tion probabilities, an over-all p_f/p_i of 3.03 is obtained for the postulated rearrangement mechanism. Figure 1 indicates that experimentally, this ratio increases as the initial pressure decreases. Consequently, the slight discrepancy between the observed and the theoretical p_f/p_i ratios can readily be accounted for by the formation of complex condensation products.

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The Chemical Thermodynamic Properties of 2-Methylthiophene[1]

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Calorimetric studies of 2-methylthiophene in the temperature range 12 to 473°K. yielded the following information: values of heat capacity for the solid, the liquid [$C_{\text{satd}} = 45.85 - 0.1754\ T + 6.772 \times 10^{-4}T^2 - 6.771 \times 10^{-7}T^3$, cal. deg.$^{-1}$ mole^{-1} (213 to 344°K.)], and the vapor [$C_p^\circ = -1.745 + 9.562 \times 10^{-2}T - 4.420 \times 10^{-5}T^2$, cal. deg.$^{-1}$ mole^{-1} (375 to 473°K.)]; the heat of fusion [2263 cal. mole^{-1}] at the triple point [209.79 ± 0.05°K.]; the entropy in the liquid state at 298.16°K. [52.22 cal. deg.$^{-1}$ mole^{-1}]; the heat of vaporization [$\Delta H_v = 11651 - 3.937\ T - 1.364 \times 10^{-2}T^2$, cal. mole^{-1} (343 to 385°K.)]; the second virial coefficient in the equation of state $PV = RT(1 + B/V)$[$B = 114 - 127 \exp (900/T)$, cc. mole^{-1} (343 to 473°K.)]; and the standard heat of formation of the liquid from graphite, hydrogen and rhombic sulfur [$\Delta Hf^\circ_{298.16} = 10.86 \pm 0.21$ kcal. mole^{-1}]. Tables of thermodynamic properties for the solid and liquid states (10 to 340°K.) were computed. The calorimetrically determined properties of the vapor were used with spectroscopic and molecular structure data to evaluate the height of the barrier hindering internal rotation (900 cal. mole^{-1}) and to compute tables of the chemical thermodynamic properties at selected temperatures from 0 to 1000°K.

Thiophene derivatives constitute an important fraction of the organic sulfur compounds found in petroleum.[2] To provide the basic information for computation, by approximate statistical mechanical methods,[3] of thermodynamic data for this class of compounds, detailed studies are being made in this Laboratory of the thermodynamic properties of selected thiophene derivatives. The results of investigations of the parent compound, thiophene,[4] and of 3-methylthiophene[5] have already been published. This paper reports data for another thiophene derivative, 2-methylthiophene.

Experimental studies on 2-methylthiophene were made by the methods of low temperature calorimetry, flow calorimetry and combustion calorimetry. The results include values of the heat capacity in the solid, liquid and vapor states and the heats of fusion, vaporization and combustion. From these data were obtained values of the entropy, heat capacity and heat of formation of 2-methylthiophene in the ideal gaseous state. The calorimetric results were used with spectroscopic and molecular structure information to calculate values of the following thermodynamic functions at selected temperatures from 0 to 1000°K.: $(F^\circ - H^\circ_0)/T$ $(H^\circ - H^\circ_0)/T$, $H^\circ - H^\circ_0$, S°, C_p°, ΔHf°, ΔFf° and $\log_{10}Kf$.

Experimental

Physical Constants.—The 1951 International Atomic Weights[6] and the 1951 values of the fundamental physical constants[7] were used for all computations described in this paper. Measurement of temperature above 90°K. was made in terms of the International Temperature Scale of 1948,[8] and International Celsius temperatures were converted to Kelvin temperatures by adding 273.16°K. Below 90°K. the temperature scale was defined by a platinum resistance thermometer calibrated at the National Bureau of Standards in terms of the provisional scale established by Hoge and Brickwedde.[9] All electrical and mass measurements were referred to standards calibrated at the National Bureau of Standards. Energy measured in joules was converted to calories by use of the definitions, 1 cal. = 4.1840 abs. j. = 4.1833 int. j.

The Material.—The sample of 2-methylthiophene used in the low temperature and combustion studies was part of the Standard Sample of Sulfur Compound, API-USBM serial no. 21, prepared and purified by American Petroleum Institute Research Project 48A at the Laramie, Wyo., Station of the Bureau of Mines. A calorimetric study of the melting point showed that the Standard Sample contains 0.036 ± 0.01 mole % of liquid-soluble, solid-insoluble impurity. A second sample, of 99.8 mole % purity, was used in studies of the heat of vaporization and vapor heat capacity. Both samples were received in ampoules with internal break-off tips and were stored in the dark at 5°. Before use in the experiments, the samples were dried in the liquid phase with calcium hydride. They were always transferred by vacuum distillations and at no time were they in contact with gases other than dry helium.

The Heat Capacity in the Solid and Liquid States.—The low temperature thermal studies were made in an adiabatic calorimeter system similar to that described by Ruehrwein and Huffman.[10] The sample of 2-methylthiophene (0.57938 mole) was sealed in a platinum calorimeter equipped with heat-distributing gold vanes. About 30 mm. helium pres-

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[1] This investigation was part of American Petroleum Institute Research Project 48A on "The Production, Isolation and Purification of Sulfur Compounds and Measurement of Their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

[2] S. F. Birch, *J. Inst. Pet.*, **39**, 185 (1953).

[3] *E.g.*, (a) K. S. Pitzer and J. E. Kilpatrick, *Chem. Revs.*, **39**, 435 (1946); (b) J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **36**, 559 (1946).

