centration exist in micelles, and the concentration of single paraffin chain ions probably decreases absolutely.[24] By extrapolation of the figures given here, the critical concentration for cetane sulfonic acid at 90° will be about 0.0015 *N*. The aggregation will therefore be almost complete in a 0.01 *N* solution. According to McBain's diagram[9] it is only just appreciable at this concentration.

Summary

The critical fall of conductivity in dilute solutions of paraffin chain salts has been examined in considerable detail in the case of cetane sulfonic acid. A stable equilibrium has been shown to exist in the solution in the neighborhood of the critical concentration. The critical concentration, about 0.008 *N* in water at 60°, has been shown to increase with temperature by about 2% per degree. Addition of glycerol raises the critical concentration, while addition of amyl alcohol or hydrochloric acid lowers it.

The conductivity data lend no support to the belief that the acid is not a strong one in concentrations where it is not aggregated.

It is concluded that aggregation must be practically complete in a 0.01 *N* solution.

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(24) See refs. 3b, 5 (pp. 25–29), and, in particular, ref. 6.

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

Heat Capacities and Entropies of Organic Compounds. II. Thermal and Vapor Pressure Data for Tetramethylmethane from 13.22°K. to the Boiling Point. The Entropy from its Raman Spectrum

BY JOHN G. ASTON AND GEORGE H. MESSERLY[1]

The high symmetry of tetramethylmethane along with the absence of polarity makes this compound an inviting one for a comparison of the entropy calculated from its Raman spectrum and moments of inertia[2] and from calorimetric data using the third law of thermodynamics. In the present paper the necessary measurements are described and such a comparison is made.[3]

Tetramethylmethane.—The partially purified compound was kindly furnished by Dr. F. C. Whitmore and his students.[4] About 700 cc. was fractionally sublimed. The resulting material (freezing point about −23°) was twice distilled, at 370–400 mm., through an efficient glass fractionating column (packed with glass spirals) in which fractionation could be carried out in the absence of air in an all glass system.[5] The middle fraction was collected in a glass bulb. A 30-cc. middle portion was distilled from this fraction into a weighed 30-cc. sample bulb connected to the line by a ground glass joint. This sample was cooled to liquid air temperature and pumped out to less than 10^{-6} mm., melted, cooled again and repumped to remove the last traces of air.

The bulb was sealed off at a constriction below the ground glass joint and reweighed along with the joint. A correction to vacuum weights was made to ascertain the weight of tetramethylmethane. The sample bulb was equipped with a side arm closed by an inner-sealed capillary. For introduction into the calorimeter, the side arm was attached to the filling line which was evacuated to less than 10^{-5} mm. After cooling the tetramethylmethane to liquid air temperature the inner-sealed capillary was broken by a piece of iron sealed in glass and activated by a solenoid. The weight of sample was checked on removal from the apparatus. The impurity was 0.73 mole per cent. as estimated from the melting point range.

The Apparatus.—This was similar to that described by Giauque and Wiebe[6] except for details mentioned below. The calorimeter was made from 2.5-cm. copper tubing (0.025 cm. wall) and was 8 cm. long. Heat conduction was furnished by thirty-nine perforated disks (0.008 cm. thick) which made a spring fit with the walls and with a central tube, re-entrant from the bottom, which served as the well for the standard thermocouple.[7] The latter was fastened in with Wood's metal. A 3-mm. soft glass filling tube was sealed onto a short platinum tube brazed to the top. The whole was gold plated inside and out.

The calorimeter was wrapped with a gold resistance thermometer-heater (No. 40 B. and S. gage, double silk insulated annealed gold wire, containing 0.175% silver and drawn using only jewel dies). It was similar to that used by Giauque and Wiebe, except that a gap was left in the center in which a constantan resistance thermometer-heater for use below 25°K. was wound. It had a resistance at room temperature of 140 ohms, and 20 ohms at 25°K. The lower half, with a resistance of 81 ohms at room temperature, was used for heat of vaporization

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(1) Submitted in partial fulfilment of the requirements for the Ph.D. degree.

(2) (a) Kassel, *J. Chem. Phys.*, **3**, 115 (1935); (b) Eidinoff and Aston, *ibid.*, **3**, 379 (1935); (c) Kassel, *ibid.*, **4**, 276 (1936).

(3) For a report of the preliminary results of this comparison see Aston and Messerly, *ibid.*, **4**, 391 (1936).

(4) Whitmore and Fleming, THIS JOURNAL, **55**, 3803 (1933). These authors discuss the previous work on this compound.

