amide is thermodynamically ideal up to one molar, *i.e.*, the factor $[1 + C \, \mathrm{d} \ln y/\mathrm{d}C]$ of the Onsager-Fuoss diffusion equation[16] is approximately equal to one,

Relative contributions of the factors in Gordon's relation are seen for glycolamide in Fig. 1 where the experimental points, represented by circles, were extrapolated to $C = 0$ to obtain D_0 for computing predicted values of D (solid line) from equation 5. The contribution of the thermodynamic term alone (dashed line) was obtained from

$$D = D_0[1 + C \, \mathrm{d} \ln y/\mathrm{d}C] \qquad (7)$$

For comparison Fig. 1 also presents corresponding data for glycine derived from previous isopiestic,[17] density,[18] viscosity[19] and diffusion[4] measurements. While for both compounds deviations from Gordon's equation are somewhat similar, the graph of D *versus* C for glycolamide has the smaller limiting slope, making for more ideal diffusion. Since the limiting diffusion coefficient for glycine is lower than that for glycolamide, it is evident that the moving aggregate is larger for the former compound, in agreement with the concept of electrostriction. The magnitude of the effects of dipole-dipole interaction is better seen by comparing equations 2 and 3 with the equations of Lyons and Thomas[4] for glycine at 25° in the form

$$D \times 10^5 = 1.063_5 - 0.192_4C \qquad (8)$$

and

$$(\Delta n/\Delta C) \times 10^3 = 13.61_4 - 0.64_2C \qquad (9)$$

Electrostriction, which makes the partial molal volume and partial molal heat capacity of glycine smaller than those of glycolamide,[16] is seen to produce an inverse effect on the limiting values of $\Delta n/\Delta C$.

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MADISON, WISCONSIN

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[18] F. T. Gucker, W. L. Ford and C. E. Moser, *J. Phys. Chem.*, **43**, 153 (1939).

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[CONTRIBUTION NO. 39 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

The Chemical Thermodynamic Properties of 3-Methylthiophene from 0 to 1000°K.[1]

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An experimental study has been made of various thermodynamic properties of 3-methylthiophene in the solid, liquid and vapor states (12 to 473°K.). The entropy of the liquid at 298.16°K., 52.18 ± 0.10 cal. deg.$^{-1}$ mole^{-1}, was computed from measured values of the heat capacity of the solid and liquid and the heat of fusion (2518 cal. mole^{-1} at the triple point, 204.19 ± 0.05°K.). Experimental results obtained for the heat capacity of the liquid [C_{satd}], the heat of vaporization [ΔH_{v}], the heat capacity in the ideal gaseous state [C_{p}°], and the second virial coefficient [$B = (PV - RT)/P$] are represented by the empirical equations: (1) $C_{\mathrm{satd}}(\mathrm{liq.}) = 46.074 - 0.17610\,T + 6.8006 \times 10^{-4}T^2 - 6.8021 \times 10^{-7}T^3$, cal. deg.$^{-1}$ mole^{-1} (207 to 337°K.); (2) $\Delta H_{\mathrm{v}} = 13{,}593 - 13.913\,T$, cal. mole^{-1} (329 to 389°K.); (3) $C_{\mathrm{p}}^{\circ} = -1.375 + 9.4508 \times 10^{-2}\,T - 4.2587 \times 10^{-5}\,T^2$, cal. deg.$^{-1}$ mole^{-1} (375 to 473°K.); and (4) $B = 75 - 94.56 \exp(1000/T)$, cc. mole^{-1} (329 to 473°K.). From determinations of the heat of combustion, the standard heat of formation [$\Delta H_{\mathrm{f}}^{\circ}$ (liq.)] of 3-methylthiophene from graphite, hydrogen and rhombic sulfur was found to be 10.49 ± 0.20 kcal. mole^{-1} at 298.16°K. Calorimetric, spectroscopic and molecular structure data were used to compute the functions $(F^{\circ} - H_0^{\circ})/T$, $(H^{\circ} - H_0^{\circ})/T$, $H^{\circ} - H_0^{\circ}$, S° and C_{p}° at selected temperatures from 0 to 1000°K. The height of the potential barrier to internal rotation (*ca.* 600 cal. mole^{-1}) required for these calculations was evaluated from the experimental entropy and vapor heat capacity data. Values of $\Delta H_{\mathrm{f}}^{\circ}$, $\Delta F_{\mathrm{f}}^{\circ}$ and $\log_{10}K_{\mathrm{f}}$, for the formation of 3-methylthiophene in the ideal gaseous state from graphite, hydrogen and gaseous diatomic sulfur, were computed from the thermodynamic functions and appropriate calorimetric data.

An investigation of the chemical thermodynamic properties of thiophene[3] initiated the experimental and computational program conducted in this Laboratory to obtain thermodynamic data for organic sulfur compounds that occur in crude petroleum or are produced in refining processes. The primary purpose of these investigations is to provide accurate data for key members of the important families of sulfur compounds. These data will then be used to construct, by approximate statistical mechanical methods,[4] relatively complete tables of the chemical thermodynamic properties of organic sulfur compounds.[5]

This paper presents the results of detailed studies of the thermodynamic properties of 3-methylthio-

[1] This investigation was performed as part of American Petroleum Institute Research Project 48A on the "Production, Isolation and Purification of Sulfur Compounds and Measurements of their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyoming.

[2] University of Lund, Lund, Sweden.

[3] G. 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).

[4] *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).

[5] The compilation and tabulation of selected values of the properties of organic sulfur compounds will be part of the program of American Petroleum Institute Research Project 44.

phene, a key member of the family of alkyl thiophenes. The experimental results include values of the heat capacity of the compound in the solid, liquid and vapor states (12 to 473°K.), and the heats of fusion, vaporization and combustion. From these data are derived values of the entropy, the standard heat of formation from the elements, and the second virial coefficient. Details of the molecular structure that are discussed include the fundamental vibrational frequencies, the moments and reduced moment of inertia, and the potential barrier to internal rotation. Values of the thermodynamic functions $(F^\circ - H^\circ_0)/T$, $(H^\circ - H^\circ_0)/T$, $H^\circ - H^\circ_0$, S°, C°_p, ΔH°_f, ΔF°_f and $\log_{10} K_f$, computed by the usual methods of statistical mechanics and chemical thermodynamics, are tabulated at selected temperatures from 0 to 1000°K.

