tions given to us by Professor Hugh M. Huffman. We also wish to express our thanks to Mr. Meyer Test, an NYA assistant, and to Dr. Robert Ruehrwein for constructing the resistance thermometers. The liquid hydrogen necessary in the measurements was kindly furnished by Professor A. Goetz of the Cryogenic Laboratory at this Institute.

Summary

A precision adiabatic low temperature calorimeter is described which is comparatively simple to construct and operate, and which requires only two liters of liquid hydrogen for a complete series of heat capacity measurements in the range 14–90°K. A calorimeter for vapor pressure and heats of vaporization measurements is also described.

The calibration of a set of four platinum resistance thermometers over the range 14°K. to 200°C. is described.

Pasadena, California Received June 23, 1941

[Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, No. 832]

The Heat Capacity, Entropy, and Heats of Transition, Fusion, and Vaporization of Dimethylacetylene. Free Rotation in the Dimethylacetylene Molecule

By Don M. Yost, Darrell W. Osborne, and Clifford S. Garner[1]

Introduction

As a result of the work of Kemp and Pitzer,[2] the existence of a barrier restricting the rotation of the methyl groups in ethane and similar molecules is now generally accepted. In ethane the barrier amounts to about 3000 cal./mole. It was the purpose of the research described in this paper to determine the extent of any barrier restricting the rotation of the methyl groups in dimethylacetylene, $H_3C—C\equiv C—CH_3$. If the barrier in ethane is due to interactions of the methyl groups, one would expect that the increased separation of the methyl groups in dimethylacetylene would lead to a small barrier. On the other hand, if the barrier is due to double-bond character of the C–C bond, then one might expect to find a large restricting potential, because the C—C bond distance in dimethylacetylene,[3] as in methylacetylene,[3,4] is 0.07 Å. shorter than the normal value; such a shortening is usually interpreted as due to considerable double bond character. Comparison of the entropy from our thermal data extending to low temperatures, a preliminary value for which has already been published,[5] with that from molecular data indicates, as is shown below, that the methyl groups in dimethylacetylene are subject to little or no restriction in their rotation.

Dimethylacetylene is of further interest because of an anomaly in the heat capacity of the solid at about 154°K.

Experimental

Preparation of the Dimethylacetylene Sample.—Dimethylacetylene was prepared by Mr. Thurston Skei by slowly adding 2,3-dibromobutane to a solution of potassium hydroxide in diethylene glycol heated to 180°C. The crude product was passed through a cuprous chloride-50% ethanolamine solution to remove ethylacetylene, and after being dried over sodium it was twice fractionated in a three-foot column packed with glass helices by Mr. Russell Doescher. The middle fraction was distilled *in vacuo* through phosphorus pentoxide into the weighing bulb and then into the calorimeter.

Heat Capacity Measurements.—The heat capacity of dimethylacetylene was determined with the adiabatic calorimeter (Gold-plated Copper Calorimeter I, and strain-free platinum resistance thermometer CT-26) described elsewhere.[6]

The data of Heisig and Davis[7] on the density of the liquid and on the vapor pressures of the liquid and solid were used to correct for vaporization into the gas space, which was about 60 cc. or about half the volume of the calorimeter. The volume of the solid was estimated. The correction amounted to approximately 0.05% at 210°K. and 1.1% at 285°K.

A small pressure of helium was present in the calorimeter to improve thermal conductivity at low temperatures, and a somewhat higher pressure was used to prevent diffusion of dimethylacetylene to cold spots in the 1-mm. monel metal filling tube when the vapor pressure became appreciable.

The results of the heat capacity measurements are presented in Table I and in Fig. 1. They are

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[1] This work was performed while C. S. Garner and D. W. Osborne were A. A. Noyes Fellows in Chemistry.

[2] J. D. Kemp and K. S. Pitzer, This Journal, **59**, 276 (1937).

[3] L. Pauling, H. D. Springall and K. J. Palmer, *ibid.*, **61**, 927 (1939).

[4] G. Herzberg, F. Patat and H. Verleger, *J. Phys. Chem.*, **41**, 123 (1937); R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 599 (1937).

