

phere and 279.12°K. is 60.16 ± 0.10 cal./deg./mole for the ideal vapor. Comparison of this value with that calculated from molecular data

leads to a barrier of 1460 ± 270 cal./mole restricting the rotation of the methyl group.

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

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The nature of the interactions between methyl or methyl-like groups in molecules to which the groups are attached by single bonds is not yet well understood. The dimethyl sulfide, $(\text{CH}_3)_2\text{S}$, molecule presents an example in which the methyl groups are attached by single bonds to a sulfur and not to a carbon atom, the latter bonds having been present in most of the substances so far studied. A careful study of dimethyl sulfide was undertaken with the hope that a knowledge of the barrier potential restricting free rotation of the methyl groups would aid eventually in throwing light on the nature of the interactions involved. This paper presents the results of a low temperature study of the substance, leading to a barrier of 2000 cal./mole restricting the rotation of each methyl group.

Purification of the Sample.—Dimethyl sulfide obtained from Eastman Kodak Co. was refluxed for several hours with copper and sodium to remove mercaptans and water, and it was twice fractionated in air through a total reflux column packed with glass helices. The middle fraction was then allowed to stand *in vacuo* for a few hours in contact with sodium wire. After being freed from non-condensable gases, a middle portion was distilled into an evacuated weighing bulb and then into the calorimeter after being weighed. The stopcocks were lubricated with Apiezon L grease. It was observed that there is a slow reaction between sodium and dimethyl sulfide at room temperature, but no appreciable amount of impurity was introduced, since the m. p. determination and the heat capacity just below the m. p. indicated an impurity of only 0.007 mole % in the final sample.

Heat Capacity Measurements.—The adiabatic calorimeter and strain-free platinum resistance thermometer CT-26 previously described¹ were

used for the heat capacity measurements. The results, expressed in terms of the defined calorie of 4.1833 international joules, are presented in Table I and Fig. 1. An estimate of the temperature intervals may be obtained from the spacing of the points. Above 30°K. the accuracy is about 0.1%, but at 15°K. it may be only 1%. A small correction was made for vaporization, using the data of Berthoud and Brum² for the density of the liquid.

TABLE I

MOLAL HEAT CAPACITY OF DIMETHYL SULFIDE
0°C. = 273.16°K., molecular weight = 62.13, 1.4432 moles in calorimeter.

T, °K.	C_p , cal. deg. ⁻¹ mole ⁻¹	T, °K.	C_p , cal. deg. ⁻¹ mole ⁻¹
Series III			
14.08	0.881	113.71	15.07
15.74	1.125	119.37	15.53
17.55	1.430	124.85	15.98
19.29	1.743	130.54	16.45
21.08	2.099	136.28	16.90
22.90	2.455	141.99	17.36
24.87	2.853	147.92	17.83
27.34	3.361	154.03	18.34
30.33	3.972	160.00	18.80
33.66	4.640	165.82	19.31 ^a
37.20	5.317	170.56	19.91 ^a
40.90	6.005	174.855	M. p.
44.97	6.736	181.30	26.89
49.67	7.555	187.94	26.87
54.77	8.381	Series II	
60.01	9.145	181.21	26.90
65.38	9.917	190.43	26.84
70.68	10.61	200.13	26.84
76.07	11.32	209.74	26.86
81.86	11.99	219.28	26.89
88.01	12.65	228.74	26.97
94.16	13.29	238.12	27.06
Series I			
96.81	13.54	247.41	27.18
102.22	14.03	257.06	27.34
107.86	14.57	267.06	27.52
		276.94	27.72
		286.69	27.95

^a Including premelting.

(1) Don M. Yost, C. S. Garner, D. W. Osborne, T. R. Rubin and H. Russell, *THIS JOURNAL*, **63**, 3488 (1941).

(2) A. Berthoud and R. Brum, *J. chim. phys.*, **21**, 143-160 (1924).