Experimental

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. The calorimetric data presented were based on a molecular weight of 98.164 for 3-methylthiophene and the following definitions: 0° = 273.16°K.; 1 cal. = 4.1840 abs. j. = 4.1833 int. j.

The Material.—The 3-methylthiophene used for the low temperature thermal studies and for determinations of the heat of combustion was part of the Standard Sample of Sulfur Compound, API–USBM serial No. 12, prepared and purified by American Petroleum Institute Research Project 48A at the Laramie (Wyo.) Station of the Bureau of Mines. In calorimetric melting point studies to be described below, the Standard Sample was found to contain 0.011 ± 0.005 mole % liquid-soluble, solid-insoluble impurity. A sample of slightly lower purity (99.8 mole %) was provided by the Laramie Station for use in the measurements of the heat of vaporization and vapor heat capacity. The samples of 3-methylthiophene were received in sealed ampoules with internal break-off tips and were stored in the dark at 40°F. Before use in the experimental studies, each sample was carefully dried in the liquid phase with calcium hydride, and transfers to appropriate receivers were made by vacuum distillations. At no time in the handling of the material or in the experiments were the samples in contact with gases other than helium.

The following physical properties of the Standard Sample of 3-methylthiophene were determined at the Laramie Station[8]: refractive index, $n^{25}\text{D}$ 1.51758; density, d^{25} 1.01647 g. ml.$^{-1}$.

The Heat Capacity in the Solid and Liquid States.—Measurements of the heat capacity of 3-methylthiophene in the solid and liquid states (12–337°K.) were made with an adiabatic calorimeter similar to that described by Ruehrwein and Huffman.[9] The sample (*ca.* 0.58 mole) was sealed in a platinum calorimeter equipped with horizontal, perforated heat-distributing disks of gold. A small amount of helium (30 mm. pressure) was left in the calorimeter to promote thermal equilibration at low temperatures. The observed heat capacities at saturation pressure (C_{satd}) of solid and liquid 3-methylthiophene are presented in Table I. The temperature increments used in the experiments were small enough that corrections for non-linear variation of C_{satd} with T were unnecessary (the increments employed 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 measurements was usually better than 0.1%; above 30°K., the accuracy uncertainty of the values of C_{satd} should not exceed 0.2%. The following empirical equation represents the heat capacity of liquid 3-methylthiophene within 0.01 cal. deg.$^{-1}$ mole^{-1} in the temperature range 207 to 337°K.

Table I

The Molal Heat Capacity of 3-Methylthiophene in Cal. Deg.$^{-1}$

T, °K.[a]	C_{satd}[b]	T, °K.	C_{satd}	T, °K.	C_{satd}
Crystals		54.05	9.399	163.12	19.725
		59.85	10.207	171.04	20.447
12.40	0.797	66.50	11.051	179.59	21.244
12.69	0.850	72.65	11.732	187.87	22.055
13.62	1.029	78.78	12.394	196.67	22.990
14.25	1.156	85.26	13.074		
14.97	1.302	91.73	13.676	Liquid	
15.78	1.468	98.39	14.235		
16.14	1.540	105.25	14.808	207.01	32.734
17.35	1.825	112.25	15.388	212.44	32.825
17.43	1.838	119.79	15.998	218.82	32.979
19.05	2.217	124.36	16.360	226.13	33.168
19.12	2.236	127.46	16.607	234.36	33.401
20.84	2.651	128.98	16.725	243.48	33.705
21.30	2.764	132.20	16.976	252.98	34.044
22.86	3.143	134.67	17.173	262.84	34.423
23.74	3.368	134.87	17.187	266.92	34.591
25.03	3.685	137.31	17.372	273.05	34.854
26.33	4.001	141.15	17.682	277.37	35.044
27.10	4.191	142.32	17.794	283.14	35.301
29.22	4.706	146.03	18.267	287.80	35.514
32.35	5.445	148.38	18.442	297.76	35.975
35.64	6.153	148.49	18.499	308.08	36.471
39.48	6.930	151.22	18.710	318.75	37.011
43.92	7.750	154.23	18.943	328.79	37.503
48.91	8.609	155.86	19.078	337.29	37.951
53.97	9.379	158.37	19.298		

[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.

$$C_{\text{satd}}(\text{liq.}) = 46.074 - 0.17610T + 6.8006 \times 10^{-4}T^2 - 6.8021 \times 10^{-7}T^3 \text{ cal. deg.}^{-1}\text{ mole}^{-1} \quad (1)$$

Fawcett[10] has reported that 3-methylthiophene may be crystallized in two distinct modifications but that the lower melting polymorph is unstable with respect to the higher melting. His results were confirmed in the present investigation. Since the instability of the lower melting polymorph made impossible reliable measurements of its heat capacity and melting point, the results in this paper concern only the stable crystalline modification.

A discontinuity was found near 145°K. in the plot of C_{satd} *vs.* T. To define better the heat capacity curve near 145°K. and to determine if the thermal treatment of the sample affected the results, a second series of measurements was made over the range 125 to 158°K. In the second series of experiments, the sample was cooled to the initial temperature (*ca.* 125°K.) at approximately one-half the rate used in the first series, and smaller temperature increments were employed. The results of the two series of observations were indistinguishable. Figure 1 shows the abrupt upward displacement (about 0.18 cal. deg.$^{-1}$ mole^{-1}) found in the heat capacity curve between 142 and 146°K. No heat effect accompanying this "transition" could be detected.