[4] (a) Guy Waddington, J. W. Knowlton, D. W. Scott, G. D. Oliver, S. S. Todd, W. N. Hubbard, J. C. Smith and H. M. Huffman, THIS JOURNAL, **71**, 797 (1949); (b) W. N. Hubbard, D. W. Scott, F. R. Frow and Guy Waddington, *ibid.*, **77**, 5855 (1955).

[5] J. P. McCullough, S. Sunner, H. L. Finke, W. N. Hubbard, M. E. Gross, R. E. Pennington, J. F. Messerly, W. D. Good and Guy Waddington, *ibid.*, **75**, 5075 (1953).

[6] Edward Wichers, *ibid.*, **74**, 2447 (1952).

[7] F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, *ibid.*, **74**, 2699 (1952).

[8] H. F. Stimson, *J. Research Natl. Bur. Standards*, **42**, 209 (1949).

[9] H. J. Hoge and F. G. Brickwedde, *ibid.*, **22**, 351 (1939).

[10] R. A. Ruehrwein and H. M. Huffman, THIS JOURNAL, **65**, 1620 (1943). Minor modifications have been described in subsequent publications: H. M. Huffman, S. S. Todd and G. D. Oliver, *ibid.*, **71**, 584 (1949), and D. W. Scott, D. R. Douslin, M. E. Gross, G. D. Oliver and H. M. Huffman, *ibid.*, **74**, 883 (1952).

sure, at room temperature, was left in the calorimeter to promote thermal equilibration at low temperatures. Observed values of the heat capacity at saturation pressure (C_{satd}) are given in Table I. The temperature increments used in the heat capacity measurements were small enough to obviate the need of corrections for non-linear variation of C_{satd} with T. The increments used were approximately 10% of the absolute temperature below 50°K., 5 to 6° from 50 to 150°K. and 8 to 10° above 150°K. The precision of the heat capacity data is, in general, within ±0.1%, and above 30°K. the accuracy uncertainty should not exceed 0.2%. An empirical equation that represents the observed heat capacity of liquid 2-methylthiophene with average and maximum deviations of 0.01 and 0.06 cal. deg.$^{-1}$ mole^{-1}, respectively, is

$$C_{satd}(\text{liq.}) = 45.85 - 17.54 \times 10^{-2}T + 6.772 \times 10^{-4}T^2 - 6.771 \times 10^{-7}T^3 \text{ cal. deg.}^{-1}\text{ mole}^{-1}\ (213\text{–}344°\text{K.}) \quad (1)$$

At about 163°K., the heat capacity of 2-methylthiophene crystals was found to increase abruptly by 0.74 cal. deg.$^{-1}$ mole^{-1}, as shown in Fig. 1. Six series of heat capacity measurements made between 150 and 180°K. gave reproducible results. The results of three direct measurements of the enthalpy increase from 150 to 175°K. agreed within ±2 cal. mole^{-1} and showed that no latent heat was involved in the transition near 163°K. The rate of cooling the sample through the region of the heat capacity anomaly was varied from 18 to 120 hr. in the experiments mentioned, but no effect of prior thermal treatment could be detected in the observed data.

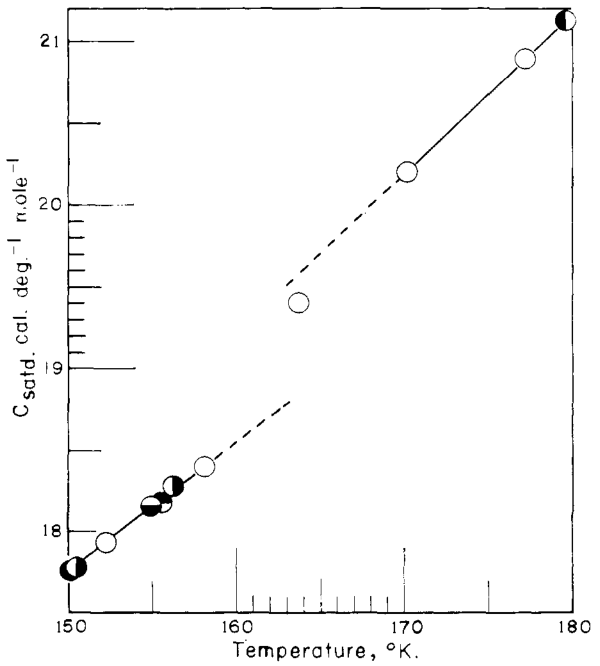

Fig. 1.—The heat capacity anomaly in 2-methylthiophene. Similar symbols are used to indicate points from a continuous series of measurements.

A similar, but smaller, discontinuity was found at 145°K. in the plot of C_{satd} *vs.* T for 3-methylthiophene.[5] Several other compounds showing related phenomena are mentioned in ref. 5. As discussed in that paper, these discontinuities in heat capacity curves probably are caused by a change in the mode of restricted internal rotation.