[5] D. W. Osborne, C. S. Garner and Don M. Yost, *J. Chem. Phys.*, **8** 131 (1940).

[6] Yost, Garner, Osborne, Rubin and Russell, This Journal, **63**, 3488 (1941).

[7] G. B. Heisig and H. M. Davis, *ibid.*, **57**, 339 (1935).

TABLE I

THE MOLAL HEAT CAPACITY OF DIMETHYLACETYLENE

0°C. = 273.16°K., molecular wt. = 54.089, 0.8671 mole in calorimeter.

T, °K.	C_p, cal./deg./mole	T, °K.	C_p, cal./deg./mole	T, °K.	ΔT, °K.	C_p, cal./deg./mole
Series 1		Series 3			Series 4	
15.15	0.791	86.95	14.27	129.31	4.780	18.67
17.26	1.094	92.37	14.94	134.20	4.992	19.18
19.40	1.459	97.54	15.50	139.29	5.191	19.72
21.67	1.890	102.49	16.06	144.57	5.365	20.81^b
24.11	2.409	107.66	16.59	149.41	4.323	32.28^b
26.47	2.926	113.04	17.13	153.24	3.329	70.11^b
29.18	3.562	118.24	17.64	158.30	6.801	26.26^b
32.79	4.409	123.64	18.10			
36.56	5.296	129.24	18.66		Series 5	
39.81	6.036					
42.82	6.708	Series 6		138.50	6.533	19.60
46.20	7.455			169.40	5.635	17.89
50.03	8.293	164.30	17.60	175.44	6.460	18.21
54.59	9.201	169.83	17.89			
		175.25	18.17		Series 9	
Series 2		180.58	18.42			
		185.83	18.75	142.98	1.871	20.10
14.70	0.735	191.01	19.02	144.83	1.842	20.53^b
16.96	1.042	196.12	19.28	147.48	3.450	27.17^b
19.08	1.398	202.06	19.64	150.83	3.247	29.47^b
21.03	1.760	209.07	20.05^a	153.83	2.752	87.88^b
23.05	2.170	216.22	20.56^a	156.82	3.226	29.43^b
25.20	2.647	223.47	21.24^a	159.53	2.209	17.59^b
27.41	3.147	230.70	23.07^a			
29.65	3.670	250.93	28.59		Series 10	
31.96	4.206	256.63	28.73			
34.37	4.787			201.58	6.933	19.59
37.66	5.551	Series 7		208.73	7.368	20.03^a
41.87	6.498			216.02	7.224	20.55^a
45.94	7.401	255.06	29.57	223.44	7.614	21.09^a
50.40	8.369	264.95	28.91	249.49	6.875	28.48
57.24	9.689	274.71	29.22	258.03	10.205	28.71
61.57	10.47	284.33	29.54	268.18	10.052	29.04
66.14	11.27			278.12	9.875	29.29
71.11	12.07					
76.40	12.90					
81.97	13.66					
87.80	14.40					

[a] Including premelting. [b] Anomalous.

expressed in the defined calorie equal to 4.1833 international joules. The temperature intervals not given may be estimated from the spacing of the mean temperature, since there were no gaps between runs in the same series. Values read from a smooth curve are given in Table II; heat capacities for temperatures below the melting point were extrapolated from temperatures where there was no premelting. The deviation from the curve was less than 0.1% for most of the data, but the probable accuracy is about 1% at 15°K. and is about 0.2% above 25°K.

Between 145 and 160°K. the apparent heat capacity of the solid was abnormally high, and equilibrium was so difficult to attain that the heat capacities given may be far from the true values. Several series of runs were made in this region, some mainly to get the total heat input (series 5 and 8), and others to get the shape of the curve as well. Values obtained for the total heat input between 142 and 162°K. were quite reproducible and were 666.0, 666.5, 666.6 and 665.0 cal./mole from series 4, 5, 8, and 9, respectively. The heat capacity curve was not reproducible, but fortunately the region of high energy absorption was sufficiently narrow to permit accurate calculation of the entropy. A typical cooling curve, which was obtained by very slowly cooling the sample in the calorimeter, is shown in Fig. 2; it shows a break at 148°K. as well as a maximum at 153.8°K.