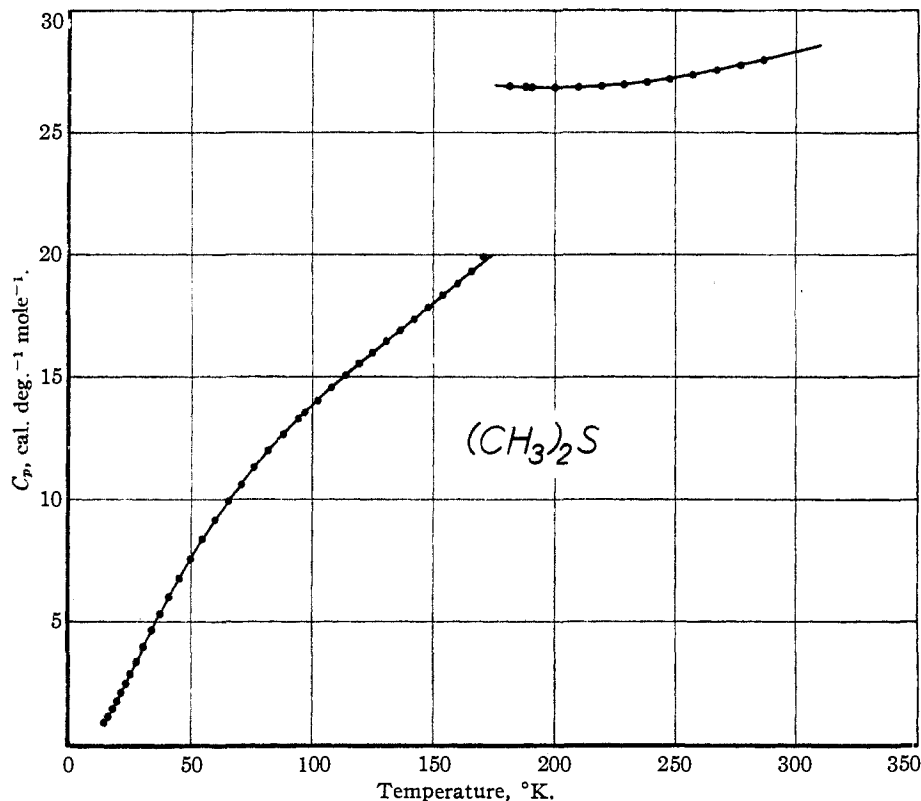


Fig. 1.—Molal heat capacity of dimethyl sulfide.

In Table II are given values of the heat capacity at rounded temperatures, read from a smooth graph of the data. The heat capacity just below the m. p. was extrapolated from temperatures where the premelting was inappreciable.

TABLE II
MOLAL HEAT CAPACITY OF DIMETHYL SULFIDE AT
ROUNDED TEMPERATURES
0°C. = 273.16°K., mol. wt. = 62.13

T , °K.	C_p , cal. deg. ⁻¹ mole ⁻¹	T , °K.	C_p , cal. deg. ⁻¹ mole ⁻¹
15	1.012	140	17.20
20	1.885	150	18.00
25	2.879	160	18.81
30	3.904	170	19.62
35	4.900	174.855	M. p.
40	5.839	180	26.91
45	6.746	190	26.86
50	7.610	200	26.84
55	8.416	210	26.86
60	9.153	220	26.90
65	9.855	230	26.98
70	10.52	240	27.08
80	11.78	250	27.22
90	12.86	260	27.39
100	13.84	270	27.58
110	14.75	280	27.79
120	15.58	290	28.03
130	16.39	300	28.28

The Melting Point and Heat of Fusion.—Table III contains the results of the melting point determination. The observed equilibrium temperatures are in agreement with temperatures calculated from Raoult's law, m. p. 174.855°K., for the pure compound, and 0.0066 mole % of solid-insoluble, liquid-soluble impurity. This same proportion of impurity was found from premelting heat capacity measurements.

TABLE III
MELTING POINT OF DIMETHYL SULFIDE
0°C. = 273.16°K.

Time, min.	% melted	T obs., °K.	T calcd., ^a °K.
0		Heated into m. p.	
33	4.4	174.807	174.807
115	42.0	174.849	174.850
232	79.6	174.851	174.852
355	98.4	174.854	174.853

M. p. pure compound = 174.855 ± 0.02°K.

^a Assuming mole % impurity = 0.0066.

Since the only other value for the m. p. of this compound which could be found in the literature, -83.2°,³ differs considerably from that found in this research, the m. p. was also determined in

(3) G. Carrara and A. Coppadoro, *Gazz. chim. ital.*, **33**, I, 329 (1903).

another apparatus with an independently calibrated thermocouple and was found to be roughly 175°K. (−98°), in substantial agreement with the value shown in the table.

The heat of fusion was measured in the same manner as the heat capacity; the results are given in Table IV.

