been reported for 3-methylthiophene (*6*), benzothiophene (*2*), 2-benzothiazole (*7*), and 2-methylfuran (*4*). A number of other benzene derivatives have more than one melting point (*8, 9*).

Third-Law Behavior. As may be seen by comparison of the two values of the entropy of the liquid at 260° K. cited in Table III, the discrepancy in closing the third-law cycle is $S_{0^\circ K.}$ (stable) $-S_{0^\circ K.}$ (metastable) = 0.23 cal./(mole ° K.). These values are based exclusively upon integration of data on the separate phases from 0° K. The entropy discrepancy is attributed not to zero point entropy of the metastable phase, but to experimental problems associated with the measurements on the metastable phase. This manner of treatment together with premelting contributions may account for the slight inversion of the Gibbs energies of the two phases in the vicinity of 220° K.

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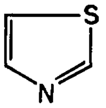
Heat Capacity and Thermodynamic Functions of Thiazole from 5° to 340° K.

PAUL GOURSOT[1] and EDGAR F. WESTRUM, Jr.

Department of Chemistry, University of Michigan, Ann Arbor, Mich. 48104

The heat capacity of thiazole was determined by adiabatic calorimetry from 5° to 340° K. A glass-type transition occurs between 145° and 175° K. Melting occurs at 239.53° K. with an entropy increment of 9.57 cal./(mole ° K.). At 298.15° K. the heat capacity, C_p, entropy, S°, and Gibbs energy function, $[(G^\circ - H^\circ_0)/T]$, are 28.92, 40.62, and −18.01 cal./(mole ° K.), respectively. The accord of the third-law, ideal-gas entropy at 298.15° K., 66.46 cal./(mole ° K.), with the spectroscopic value, 66.41 cal./(mole ° K.), indicates that the crystal is an ordered form at 0° K.

THIS is the first in a series of thermodynamic investigations of the properties of thiazole and its derivatives, which



extends a program of studies under way in the Organic Chemistry Department of the University of Marseilles (France) and correlates physicochemical properties with structural parameters. Results of thermal measurements on the solid through fusion and liquid phase yield values for chemical thermodynamic functions. The entropy of gaseous thiazole derived from the above results is compared with those calculated from spectroscopic measurements.

EXPERIMENTAL

Cryostat and Calorimeter. Measurements were made at temperatures between 5° and 340° K. by quasi-adiabatic calorimetry using the Mark III cryostat (*21*). The adiabatic shield was controlled to within 0.001° C. Manual shield operation was used below 50° K., and recording electronic circuitry provided with proportional, rate, and reset control action was used above this temperature. Energy exchange between calorimeter and surroundings was thereby reduced so that it was negligible in comparison with other sources of error. The sample was transferred in vacuo from a storage bulb to the gold-plated calorimeter (laboratory designation W-24A) sealed with a demountable valve in which a gold disk is pressed against a circular edge. Temperature was determined by an encapsulated platinum thermometer

[1] Present address: Department de Chimie Organique, Faculté des Sciences, 13 Traverse de la Barassee, 13 Marseille, France.

(laboratory designation A-3). The mass of the sample was 53.9424 grams in vacuo, and its heat capacity ranged from 92% of the total at 5° K. to 65% at 340° K. Buoyancy corrections used in determining the mass were made using a density of 1.18 grams per cc. (*13*). A helium pressure of 113 torr at 300° K. was used to facilitate thermal equilibration in the sample space. All measurements of mass, temperature, resistance, potential, and time are referred to standardizations and calibrations by the National Bureau of Standards. Adjustment for vaporization of the sample into the gas space (40 cc.) in the calorimeter based on the vapor pressure equation (*17*), $\log P$ (torr) $= 7.1411 - 1424.80/(t + 216.694)$ (t in ° C.), was found to be negligible, even in the liquid region.