It is believed that the anomaly near 145°K. may be caused by the onset of internal rotation of the methyl group. Since, as will be shown later, the potential barrier to internal rotation in gaseous 3-methylthiophene is quite low (500 to 600 cal. mole^{-1}), it is possible that internal rotation may occur in the solid phase. Anomalies similar to that described above have been reported by other investigators, or may be detected in the results of several earlier low temperature heat capacity studies. Pitzer and Scott[11] have ascribed broad "humps" in the heat capacity curves for *m*- and *p*-xylene (near 50 and 100°K., respectively) to the beginning

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(6) Edward Wichers, This Journal, **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) W. E. Haines, R. V. Helm and J. S. Ball, unpublished data from American Petroleum Institute Research Project 48A, Bureau of Mines, Laramie, Wyo.

(9) (a) R. A. Ruehrwein and H. M. Huffman, This Journal, **65**, 1620 (1943); (b) H. M. Huffman, S. S. Todd and G. D. Oliver, *ibid.*, **71**, 584 (1949).

(10) F. S. Fawcett, *ibid.*, **68**, 1420 (1946).

(11) K. S. Pitzer and D. W. Scott, *ibid.*, **65**, 803 (1943).

of internal rotation. Inspection of Kelley's heat capacity data for toluene[12] and methyl alcohol[13] shows in each case a discontinuity near 125°K. that is similar to the results shown in Fig. 1; but the lower precision of Kelley's early work makes somewhat doubtful the reality of the discontinuities noted. The precise data presented by Jones and Giauque for nitromethane[14] show a definite point of inflection, and possibly a slight discontinuity, in the heat capacity curve near 150°K. Since these several compounds all have low potential barriers to internal rotation (0 to 1000 cal. mole^{-1}), it is reasonable to conclude with Pitzer and Scott[11] that the anomaly noted in each case is caused by the beginning of internal rotation in the solid phase. As would be expected if this explanation is valid, a discontinuity in the heat capacity curve for 2-methylthiophene was found near 160°K. in a study recently concluded in this Laboratory (to be published). The abrupt nature of the "transitions" in those compounds that possess only one internal rotational degree of freedom, as contrasted with the broad "humps" found for the xylenes, suggests that the onset of internal rotation in the monomethyl compounds is a more nearly cooperative phenomenon than in the dimethylbenzenes.

The Triple Point and Sample Purity.—As part of the low temperature calorimetric investigation, a study of the equilibrium melting temperature as a function of the fraction of sample melted was made by the method outlined in an earlier publication from this Laboratory.[15] The results of these observations are presented in Table II. The equilibrium melting temperatures, T_{obsd}, were plotted against the reciprocal of the fraction melted, $1/F$. The triple point, $T_{\text{T.P.}}$, was determined by linear extrapolation of these data to $1/F = 0$. The mole fraction of total impurity in the sample, N_2^*, was calculated by the relationship, $N_2^*/F = A(T_{\text{T.P.}} - T_{\text{obsd}})$, where A is the cryoscopic constant, $\Delta H_{\text{fusion}}/RT^2_{\text{T.P.}}$. This procedure is based on the assumption that ideal solutions are formed in the liquid phase and that the impurity is insoluble in the solid phase.

TABLE II

3-METHYLTHIOPHENE: MELTING POINT SUMMARY

Triple point, $T_{\text{T.P.}} = 204.19 \pm 0.05$°K.; cryoscopic constant, $A = 0.0304$ deg.$^{-1}$; impurity $= 0.011 \pm 0.005$ mole %.

Melted, %	$1/F$	T, °K. Obsd.	Graph[b]
10.02	9.99	204.1636	204.1576
26.21	3.816	.1814	.1793
50.52	1.979	.1858[a]	.1858
69.95	1.430	.1877	.1877
90.99	1.099	.1889[a]	.1889
100.00	1.000		.1892
Pure	*0.0*		*.1928*[c]

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

The Heat of Fusion.—Duplicate determinations of the heat of fusion of 3-methylthiophene both yielded the value 2518 cal. mole^{-1}. A third value of the heat of fusion, obtained in the melting point study, was only 0.5 cal. mole^{-1} lower than the results of the two direct measurements. To compute the isothermal heat of fusion from observed enthalpy changes over finite temperature intervals, the heat capacity data from Table I were approximately corrected for premelting, and a smooth curve through the corrected data was extrapolated to the triple point temperature.

The Heat of Vaporization.—Measurements of the heat of vaporization and vapor heat capacity of 3-methylthiophene were made with the flow calorimeter system described in previous publications from this Laboratory.[16] The vaporizer described in ref. 16a has been replaced by one constructed of metal, but the principle of operation remains the same. The heating element used for this investigation consisted of glass-insulated Nichrome wire sheathed by thin-walled copper tubing to prevent contact with the liquid under study. Glass thread wrapped around the copper sheath served to promote smooth ebullition.

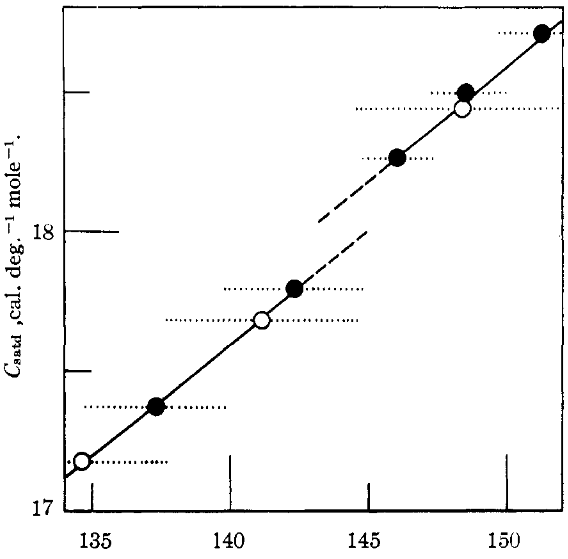

Fig. 1.—The discontinuity in the heat capacity curve of 3-methylthiophene. The open and solid circles represent points from two different series of measurements. The dotted lines show the temperature interval over which each measurement extended.