TABLE IV

MOLAL HEAT OF FUSION OF DIMETHYL SULFIDE

0°C. = 273.16°K., mol. wt. = 62.13, 1.4432 moles in calorimeter, m. p. = 174.855°K.

Temperature interval, °K.	Heat input, cal./mole	$C_p dT$, cal./mole	Premelting, cal./mole	ΔH fusion, cal./mole
172.422–177.867	2036.6	129.6	1.1	1908.1
170.552–177.975	2077.5	169.4	0.6	1908.7

Mean 1908.4 ± 1

The Vapor Pressure and Heat of Vaporization.—The adiabatic calorimeter was used for measuring the vapor pressure and heat of vaporization, but the whole apparatus was maintained warmer than the calorimeter itself.

Vapor pressure readings were made with a calibrated Hensen cathetometer and an enclosed mercury-in-glass manometer of 18.65 mm. diameter. The accuracy was about 0.1 mm. Correction was made for the vapor column connecting calorimeter and manometer and for capillary depression by means of the data of Cawood and Patterson.⁴ The observations were reduced to mm. of Hg at standard gravity of 980.665 cm./sec.² and at 0°C. (international mm.). They are tabulated in Table V, together with an equation which represents them satisfactorily. The b. p. calculated from this equation is 310.49°K. (37.33°C.), in agreement with the b. p. observed during distillation of the sample.

TABLE V

VAPOR PRESSURE OF DIMETHYL SULFIDE

0°C. = 273.16°K., g at Pasadena = 979.57 cm./sec.²

T , °K.	p obs., int. mm. Hg	p obs. − p calcd., int. mm. Hg
250.603	52.46	+0.05
263.122	102.75	+ .03
273.246	168.29	+ .05
278.093	210.33	− .15
283.007	260.85	+ .11
288.288	326.37	− .11
293.237	398.84	+ .08

p calcd. from $\log_{10} p$ (mm.) = 16.51798 − 1876.370/ T − 3.04727 $\log_{10} T$.

Table VI gives the results of the direct measurements of the heat of vaporization. The method of collecting the sample and of maintain-

ing constant pressure was the same as that employed with dimethyl acetylene.⁵ Included in the same table is a value calculated from the v. p. equation given in Table V and the Berthelot equation of state, the critical constants used being 503.0°K. and 54.6 atm.² The agreement between the measured and calculated heats of vaporization affords justification for later use of the Berthelot equation in correcting the entropy for gas imperfection.

TABLE VI

MOLAL HEAT OF VAPORIZATION OF DIMETHYL SULFIDE AT 291.06°K. AND 365.5 MM.

0°C. = 273.16°K., mol. wt. = 62.13

Moles vaporized	Time, min.	ΔH vap., cal./mole
0.06787	33	6687
0.11373	40	6688
	Measured (mean)	6688 ± 7
	Calculated	6689

The Entropy of Dimethyl Sulfide.—The evaluation of the entropy is itemized in Table VII, which is self-explanatory.

TABLE VII

MOLAL ENTROPY OF DIMETHYL SULFIDE FROM CALORIMETRIC DATA

0°C. = 273.16°K., mol. wt. = 62.13

	ΔS , cal. deg. ^{−1} mole ^{−1}
0–15°K. Debye extrapolation	0.369
15–174.855°K. graphical	21.156
Fusion (1908.4/174.855)	10.914
174.855–291.06°K. graphical	13.825
Vaporization (6688/291.06)	22.978
Entropy of actual gas, 291.06°K., 265.5 mm.	69.24 ± 0.1
Correction for gas imperfection ^a	0.08
Compression to 1 atm.	−1.45
Entropy of ideal gas at 291.06°K., 1 atm.	67.87 ± 0.1
291.06–298.16°K. from molecular data	0.41

Entropy of ideal gas at 298.16°K., 1 atm. 68.28 ± 0.1

Entropy of liquid at 298.16°K. 46.94 ± 0.07

^a $S_{ideal} - S_{actual} = 27RT_c^2 P / 32T^2 P_c$, $T_c = 503$ °K., $P_c = 54.6$ atm.²

The Entropy from Molecular Data.—The Raman and infrared spectra of dimethyl sulfide have been carefully analysed by Thompson,⁶ who gives the following fundamental frequencies and, in parentheses, degeneracies: 285, 693, 742, 917, 1040, 1242, 1274, 1315, 1325, 1426, 1440 (2), 1460, 2800, 2832, 2850 (2), 2911 and 2980 cm.^{−1}. The vibrations were assumed to be harmonic. The

(5) D. M. Yost, D. W. Osborne and C. S. Garner, *THIS JOURNAL*, **63**, 3492 (1941).

