

pared with that expected on the basis of published photochemical results; there appears to be an alternative two electron process for the

reactions of  $S_2O_8^{2-}$  and acetyl peroxide with  $I^-$ .

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## The Heat Capacity, Entropy, Heats of Fusion, Transition, and Vaporization and Vapor Pressures of Methyl Mercaptan

By HORACE RUSSELL, JR., DARRELL W. OSBORNE AND DON M. YOST

**Introduction.**—Methyl mercaptan,  $HSCH_3$ , represents an interesting and relatively simple case in which one may expect to find hindered internal rotation. The comparison between the accurately determined calorimetric entropy and the entropy calculated from structural and spectroscopic data should give a reliable value of the barrier, since the calculation may now be carried out quite exactly.<sup>1</sup> By analogy with methyl alcohol,<sup>2</sup> a transition in the solid should be found, the investigation of which should throw further light on the nature of the two substances. In the present paper there are presented the results of an investigation of the thermodynamic and structural properties of methyl mercaptan as deduced from a low temperature study of the substance.

**Purification of Methyl Mercaptan.**—The material used was an Eastman Kodak Company product which was purified by two careful fractionations in a closed, meter and a half, vacuum-jacketed column packed with glass helices. The final distillation was done at a reflux ratio of 30:1. Ninety-four grams was collected from an original sample of 200 g. The mercaptan was dried with phosphorus pentoxide before each of the distillations. The substance reacts slightly with moist phosphorus pentoxide to give a yellow, non-volatile product. The air-free sample was sealed in a weighed bulb with a fragile tip and weighed. It was then distilled into the calorimeter through a single stopcock lubricated with Apiezon L grease. The liquid-soluble, solid-insoluble impurity as determined from the premelting was 0.05 mole %.

**The Heat Capacities.**—All measurements except the heat of vaporization were made in an adiabatic calorimeter (gold-plated copper calorimeter I) and the temperatures were measured with the strain-free platinum resistance thermometer of laboratory designation CT-26. The heat of vaporization was measured in a non-adiabatic calorimeter specially designed for such measurements, using thermometer CT-4. The construction and operation of the apparatus and the calibration of the thermometers are described elsewhere.<sup>3</sup>

The defined calorie of 4.1833 international joules was used throughout, and the ice-point was taken as 273.16°K.

TABLE I

MOLAL HEAT CAPACITY OF METHYL MERCAPTAN  
0°C. = 273.16°K., molecular weight = 48.102, 1.9462 moles in calorimeter.

Run	T, °K.	$C_p$ , cal./deg./mole	Run	T, °K.	$C_p$ , cal./deg./mole
55	14.97	0.773	12	94.12	11.38
72	15.82	0.885	13	99.38	11.74
56	16.47	0.983	14	104.87	12.10
73	17.48	1.126	15	110.37	12.47
57	17.98	1.226	16	115.70	12.81
74	19.35	1.435	25	117.20	12.89
58	19.49	1.476	17	120.87	13.15
59	21.17	1.773	26	122.29	13.23
75	21.50	1.835	18	125.90	13.46
60	23.26	2.168	27	128.06	13.61
76	23.94	2.300	19	130.81	13.80
61	25.63	2.641	45	133.03	13.95
77	26.57	2.831	28	133.21	13.97
62	28.17	3.155	49	133.22	13.96
78	29.37	3.396		137.6	Transition
63	30.97	3.719	51	140.42	14.87 <sup>a</sup>
79	32.51	4.022	47	140.60	14.97 <sup>a</sup>
64	33.86	4.285	30	141.09	15.66 <sup>a</sup>
80	35.96	4.690	52	143.45	16.62 <sup>a</sup>
65	37.09	4.902	31	145.88	16.98 <sup>a</sup>
81	39.61	5.352	53	146.57	17.47 <sup>a</sup>
66	40.73	5.555		150.16	M. p.
82	43.61	6.038	85	154.16	21.27
67	44.40	6.170	33	155.62	21.27
83	48.08	6.763	86	160.50	21.17
68	48.30	6.798	34	162.07	21.12
69	52.64	7.435	87	166.80	21.07
84	53.04	7.486	88	174.47	20.97
35	56.72	7.948	89	184.11	20.87
70	57.46	8.038	90	194.31	20.80
36	61.86	8.548	91	204.51	20.75
71	62.53	8.625	92	214.63	20.71
37	67.00	9.106	93	224.68	20.70
38	72.15	9.600	94	234.63	20.73
39	77.34	10.09	95	244.48	20.81
40	82.58	10.51	96	254.23	20.88
41	87.89	10.93	97	263.89	21.00
11	88.84	10.99	98	271.06	21.13
42	93.26	11.33		279.12	B. p.