Triplicate measurements of the heat of vaporization were made at each of four temperatures from 329 to 389°K. (corresponding to vapor pressures of $^1/_8$, $^1/_4$, $^1/_2$ and 1 atm.). The results of these experiments are recorded in Table III. It is believed that the accuracy uncertainty of these values of the heat of vaporization should not exceed 0.1%. The following empirical equation represents the experimental data within ±2 cal. mole^{-1}

$$\Delta H_{\text{v}} = 13{,}593 - 13.913T,\ \text{cal. mole}^{-1} \quad (329 \text{ to } 389\text{°K.}) \qquad (2)$$

TABLE III

THE MOLAL HEAT OF VAPORIZATION AND GAS IMPERFECTION OF 3-METHYLTHIOPHENE

T,°K.	ΔH_{v}, cal.	$-B$ (obsd.), cc.	$-B$ (calcd.),[a] cc.	V,[a,b] cc.	$(\partial V/\partial T)_P$,[a,b] cc. deg.$^{-1}$
328.69	9019 ± 2[c]	1640	1900	213,870	674.79
346.11	8779 ± 3[c]	1510	1620	111,980	342.42
365.90	8502 ± 1[c]	1405	1375	58,675	174.98
388.60	8186 ± 2[c]	1215	1160	30,725	90.268

[a] Calculated with the aid of eq. 4. [b] At saturation pressure. [c] Maximum deviation of experimental results from the mean.

The Vapor Heat Capacity.—The vapor heat capacity of 3-methylthiophene was measured at 2 or more pressures at each of 4 temperatures between 375 and 473°K. The results are listed in Table IV. Values of the heat capacity in the ideal gaseous state, C_p°, were determined from the data at finite pressures by linear extrapolations to zero pressure.[16a] It is estimated that the accuracy uncertainty of these values of C_p° is less than 0.2%. The following empirical equation represents the "observed" values of C_p° within 0.01 cal. deg.$^{-1}$ mole^{-1}

$$C_p^\circ = -1.375 + 9.4508 \times 10^{-2}T - 4.2587 \times 10^{-5}T^2 \quad \text{cal. deg.}^{-1}\,\text{mole}^{-1}\ (375 \text{ to } 473\text{°K.}) \qquad (3)$$

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[12] K. K. Kelley, THIS JOURNAL, **51**, 2738 (1929).

[13] K. K. Kelley, *ibid.*, **51**, 180 (1929).

[14] W. M. Jones and W. F. Giauque, *ibid.*, **69**, 983 (1947).

[15] S. S. Todd, G. D. Oliver and H. M. Huffman, *ibid.*, **69**, 1519 (1947).

[16] (a) G. Waddington, S. S. Todd and H. M. Huffman, *ibid.*, **69**, 22 (1947); (b) G. Waddington and D. R. Douslin, *ibid.*, **69**, 2275 (1947).

TABLE IV

THE MOLAL VAPOR HEAT CAPACITY OF 3-METHYLTHIOPHENE IN CAL. DEG.$^{-1}$

T, °K.	375.20	398.25	438.25	473.25
C_p (760.0 mm.)		30.388	32.376	34.126
C_p (380.0 mm.)	28.627	29.902		
C_p (190.0 mm.)	28.367	29.712	31.999	33.889
C_p (95.0 mm.)	28.225			
C_p° (obsd.)	28.10	29.50	31.87	33.81
C_p° (calcd.)^a	27.85	29.27	31.62	33.52
$(\partial C_p/\partial P)_T$ (obsd.)	1.07	0.84	0.50	0.32
$(\partial C_p/\partial P)_T$ (calcd.)^b	1.09	0.80	0.50	0.35

^{a} Calculated from spectroscopic and molecular structure data. ^{b} Calculated by use of eq. 4; units of $(\partial C_p/\partial P)_T$ are cal. deg.$^{-1}$ mole^{-1} atm.$^{-1}$.

TABLE V

THE MOLAL ENTROPY OF 3-METHYLTHIOPHENE IN CAL. DEG.$^{-1}$

0–12°K.	Debye extrapolation^a	0.251
12–204.19°	Graphical, $\int C_{satd}\ d \ln T$	26.734
204.19°	Fusion, 2518/204.19	12.332
204.19–298.16°	Graphical, $\int C_{satd}\ d \ln T$	12.868
S_{satd}, liq., 298.16°K. (±0.10)^b		52.185

T, °K.	328.69	346.11	365.90	388.60
S_{satd}, liq.	55.764	57.724^c	59.886^c	62.287^c
$\Delta H_v/T^d$	27.438	25.365	23.236	21.065
$P(dB/dT)^e$	0.056	0.086	0.132	0.199
$R \ln (p/760)^f$	−4.128	−2.755	−1.377	0.000
$S°$, gas (obsd.)(±0.20)^b	79.13	80.42	81.88	83.55
$S°$, gas (calcd.)^g	79.11	80.42	81.90	83.58

^{a} A Debye function for 4 degrees of freedom with θ = 111.9° was used for this extrapolation. ^{b} Estimated accuracy uncertainty. ^{c} Extrapolated values; calculated with the aid of eq. 1. ^{d} Entropy of vaporization; from data of Table III. ^{e} Entropy of gas imperfection; from data of Table III. ^{f} Entropy of compression; from data of ref. 17. ^{g} Calculated from spectroscopic and molecular structure data.

Gas Imperfection and the Second Virial Coefficient.—The experimental values of the heat of vaporization and the vapor pressure data of White, Barnard-Smith and Fidler[17] were used to compute values of the second virial coefficient, $B = (PV - RT)/P$, from the Clapeyron equation in the form, $B = [\Delta H_v/T(dP/dT)] - RT/P + V_L$. where V_L is the molal volume of the liquid. Values of (d^2B/dT^2) were calculated from the observed pressure dependence of the vapor heat capacity by use of the relationship, $(\partial C_p/\partial P)_T = -T(\partial^2 V/\partial T^2)_P = -T(d^2B/dT^2)$. These results for B and its second derivative were correlated by means of the empirical equation

$$B = 75 - 94.56 \exp (1000/T), \text{ cc. mole}^{-1}\ (329 - 473\text{°K.}) \qquad (4)$$

in which T is in °K.; the numerical constants were evaluated by methods outlined in an earlier paper.[18] The values of B calculated from the Clapeyron equation and values of B and $(\partial V/\partial T)_P$ computed with eq. 4 are included in Table III.