TABLE II

THE MOLAL HEAT CAPACITY OF DIMETHYLACETYLENE AT ROUNDED TEMPERATURES

0°C. = 273.16°K., molecular wt. = 54.089

T, °K.	C_p, cal./deg./mole	T, °K.	C_p, cal./deg./mole
15	0.772	110	16.83
20	1.567	120	17.79
25	2.603	130	18.74
30	3.750	140	19.79
35	4.932	150	Anomalous
40	6.079	160	17.37
45	7.190	180	18.43
50	8.289	200	19.49
55	9.277	220	20.55
60	10.18	240	21.60
70	11.91	240.93	M. p.
80	13.39	250	28.49
90	14.65	270	29.08
100	15.78	290	29.67

An X-ray study of the material in the anomalous region was made by Dr. Lindsay Helmholz, but no definite decision regarding the nature of the transition could be made from the results.

The Melting Point and Heat of Fusion.—Equilibrium temperatures with various amounts melted are shown in Table III together with the temperatures calculated assuming that Raoult's law holds, that there are no solid solutions, that the melting point is 240.93°K. (−32.23°C.), and that the proportion of impurity is 0.25 mole per cent. Values of the melting point reported in

TABLE III

MELTING POINT OF DIMETHYLACETYLENE

0°C. = 273.16°K.

Time	% melted	T obsd., °K.	T calcd.,[a] °K.
2:13 p.m.	Heated into m. p.		
3:30	29.9	240.497	240.49
4:30	49.8	240.647	240.67
5:40	95.4	240.799	240.79

M. p. this sample = 240.80 ± 0.05°K.
M. p. pure compound = 240.93 ± 0.05°K.

[a] Assuming mole per cent. impurity = 0.25.

the literature are −32.5 to −32.8°C.[7] and −24.0°C.[8]

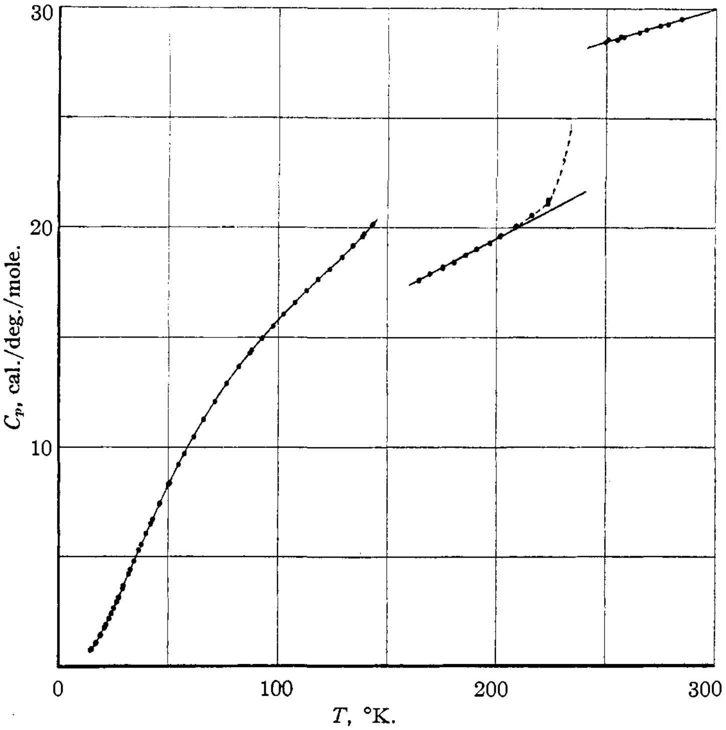

Fig. 1.—The molal heat capacity of dimethylacetylene, $H_3C—C≡C—CH_3$.

Table IV presents the results of measurements on the heat of fusion. The procedure was the same as for the heat capacities, the runs starting below the melting point and ending above; the heating period was seventy-five to eighty-five minutes. The heat capacities of the solid used in the calculation were corrected for premelting. The difference between the heat input in the heat capacity runs immediately preceding each heat of fusion measurement (series 6 and 10, respectively) and that calculated from the extrapolated values of the heat capacity is tabulated as premelting and included in the heat of fusion. Any error in the heat capacity of the solid below the melting point introduced by this extrapolation is compensated for by an error in the heat of fusion, and makes little difference in the entropy.