<sup>a</sup> Not corrected for premelting.

(1) K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **9**, 485 (1941).

(2) K. K. Kelley, *THIS JOURNAL*, **51**, 181 (1929).

(3) D. M. Yost, C. S. Garner, D. W. Osborne, T. R. Rubin and H. Russell, *ibid.*, **63**, 3488 (1941).

TABLE II  
MOLAL HEAT CAPACITY OF METHYL MERCAPTAN AT  
ROUNDED TEMPERATURES

T, °K.	$C_p$ , cal./deg./mole	T, °K.	$C_p$ , cal./deg./mole
15	0.777	140	14.54 <sup>a</sup>
20	1.565	150	16.58 <sup>a</sup>
25	2.515	150.16	M. p.
30	3.523	160	21.18
35	4.508	170	21.03
40	5.425	180	20.91
45	6.265	190	20.83
50	7.053	200	20.77
60	8.333	210	20.73
70	9.411	220	20.70
80	10.300	230	20.72
90	11.081	240	20.76
100	11.785	250	20.84
110	12.438	260	20.96
120	13.080	270	21.11
130	13.740	280	21.28
137.6	Transition		

<sup>a</sup> Corrected for premelting.

Corrections for vaporization were made using the observed vapor pressures and the density data of Ellis and Reid.<sup>4</sup>

Errors in the heat capacity vary with the temperature, being possibly 1% at 15°K. but decreasing rapidly so that above about 30°K. and below the transition at 137.6°K., the errors are only 0.1%. Between the transition and melting points, measurements were difficult due to the combination of a slow transition and premelting. Values of the heat capacity may be in error by several per cent. in that range. The total heat added, however, was accurately measured so that the uncertainty in the entropy is negligible. Error in the liquid heat capacities varies from 0.1 to 0.2% near the boiling point. The results of the measurements are presented in Tables I and II and in Fig. 1.

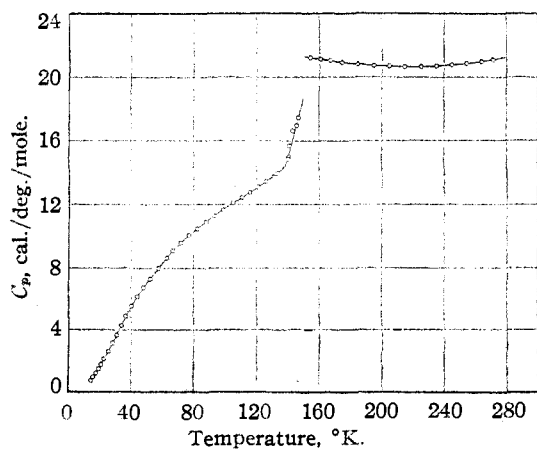


Fig. 1.—Molal heat capacity of methyl mercaptan.

**The Vapor Pressure and Melting Point.**—Vapor pressure measurements were made with a mercury manometer to be described.<sup>3</sup> Readings

(4) M. L. Ellis and E. Reid, *THIS JOURNAL*, **54**, 1674 (1932).

were made with a calibrated Henson cathetometer, and the results given in Table III are expressed in international mm. of mercury and are accurate to  $\pm 0.20$  mm.

TABLE III  
VAPOR PRESSURES OF METHYL MERCAPTAN  
0°C. = 273.16°K.

Temp., °K.	$p_{\text{obs.}}$ , Int. mm. of Hg	$p_{\text{calcd.}}^a$ , mm.	$p_{\text{calcd.}} - p_{\text{obs.}}$ , mm.
221.880	41.13	41.19	+0.06
249.288	201.46	201.44	- .02
263.686	399.30	399.34	+ .04
273.189	599.40	599.50	+ .10
279.137	760.64	760.57	- .07

<sup>a</sup>  $\log_{10} p_{\text{mm.}} = 18.27429 - (1769.05/T) - 3.70248 \log_{10} T$ .