(6) H. W. Thompson, *Trans. Faraday Soc.*, **37**, 38 (1941).

(4) Cawood and Patterson, *Trans. Faraday Soc.*, **29**, 514 (1933).

S-C distance has been determined by Brockway and Jenkins⁷ and more recently by Schomaker and Stevenson,⁸ the results of the latter authors agreeing completely with those of the former. Inasmuch as the electron diffraction method does not yield accurate values for the C-S-C bond angle and gives no information about the H-C distance, the reasonable value 105° has been assumed for the former and 1.09 Å. for the latter; the methyl groups have been assumed to have a tetrahedral structure. With these molecular constants, and the formulas developed by Kassel⁹ from the considerations of Eidinoff and Aston,¹⁰ the entropy calculation assuming free rotation was made. In order to evaluate the barrier, use was made of Crawford's¹¹ method for arriving at the reduced moments of inertia, which were used with Pitzer's¹² tables of $S_f - S$, the difference between the entropy for free and restricted rotation. Table VIII contains a summary of the entropy

TABLE VIII

COMPARISON OF ENTROPIES OF DIMETHYL SULFIDE FROM CALORIMETRIC AND FROM MOLECULAR DATA, AT 291.06°K. AND 1 ATM.

	S , cal./deg./mole
Translational	38.18
Vibrational	2.35
Rotational (free)	29.08
Total with free rotation	69.61
Calorimetric value	67.87
Difference	1.74
$2(S - S_f)$ for $V = 2000$ cal./mole, I_{red} , $= 4.81 \times 10^{-40}$	1.74

(7) L. O. Brockway and H. O. Jenkins, *THIS JOURNAL*, **58**, 2036 (1936).

(8) V. Schomaker and D. P. Stevenson, private communication.

(9) L. S. Kassel, *J. Chem. Phys.*, **4**, 276 (1936).

(10) M. L. Eidinoff and J. G. Aston, *J. Chem. Phys.*, **3**, 379 (1935).

(11) B. L. Crawford, *ibid.*, **8**, 273 (1940).

(12) K. Pitzer, *ibid.*, **5**, 469 (1937).

calculations just described. The values of the physical constants used were those given in a previous paper.¹³

It is evident that the best agreement between the calculated and experimental entropy is obtained with a barrier potential of about 2000 cal./mole for each methyl group. This barrier is smaller than that found for methyl ether,¹⁴ 3100 cal./mole, and is larger than that for methyl mercaptan,¹⁵ 1500 cal./mole. The relative values of these potentials are those to be expected, if the barrier arises mainly from the interaction of the electrons involved in the bonds to the hydrogen atoms.

Summary

The heat capacity of dimethyl sulfide has been determined over the range 13.3–292°K.

The melting point is $174.86 \pm 0.02^\circ\text{K}$., the heat of fusion is 1908.4 ± 1 cal./mole, the directly measured heat of vaporization is 6688 ± 7 cal./mole, and the vapor pressure may be represented by the equation $\log_{10} p_{\text{mm.}} = 16.51798 - (1876.370/T) - 3.04727 \log_{10} T$ over the range 250.6–290.2°K. ($0^\circ\text{C.} = 273.16^\circ\text{K.}$).

From the calorimetric data the standard entropy of the ideal gas is 67.87 ± 0.1 and 68.28 ± 0.1 cal./deg./mole at 291.06°K. and 298.16°K., respectively. The entropy of the liquid at 298.16°K. is 46.94 ± 0.07 cal./deg./mole.

Comparison of the experimental and statistical entropies of dimethyl sulfide leads to a barrier potential of 2000 cal./mole hindering the rotation of each methyl group.

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(13) H. Russell, R. Rundle and Don M. Yost, *THIS JOURNAL*, **63**, 2825 (1941).

(14) R. M. Kennedy, M. Sagenkahn and J. G. Aston, *ibid.*, **63**, 2267 (1941).

(15) H. Russell, D. W. Osborne and Don M. Yost, *ibid.*, **64**, 165 (1941).