Table IV

The Molal Heat of Fusion of Dimethylacetylene

0°C. = 273.16°K., molecular wt. = 54.089, 0.8671 mole in calorimeter, m. p. = 240.93° K.

Temp. interval, °K.	Heat input, cal./mole	C_pdT, cal./mole	Pre-melting, cal./mole	ΔH fusion, cal./mole
227.182–248.061	2695.8	494.7	6.2	2207.3
227.248–246.107	2639.8	437.8	5.1	2207.1
			Mean	2207.2 ± 2

The Heat of Vaporization.—Measurements of the heat of vaporization, which are summarized in Table V, were made with the whole apparatus warmer than the calorimeter, and correction for heat interchange was made from frequent readings of the difference thermocouples, and from drift measurements before and after each run. These readings were also used to determine the mean temperature of the calorimeter exterior during the vaporization, which was taken to be the temperature of the gas leaving the calorimeter. Constant pressure was maintained by having the vapor bubble through a small mercury trap into a receiver immersed in liquid air and connected to a 20-liter bulb filled with dry nitrogen. The heating period was thirty-three minutes for each run.

The Entropy of Dimethylacetylene.—The calculation of the entropy from our calorimetric data is summarized in Table VI. The extrapolation below 14.7°K. was made with a Debye function with three degrees of freedom and $\theta = 123$; this function fits the points up to 20°K. to 3% or better.

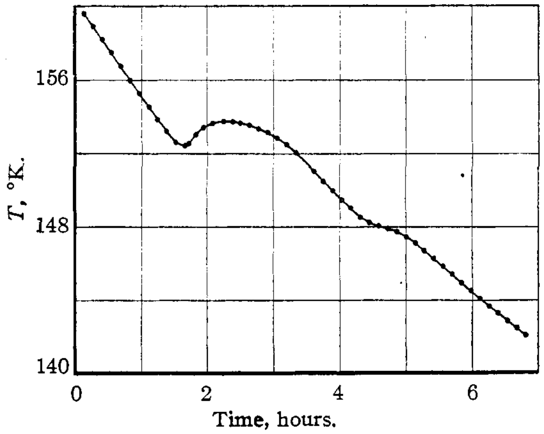

Fig. 2.—Cooling curve for dimethylacetylene.

The entropy change, between 142.0° and 162.0°K., was evaluated by summing the energy input divided by the average temperature for two uninterrupted series of runs in the range in question; in series 4 and 9 the entropy changes cal-

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(8) F. R. Morehouse and O. Maass, *Can. J. Res.*, **11**, 637 (1934).

TABLE V

THE MOLAL HEAT OF VAPORIZATION OF DIMETHYLACETYLENE AT 291.00°K. AND 536 MM.

0°C. = 273.16°K., molecular wt. = 54.089

Moles vaporized	ΔH vap., cal./mole
0.07310	6434
.07209	6447
.07042	6438
.08068	6442
	Mean 6440 ± 6

culated in this way are 4.375 and 4.373 cal./deg.-mole, respectively. This procedure for calculating the entropy change over the region of anomalous heat capacity is possible only if an adiabatic calorimeter is used. Essentially the same value, 4.369 cal./deg./mole, may be obtained by assuming the existence of an isothermal transition at 153.8°K., the temperature of the cooling curve maximum, and extrapolating the heat capacity curve from both sides to this temperature.

The correction for gas imperfection was made on the basis of the modified Berthelot equation of state, using as critical constants 489°K.[8] and 41 atm., the latter being obtained by extrapolating the vapor pressure[7] to the critical temperature.

TABLE VI

THE MOLAL ENTROPY OF DIMETHYLACETYLENE FROM CALORIMETRIC DATA

0°C. = 273.16°K., molecular wt. = 54.089.