(5) We wish to thank Professor J. H. Simons for the loan of the column and help in the purification.

(6) Giauque and Wiebe, THIS JOURNAL, **50**, 101 (1928).

(7) Parks, *ibid.*, **47**, 338 (1925).

measurements. The constantan resistance thermometer-heater, which was of No. 40 B. and S. gage double silk insulated thermocouple wire had a room temperature resistance of 114 ohms and below 25°K. an approximately constant temperature coefficient of 0.00145 deg.$^{-1}$. Both were wound as described by Ahlberg and Latimer,[8] and cooled several times to liquid air temperatures before use. However, both were continuously calibrated during the calorimetric measurements against the standard copper-constantan thermocouple S-2 whose calibration has already been described.[9a] The temperature scale was extended above 273°K. using carbon bisulfide vapor pressures.[9b]

The temperature head between the gold heater wire and the inside of the calorimeter was about 0.05°K. for a one cal. per minute energy input. In the case of the constantan heater below 25°K. it was several times this value.

The radiation shield together with the massive cylinder, which formed its top and with which the lead wires and the filling tube made good thermal contact, contained 1890 g. of copper and 4800 g. of lead.

The built-in hydrogen liquefier and cryostat were exactly as described by Latimer and Greensfelder.[10]

In cooling the calorimeter after filling it was found necessary to keep the entire filling tube hotter than the calorimeter at all times. Otherwise solid tetramethylmethane condensed in the tube as a solid plug which was very difficult to drive back into the calorimeter. A stream of warm air passing over the tube leading to the cryostat and onto the top of the cryostat allowed the temperature of these to be kept considerably above the temperature of the calorimeter, while allowing the cooling to proceed from the bottom. Liquid air was added at the bottom of the Dewar. In addition the tube and the heavy top of the radiation shield were electrically heated while cooling.

The Heat Capacity Measurements.—The electrical connections and method of measurement were as described by Giauque and Wiebe.[6,11]

The White potentiometer and standard resistances were calibrated by (or against standards calibrated by) the Bureau of Standards. The one-tenth second stop watch was calibrated frequently against an astronomical clock set with the Arlington time signals.

Three standard cells were constantly intercompared and frequently checked by the Bureau of Standards during the measurements. A thermometer current was chosen to give in most cases a sensitivity of 0.001° in reading the temperature rise.

The various corrections described by Giauque and Wiebe have been applied. In addition a correction was applied to the resistance for the temperature of the pair of 5-cm. leads from the terminals on the radiation shield to each of the resistance thermometers. This was taken as the mean of the shield and calorimeter temperatures. This correction was necessary because these leads formed part of the measured resistance, and during calibration the shield was at the same temperature as the calorimeter; it reduced the heat capacity by 0.14% at all temperatures above 60°K. For the calorimeter of G. and W. this correction was negligible (0.025%). The shield was kept above the calorimeter at all temperatures above 110°K. to prevent condensation. The vapor pressure measurements described later were used in correcting for material vaporized into the filling line, whose volume was determined accurately. In the calculation the density taken for the liquid was that given by Whitmore and Fleming[4]; that for the solid (0.73 g./cc.) was ascertained by the contraction on freezing.

The molal heat capacities are given in Table I and Fig. 1.

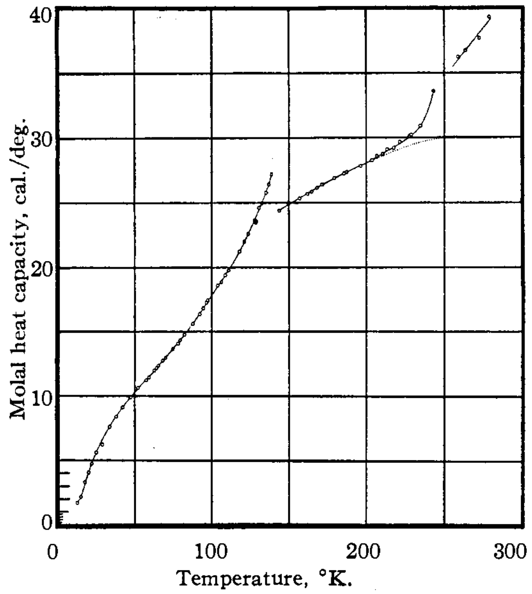

Fig. 1.—Heat capacity of tetramethylmethane.