The Entropy.—The entropy of the saturated liquid, S_{satd}, was computed from the low temperature calorimetric data. The entropy in the ideal gaseous state at 1 atm., $S°$, was calculated from values of S_{satd}, the data of Table III, and vapor pressure data.[17] Table V contains a summary of these calculations.

The Heat of Combustion.—The heat of combustion of 3-methylthiophene was determined in a rotating-bomb combustion calorimeter. The apparatus and method used for this investigation will be described in a forthcoming publication.[19] The results of 15 combustion experiments are summarized in Table VI. To determine if a heat effect resulted from reaction of the combustion products with the ampoule material, 3 series of combustions were made, in which the samples were contained in ampoules of soft (A), Pyrex (B) and Vycor glass (C).

All combustions were made in the platinum-lined bomb (Pt-4) described in ref. 19. The air originally present in the bomb was not removed, since small amounts of nitrogen oxides, formed from N_2 from the air, effectively catalyze the conversion of sulfur combustion products to H_2SO_4.[19] The bomb was charged with pure O_2 to a pressure of 30 atm. Each combustion was initiated at 23.00°, and the quantities of sample and auxiliary oil were chosen to produce approximately a 2° temperature increment in the calorimetric system. Approximately 70 sec. after ignition of the sample, the bomb was rotated simultaneously about 2 perpendicular axes for 90 sec. to rinse the interior parts with the bomb solution (*ca.* 11 ml.) and ensure that the solution was homogeneous and in equilibrium with the bomb gases.

The energy equivalent of the calorimetric system was determined from combustion experiments with benzoic acid, NBS Standard Sample 39g, which was certified to evolve 26.4338 abs. kj. per gram mass by combustion under specified conditions.[20] For the conditions of the calibration experiments, which were essentially those specified in ref. 20, a value of 26.4339 abs. kj. per gram mass was used. From six determinations, the energy equivalent of the calorimetric system, $\mathcal{E}_{eff}$(Calor.), was found to be 3909.4 ± 0.3[21] cal. deg.$^{-1}$. In each experiment, the energy equivalent of the initial contents of the bomb, $\mathcal{E}^i_{eff}$(Cont.), was approximately 13.7 cal. deg.$^{-1}$.

The last column of Table VI presents the experimentally determined values of $\Delta U_c^\circ/M$, the change in internal energy per gram mass of 3-methylthiophene for the idealized combustion reaction

$$C_5H_6S(\text{liq.}) + 8O_2(\text{gas}) + 68H_2O(\text{liq.}) \longrightarrow 5CO_2(\text{gas}) + H_2SO_4 \cdot 70H_2O(\text{aq.}) \qquad (I)$$

when each reactant and product is in the appropriate standard reference state at 25°.[22] The corrections listed in columns 5 to 10, Table VI, were used to compute the values of $\Delta U_c^\circ/M$ from the observed values of the energy of the isothermal bomb process. Since the methods for evaluating these corrections will be described in detail in ref. 22, only their magnitudes are given here.

Previous experience in this Laboratory had indicated that,

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

[18] D. W. Scott, G. Waddington, J. C. Smith and H. M. Huffman, *J. Chem. Phys.*, **15**, 565 (1947).

[19] W. N. Hubbard, Charles Katz and Guy Waddington, accepted for publication by *J. Phys. Chem.*

[20] (a) NBS certificate for Standard Sample 39g; (b) R. S. Jessup, *J. Research Natl. Bur. Standards*, **36**, 421 (1946).

[21] The uncertainty given is the standard deviation of the mean.

[22] W. N. Hubbard, D. W. Scott and Guy Waddington, accepted for publication by *J. Phys. Chem.*

TABLE VI[a,b]

SUMMARY OF 3-METHYLTHIOPHENE COMBUSTION EXPERIMENTS

Ampoule material	Comb. no.	m', g.	ΔT_0, °C.	Corrections, cal. q_{oil}	q_{fuse}	q_N	q_{diln}	q_{CO_2}	q_{corr}	$\Delta U_c^\circ/M$, cal. g.$^{-1}$
Soft glass	A_1	0.81344	1.99914	− 954.27	−15.46	8.50	0.00	3.46	0.76	−8432.0
	A_2	.80625	1.99981	−1018.64	−15.46	8.50	+ .03	3.47	.76	−8430.5
	A_3	.84394	1.99794	− 693.30	−15.18	8.02	− .07	3.42	.72	−8432.0
	A_4	.85810	1.99885	− 575.88	−15.34	7.39	− .09	3.42	.70	−8334.4
	A_5	.86658	1.99936	− 508.00	−16.16	7.39	− .12	3.40	.69	−8431.7
	A_6	.91454	1.99946	− 101.82	−15.22	8.92	− .22	3.35	.62	−8433.7
Pyrex	B_1	.82302	1.99988	− 877.50	−15.81	8.29	− .02	3.45	.75	−8430.5
	B_2	.85715	1.99972	− 588.08	−16.09	9.68	− .09	3.47	.62	−8430.2
	B_3	.86361	1.99846	− 530.30	−15.85	8.29	− .11	3.41	.70	−8430.0
	B_4	.86172	2.00049	− 553.69	−15.46	8.85	− .10	3.42	.70	−8430.4
	B_5	.90225	1.99833	− 205.40	−15.84	9.47	− .19	3.37	.64	−8427.4
Vycor	C_4	.79149	2.00217	−1150.77	−15.34	9.61	+ .04	3.50	.78	−8431.2
	C_5	.83019	1.99898	− 814.56	−16.28	8.22	− .04	3.44	.75	−8428.9
	(C_7)[c]	.87170	1.99702	− 461.65	−15.42	6.15	− .11	3.39	.68	−(8427.1)[c]
	C_8	.88459	1.99782	− 350.93	−15.57	8.71	− .15	3.38	.66	−8430.0