The boiling point calculated from the equation in Table III is 279.12°K. (5.96°C.). Previous values found are 5.8° at 752 mm.,<sup>5</sup> 6° with no pressure specified,<sup>6</sup> and 7.6° at 760 mm.<sup>7</sup>

The results of the melting point determination are given in Table IV.

TABLE IV  
MELTING POINT OF METHYL MERCAPTAN  
0°C. = 273.16°K.

% melted	$T_{\text{obs.}}$ , °K.	$T_{\text{calcd.}}$ , °K. <sup>a</sup>
10.3	150.002	150.002
31.4	150.108	150.109
50.5	150.129	150.129
69.6	150.138	150.138
88.8	150.143	150.143

M. p. this sample = 150.14  $\pm$  0.02°K.

M. p. pure compound = 150.16  $\pm$  0.02°K. (-123.00°C.)

<sup>a</sup> Assuming 0.052 mole % impurity.

Previously reported values of the melting point are -121.0°<sup>8</sup> and -123.1°C.<sup>4</sup>

**The Heats of Transition and Fusion.**—A narrow transition region was found about 13° below the melting point. This region was investigated by heating into the anomalous region from a point about one degree below it and attempting to reach an equilibrium temperature. The results are shown in Table V; it is evident that equilibrium is not completely reached, in general, even after several hours, but it is also clear that the change in state takes place over a very small range if not at a single temperature. An adiabatic calorimeter with its negligible temperature drift is very

(5) P. Klason, *Ber.*, **20**, 3409 (1887). Klason remarks that small amounts of methyl sulfide raise the boiling point markedly.

(6) F. Arndt, E. Milde and G. Eckert, *ibid.*, **54**, 2238 (1921).

(7) A. Berthoud and R. Brum, *J. chim. phys.*, **21**, 143 (1924). The vapor pressure at 0°, however, is given as 595 mm., which agrees fairly well with the value found in this research.

(8) "International Critical Tables," Vol. I, 1928, p. 177.

valuable in studying such slow transitions. The total heat involved in the transition was found by heating through the region to a temperature at which equilibrium could be obtained readily (Table VI). At the upper temperature equilibrium was reached after forty to sixty minutes; the moderate slowness here was due mainly to premelting and possibly to some incompleteness of transition. Tables V and VI show that the transition occurs over a narrow temperature range and that it may well be isothermal at  $137.6 \pm 0.1^\circ\text{K}$ . The entropy calculation was made on the latter assumption, but any other reasonable method would give very closely the same result.

A similar transition has been found in methyl alcohol,<sup>2</sup> where it is accompanied by a change in the dielectric constant.<sup>9</sup> The transitions in each case are probably due to the setting in of rotation of the entire molecule in the crystal.

TABLE V

THE TRANSITION TEMPERATURE OF METHYL MERCAPTAN  
 $^\circ\text{C.} = 273.16^\circ\text{K.}$

Date	Per cent. high temp. form	Time after heating, hrs.:min.	Temp., $^\circ\text{K.}$
7/6/40	84.7	0:15	137.676
		0:30	.632
		1:00	.605
		1:30	.591
		2:00	.583
7/10/40	72.2	0:12	137.664
		0:25	.622
7/12/40	88.7	0:05	138.017
		0:15	137.864
		0:30	.805
		1:00	.756
		2:30	.716
		4:00	.699
		5:00	.692
		6:00	.685
		7:30	.678
		8:00	.677
7/19/40	18.1	0:30	137.561
		1:00	.531
		2:00	.514
		3:00	.506
		4:00	.501
		5:00	.499
		5:30	.497

The determinations of the heat of transition are given in Table VI and of the heat of fusion in Table VII.

**The Heat of Vaporization.**—Two determinations made using the adiabatic calorimeter dif-

(9) C. P. Smyth and S. A. McNeight, *THIS JOURNAL*, **58**, 1597 (1936).

TABLE VI

HEAT OF TRANSITION OF METHYL MERCAPTAN			
Temp. interval, $^\circ\text{K.}$	Heat input, cal./mole	$\int \bar{C}_p dT^a$	$\Delta H$ , cal./mole
135.925-138.618	91.04	38.38	52.64
135.382-139.021	104.19	51.91	52.28
135.887-138.833	94.57	42.04	52.53
		Average	$52.5 \pm 0.5$

<sup>a</sup> Including premelting.

