The values obtained for the virial coefficients and those obtained from the least squares equation (equation 5) are listed in Table VIII. The volumes of the saturated vapor are also given in this table.

Table VIII

The Volumes of Saturated Vapor and Second Virial Coefficients of 1-Butyne from Heats of Vaporization and Vapor Pressure Data

T, °K.	P, atm.	H,[a] cal./mole	V_g, liters/mole	B, liters/mole Exptl.	Calcd.[b]	Berthelot[c]
262	0.44108	6173.8	47.743	−0.98	−1.05	−0.97
266	.52904	6108.6	40.221	−1.01	−1.02	− .94
270	.63063	6043.5	34.085	−1.10	−0.99	− .91
274	.74695	5978.3	29.062	−1.00	−0.96	− .88
278	.87975	5913.2	24.912	−0.98	−0.94	− .84
282	1.03046	5848.1	21.469	−0.94	−0.91	− .81

[a] Calcd. from the equation given in Table VI. [b] Calculated from the equation $B = -2.882 + 0.0070T$ (5) obtained by applying the method of least squares to the values of B in the experimental column and the value of B at 298.16. [c] Calculated from the equation $B = 0.00805T - 3.0821$ obtained by plotting the values of B against T using the Berthelot expression $B = \frac{9PV_gT_c}{128P_cT}\left(1 - 6\frac{T_c^2}{T^2}\right)$ which gives B a linear dependence over the relatively small temperature range considered. No experimental value of P_c is available so a value of P_c was obtained by substitution of $T_c = 463.7$°K. in this expression for B using the direct experimental value of B at 1 atm. and 298.16°K. These values of B were calculated as a test of the validity of the Berthelot equation since we later consider it in calculating the correction of the entropy to the ideal gas state.

In order to check the consistency of the heat of vaporization, heat capacity, vapor pressure and state data the heat capacity of the gas was calculated using the equation

$$C_p(\mathrm{g}) = C_p(\mathrm{l}) + \left(\frac{\mathrm{d}\,\Delta H_v}{\mathrm{d}T}\right)_{\mathrm{satd.}} - \left[V(\mathrm{g}) - \left(\frac{\partial V(\mathrm{g})}{\partial T}\right)_p\right]\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{\mathrm{satd.}} \qquad (6)$$

where the volume of the liquid is neglected. The heat capacity of the gas corrected to the ideal gas state at 273.2 and 282.0°K. was calculated and these values compared with the values calculated from spectroscopic data. The calorimetric values are 16.94 and 17.82, respectively, and the spectroscopic values are 18.28 and 18.70, respectively. The discrepancy between these respective values can be accounted for by permitting an error of ±0.1% in the heats of vaporization, ±0.3% in the heat capacity of the liquid, ±10.0% in the second virial coefficients and about ±20% in their temperature derivatives, assuming the spectroscopic values to be absolutely correct.

The Entropy from Calorimetric Data.—The entropy of 1-butyne at the normal boiling point for the ideal gas is 68.21 e. u. The calculation is shown in Table IX.

Table IX

The Entropy of 1-Butyne in the Ideal Gas State from Calorimetric Data

Conditions	Entropy, e. u.
0–14°K., Debye extrapolation ($\theta = 133.6$, 5 degrees of freedom)	0.2993
14–30°K., $\int C_p/T\,\mathrm{d}T$	1.6934
0–30°K., Debye extrap. and $\int C_p/T\,\mathrm{d}T$	1.993 (2.087 e. u. by Debye extrap. from 30°K.)
30–147.430°K., $\int C_p/T\,\mathrm{d}T$	16.998
147.430°K., fusion (1441.36/147.43)	9.774
147.430–281.22°K., $\int C_p/T\,\mathrm{d}T$	18.435
281.23°K., vaporization (5860.6/281.23)	20.840
$S^0 - S$, correction to ideal gas state	0.170
Entropy ideal gas at 281.23°K., 1 atm.	68.21 ± 0.18