In this and all other tables the molecular weight of tetramethylmethane was taken as 72.09. and the ice point as 273.16°K. One calorie (15°) was taken equal to 4.1852 absolute joules and one international joule to 1.00041 absolute joules.[12a] The present United States Standards were taken as yielding energy in international joules.[12b]

The error in these measurements from the various sources depends on the temperature. Below 25°K. the results may be in error by more than 1% due largely to the short range of calibration of the constantan resistance thermometer (10.9–26.2°K.) and the comparative insensitivity of the thermocouple in this range. Between 25 and 40°K. the lower points may be in error by about 1% due to the rapid change of derivative of the gold resistance thermometer. From 40 to 240°K. the error does not exceed a few tenths of a per cent. In the case of the points for the liquid the error may be somewhat above 0.5%. The error

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(8) Ahlberg and Latimer, This Journal, **56**, 856 (1934).

(9) (a) Aston, Willihnganz and Messerly, *ibid.*, **57**, 1642 (1935); (b) Henning and Stock, *Z. Physik*, **4**, 226 (1921).

(10) Latimer and Greensfelder, This Journal, **50**, 2202 (1928).

(11) See also Gibson and Giauque, *ibid.*, **45**, 93 (1923).

(12) (a) Birge, *Rev. Modern Phys.*, **1**, 30 (1929); (b) Vinal, *Bur. Standards J. Research*, **8**, 729 (1932).

TABLE I

HEAT CAPACITY OF TETRAMETHYLMETHANE

Molecular weight 72.09. 0°C. = 273.16°K.
Series I, 0.2419 mole; Series II and III, 0.2578 mole.

Temp., °K.	Rise, °K.	C_p, cal./deg./mole	Series number
13.14	0.453	1.688	I
15.24	2.244	2.134	I
18.05	2.042	3.281	I
20.28	2.206	4.061	I
22.40	2.615	4.734	I
25.22	3.873	5.583	I
29.12	3.160	6.203	I
33.83	4.695	7.579	I
38.12	3.852	8.380	I
42.28	4.951	9.087	I
47.30	5.170	9.854	I
52.11	4.407	10.544	I
57.45	6.244	11.190	I
59.29	3.377	11.403	II
62.72	5.138	11.946	III
63.17	5.336	11.965	I
64.19	5.891	12.126	II
65.56	4.849	12.303	I
68.03	4.572	12.696	I
69.69	5.125	12.906	II
70.05	4.183	12.918	III
70.86	5.454	13.043	I
72.90	5.111	13.336	I
74.70	4.560	13.623	II
74.81	4.780	13.615	III
78.12	4.569	14.009	I
79.47	4.965	14.266	II
82.13	4.079	14.712	III
82.50	4.163	14.673	I
87.12	5.327	15.623	I
87.34	5.263	15.501	II
87.81	3.615	15.632	III
92.20	4.838	16.407	I
92.21	4.629	16.287	II
94.57	4.561	16.772	III
96.70	4.445	17.191	I
97.39	4.283	17.372	II
103.89	5.280	18.488	I
104.14	3.842	18.514	III
106.53	5.326	18.808	II
108.95	4.846	19.350	I
111.14	4.516	19.711	III
118.22	4.035	21.20	III
121.35	7.441	21.96	II
124.00	3.686	22.53	III
128.07	3.453	23.59	III
128.84	3.571	23.40	IIIy
129.09	3.348	23.52	IIIx
130.87	6.376	24.53	II
132.87	3.200	24.90	III
135.50	1.533	25.72	III
137.06	1.485	26.36	III
138.81	1.438	27.15	III
140.02	"Transition"		
143.75	4.446	24.32	III
149.59	2.768	24.83	II
149.99	5.245	24.85	III
155.97	4.201	25.11	II
156.89	4.947	25.28	III
161.82	4.996	25.62	II
164.56	4.659	25.77	III
168.07	3.802	26.08	II
171.41	5.313	26.34	III
173.61	4.501	26.94	II
179.14	5.021	26.84	III
179.26	5.496	26.77	II
185.26	5.257	27.21	II
187.20	4.733	27.32	III
196.09	4.457	27.79	III
203.35	3.396	28.23	III
206.59	4.556	28.56	II
210.29	4.309	28.72	III
213.14	4.360	29.05	II
217.38	5.148	29.16	III
221.19	6.249	29.62	II
227.61	4.777	30.07	III
228.15	5.976	30.19	II
234.54	4.569	30.89	II
243.04	4.099	33.55	III
256.53	Fusion		
258.96	2.600	36.10	II
263.76	3.650	36.67	II
272.57	4.385	37.59	II
278.92	4.091	39.17	II
282.61	Boiling point		

due to the increased heat leak correction at the higher temperatures has been reduced by an accurate treatment of the drifts where these were non-linear.[13]