TABLE I

THE MOLAL HEAT CAPACITY OF 2-METHYLTHIOPHENE IN CAL. DEG.$^{-1}$

T, °K.[a]	C_{satd}[b]	T, °K.	C_{satd}	T, °K.	C_{satd}
Crystals		78.80	12.594	156.31	18.285
		79.38	12.665	158.17	18.399
12.46	1.567	81.02	12.798	163.83	19.398
13.35	1.783	83.85	13.041	170.19	20.201
14.19	2.009	86.47	13.243	177.25	20.884
14.62	2.123	89.20	13.454	179.64	21.119
15.86	2.423	92.21	13.656	184.86	12.666
16.10	2.497	94.84	13.834	189.09	22.144
17.52	2.893	95.66	13.887	192.84	22.555
17.84	2.957	98.12	14.058	197.09	23.118
19.22	3.347	100.32	14.206	198.54	23.263
19.86	3.512	102.02	14.324	202.57	23.986[c]
21.26	3.901	104.21	14.477		
22.03	4.110	108.17	14.750	Liquid	
23.61	4.539	114.57	15.197		
24.27	4.722	121.20	15.663	213.30	32.676
26.29	5.257	121.33	15.668	219.53	32.816
26.55	5.332	127.65	16.122	227.40	33.021
29.37	6.043	127.80	16.131	236.88	33.316
32.61	6.816	133.93	16.573	247.37	33.655
36.38	7.577	135.79	16.707	258.29	34.048
40.72	8.373	140.05	17.016	269.08	34.487
45.59	9.136	140.75	17.070	279.74	34.965
51.08	9.897	144.11	17.306	290.25	35.458
53.43	10.195	144.61	17.336	294.87	35.636
56.57	10.547	146.34	17.479	300.63	35.923
58.38	10.755	150.14	17.757	304.94	36.116
63.45	11.293	150.52	17.798	314.87	36.599
68.82	11.762	152.32	17.936	324.68	37.098
73.94	12.208	154.94	18.159	334.37	37.538
75.85	12.360	155.56	18.176	343.94	38.084

[a] T is the mean temperature of each heat capacity measurement. [b] C_{satd} is the heat capacity of the condensed phase under its own vapor pressure. [c] Corrections for hetero-phase premelting have *not* been applied to these data.

The Heat of Fusion.—Three determinations were made of the heat of fusion of 2-methylthiophene. In each experiment the enthalpy change was measured over a finite temperature interval that included the triple point. The latent heat of fusion was calculated from these results by subtraction of the energy absorbed non-isothermally, as computed from the heat capacity data. Corrections were applied for the effects of premelting caused by the presence of impurity in the sample. The average value found for the heat of fusion is 2263 ± 1[11] cal. mole^{-1}.

The Triple Point, Cryoscopic Constants and Sample Purity.—A study of equilibrium melting temperature as a function of fraction of sample melted was made by the procedure described in an earlier publication.[12] The results are summarized in Table II. The observed equilibrium tem-

TABLE II

2-METHYLTHIOPHENE: MELTING POINT SUMMARY

Heat of fusion, ΔH_{fusion} = 2263 cal. mole^{-1}; triple point, $T_{T.P.}$ = 209.79 ± 0.05°K.; cryoscopic constant, A = 0.0259 deg.$^{-1}$; impurity = 0.036 ± 0.01 mole %

Melted, %	$1/F$	T, °K. Obsd.	T, °K. Graph.[b]
8.76	11.41	209.6295[a]	209.6295
23.40	4.274	209.7244	209.7288
47.35	2.112	209.7583	209.7588
65.78	1.520	209.7665	209.7671
84.23	1.187	209.7717[a]	209.7717
100.0	1.000		209.7743
Pure	0.000		209.7882[c]

[a] A straight line through these two points was extrapolated to $1/F = 0$ to obtain the triple point temperature, $T_{T.P.}$. [b] Temperatures read from the straight line of footnote *a*. [c] Triple point temperature.

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(11) The uncertainty given is the maximum deviation from the mean.

(12) S. S. Todd, G. D. Oliver and H. M. Huffman, THIS JOURNAL, **69**, 1519 (1947).

peratures, T_{obsd} were plotted as a function of $1/F$, the reciprocal of fraction of total sample in the liquid phase. The triple point temperature, $T_{\text{T.P.}} = 209.79 \pm 0.05$°K., was obtained by linear extrapolation to zero value of $1/F$. If the impurities present form ideal solutions in the liquid phase and are insoluble in the solid phase, the relation between mole fraction of total impurity, N_2^*, and melting point depression $\Delta T = T_{\text{T.P.}} - T_{\text{obsd.}}$ is[13]

$$-\ln (1 - N_2) = A\Delta T(1 + B\Delta T + \ldots\ldots..) \quad (2)$$

where $N_2 = N_2^*/F$. The cryoscopic constants, $A = \Delta H_{\text{fusion}}/RT_{\text{T.P.}}^2 = 0.0259$ deg.$^{-1}$ and $B = 1/T_{\text{T.P.}} - \Delta C_{\text{fusion}}/2\Delta H_{\text{fusion}} = 0.00294$ deg.$^{-1}$, were evaluated from the data above and from $\Delta C_{\text{fusion}} = 8.27$ cal. deg.$^{-1}$ mole^{-1} from Table III.