[a] Auxiliary data: C_{eff}(Calor.), 3909.4 cal. deg.$^{-1}$; C^{i}_{eff}(Cont.), 13.7 cal. deg.$^{-1}$; volume of bomb, 0.3471 l.; initial total pressure, 30 atm.; electrical ignition energy, 1.35 cal.; $\Delta U_c^\circ/M$(oil), 10,983.8 cal. g.$^{-1}$; $\Delta H_c^\circ/M$(fuse), 3,923 cal. g.$^{-1}$; $\Delta U_{decomp.}(HNO_3)$, +14,074 cal. mole^{-1}; $\Delta U_{decomp.}(HNO_2)$, −6,600 cal. mole^{-1}. [b] The column headings of this table correspond to the following computation item numbers of ref. 22: m', mass of sample, item 2; ΔT_c, items 79 − 78 − 80; q_{oil}, item 96; q_{fuse}, item 97; q_N, item 92; q_{diln}, items 90 + 91; q_{CO_2}, item 87; q_{corr}, items 81 + 82 + 83 + 84 + 85 + 88 + 89 + 93 + 94; $\Delta U_c^\circ/M$, item 99, is the change in internal energy for the idealized combustion reaction I at 25°. In these experiments, the total acid recovery ($H_2SO_4 + HNO_3 + HNO_2$) ranged from 99.6 to 100.7% theoretical. [c] The datum from comb. no. C_7 was not accepted, since deposits of carbon indicated the combustion reaction was incomplete.

in the combustion of sulfur-containing compounds, a significant heat effect might result from an unknown reaction that involved the glass of the ampoules used to contain liquid compounds.[19] It had been found that the fused remnants of soft glass ampoules were usually colored amber to dark brown but that the remnants of Pyrex or Vycor glass ampoules were clear. Furthermore, values of $\Delta U_c^\circ/M$ obtained when soft glass ampoules were employed usually differed slightly from those obtained when Pyrex or Vycor glass ampoules were used. The results of Table VI clearly show the magnitude of such a thermal effect in the combustion experiments for 3-methylthiophene. The average values of $\Delta U_c^\circ/M$ from the combustion experiments made with Pyrex and Vycor glass ampoules are in excellent accord ($-8429{.}_7 \pm 0{.}_6$[21] and $-8430{.}_0 \pm 0{.}_7$[21] cal. g.$^{-1}$, respectively) but differ significantly from the value obtained in the experiments made with soft glass ampoules ($-8432{.}_4$ $\pm 0{.}_6$[21] cal. g.$^{-1}$). Since, as usual, only the remnants of the soft glass ampoules were colored, it is believed that only in the experiments made with soft glass ampoules did significant reaction with the ampoule material occur. Therefore, the value selected for $\Delta U_c^\circ/M$, *as determined from 8 experiments conducted with Pyrex and Vycor glass ampoules*, is $-8429{.}_8 \pm 0{.}_4$[21] cal. g.$^{-1}$. From this value for $\Delta U_c^\circ/M$, the standard heat of combustion, ΔH_c°, for reaction I, was computed to be $-829.2_8 \pm 0.0_4$[21] kcal. mole^{-1} at 25°.

The Heat of Formation.—To compute the heat of formation of 3-methylthiophene from the above value of the heat of combustion, it was necessary to determine the standard heat of combustion of rhombic sulfur, *according to reaction* II

$$S(\text{rhombic}) + 3/2O_2(\text{gas}) + 71H_2O(\text{liq.}) \longrightarrow H_2SO_4\cdot 70H_2O(\text{aq.}) \quad \text{(II)}$$

when each reactant and product is in the appropriate standard reference state at 25°. This quantity was determined by combustion experiments made with mixtures of paraffin oil and rhombic sulfur. The amounts of oil and sulfur and the amount of water added to the bomb were adjusted to result in nearly the same final state as in the combustion experiments with 3-methylthiophene. The heat of combustion of the paraffin oil was determined in separate experiments. The value of ΔH_c° for reaction II was found to be $-143.5_8 \pm 0.0_9$[23] kcal. mole^{-1}. Determinations of the heats of combustion of 3-methylthiophene and rhombic sulfur under essentially identical conditions had the advantage that any systematic errors, if present, would largely cancel in the computation of the heat of formation.[19] The values obtained for the heats of combustion of 3-methylthiophene (reaction I) and rhombic sulfur (reaction II) were used with the heats of formation of carbon dioxide[24] and water[24] to compute ΔH_f°(liq.), the standard heat of formation (at 25°) of liquid 3-methylthiophene from C(graphite), H_2(gas) and S(rhombic). The standard heat of formation in the ideal gaseous state, ΔH_f°(gas), was computed from ΔH_f°(liq.) by addition of the standard heat of vaporization at 25°, as calculated by use of eqs. 2 and 4. Values of the standard free energy, ΔF_f°, and the logarithm of the equilibrium constant, $\log_{10}K_f$, for the formation of both liquid and gaseous 3-methylthiophene were calculated from the values for the heat of formation, the entropy at 25° (Tables V and IX), and thermodynamic functions for graphite,[24] hydrogen[24] and rhombic sulfur.[25] The heat of formation of S_2(gas) from rhombic sulfur and the thermodynamic functions of S_2(gas)[26] were used to compute ΔH_f°, ΔF_f° and $\log_{10} K_f$ for the formation (at 25°) of gaseous 3-methylthiophene from C(graphite), S_2(gas) and H_2(gas). These data are presented in Table VII.

TABLE VII

THE MOLAL HEAT AND FREE ENERGY AND THE LOGARITHM OF THE EQUILIBRIUM CONSTANT FOR THE FORMATION OF 3-METHYLTHIOPHENE AT 298.16°K.