The High Energy Absorption near 140°K.—The abnormal rise in the heat capacity curve for the solid precedes what is perhaps an isothermal transition at 140.02°K.[14] However, the "transition" may be purely of the ammonium chloride type,[15] with very high heat capacities over a short range. In this connection it is noteworthy that up to almost 140°K. equilibrium was rapidly attained, whereas when energy was supplied in the neighborhood of 140.02°K. equilibrium was attained much more slowly (almost an hour). Table II records equilibrium temperatures at various fractions "transformed" as estimated from the fraction of the "transition" heat supplied, assuming this to be isothermal. The temperature at 80% transformed may be high due to difficulty in attaining equilibrium and less probably due to impurity.

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(13) See Keesom and Kok, *Comm. Phys. Lab. Univ. of Leiden*, 219c (1932).

(14) Wahl, *Z. physik. Chem.*, **88**, 135 (1914), states that solid tetramethylmethane is probably tetragonal (slightly birefringent) at low, and cubic (isotropic) at high, temperatures but no transition temperature is given.

(15) (a) Simon, *Ann. Physik*, **68**, 241 (1922); (b) see also Giauque and Blue, THIS JOURNAL, **58**, 833 (1936) for a very similar region of high energy absorption in the case of hydrogen sulfide between 126 and 127°K.

TABLE II

TEMPERATURES IN THE REGION OF HIGH ENERGY ABSORPTION

Per cent. transformed	Temp., °K. Thermocouple S-2	Temp., °K. Resistance thermometer
10	139.954	139.959
30	140.008	140.006
50	140.020	140.016
60	140.020	140.025
80	140.112	140.087
Mean	140.023	140.017

Mean 140.020

TABLE III

HEATS OF "TRANSITION" AND FUSION OF TETRAMETHYLMETHANE

(Mol. wt. 72.09; 0.25778 mole)

Temperature interval, °K.	Corrected heat input, cal./mole	$\int C_p dT$ cal./mole	Pre-melting, cal./mole	ΔH, cal./mole
"Transition" at 140.02° K.				
133.661–145.871	1054.5	438.6		615.9
135.534–146.911	1023.7	407.9		615.9
			Mean	615.9 ± 0.6
Fusion at 256.53°K.				
240.407–259.847	1609.9	854.1	23.5	779.3
240.913–261.442	1662.7	910.7	25.0	777.0
			Mean	778.2 ± 3.5

Table III contains a summary of data on the heat of "transition." For the calculation of $\int C_p dT$ the heat capacity curves on either side were extrapolated linearly to 140.02°K.

The two heat capacity measurements IIIx and IIIy recorded in Table I are lower than the best curve through the other series by 1.3%. This may indicate hysteresis in the neighborhood of the "transition" point. For this reason a history of the cooling for, and of the course of, the various series of heat capacity determinations is of interest. Before series I the solid material was heated until melting started and then cooled over two days to 10°K. Up to 70°K. the points were taken continuously. The apparatus was then cooled to 60°K. and the rest of the points of series I taken. Series II and III were taken on another filling from the same sample. In series II the cooling procedure was essentially the same except the calorimeter was cooled only to slightly below 60°K. Points were taken continuously to below the "transition" point; the material was carried through the transition with one application of energy. In series III the cooling to 60°K. occupied nine days. Points were taken continuously to just above the "transition" point. The calorimeter was then slowly cooled to obtain the point III$_x$, which was taken at the temperature where cooling stopped. The first heat of "transition" measurement was then taken. Point IIIy was taken after a similar cooling, and followed by the second heat of "transition" measurement. The rest of the points of series III were taken continuously to the melting point. Apparently hysteresis occurs only in the neighborhood of the "transition" point.

The Melting Point.—The equilibrium temperature of the system was observed with 50 and 97% of the sample melted as ascertained by measuring the heat required to melt the remaining solid as in a regular heat of fusion measurement. From the results and the heat of fusion the impurity present was found to be 0.727 mole per cent., assuming no solid solution. The melting point of pure tetramethylmethane calculated on this basis is 256.53 ± 0.10°K. (The freezing point of our sample was 255.31°K.) Previous melting points recorded in the literature[4] are: 253°K. (Lwow, 1871); 253.7°K. (Whitmore and Fleming, 1933).