TABLE VII

HEAT OF FUSION OF METHYL MERCAPTAN

Temp. interval, $^\circ\text{K.}$	Heat input, cal./mole	$\bar{C}_p dT$ , cal./mole	Pre-melting below starting temp., cal./mole	$\Delta H$ , cal./mole
148.196-152.390	1481.0	79.8	10.0	1411.2
148.238-153.519	1504.5	103.1	10.2	1411.6
			Average	$1411.4 \pm 2$

ferred by 1%. Five more determinations were made using the improved non-adiabatic calorimeter.<sup>3</sup> Two heaters were used, one wound on the outside of the calorimeter and the other inside the reentrant thermometer. The agreement between runs with different heaters and heating rates shows that heat leak corrections were properly made and that the method of evaporation does not influence the results. Results are given in Table VIII.

TABLE VIII

HEAT OF VAPORIZATION OF METHYL MERCAPTAN

$\Delta H_v$  calculated from the vapor pressure equation and Berthelot's equation of state is 5866 cal./mole;  $T_0 = 470.0^\circ\text{K.}$ ,  $p_0 = 71.4 \text{ atm.}$ <sup>7</sup>

Run	Heater	Moles vaporized	Time required, sec.	$\Delta H_v$ at $279.12^\circ$ , cal./mole
1 <sup>a</sup>	Inside	0.17335	3000	5815 <sup>b</sup>
2 <sup>a</sup>	Inside	.19343	3600	5871
3	Inside	.17313	3600	5876
4	Inside	.17401	3600	5868
5	Outside	.13943	4200	5869
6	Inside	.11630	3000	5874
7	Outside	.11075	3000	5876
			Average	$5872 \pm 4$

<sup>a</sup> Using adiabatic calorimeter. <sup>b</sup> Given no weight in average.

**The Entropy.**—The entropy calculation from calorimetric measurements is summarized in Table IX.

**The Entropy from Molecular Data.**—Standard statistical mechanical formulas were used in the calculation of the entropy. The constants used in the calculation were those recommended by Professor R. T. Birge in a private communication except for changes required by our values of the ice-point and calorie. The values are  $0^\circ\text{C.} =$

TABLE IX

THE MOLAL ENTROPY OF METHYL MERCAPTAN  
 0°C. = 273.16°K., molecular weight = 48.102.

	$\frac{\Delta S}{\text{cal./deg./mole}}$
0-15°K. Debye function, $\theta = 122.8^\circ$	0.274
15-137.6°K. graphical	14.679
Transition 52.5/137.6	0.350
137.6-150.16°K. graphical	1.339
Fusion 1411.4/150.16	9.399
150.16-279.12°K. graphical	12.968
Vaporization 5872/279.12	21.038
Entropy of actual gas at b. p. and 1 atm.	60.047
Correction for gas imperfection <sup>a</sup>	0.112
Entropy of ideal gas at 279.12°K. and 1 atm.	60.16 ± 0.10

<sup>a</sup>  $S_{\text{ideal}} - S_{\text{actual}} = 27RT_0^2P/32T^3P_0$ .  $T_0 = 470.0^\circ\text{K.}^7$ ,  $P_0 = 71.4 \text{ atm.}^7$ .

273.16°K.,  $R = 1.9871 \text{ cal./deg./mole}$ , and  $h = 1.3805 \times 10^{-16} \text{ erg./deg./molecule}$ ,  $N = 6.023 \times 10^{23}$ ,  $\hbar = 6.624 \times 10^{-27} \text{ erg. sec.}$

The rotational entropy was calculated from the classical partition function for an asymmetric rotator, neglecting the internal rotation. Since this molecule may be regarded as a symmetrical top (the methyl group) fastened to a rigid framework, its moments of inertia about the principal axes are independent of the orientation of the top about the symmetry axis of the top. Thus the rotational entropy calculation (exclusive of internal rotation) is the same as for DSH, for example, except, of course, that different moments of inertia are used.