State[a]	Reference state[b]	ΔH_f°, kcal.	ΔF_f°, kcal.	$\log_{10} K_f$
Liquid	S(rhombic)	10.49 ± 0.20[c]	27.15	−19.90
Gas	S(rhombic)	19.94 ± 0.23[c]	29.26	−21.45
	S_2(gas)	4.54	19.72	−14.45

[a] Standard state of 3-methylthiophene. [b] Reference state for elemental sulfur in the reactions: (A) 5C(graphite) + $3H_2$(gas) + S(rhombic) → C_5H_6S(liq. or gas); (B) 5C(graphite) + $3H_2$(gas)) + $^1/_2S_2$(gas) → C_5H_6S(gas). [c] See ref. 23.

Calculation of Thermodynamic Functions

The Vibrational Assignment.—To compute the thermodynamic functions of 3-methylthiophene by

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[23] The uncertainty given is twice the "over-all" standard deviation. See F. D. Rossini and W. E. Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

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

[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] National Bureau of Standards Report No. 1037, by W. H. Evans and D. D. Wagman.

appropriate methods of statistical mechanics, it was necessary to select the fundamental vibrational frequencies of the compound. The Raman[27] and infrared spectral data[28] used for this purpose are recorded in Table VIII. All of the data in Table VIII were determined from measurements made on portions of the Standard Sample of 3-methylthiophene, API–USBM 12, and will be published in the API 44 catalogs of Raman and infrared spectral data.

Table VIII

The Vibrational Spectra and Assignment for 3-Methylthiophene

3-Methylthiophene		Assignment			
Raman,[a] liq. cm.$^{-1}$	Infrared,[b] liq. cm.$^{-1}$	3-Methylthiophene cm.$^{-1}$	Thiophene cm.$^{-1}$	Designation No.	Class
236(30)		236	1290	20	A_2
323(20)	324	324	748	12	B_1
457(10)	459	458	453	23	B_2
485(10)				$(2 \times 236 = 472)$	
541(60)	544	543	604	1	A_1
	594	594	565	18	A_2
655(40)	*ca.* 661	655	686	19	A_2
	685	685	710	22	B_2
	760	760	832	10	B_1
	810			$(1036 - 236 = 800)$	
827(80)	831	829	832	3	A_1
853(70)	858	856	872	11	B_1
	877			$(324 + 543 = 867)$	
	913	913	909	24	B_2
928(80)	931	929		(CH_3 rock.)	
987(30)	993	990		(CH_3 rock.)	
	1036	1036	1032	2	A_1
	1050			$(236 + 829 = 1065)$	
1078(60)	1080	1079	1079	4	A_1
1152(80)	1156	1154		(C–C stretch.)	
	1205			$(655 + 543 = 1198)$	
	1239	1239	1252	14	B_1
	1282			$(594 + 685 = 1279)$	
1346(10)				$(594 + 760 = 1354)$	
1376(20)	1377	1377	1358	5	A_1
	1387	1387		(CH_3 bend.)	
1404(100)	1412	1408	1404	6	A_1
1450(40)	1456	1453(2)		(CH_3 bend.)	
1532(10)	1543	1538	1590	15	B_1
The region from 1600 to 2900 cm.$^{-1}$ has been omitted					
2921(90)	2933				
3058(60)		3000(6)		(C–H stretch.)	
3079(40)					
3107(100)	3125				

[a] Reference 27; relative intensities are given by the numbers in parentheses. [b] Reference 28.

The complex structure of 3-methylthiophene and its low symmetry precluded a detailed analysis of its vibrational spectrum. However, a schematic assignment of fundamental vibrational frequencies was made by comparison with assignments for pyrrole,[29] thiophene[3] and furan.[30] The assignment used in the calculations is given in Table VIII, along with the slightly revised assignment for thiophene.[30] The designation of the normal modes for the thiophene ring follows the terminology of Lord and Miller,[29] and the assignments to symmetry classes are, of course, valid only for thiophene.

In general, the frequencies not assigned to motions of the methyl group correspond closely (in activity, intensity and position) to fundamental frequencies of thiophene. The frequencies assigned to vibrations of the methyl group are in the expected regions of the spectra. It is reasonable to expect that of the 6 frequencies that appear below 600 cm.$^{-1}$, only 5 are fundamentals (2 from C–C–C bending modes involving the methyl group, and 3 analogous to the ring deformation modes, ν_1, ν_{18} and ν_{23} of thiophene). Best agreement with the calorimetric data was obtained by interpreting the weak Raman displacement at 485 cm.$^{-1}$ as the overtone, $2 \times 236 = 472$. Not all of the hydrogen frequencies above 1300 cm.$^{-1}$ were resolved, and average values were used for the CH_3 bending and C–H stretching frequencies.

Although the assignments to particular vibrational modes are doubtful in several instances, it is believed that all fundamental frequencies of 3-methylthiophene have been chosen, and that the assignment is adequate for use in the computation of thermodynamic functions. All frequencies not assigned as fundamentals have very low intensities and are readily explained as combination tones.

The Moments and Reduced Moment of Inertia.—The molecular structure of 3-methylthiophene has not been studied experimentally, but the results of Schomaker and Pauling's[31] electron diffraction investigation of thiophene were assumed to be applicable to the 3-methylthiophene ring. The length of the C–C bond joining the methyl group to the ring was taken as 1.54 Å., and the C–C–C angles involving the methyl group were assumed to be the same as the H–C–C angles at the β-carbon atoms of thiophene. The conventional tetrahedral configuration of the methyl group, with C–H bond distances of 1.09 Å., was used. On the basis of the assumed molecular structure, the product of the three principal moments of inertia was calculated to be 19.48×10^{-114} g.^{3} cm.^{6} The reduced moment of inertia for internal rotation, 5.182×10^{-40} g. cm.^{2}, was computed by the general method of Kilpatrick and Pitzer.[32]

The Potential Barrier to Internal Rotation.—Although the symmetry number for internal rotation in 3-methylthiophene is 3, the potential barrier is undoubtedly more complex than threefold. In molecules such as toluene, a sixfold barrier has been assumed,[11] but for 2-methylpropene[33] a threefold barrier was used. From molecular structure in-

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(27) Measurements of Dr. F. A. Miller, Mellon Institute of Industrial Research.