The correction to the ideal gas state from the Berthelot equation is given by

$$S^0 - S = \frac{27}{32}R\frac{T_c^3}{T^3}\frac{P}{P_c} \qquad (7)$$

with $T_c = 463.7$ and $P_c = 48$ atm. This yields a value of 0.16 e. u. Since the value of P_c was calculated to fit the value of B from direct experiment, this calculation should be more reliable than if the actual value of P_c were used. However,

$$S^0 - S = (\partial PB/\partial T)\,P \qquad (8)$$

is the expression used for calculating the correction of the entropy to the ideal gas state. Substituting equation (5) for B in equation (8) the correction of the entropy to the ideal gas state becomes $S^0 - S = 0.0070\ P$ liter-atm.-deg.$^{-1}$ or 0.17 e. u. at 1 atm. We have preferred to use the latter value in correcting the entropy to the ideal gas state although the choice is within experimental error.

The Entropy from Spectroscopic and Molecular Data.—The entropy from spectroscopic and molecular data has been obtained by Wagman.

Kilpatric, Pitzer and Rossini.[11] A new frequency assignment made by N. Sheppard[12] was used in recalculating the entropy. The latter assignment is given in Table II of Sheppard.[12] The atomic parameters used in the calculation of the entropy were: $-\text{C}-\text{C}\equiv$, 1.462 Å.; $-\text{C}\equiv\text{C}-$, 1.207 Å.; $\equiv\text{C}-\text{H}$, 1.06 Å.; $-\text{C}-\text{C}-$, 1.54 Å., methylene C–H, 1.1 Å.; methyl C–H, 1.09 Å. Tetrahedral angles were assumed. The values used by Wagman, Kilpatric, Pitzer and Rossini[11] are identical with the values stated above. They were taken from electron diffraction and spectroscopic data.[13a,b,c] The values obtained for the product of the principal moments of inertia and the reduced moment of the methyl group about the $-\text{C}\equiv\text{C}-\text{C}-$ axis were 1.1643×10^{-114} (g. sq. cm.)[3] and 4.847×10^{-40} g.-sq. cm., respectively. The symmetry number of the rigid molecule is 1. The entropy of the ideal gas at the normal boiling point calculated from spectroscopic and molecular data is given in Table X. The value obtained is 69.618 e. u. assuming free internal rotation.

TABLE X

THE ENTROPY OF 1-BUTYNE IN THE IDEAL GAS STATE FROM SPECTROSCOPIC DATA

Entropy in the ideal gas state at the normal b. p.	E. u.
Translation	37.395
External rotation	23.791
Vibration	4.985
Free internal rotation	3.447
Entropy ideal gas at 281.23°K., 1 atm.	69.618

The barrier assumed by Wagman, Kilpatric, Pitzer and Rossini was 2710 cal./mole. They assumed the barrier restricting internal rotation of the methyl group was the same as the barrier in ethane. This barrier gives a value of 68.34 e. u. for the entropy of the ideal gas at 1 atm. and 281.23°K. The barrier calculated from the tables of Pitzer and Gwinn[14] to fit the calorimetric data is 3000 cal./mole.

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Summary

1. The heat capacities of 1-butyne have been measured from 12 to 275°K.

2. The solid–liquid equilibrium temperature and heat of fusion have been determined. The melting point is 147.43 ± 0.05°K.

3. The vapor pressures have been determined from 194.4 to 282.7°K. and the results represented by an equation giving the value of 281.23°K. for the normal boiling point.

4. The heat of vaporization has been determined at various temperatures.

5. The vapor density has been determined at 298.16°K.

6. The vapor density at various temperatures has been calculated from the vapor pressure and heat of vaporization data.

7. Virial coefficients have been obtained from the density data. Comparison of these with the Berthelot equation yields a value of $P_c = 48$ atm.

8. The entropy has been calculated from spectroscopic and molecular data and comparison between the calculated and observed entropies yielded a value of 3000 cal./mole for the potential barrier hindering the internal rotation of the methyl group.

STATE COLLEGE, PA.

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[11] Wagman, Kilpatric, Pitzer and Rossini, *J. Research Natl. Bur. Standards*, **35**, 467 (1945).

[12] N. Sheppard, *J. Chem. Phys.*, **17**, 74 (1949).

[13] (a) Pauling, Springall and Palmer, THIS JOURNAL, **61**, 927 (1939); (b) **63**, 3492 (1941); (c) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1945.

[14] Pitzer and Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).