TABLE III

THE MOLAL THERMODYNAMIC PROPERTIES OF 2-METHYLTHIOPHENE IN THE SOLID AND LIQUID STATES[a]

T, °K.	$-(F_{\text{satd.}} - H_0^\circ)/T$, cal. deg.$^{-1}$	$(H_{\text{satd.}} - H_0^\circ)/T$, cal. deg.$^{-1}$	$H_{\text{satd.}} - H_0^\circ$, cal.	$S_{\text{satd.}}$, cal. deg.$^{-1}$	$C_{\text{satd.}}$, cal. deg.$^{-1}$
			Crystals		
10	0.082	0.242	2.42	0.324	0.916
15	.258	.684	10.26	.942	2.208
20	.529	1.232	24.64	1.761	3.552
25	.867	1.834	45.84	2.701	4.920
30	1.257	2.456	73.69	3.713	6.201
35	1.682	3.074	107.59	4.756	7.308
40	2.132	3.663	146.52	5.795	8.246
45	2.595	4.218	189.81	6.813	9.047
50	3.067	4.737	236.84	7.804	9.753
60	4.015	5.675	340.5	9.690	10.933
70	4.953	6.496	454.7	11.449	11.878
80	5.868	7.222	577.7	13.090	12.717
90	6.757	7.877	708.9	14.634	13.497
100	7.619	8.473	847.3	16.092	14.182
110	8.452	9.024	992.6	17.476	14.875
120	9.261	9.540	1144.9	18.801	15.574
130	10.044	10.032	1304.2	20.076	16.288
140	10.805	10.505	1470.7	21.310	17.006
150	11.545	10.963	1644.4	22.508	17.752
160	12.267	11.412	1825.9	23.679	18.540
163	12.480	11.545	1881.9	24.025	18.780
163	12.480	11.545	1881.9	24.025	19.505
170	12.972	11.887	2020.7	24.859	20.165
180	13.666	12.373	2227.2	26.039	21.130
190	14.348	12.861	2443.6	27.209	22.168
200	15.020	13.354	2670.8	28.374	23.263
209.79	15.670	13.842	2904.0	29.512	24.330
			Liquid		
209.79	15.670	24.628	5167	40.30	32.60
210	15.69	24.636	5174	40.33	32.60
220	16.85	25.003	5501	41.85	32.83
230	17.97	25.349	5830	43.32	33.10
240	19.05	25.678	6163	44.73	33.41
250	20.11	25.994	6499	46.10	33.74
260	21.13	26.299	6838	47.43	34.12
270	22.13	26.597	7181	48.73	34.54
273.16	22.44	26.689	7290	49.13	34.67
280	23.10	26.888	7529	49.99	34.98
290	24.05	27.175	7881	51.23	35.43
298.16	24.81	27.406	8171	52.22	35.81
300	24.98	27.458	8237	52.44	35.89
310	25.88	27.738	8599	53.62	36.38
320	26.76	28.015	8965	54.78	36.86
330	27.64	28.291	9336	55.93	37.37
340	28.48	28.566	9712	57.05	37.88

[a] The values tabulated are the free energy function, heat content function, heat content, entropy and heat capacity of the condensed phases at saturation pressure.

The Thermodynamic Properties in the Solid and Liquid States.—Values of the entropy, free energy function, heat content function and heat content of 2-methylthiophene in the solid and liquid states at saturation pressure were computed from the thermal data presented in the foregoing sections. The results, at selected temperatures between 10 and 340°K., are given in Table III. The values at 10°K. were computed from a Debye function for 3.5 degrees of freedom and characteristic temperature of 81.5°; these parameters were selected to fit the observed values of $C_{\text{satd.}}$ between 13 and 20°K. Values of the thermodynamic properties above 10°K. were calculated by appropriate numerical integration of values of $C_{\text{satd.}}$ read from a large scale plot of the data in Table I. Corrections for the effects of heterophase premelting were applied in computing the data in Table III.

The Heat of Vaporization.—The heat of vaporization and vapor heat capacity of 2-methylthiophene were determined in the flow calorimeter system described in previous publications.[14] Presented in Table IV are the results obtained from triplicate measurements of the heat of vaporization at each of three temperatures ranging from 343 to 386°K. The estimated accuracy uncertainty of the results is ±0.1%. The following empirical equation may be used for interpolation in the temperature range of the measurements.

$$\Delta H_{\text{v}} = 11651 - 3.937T - 1.364 \times 10^{-2}T^2\text{, cal. mole}^{-1} \quad (3)$$

TABLE IV

THE MOLAL HEAT OF VAPORIZATION AND SECOND VIRIAL COEFFICIENT OF 2-METHYLTHIOPHENE

T, °K.	P, atm.	ΔHv, cal.	$B_{\text{obsd.}}$, cc.	$B_{\text{calcd.}}$,[a] cc.
343.49	0.250	8689 ± 2[b]	−1780	−1630
363.14	.500	8422 ± 1[b]	−1400	−1400
385.72	1.000	8103 ± 3[b]	−1160	−1190

[a] Calculated with eq. 5. [b] Maximum deviation of experimental results from the mean.

The Vapor Heat Capacity and the Effects of Gas Imperfection.—Measurements of the heat capacity of 2-methylthiophene in the vapor state were made at two or more pressures at each of four temperatures between 375 and 473°K. The results are summarized in Table V.

TABLE V

THE MOLAL VAPOR HEAT CAPACITY OF 2-METHYLTHIOPHENE IN CAL. DEG.$^{-1}$

T, °K.	375.20	395.20	438.25	473.25
C_p (1.000 atm.)		29.946	32.156	33.935
C_p (0.500 atm.)	28.401	29.525		
C_p (0.272 atm.)				33.693
C_p (0.250 atm.)	28.153	29.320	31.792	
C_p° (obsd.)	27.92	29.13	31.68	33.61
C_p° (calcd.)[a]	27.89	29.13	31.68	33.61
[C_p (1 atm.) − C_p°] obsd.		0.82	0.48	0.33
[C_p (1 atm.) − C_p°] calcd.[b]		0.80	0.48	0.33

[a] Calculated from spectroscopic and molecular structure data. [b] Calculated from eqs. 4 and 5.