Heat Capacities in the Premelting Range.—In the range between 200°K. and the melting point the tabulated heat capacities require correction for heat absorbed in fusion. The lower curve in Fig. 1 has been obtained from the upper one through the experimental points by subtracting this correction. obtained from the thermodynamic freezing point equation and the heat of fusion at the melting point without allowance for its change with temperature. (The heat capacity of the increasing quantity of liquid could be assumed equal to that of the solid without serious error.) This lower curve was extrapolated to the melting point as indicated by the extension to obtain heat capacities used in calculating the heat of fusion.

The Heat of Fusion.—The method described by Gibson and Giauque[11] was used. The results are recorded in Table III.

The correction for premelting (col. 4) is the area between the upper and lower curves (Fig. 1). The estimated error does not include the error due to our estimation of this correction. This may produce about 1% error in the heat of fusion, but does not seriously affect the entropy. Indeed if the whole fusion had been treated as a heat capacity in calculating the entropy, the effect on the final entropy would have been only to add the almost negligible entropy of mixing of the impurity—($-0.0073\ R \ln 0.0073 - 0.9927\ R \ln 0.9927 = 0.088$ e. u.).

The Vapor Pressure Measurements.—The measurements were made as already described.[9] The results for the liquid are given in Table IV. Column 1 gives the absolute temperature as read by the thermocouple; col. 2 gives the observed pressure, and col. 3 the pressure calculated from equation (1).

$$\log_{10} P_{\text{mm.}} = -1525.0/T - 2.16979 \log_{10} T + 13.59527 \quad (1)$$

Column 4 gives the temperature deviation corresponding to the pressure difference. Since the boiling range of the sample used was about 0.1°, as ascertained by vapor pressure measurements on fractions distilled from it, these measurements should hold for pure tetramethylmethane to about 0.1° in the temperature. Vapor pressure data were also obtained on the solid, but are without significance as the partial pressure of impurity above the liquid is steadily increased as the solid crystallizes. For completeness we give equation (2), which represented our data on the solid between 230°K. and the melting point.

$$\log_{10} P_{\text{mm.}} = 11642.30/T + 258.6890 \log_{10} T - 0.241380\,T - 604.2570 \quad (2)$$

The only other data on tetramethylmethane are the measurements of Whitmore and Fleming.[4] A comparison of their results on the solid with equation (2) shows that their material contained more impurity than ours, as does also the freezing point which they record for it. In col. 5 of Table IV are given the deviations (W. and F.-A. and M.) between the pressures observed by Whitmore and Fleming at their nearest temperature and those calculated from equation (1). From equation (1) the boiling point has been found to be 282.61°K. Previous boiling points recorded in the literature[4] are: 282.7°K. (Lwow, 1871); 282.6°K. (Whitmore and Fleming, 1933).

TABLE IV

VAPOR PRESSURES OF LIQUID TETRAMETHYLMETHANE

(*g* for State College, 980.124 ("I. C. T.")) (0°C. = 273.16°K.). Boiling point 282.61°K.

Temp., °K.	Pressure (obsd.) int. mm.	Pressure (calcd.) int. mm.	ΔT., °K. (calcd. − obsd.)	ΔP (mm.) (W. and F.-A. and M.)
258.036	283.71	283.64	−0.011	10.7
262.766	348.41	348.33	−.005	
267.847	430.66	430.46	−.009	8.1
272.292	515.02	514.48	−.021	9.0
277.865	637.77	637.70	−.003	4.7
280.396	700.30	700.82	+.017	
282.897	767.72	767.93	+.006	0.3

The Heat of Vaporization.—Our procedure differed from that described by Giauque and Wiebe (method II)[6] only in the method of collecting the vaporized material. A thin-walled glass bulb, connected to the line by a vaseline sealed glass joint, was used for this purpose. It was immersed in a well-stirred bath of benzene and benzene ice, along with excess water, contained in a silvered dewar. During vaporization the pressure remained constant to within a few millimeters except during the initial period required to build up the head necessary for heat transfer across the bulb, when it rose by about 20 mm. Before a measurement the calorimeter was brought to within a degree of the temperature of the bath of benzene–benzene ice. The surroundings were at such a temperature as to be above that of the calorimeter at all times during the vaporization. The drift of the calorimeter was observed with the resistance thermometer until a sudden decrease in its value indicated that material had started to condense in the bulb. The heater was then turned on. The energy for the vaporization before the heater was turned on was calculated from the heat leak. At the end of the measurement the heater was shut off at a predetermined time and a stopcock connecting the calorimeter to the rest of the line (manometer, condensing bulb, etc.) simultaneously closed. The drifts were followed until the calorimeter reached equilibrium. The correction for the varying pressure and hence temperature of the surface from which vaporization occurred was simply made as follows.