The structural parameters taken were C-S distance = 1.83 Å. as determined by electron diffraction,<sup>10</sup> S-H distance = 1.35 Å. from hydrogen sulfide, C-S-H angle = 100° from similar sulfur compounds, and a tetrahedral methyl group with C-H distance = 1.09 Å. The principal moments of inertia are  $A = 68.78 \times 10^{-40}$ ,  $B = 65.94 \times 10^{-40}$ ,  $C = 8.14 \times 10^{-40} \text{ g. cm.}^2$ . For the vibrational entropy the assignments of Thompson and Skerrett<sup>11</sup> from infrared data for the vapor and Raman data for the liquid were used. The frequencies in  $\text{cm.}^{-1}$  are 3000 (2), 2870, 2597, 1475, 1430, 1335, 1060, 975, 803, 704. The torsional frequency is omitted. The entropy so calculated is compared in Table X with the calorimetric entropy; the observed discrepancy is attributed to the internal, torsional motion. From the tables of Pitzer,<sup>12</sup> which are quite accurate for this type of molecule,<sup>1</sup> the barrier height necessary to

(10) Private communication from Dr. D. P. Stevenson.

(11) H. W. Thompson and N. P. Skerrett, *Trans. Faraday Soc.*, **36**, 812 (1940).

(12) K. S. Pitzer, *J. Chem. Phys.*, **5**, 469 (1937).

give the desired contribution was calculated. The reduced moment of the methyl group is  $1.853 \times 10^{-40} \text{ g.-cm.}^2$ . A summary of the calculations is presented in Table X.

TABLE X

SUMMARY OF THE BARRIER CALCULATION FOR METHYL MERCAPTAN  
 279.12°K. and 1 atm.

	Entropy, cal./deg./mole
Translational	37.207
Rotational (omitting internal rotation)	20.338
Vibrational	0.592
Total omitting internal rotation	58.137 ± 0.10
Calorimetric entropy	60.16 ± 0.10
Contribution of torsional motion as experimentally determined	2.02 ± 0.14
Contribution assuming free rotation	2.50
Contribution of hindered rotation with barrier of 1460 cal./mole	2.02

The height of the barrier for methyl mercaptan is seen from Table X to be  $1460 \pm 270 \text{ cal./mole}$ , and this value appears to be a reasonable one in view of the value of about 3000 cal. calculated in the same manner for methyl alcohol.<sup>13</sup> It should be remarked, however, that Koehler and Dennison<sup>14</sup> from spectroscopic considerations alone find a barrier of about 1300 cal./mole for methyl alcohol. The difference between these two values has not yet been explained. It does seem, at this time, that the method employed here for the evaluation of barrier heights is the more reliable.

### Summary

The heat capacities of solid and liquid methyl mercaptan have been measured over the temperature range 14-273°K.

There is a slow isothermal transition at  $137.6 \pm 0.1^\circ\text{K.}$  ( $0^\circ\text{C.} = 273.16^\circ\text{K.}$ ) the heat of transition being  $52.5 \pm 0.5 \text{ cal./mole}$ .

The melting point of pure methyl mercaptan is  $150.16 \pm 0.02^\circ\text{K.}$ , and the heat of fusion is  $1411.4 \pm 2.0 \text{ cal./mole}$ .

The vapor pressure has been measured in the range 222-279°K. and can be accurately represented by the equation  $\log_{10} p_{\text{mm.}} = 18.2749 - (1769.05/T) - 3.70248 \log_{10} T$ ; the boiling point from this equation is 279.12°K. ( $5.96^\circ\text{C.}$ ). The directly measured heat of vaporization at the normal boiling point is  $5872 \pm 4 \text{ cal./mole}$ .

The entropy of methyl mercaptan at one atmos-

(13) For this calculation the data summarized by B. L. Crawford, *J. Chem. Phys.*, **8**, 744 (1940), were used.

(14) J. S. Koehler and D. M. Dennison, *Phys. Rev.*, **57**, 1006 (1940).

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

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

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 described<sup>1</sup> 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 Brum<sup>2</sup> 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. <sup>-1</sup> mole <sup>-1</sup>	T, °K.	$C_p$ , cal. deg. <sup>-1</sup> mole <sup>-1</sup>
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 <sup>a</sup>
37.20	5.317	170.56	19.91 <sup>a</sup>
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

<sup>a</sup> 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).