For use in correlation of the thermal data, an equation of state for 2-methylthiophene was obtained from the heat of vaporization and vapor heat capacity data of this investigation and the vapor pressure data reported by White, Barnard-Smith and Fidler.[15] Values of the second virial coefficient, B, in the equation of state, $PV = RT\,(1 + B/V)$, were computed by use of the Clapeyron equation. Values of $\mathrm{d}^2B/\mathrm{d}T^2$ were determined from the thermodynamic

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(13) A. R. Glasgow, Jr., A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

(14) (a) Guy Waddington, S. S. Todd and H. M. Huffman, THIS JOURNAL, **69**, 22 (1947). (b) J. P. McCullough, D. W. Scott, R. E. Pennington and Guy Waddington, *ibid.*, **76**, 4791 (1954).

(15) P. T. White, D. G. Barnard-Smith and F. A. Fidler, *Ind. Eng. Chem.*, **44**, 1430 (1952).

relationship, $(\partial^2 V/\partial T^2)_P = -1/T(\partial C_p/\partial P)_T$, in terms of which the variation of vapor heat capacity with pressure is represented, with slight approximations,[14b] by

$$C_p = C_p^\circ - PT(d^2B/dT^2) + 2[P^2/R][B(d^2B/dT^2)] \times [1 - 3BP/RT] \quad (4)$$

The numerical constants of the following empirical equation for B were determined by the method described in ref. 14b.

$$B = 114 - 127 \exp(900/T), \text{ cc. mole}^{-1} \text{ (343–473°K.)} \quad (5)$$

Values of B, computed by use of eq. 5, and values of C_p (1 atm.) $- C_p^\circ$, computed by use of eq. 4 and 5, are compared with experimental data in Tables IV and V, respectively.

To determine the "observed" values of C_p° listed in Table V, the last term in eq. 4 was evaluated for each experimental point by use of eq. 5, and the result[16] was subtracted from C_p(obsd.). The adjusted values of C_p at each temperature were then extrapolated linearly to zero pressure to obtain C_p° (obsd.).[17]

The accuracy uncertainty of the values of C_p° (obsd.) listed in Table V should not exceed ±0.2%. The following empirical equation represents the experimental data within 0.05% between 375 and 473°K.

$$C_p^\circ = -1.745 + 9.562 \times 10^{-2}T - 4.420 \times 10^{-5}T^2, \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (6)$$

The Entropy in the Ideal Gaseous State.—The experimental and derived data given in previous sections were used in computing "observed" values of the entropy in the ideal gaseous state at one atmosphere pressure. These calculations are summarized in Table VI.

TABLE VI

THE MOLAL ENTROPY OF 2-METHYLTHIOPHENE IN CAL. DEG.$^{-1}$

0–13°K.	Debye extrapolation[a]	0.659
13–209.79°	Crystals, numerical $\int C_{satd}\, d \ln T$	28.850
209.79°	Fusion, 2263/209.79	10.787
209.79–298.16°	Liquid, numerical $\int C_{satd}\, d \ln T$	11.919
S_{satd} (liq.), 298.16°K. (±0.12)[b]		52.22

T, °K.	343.49	363.14	385.72
S_{satd} (liq.)[c]	57.439	59.584	61.969
$\Delta H_v/T$[d]	25.296	23.192	21.007
S (ideal) $-$ S (real)[e]	0.084	0.129	0.200
$R \ln (p/760)$[f]	−2.755	−1.377	0.000
S°, gas (obsd.) (±0.15)[b]	80.06	81.53	83.18
S°, gas (calcd.)[g]	80.06	81.52	83.20

[a] A Debye function for 3.5° of freedom with $\theta = 81.5$°K. was used for this extrapolation. [b] Estimated accuracy uncertainty. [c] Calculated from the value at 298.16°K. by integrating eq. 1. [d] Entropy of vaporization; calculated from data of Table IV. [e] Entropy of gas imperfection, calculated by use of eq. 5. [f] Entropy of compression; calculated from data of ref. 15. [g] Calculated from spectroscopic and molecular structure data.

The Heat of Combustion.—The heat of combustion of 2-methylthiophene was determined in the rotating-bomb calorimetric system described in a recent publication.[18] The energy equivalent of the calorimetric system was determined by combustion experiments with benzoic acid (National Bureau of Standards Sample 39g), which was certified to evolve 26.4338 abs. kj. g.$^{-1}$ (weight in vacuum) under specified conditions.[19] For the calibration experiments, in which conditions were slightly different from those specified in reference 19, an adjusted value of 26.4343 abs. kj. g.$^{-1}$ (weight in vacuum) was used.

The samples for combustion experiments were contained in thin-walled, flat-sided Pyrex ampoules. Recent investigations have shown that soft-glass ampoules are not satisfactory for sulfur-containing compounds.[5] All experiments were made in a platinum-lined bomb (Pt-4).[18] The amount of water initially added to the bomb was 10 g. Each combustion experiment was initiated at 296.16°K., and the quantities of sample and auxiliary oil (Sample USBM-P3a) were chosen to produce a 2° temperature rise in the calorimeter.

In Table VII the details of the combustion experiments are summarized; in the last column of the table are the observed values of $\Delta U_c^\circ/M$, the change in internal energy per gram mass of 2-methylthiophene for the idealized combustion reaction

$$C_6H_5S(l) + 8O_2(g) + 68H_2O(l) \longrightarrow 5CO_2(g) + H_2SO_4 \cdot 70H_2O(l) \quad (I)$$

in which all reactants and products are in the appropriate standard states.[20] The average of the nine acceptable values of $\Delta U_c^\circ/M$ is 8433.5 ± 0.80[21] cal. g.$^{-1}$ From the datum for $\Delta U_c^\circ/M$, the value of the heat of combustion, ΔH_c°, for reaction I was found to be −829.65 ± 0.18[22] kcal. mole^{-1} at 298.16°K.