Consider n moles of liquid whose initial temperature is T' and whose vaporization temperature varies from T' to T. Let Q be the heat absorbed in heating the n moles from T' and vaporizing them. Let C_p be the heat capacity of the gas (assumed constant), and $\Delta H'$ the heat of vaporization at the temperature T'. Then

$$Q = \int_0^n [\Delta H' + C_p(T - T')]\,\mathrm{d}n \qquad (3)$$

Over the small range of temperatures involved $(T - T') = k(P - P')$, where P and P' are the vapor pressures at T and T'. Substituting in (3) and integrating

$$Q = \Delta H'n - \alpha P'n + \int_0^n \alpha P\,\mathrm{d}n \; (\alpha = kC_p) \qquad (4)$$

As the number of moles vaporized is proportional to the time of energy input

$$Q = \Delta H'n - \alpha P'n + \beta \int_0^t P\,\mathrm{d}t \qquad (5)$$

where β is a new constant. If P had a constant value P_e

$$Q = \Delta H'n - \alpha P'n - \beta P_e t \qquad (6)$$

Comparing (5) and (6) it is seen that the vaporization may be considered as occurring at an effective pressure

$$P_e = 1/t \int_0^t P \, dt \qquad (7)$$

The integral (7) accordingly was evaluated graphically to obtain the effective pressure (and temperature) of the vaporization.

The number of moles of liquid vaporized was calculated from the increase of pressures in the line, and the weight of material condensed in the bulb. The pressure in the calorimeter line up to the closed stopcock was obtained from its equilibrium temperature at the end of the vaporization period; that in the manometer and bulb from the manometer reading when the bulb was sealed off.[16] The results are given in Table V.

TABLE V

HEAT OF VAPORIZATION OF TETRAMETHYLMETHANE

(662.2 int. mm. (278.59°K.)) (mol. wt. 72.09)

Moles vaporized	Time of energy input, min.	Total input, cal./mole	$\int C_p dT$, cal./mole	ΔH, cal./mole
0.05545	25.50	6281	797	5484
.06378	28.00	5980	447	5528[a]
			Mean	5506 ± 30
Corrected to one atm. (282.61°K.)				5438 ± 30
Calculated at one atm. from equation (1) and thermodynamics; Berthelot correction = 244 cal.				5490

[a] A correction of −5 cal. applied for difference in effective pressure.

The correction for raising the temperature of the liquid remaining in the calorimeter to the final temperature and the number of moles of liquid vaporized to the effective temperature of vaporization are given in col. 4. The mean value has been corrected to the boiling point using the measured heat capacities for the liquid and for the gas the heat capacities calculated by adding to 12/2 R (the translational and rotational heat capacity + $C_p - C_v$) the vibrational heat capacity calculated from the Raman spectrum using the equation

$$C_{\text{vib.}} = R \sum x_i^2 e^{x_i}/(e^{x_i} - 1)^2 \ (x_i = hc\tilde{\nu}/kT) \qquad (8)$$

with frequencies and constants discussed later. (The correction to the real gas state is here negligible.) It is of interest to compare the measured heat of vaporization with the one calculated from the vapor pressures (equation (1)) and thermodynamics using the modified Berthelot equation

$$PV = RT\,[1 - 9PT_c(1 - 6T_c^2/T^2)/128P_cT] \qquad (9)$$

$$T_c = 432\text{°K.}; \quad P_c = 33 \text{ atm.}^{17}$$

to calculate the volume of the gas. The heat of vaporization, thus calculated from the vapor pressures, at the boiling point, is included in Table V. The agreement justifies the equation of state chosen for the later correction of the entropy.

The Entropy.—Table VI summarizes the calculation of the entropy of the gas at the boiling point from the experimental data. The correction to the perfect gas state has been made using equation (9) and thermodynamics.[6]

TABLE VI

THE ENTROPY OF TETRAMETHYLMETHANE

(Mol. wt. 72.09)

	E. u./mole
0–13.14°K. Debye function $h\partial_m/k$ = 106.7 (six degrees of freedom)	0.56
13.14–140.02°K. graphical[a]	24.13
"Transition" 615.9/140.02	4.39
140.02–256.53°K. graphical[a]	16.55
Fusion 778.2/256.53	3.03
256.53–282.61°K. graphical[a]	3.63
Vaporization 5438/282.61	19.24
Entropy of actual gas at boiling point	71.53 ± 0.3
correction for gas imperfection	0.18
Entropy of ideal gas at boiling point	71.71 ± 0.3

[a] $\Delta S = \int C_p d \ln T$.