	ΔS, cal. deg.$^{-1}$/mole^{-1}
0–14.70°K., Debye extrapolation	0.258
14.70–142.0°K., graphical	18.929
142.0–162.0°K., $\Sigma Q/\bar{T}$	4.374
162.0–240.93°K., graphical	7.711
Fusion (2207.2/240.93)	9.161
240.93–291.00°K., graphical	5.464
Vaporization (6440/291.00)	22.131
Entropy of actual gas, 291.00°K., 536 mm.	68.03 ± 0.15
Correction for gas imperfection[a]	0.14
Compression to 1 atm.	− .69
Entropy of ideal gas, 291.00°K., 1 atm.	67.48 ± 0.2
291.00–298.16°K. (molecular data)	0.45
Entropy of ideal gas, 298.16°K., 1 atm.	67.93 ± 0.2
Entropy of liquid, 298.16°K.	46.63 ± .1

[a] $S_{\text{ideal}} - S_{\text{actual}} = 27RT_c^3P/32T^3P_c$, T_c = 489°K.,[8] P_c = 41 atm. estimated.

TABLE VII

THE STANDARD MOLAL ENTROPY OF GASEOUS DIMETHYLACETYLENE AT 291.00°K. FROM MOLECULAR DATA

0°C. = 273.16°K., molecular wt. = 54.089

	S, cal./deg./mole
Translational	37.76
Vibrational	6.71
Rotational (free)	22.61
Total with free rotation	67.08
Total with 1000 cal./mole barrier	66.79
Calorimetric	67.48

It should be pointed out here that since the 0.25 mole % impurity is probably 1-butyne or 1,2-butadiene, its effect on the calorimetric entropy will amount at most to 0.05 cal./deg./mole. This is true because the entropies of these possible impurities at room temperature are nearly the same as that for dimethylacetylene, and furthermore the entropy of mixing has been taken into account by correcting for premelting.

Table VII shows the various contributions to the entropy calculated from molecular data. The vibrations were assumed to be harmonic and the frequencies and assignments were those given by Crawford,[9] namely: 213 (2), 371 (2), 725 (1), 1029 (2), 1050 (2), 1126 (1), 1380 (2), 1448 (2), 1468 (2), 2270 (1), 2916 (1), 2966 (2) and 2976 (3) cm.$^{-1}$. The moments of inertia were computed using tetrahedral angles for the methyl groups and the following interatomic distances: C—H, 1.09 Å.; C—C, 1.47 Å.[3]; C≡C, 1.20 Å.[3] The calculation for a barrier of 1000 cal./mole was made with Pitzer's tables.[10]

The natural constants used were those recommended by Professor R. T. Birge in a private communication, except for changes required by our conventional values of the ice point and calorie. The important values are: R = 1.9871 cal./deg.$^{-1}$/mole^{-1}, $k = 1.3805 \times 10^{-16}$ erg/deg.$^{-1}$, $N = 6.023 \times 10^{23}$, $h = 6.624 \times 10^{-27}$ erg sec.

The deviation of the calorimetric value for the entropy from the value calculated using molecular data and free rotation is 0.40 cal./deg./mole, and is in such a direction that it will be increased by the assumption of any barrier hindering the rotation of the methyl groups. It is highly improbable that the molecular model chosen could be so inaccurate as to permit a barrier higher than 500 cal./mole. This same conclusion has been reached by Crawford and Rice[11] using the data of Kistiakowsky and Rice[12] on the heat capacity of gaseous dimethylacetylene, and Crawford's vibrational analysis.[9]

We wish to thank Professor Alexander Goetz for supplying us with liquid hydrogen. Assistance from the Works Project Administration,

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(9) B. L. Crawford, Jr., *J. Chem. Phys.*, **7**, 555 (1939).

(10) K. S. Pitzer, *ibid.*, **6**, 470 (1937).

(11) B. L. Crawford, Jr., and W. W. Rice, *ibid.*, **7**, 437 (1939).

(12) G. B. Kistiakowsky and W. W. Rice, *ibid.*, **8**, 618 (1940).

Project No. 165-1-08-72 (Unit C-2), in preparing some of the graphs and tables is gratefully acknowledged.

Summary

The heat capacity of dimethylacetylene has been measured from 14°K. to room temperature. There is an anomaly in the heat capacity near 154°K.