The Heat, Free Energy and Equilibrium Constant of Formation at 298.16°K.—For the formation of $H_2SO_4 \cdot 70H_2O$ (1) at 298.16°K., according to the reaction

$$S(\text{rhombic}) + 3/2O_2(g) + 71H_2O(l) \longrightarrow H_2SO_4 \cdot 70H_2O(l) \quad (II)$$

the values, $\Delta U_c^\circ = -142.69$ kcal. mole^{-1} and $\Delta H_c^\circ = -143.58$ kcal. mole^{-1} were obtained by adding a small dilution term to the value of ΔU_c° reported for the formation of $H_2SO_4 \cdot 115H_2O(l)$.[18] The foregoing value of ΔH_c° for reaction II and values of the standard heats of formation of water[23] and carbon dioxide[24] were used in computing the standard heat of formation of liquid 2-methylthiophene, ΔHf° (liq.) $= +10.86 \pm 0.21$[22] kcal. mole^{-1} at 298.16°K., according to the reaction

$$5C(\text{graphite}) + 3H_2(g) + S(\text{rhombic}) \longrightarrow C_5H_6S(l) \quad (III)$$

With the aid of a thermodynamic network that used the thermodynamic properties of the liquid (Table III), the heats of vaporization (Table IV), the equation of state (eq. 5) and the thermodynamic functions of the ideal gas (Table X of the next section), the standard molal heat, free energy and entropy of vaporization were calculated to be 9.30 kcal., 2.03 kcal. and 24.41 cal. deg.$^{-1}$, respectively. These values, the experimental values of the entropy and heat of formation of liquid 2-methylthiophene and values of the thermodynamic functions of graphite,[23] hydrogen,[23] rhombic sulfur[25] and $S_2(g)$[26] were used in computing the values given in Table VIII for the standard heat, $\Delta Hf^\circ_{298.16}$, free energy, $\Delta Ff^\circ_{298.16}$ and logarithm of the equilibrium constant, $\log_{10} Kf_{298.16}$, of formation of 2-methylthiophene in the liquid and gaseous states.

Calculation of Thermodynamic Properties

The Vibrational Assignment.—For calculation of the thermodynamic properties of 2-methylthiophene by the methods of statisical mechanics, an assignment of the fundamental vibrational fre-

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(16) The maximum value of the last term in eq. 4 was 0.06 cal. deg.$^{-1}$ mole^{-1}.

(17) For a discussion of the reasons for using this procedure, see: J. P. McCullough, H. L. Finke, J. F. Messerly, R. E. Pennington, I. A. Hossenlopp and Guy Waddington, THIS JOURNAL, **77**, 6119 (1955).

(18) W. N. Hubbard, C. Katz and Guy Waddington, *J. Phys. Chem.*, **58**, 142 (1954).

(19) National Bureau of Standards Certificate for Standard Sample 39g.

(20) W. N. Hubbard, D. W. Scott and Guy Waddington, *J. Phys. Chem.*, **58**, 152 (1954).

(21) Standard deviation of the mean.

(22) The uncertainty interval is twice the "over-all standard deviation of the mean"; see F. D. Rossini and W. E. Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

(23) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

(24) E. J. Prosen, R. S. Jessup and F. D. Rossini, *ibid.*, **33**, 447 (1944).

(25) "Selected Values of Chemical Thermodynamic Properties," Circular 500 of the National Bureau of Standards, Washington, D. C., 1952; Series I, Table 14-1.

(26) W. H. Evans and D. D. Wagman, *J. Research Natl. Bur. Standards*, **49**, 141 (1952).

TABLE VII[a,b]

SUMMARY OF 2-METHYLTHIOPHENE COMBUSTION EXPERIMENTS

Comb. no.	C^{i}_{eff} (cont.), cal. deg.$^{-1}$	C^{f}_{eff} (cont.), cal. deg.$^{-1}$	ΔT_c, deg.	Corrections, cal.						m', g.	$\Delta U^{\circ}_{c}/M$, cal. g.$^{-1}$
				q_{fuse}	q_{oil}	q_{CO_2}	q_N	$q_{diln.}$	q_{corr}		
1	13.83	13.91	2.03680	−15.77	−168.93	3.47	8.81	−0.23	+0.60	0.92337	−8437.92
2	13.82	13.92	1.95438	−16.40	−756.56	3.44	9.46	− .01	.64	.81596	−8430.36
3	13.82	13.92	1.99635	−16.12	−615.53	3.48	8.11	− .09	.65	.85237	−8430.81
4	13.82	13.92	1.99598	−15.97	−528.65	3.47	9.55	− .11	.62	.86200	−8434.30
5	13.82	13.91	2.00079	−15.38	−174.31	3.42	9.61	− .20	.61	.90636	−8434.02
6	13.83	13.94	2.00051	−15.18	2628.31	3.78	8.97	+ .42	.80	.61526	−8433.59
7	13.82	13.91	2.00385	−15.18	−176.40	3.42	15.79	− .20	.60	.90713	(−8431.2)[c]
8	13.77	13.87	2.04764	−15.61	−270.31	3.51	8.60	− .22	.61	.91664	−8435.87
9	13.83	13.92	2.04483	−15.10	−257.68	3.50	9.05	− .22	.62	.91716	−8433.04
10	13.78	13.87	2.05722	−16.20	−215.06	3.52	9.91	− .25	.60	.92787	−8431.82
										Av. value of $\Delta U^{\circ}_{c}/M$	−8433.53
										Standard dev. of the mean	±0.80