The classical rotational and translational entropy of the gas at 298.16°K. and one atm. has been calculated by Kassel to be 73.957 e. u.[2c] using 1.53 and 1.11 Å. for the C–C and C–H distances respectively. We have used 1.54 Å. for the former throughout, but have retained the latter.

The equation for the translational and classical rotational entropy, assuming zero potential associated with the rotation of the methyl groups, neglecting nuclear spin, and using 972 for the symmetry number, is then

$$S_{T,R} = 27.45011 \log_{10} T - 4.57504 \log_{10} P_{\text{atm.}} + 6.05751 \qquad (10)$$

The vibrational entropy has been calculated by the equation

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(16) To seal off the bulb a stopcock leading to it was closed before cooling in liquid air and sealing off at a constriction.

(17) T_c and P_c were ascertained as follows. An inspection of the data in the "I. C. T." reveals that for isomers of a given class P_c and T_c/T_b are respectively about the same (where T_b is the normal boiling point); *e. g.*, for *n*-pentane P_c = 33.0; T_c/T_b = 1.521, while for isopentane P_c = 32.8, and T_c/T_b = 1.529. For *n*-butane and isobutane P_c = 35.5, 37; T_c/T_b = 1.558, 1.546. With some confidence therefore we take P_c and T_c/T_b for neopentane the same as for isopentane.

$$S_{\text{vib.}} = R \sum x_1/(e^{x_1} - 1) - \ln (1 - e^{-x_1}) \; (x_i = hc\tilde{\nu}_1/kT) \quad (11)$$

using the Raman frequencies determined by Rank and Bordner.[18] These are, respectively, 335 (2), 414 (3), 733 (1), 925 (3), 1252 (4), and 1455 (8) cm.$^{-1}$, where the figures in parentheses give the multiplicities. For the first four frequencies which are due to the carbon skeleton this assignment is that of Rank and Bordner and is based on analogy with the Raman spectrum of carbon tetrachloride. The two higher frequencies, as Rank and Bordner point out, undoubtedly are due to deformation of the methyl groups, but they hesitate to estimate the multiplicity. Two similar frequencies appear in methyl chloride, namely, 1355 (1) and 1460 (2).[19] It seems justifiable to take four times these multiplicities in the case of tetramethylmethane where there are four methyl groups. The effect of the higher frequencies is negligible. In the calculation the constants R = 1.9869 cal.$_{15}$/deg./mole, hc/k = 1.4325 cm. deg., were used. A comparison of the calorimetric and spectroscopic values of the entropy is given in Table VII.

TABLE VII

COMPARISON OF CALORIMETRIC AND "SPECTROSCOPIC" ENTROPIES OF TETRAMETHYLMETHANE AT ONE ATMOSPHERE

	Temperature, °K.	282.61 E. u./mole	298.16 E. u./mole
I	Translational and rotational	73.34	73.98
II	Vibrational (carbon skeleton)	5.38	5.89
III	Vibrational (other modes)	0.17	0.25
IV	Absolute	95.42	96.65
V	Total (less nuclear spin)	78.89	80.12
VI	Calorimetric corrected to ideal gas state	71.71	
VII	Discrepancy	7.18	
		($5\,R \ln 2 = 6.89$)	

Discussion.—The spectroscopic entropy exceeds that calculated from the calorimetric data by 5 R ln 2 within experimental error. The chief experimental errors lie in the heat of vaporization and in the extrapolation. That due to the former could hardly exceed 0.2 e. u. Any serious error in the extrapolation (on the basis of the actual crystal) is unlikely as the results fit a Debye function, calculated for six degrees of freedom, within experimental error.

The specific entropy of the impurity (probably isobutylene, $S_{298.1,\,1\text{ atm.}}$ = 67.3 e. u. per mole)[20] would be sufficiently similar so that the error on this account should be less than 0.1 e. u.; the entropy of mixing has already been eliminated without appreciable error as evident from its magnitude.

In the absence of any other calorimetric data on tetramethylmethane which might serve as an over-all check, we have made several isolated heat capacity measurements on methyl alcohol between 90°K. and room temperature, and the results have always been in agreement with those of Kelley[21] within the estimated accuracy of the respective observers.

An examination of the assignment of the four Raman frequencies due to the carbon skeleton also furnishes no obvious method of eliminating or materially reducing the discrepancy. Of the single frequency there is little doubt. Indeed this is true of the two highest pentatomic frequencies, of which the lower is a singlet and the higher a triplet, in the case of both methane and carbon tetrachloride. Inversion of the multiplicities of the two lower frequencies would raise the entropy calculated by 0.33 e. u.