(28) (a) (14–40 μ) Measurements of Dr. F. F. Bentley, Materials Laboratory, Wright–Patterson Air Force Base; (b) (14–24 μ) Measurements made at the Laramie (Wyo.) Station, Bureau of Mines; (c) (2–15 μ) American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology, Catalog of Infrared Spectral Data, Serial No. 1301.

(29) R. C. Lord, Jr., and F. A. Miller, *J. Chem. Phys.*, **10**, 328 (1942).

(30) G. B. Guthrie, Jr., D. W. Scott, W. N. Hubbard, C. Katz, J. P. McCullough, M. E. Gross, K. D. Williamson and Guy Waddington, This Journal, **74**, 4662 (1952).

(31) V. Schomaker and L. Pauling, *ibid.*, **61**, 1769 (1939).

(32) J. E. Kilpatrick and K. S. Pitzer, *J. Chem. Phys.*, **17**, 1064 (1949).

(33) J. E. Kilpatrick and K. S. Pitzer, *J. Research Natl. Bur. Standards*, **37**, 163 (1946).

TABLE IX

THE MOLAL THERMODYNAMIC PROPERTIES OF 3-METHYLTHIOPHENE[a]

T, °K.	$(F° - H°_0)/T$, cal. deg.$^{-1}$	$(H° - H°_0)/T$, cal. deg.$^{-1}$	$H° - H°_0$, kcal.	$S°$, cal. deg.$^{-1}$	$C°_p$, cal. deg.$^{-1}$	$\Delta H°_f$,[b] kcal.	$\Delta F°_f$,[b] kcal.	$\log_{10} K_f$[b]
0	0	0	0	0	0	8.81	8.81	Infinite
273.16	−61.74	13.15	3.591	74.89	20.87	4.79	18.45	−14.76
298.16	−62.93	13.86	4.133	76.79	22.67	4.54	19.72	−14.45
300	−63.01	13.92	4.175	76.93	22.80	4.52	19.81	−14.43
400	−67.44	16.98	6.792	84.42	29.38	3.42	25.08	−13.70
500	−71.55	20.04	10.02	91.59	34.89	2.54	30.60	−13.38
600	−75.46	22.90	13.74	98.36	39.34	1.85	36.28	−13.21
700	−79.19	25.51	17.86	104.7	42.95	1.32	42.09	−13.14
800	−82.75	27.89	22.31	110.6	45.95	0.91	47.91	−13.09
900	−86.17	30.03	27.03	116.2	48.47	.63	53.81	−13.07
1000	−89.43	31.99	31.99	121.4	50.59	.46	59.73	−13.06

[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 3-methylthiophene by the reaction: $5C(\text{graphite}) + 3H_2(\text{gas}) + {}^1/_2S_2(\text{gas}) \rightarrow C_5H_6S(\text{gas})$.

formation and the value of the resonance energy, the C–C "single" bonds of thiophene have been shown to possess about 28% "double-bond character."[34] Thus, the ring C–C bonds of carbon atom 3 in 3-methylthiophene are probably intermediate between those of "1-$^1/_2$ order" in toluene and the single and double bonds in 2-methylpropene. Consequently, the potential barrier in 3-methylthiophene should be intermediate to these two extremes. Since, at temperatures at which experimental values of $S°$ and $C°_p$ are available, internal rotation in 3-methylthiophene is only slightly restricted, the calorimetric data cannot be used to obtain more detailed information as to the form of the potential barrier. Either a sixfold potential function, $V(\phi) = {}^1/_2\, V_0(1 + \cos 6\,\phi)$, with $V_0 = 600$ cal. mole^{-1}, or a threefold function, $V'(\phi) = {}^1/_2\, V'_0\,(1 + \cos 3\phi)$, with $V'_0 = 525$ cal. mole^{-1}, fits the calorimetric entropy and heat capacity data equally well.[35] These values of the barrier height were determined from the experimental entropy value alone, since the expected large effect of anharmonicity on the heat capacity could not be estimated reliably. The values of the functions $(H° - H°_0)/T$, $H° - H°_0$ and $(F° - H°_0)/T$, vary slightly depending upon which barrier form is assumed, for the zero point energies of the internal rotation are different in the two cases. However, the values calculated for $\Delta H°_f$, $\Delta F°_f$ and $\log_{10} K_f$, to be discussed in a later section, are not affected by any error from this source.

The Chemical Thermodynamic Properties.—The vibrational assignment, product of principal moments of inertia, reduced moment of inertia and potential barriers to internal rotation discussed in previous sections were used to compute values of the following thermodynamic functions of 3-methylthiophene at selected temperatures to 1000°K.: $(F° - H°_0)/T, (H° - H°_0)/T, H° - H°_0, S°$ and $C°_p$ (Table IX). In these calculations the molecule was treated as an harmonic oscillator, rigid rotator with independent internal rotation. Comparisons of the calculated heat capacity and entropy with the calorimetric data are made in Tables IV and V. The differences between $C°_p$ (obsd.) and $C°_p$ (calcd.), which are attributed to the unavoidable neglect of anharmonicity, are of the same order of magnitude as those found for thiophene.

The data of Tables VII and IX were used with thermodynamic data for C(graphite),[24] H_2(gas)[24] and S_2(gas)[26] to compute values of the standard heat, $\Delta H°_f$, standard free energy, $\Delta F°_f$, and common logarithm of the equilibrium constant, $\log_{10} K_f$, for the formation of gaseous 3-methylthiophene from the elements. Values of these functions at selected temperatures to 1000°K. are included in Table IX.

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(34) L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithaca, New York, 1940, p. 226.

(35) The contribution to the thermodynamic functions of restricted internal rotation was obtained by averaging the values calculated by use of the threefold and sixfold potential functions.