[a] Auxiliary data: C_{eff}(calor.) = 3909.0 ± 0.08 (standard deviation of the mean) cal. deg.$^{-1}$ from six determinations; volume of bomb = 0.3471 l.; initial total pressure = 30 atm.; electrical ignition energy = 1.35 cal.; ρ, density of 2-methylthiophene = 1.01422 at 25°. [b] The column headings of this table correspond to the following computation item numbers of ref. 20: C^{i}_{eff}(cont.), item 75; C^{f}_{eff}(cont.), item 76; ΔT_c items 79-78-80; q_{fuse}, item 97; q_{oil}, item 96; q_{CO_2}, item 87; q_N, item 92; q_{diln}, items 90 and 91; q_{corr}, items 81 + 82 + 83 + 84 + 85 + 88 + 89 + 93 + 94; m', mass of compound, item 2; $\Delta U^{\circ}_{c}/M$, item 99. [c] This result was discarded because residual carbon was observed on the baffle and head of the bomb and in the bomb solution.

TABLE VIII

THE MOLAL HEAT AND FREE ENERGY AND THE LOGARITHM OF THE EQUILIBRIUM CONSTANT FOR THE FORMATION OF 2-METHYLTHIOPHENE AT 298.16°K.

State[a]	Ref. state[b]	$\Delta Hf^{\circ}_{298.16}$, kcal.	$\Delta Ff^{\circ}_{298.16}$, kcal.	$\log_{10} Kf_{298.16}$
Liquid	S(rhombic)	10.86 ± 0.21[c]	27.51	−20.16
Gas	S(rhombic)	20.16 ± 0.22[c]	29.53	−21.65
Gas	S_2(gas)	4.74	19.97	−14.63

[a] Standard state of 2-methylthiophene. [b] Reference state for elemental sulfur in the reactions: 5C(graphite) + $3H_2(g)$ + S(rhombic) → C_6H_5S(l or g); and 5C(graphite) + $3H_2(g)$ + $^1/_2S_2(g)$ → $C_6H_5S(g)$. [c] See footnote 22.

TABLE IX

THE VIBRATIONAL ASSIGNMENT FOR 2-METHYLTHIOPHENE[a]

2-Methylthiophene,[b] cm.$^{-1}$	3-Methylthiophene,[c] cm.$^{-1}$	Thiophene,[d] cm.$^{-1}$	Designation[e] No.	Class
238	236	1290	20	A_2
303	324	748	12	B_1
470	458	453	23	B_2
547	543	604	1	A_1
563	594	565	18	A_2
664	655	686	19	A_2
692	685	710	22	B_2
743	760	832	10	B_1
766			(303 + 470 = 773)	
818	829	832	3	A_1
848	856	872	11	B_1
891			(238 + 664 = 902)	
940			(2 × 470 = 940)	
976	913	909	24	B_2
1036	1036	1032	2	A_1
1047	990		(CH_3 rock.)	
1079	1079	1079	4	A_1
1131	929		(CH_3 rock.)	
1163	1154		(C—C stretch)	
1215			(238 + 976 = 1214)	
1240	1239	1252	14	B_1
1332			(2 × 664 = 1328)	
1352	1377	1358	5	A_1
1393	1387		(CH_3 bend.)	
1400	1408	1404	6	A_1
1440 (2)	1453 (2)		(CH_3 bend.)	
1511			(470 + 1047 = 1517)	
1538	1538	1590	15	B_1

[a] The region of spectra above 1600 cm.$^{-1}$ has been omitted. [b] Chosen from data of ref. 27. [c] Ref. 5. [d] Refs. 4 and 28. [e] Ref. 28.

quencies was necessary. Raman and infrared spectral data obtained from measurements on Standard Sample API-USBM serial no. 21 were used for this purpose.[27] A detailed analysis of the spectra was not possible because of the difficulties introduced by the lack of symmetry and complicated structure of the 2-methylthiophene molecule. The schematic assignment given in Table IX[28] was made by analogy with assignments for thiophene[4] and 3-methylthiophene.[5] The six hydrogen-stretching frequencies were assigned an average value of 3000 cm.$^{-1}$. All frequencies not chosen as fundamentals are readily explained as overtones or sum combinations. Although the designations of particular vibrational modes are uncertain, this assignment provides a satisfactory basis for the calculation of thermodynamic quantities.

The Moments and Reduced Moment of Inertia.—The product of the principal moments of inertia and the reduced moment of inertia for internal rotation were computed by the formalized method of Kilpatrick and Pitzer.[29] Since the structural parameters of 2-methylthiophene have not been determined experimentally, the molecular dimensions were estimated from those of related molecules. The results of Schomaker and Pauling[30] were used for the thiophene ring, and it was assumed that the C-C-C angles of the attached methyl group are the same as the analogous C-C-H angles of thiophene.

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[27] American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology, Catalogues of Spectral Data; Raman spectrum No. 214; infrared spectra Nos. 365, 942, 1463, 1510 and 1628.

[28] The designations of the normal modes of thiophene are those of R. C. Lord, Jr., and F. A. Miller, *J. Chem. Phys.*, **10**, 328 (1942).

[29] J. E. Kilpatrick and K. S. Pitzer, *ibid.*, **17**, 1064 (1949).