If the above agreement of the discrepancy with 5 R ln 2 is not fortuitous, it might be taken to indicate 2^5 possible arrangements in the crystal such as have been proposed by Giauque to explain discrepancies of a similar nature in the case of carbon monoxide,[22,23] and nitrous oxide;[24,25] and by Pauling for water,[26,27] although the possibility of rotation of the methyl groups in certain of the symmetry varieties must not be overlooked. A situation similar to the latter for the case of hydrogen has been discussed by Giauque and Johnston.[28,29]

In this connection it is to be noted that for methane the calorimetric and spectroscopic entropies are in agreement,[30] but there is a peak in the heat capacity curve at 20.4°K.[31]

The entropy corresponding to the area between the peak and the normal heat capacity curve is 1.78 e. u. This is close to the sum (1.63 e. u.) of the entropy of mixing of the degenerate lowest

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(18) Rank and Bordner, *J. Chem. Phys.*, **3**, 248 (1935).

(19) For discussion and references see Vold, THIS JOURNAL, **57**, 1192 (1935).

(20) Parks and Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., New York, 1932, p. 81.

(21) Kelley, THIS JOURNAL, **51**, 180 (1929).

(22) Clusius, *Z. physik. Chem.*, **B6**, 135 (1929).

(23) Clayton and Giauque, THIS JOURNAL, **54**, 2610 (1932).

(24) Clusius, *Z. Elektrochem.*, **40**, 98 (1935).

(25) Giauque and Blue, THIS JOURNAL, **57**, 991 (1935).

(26) Pauling, *ibid.*, **57**, 2680 (1935).

(27) Giauque and Stout, *ibid.*, **58**, 1144 (1936).

(28) Giauque and Johnston, *ibid.*, **50**, 3221 (1928).

(29) Giauque, *ibid.*, **52**, 4816 (1930).

(30) Giauque, Blue and Overstreet, *Phys. Rev.*, **38**, 197 (1932).

(31) (a) Clusius, *Z. physik. Chem.*, **B3**, 65 (1929); (b) Clusius and Perlick, *ibid.*, **B24**, 313 (1934).

rotational states of the triplet ($9/16\ R \ln 3 = 1.23$ e. u.) and the corresponding quantity for the quintet variety ($2/16\ R \ln 5 = 0.40$ e. u.) assuming the high temperature equilibrium mixture. It therefore seems probable that rotational states are present in methane down to this temperature and there rotation practically ceases. The energy differences between the orientations of minimum potential energy are then evidently sufficiently large compared with kT to cause a unique arrangement of all but a small fraction of the molecules.

It is likely that the abnormal heat capacity rise prior to the "transition" of tetramethylmethane is caused by rotation starting for at least one degree of freedom and perhaps not unreasonable that this is one of the angular coördinates for the carbon skeleton.

It would be of interest to investigate the heat capacity of methyl deuteride from 10 to 30°K. as the symmetry situation is changed and hence if the above interpretation for methane is correct it should present a peak of quite a different kind.

Data on the heat capacity of ethane[32] below 67°K. would make possible a third law comparison which might throw light on the tetramethylmethane discrepancy.

The apparatus for the investigation of both of these compounds down to 10°K. is now practically complete. It is also planned in the near future to investigate tetramethylmethane, and, if necessary, ethane, down to 1°K.

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Summary

1. The heat capacities of tetramethylmethane have been determined from 13°K. to the boiling point.

2. The vapor pressure of liquid tetramethylmethane has been determined from the melting point to the boiling point, and an equation derived to represent the data. An equation for the vapor pressure below the freezing point is given but not considered significant.

3. The melting point of tetramethylmethane is 256.53°K. (−16.63°C.) and the boiling point 282.61°K. (9.45°C.). There is an energy absorption which is perhaps isothermal at 140.02°K. (−133.14°C.) but which is preceded by an abnormal rise in the heat capacity.

4. The molal entropy of the ideal gas at the boiling point, calculated from the experimental data, is 71.71 ± 0.3 e. u. This value is, within experimental error, $5\ R \ln 2$ lower than the corresponding value of 78.89 e. u. calculated from the Raman spectrum and moments of inertia.

5. The "spectroscopic" entropy, calculated from the Raman spectrum and moments of inertia, is 80.12 e. u. per mole at 298.16°K. and one atmosphere neglecting nuclear spin.

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[32] For data above 67°K. see Wiebe, Hubbard and Brevoort, THIS JOURNAL, 52, 611 (1930).