The melting point of dimethylacetylene is 240.93 ± 0.05°K. (0°C. = 273.16°K.), the heat of fusion is 2207 ± 2 cal./mole, and the heat of vaporization is 6440 ± 6 cal./mole at 291.00°K. and 536 mm.

The entropy of the ideal gas from the calorimetric data is 67.48 ± 0.20 cal./deg./mole and 67.93 cal./deg./mole at 1 atm., 291.00°K. and 298.16°K., respectively. That of the liquid at 298.16°K. is 46.63 ± 0.1 cal./deg./mole.

Comparison of the statistical and calorimetric entropies indicates that the barrier restricting rotation of the methyl groups is not more than 500 cal./mole.

PASADENA, CALIFORNIA RECEIVED JUNE 23, 1941

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 837]

The Heat Capacity, Entropy, Heats of Fusion and Vaporization and Vapor Pressure of Fluorotrichloromethane

BY DARRELL W. OSBORNE, CLIFFORD S. GARNER, RUSSELL N. DOESCHER AND DON M. YOST

Introduction

Because of the interesting properties of the fluorochloromethanes and their increasing use as refrigerants, they have received attention[1] with the view of determining their thermodynamic properties. These investigations, however, have not been of such a character as to permit the calculation of the entropies of these substances.

This paper presents the results of a low temperature calorimetric investigation of fluorotrichloromethane, CCl_3F, together with a comparison of the calorimetric entropy of this substance with that calculated from spectroscopic and electron-diffraction data. Since in the fluorotrichloromethane molecule there is no possibility of hindered internal rotation of the type found in ethane and similar molecules or little probability of randomness of molecular orientation in the crystals of the solid, the excellent agreement found in this comparison is an indication of the reliability of measurements[2] made with the low temperature calorimeters recently constructed in this Laboratory.

Experimental

Purification of the Fluorotrichloromethane Sample.—Commercial fluorotrichloromethane, manufactured by Kinetic Chemicals, Inc., Wilmington, Delaware, was purified by fractionation at atmospheric pressure in a 70 cm. column packed with glass helices. It was fractionated twice (reflux ratio of about 15 to 1), and only the middle cut of the last fractionation was utilized further. This portion was distilled through phosphorus pentoxide into a glass vessel in which it was repeatedly frozen and melted under high vacuum. Some of this purified sample was then distilled into an evacuated, weighed sample bulb, from which it was condensed into the evacuated calorimeter.

An impurity of 0.050 mole per cent. in the sample was estimated from measurements on its melting point.

Heat Capacity Measurements.—The heat capacities were determined with the adiabatic calorimeter (gold-plated copper calorimeter I) and strain-free platinum resistance thermometer CT-26 described elsewhere.[3] Our vapor pressure measurements and the data of Benning and McHarness[1] on the density of the liquid were used to correct for vaporization into the gas space. This correction amounted at most to 0.3%.

The results of these measurements are given in Table I and are shown graphically in Fig. 1. They are expressed in defined calories (1 cal. = 4.1833 international joules). In Table II are presented heat capacities at rounded temperatures read from a smooth curve through the experimental points; those given for temperatures just below the melting point have been corrected for premelting, using Raoult's law and the mole fraction of liquid-soluble, solid-insoluble impurity found in the melting point determination. The probable accuracy of the heat capacities is about 0.5% at 15°K. due to decreased sensitivity of the

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[1] A. Benning and R. McHarness, *Ind. Eng. Chem.*, **31**, 912 (1939); *ibid.*, **32**, 497, 698 and 814 (1940); A. Benning, R. McHarness, W. Markwood and W. Smith, *ibid.*, **32**, 976 (1940).

[2] (a) D. Osborne, C. Garner and D. Yost, *J. Chem. Phys.*, **8**, 131 (1940); (b) D. Osborne, R. Doescher and D. Yost, *ibid.*, **8**, 506 (1940); (c) D. Yost, D. Osborne and C. Garner, THIS JOURNAL, **63**, 3492 (1941).

[3] D. Yost, C. Garner, D. Osborne, T. Rubin and H. Russell, THIS JOURNAL, **63**, 3488 (1941).