[30] V. Schomaker and L. Pauling, THIS JOURNAL, **61**, 1769 (1939).

TABLE X

THE MOLAL THERMODYNAMIC FUNCTIONS OF 2-METHYLTHIOPHENE IN THE IDEAL GASEOUS STATE[a]

T, °K.	$(F^\circ - H_0^\circ)/T$, cal. deg.$^{-1}$	$(H^\circ - H_0^\circ)/T$ cal. deg.$^{-1}$	$H^\circ - H_0^\circ$, kcal.	S°, cal. deg.$^{-1}$	C_p°, cal. deg.$^{-1}$	ΔHf°,[b] kcal.	ΔFf°,[b] kcal.	$\log_{10} Kf$[b]
0	0	0	0	0	0	8.93	8.93	Infinite
273.16	−61.29	13.41	3.662	74.70	21.09	5.04	18.73	−14.98
298.16	−62.49	14.13	4.212	76.62	22.80	4.74	19.97	−14.63
300.00	−62.58	14.18	4.254	76.76	22.92	4.72	20.06	−14.61
400	−67.07	17.18	6.873	84.25	29.43	3.62	25.35	−13.85
500	−71.23	20.21	10.105	91.44	35.01	2.75	30.86	−13.49
600	−75.17	23.07	13.84	98.24	39.57	2.08	36.58	−13.32
700	−78.93	25.71	18.00	104.64	43.32	1.58	42.37	−13.22
800	−82.51	28.11	22.49	110.62	46.43	1.22	48.23	−13.18
900	−85.96	30.30	27.27	116.26	49.06	0.99	54.11	−13.14
1000	−89.25	32.28	32.28	121.53	51.30	.88	60.03	−13.12

[a] To form an internally consistent set of values of the thermodynamic properties and to retain the higher accuracy of increments with temperature of a given property, the values in this table are given to more significant figures than are justified by their absolute accuracy. [b] The standard heat, standard free energy and common logarithm of the equilibrium constant for the formation of 2-methylthiophene by the reaction: 5C(graphite) + $3H_2$(g) + $^1/_2S_2$(g) → C_5H_6S (g).

The methyl group was taken to be tetrahedral with C–H bond distances of 1.09 Å., and the methyl-to-ring C–C bond distance was taken to be 1.54 Å. The value of the product of principal moments of inertia for this structure is 18.90×10^{-114} g.^{3} cm.,^{6} and the reduced moment for internal rotation is 5.128×10^{-40} g. cm.^{2}

The Potential Barrier to Internal Rotation.—A simple three-fold cosine type potential barrier to internal rotation gives satisfactory agreement between calculated and experimental values of C_p° and S° when the barrier height is taken to be 900 cal. mole^{-1}. Undoubtedly, the barrier to internal rotation in 2-methylthiophene is of a more complex nature,[5] but for the temperatures at which calorimetrically determined data are available, the contributions of internal rotation are not particularly sensitive to the shape of the assumed barrier. The value of 900 cal. mole^{-1} is consistent with values previously found for other methyl aromatic compounds.[5,31]

The Effect of Anharmonicity.—The vibrational assignment, moments and reduced moment of inertia and barrier to internal rotation provide a basis for the calculation of thermodynamic functions to the rigid-rotator, harmonic-oscillator approximation. However, as in thiophene[4] and 3-methylthiophene,[5] the effect of anharmonicity of the normal vibrations is large. At 473°K. this effect amounts to almost 1% of C_p°. The contributions of anharmonicity to the calculated thermodynamic functions were estimated by the empirical procedure outlined in an earlier paper.[32] The best agreement between calculated and calorimetric values of C_p° was obtained when ν and Z, the empirical constants defined in ref. 32, were assigned the values ν = 650 cm.$^{-1}$, and Z = 0.40 cal. deg.$^{-1}$ mole^{-1}.

The Chemical Thermodynamic Properties.—The method of calculation just outlined was used in computing values of $(F^\circ - H_0^\circ)/T$, $(H^\circ - H_0^\circ)/T$, $H^\circ - H_0^\circ$, S° and C_p° from 0 to 1000°K.[33] The results are listed in Table X. Comparisons of the experimental and calculated values of C_p° and S° are presented in Tables V and VI, respectively. The agreement is within ±0.1% at all temperatures for which experimental data were obtained.

The values of the thermodynamic functions of 2-methylthiophene and of graphite,[23] hydrogen[23] and gaseous diatomic sulfur[26] were used with the value of $\Delta Hf^\circ_{298.16}$ from Table VIII to compute values of ΔHf°, ΔFf° and $\log_{10} Kf$ for gaseous 2-methylthiophene. These values also are listed in Table X.

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(31) K. S. Pitzer and D. W. Scott, THIS JOURNAL, **65**, 803 (1943).

(32) J. P. McCullough, H. L. Finke, W. N. Hubbard, W. D. Good, R. E. Pennington, J. F. Messerly and Guy Waddington, *ibid.*, **76**, 2661 (1954).

(33) The vibrational contributions to the thermodynamic functions were taken from H. L. Johnston, L. Savedoff and J. Belzer, "Contributions to the Thermodynamic Functions by a Planck–Einstein Oscillator in One Degree of Freedom," NAVEXOS P-646, Office of Naval Research, Department of the Navy, Washington, D. C., July, 1949. Restricted internal rotation contributions were computed from the tables published by K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942). The contributions of anharmonicity were calculated with data from the tables of R. E. Pennington and K. A. Kobe, *ibid.*, **22**, 1442 (1954).