Sample Preparation and Characterization. Thiazole was synthesized by standard procedures used at Marseilles (*14*). Amino-2-thiazole, commercially available, was converted by diazotization into 2-chlorothiazole and reduced to thiazole. This product was purified by distillation through a column packed with Tantal rings and subsequently through a spinning band column. Thiazole was characterized by its infrared spectra and stored under vacuum in sealed glass ampoules.

Table I. Fractional Melting of Thiazole[a]

$\bar{T}$	$\Sigma\Delta H_{excess}$	T_{final}	$1/F$
238.869	397.98	239.270	5.75
239.327	722.39	239.385	3.17
239.406	1049.55	239.425	2.18
239.441	1494.85	239.456	1.53
239.466	1937.34	239.475	1.18

Triple point of sample $T = 239.48°$ K.
Triple point of pure compound $T = 239.53°$ K.
Mole fraction of impurity 0.0009_3

[a] Units. Cal., mole, ° K. Data from melting determination Series IV.

Table II. Experimental Heat Capacity of Thiazole[a]

$\bar{T}$	C_s
Series I	
187.53	16.38
194.26	16.81
Series II	
206.38	17.58
222.67	19.03
231.21	21.12
237.32	74.86
239.26	1160
239.42	4780
239.46	11900
239.49	19000
242.19	76.98
Series III	
225.63	19.30
234.36	29.60
238.87	400
239.33	2839
239.41	8270
239.44	14500
239.47	24200
240.56	189
244.85	27.30
Series IV	
232.05	25.83
Series IV	
ΔHm detns. *A*	
244.63	27.66
Series V	
ΔHm detns. *B*	
Series VI	
180.25	16.01
190.21	16.54
209.69	17.73
Series VII	
177.57	15.85
ΔHm detns. *C*	
194.88	16.85
203.82	17.42
Series VIII	
250.67	27.33
256.96	27.62
265.81	27.97
275.69	28.23
284.40	28.53
292.60	28.78
301.39	29.00
310.12	29.44
318.76	29.94
327.32	30.61
336.57	31.58

[a] Units. Cal., mole, ° K.

Table II. Continued

$\bar{T}$	C_s
Series IX	
171.80	15.51
179.22	15.95
187.37	16.38
Series X	
58.46	8.827
61.87	9.153
66.87	9.565
74.41	10.052
82.48	10.553
90.57	10.978
101.23	11.414
112.37	11.889
122.79	12.356
ΔHt detns. *D*	
Series XI	
126.57	12.53
131.10	12.74
137.58	13.05
143.25	13.31
148.81	13.62
Series XII	
112.89	11.912
115.06	12.023
117.87	12.124
120.03	12.222
125.54	12.474
127.35	12.555
129.14	12.641
130.91	12.73
132.67	12.82
134.99	12.94
137.86	13.04
Series XIII	
134.91	12.93
141.93	13.42
146.53	13.11
149.18	13.67
152.15	13.85
154.50	14.00
156.24	14.09
157.99	14.25
159.71	14.52
161.41	14.60
162.81	14.76
163.94	14.90
165.06	15.10
166.44	15.27
168.10	15.31
169.75	15.37
174.57	15.67
182.48	16.12
Series XIV	
119.14	12.18
121.26	12.26
122.46	12.32
123.66	12.38
124.85	12.43
126.08	12.50
142.50	13.28
145.17	13.43
ΔHt detns. *E*	
Series XV	
144.41	13.41
147.16	13.54
150.13	13.69
152.18	14.04
153.33	14.21
154.49	14.07
155.65	14.17
156.80	14.54
157.92	14.85
159.04	14.76
160.18	14.66
161.30	14.92
162.41	15.06
163.52	14.95
164.64	15.02
165.76	15.13
166.86	15.27
Series XVI	
148.28	13.61
151.19	13.86
153.20	13.94
154.32	14.34
155.43	14.32
156.53	14.49
157.63	14.54
158.72	14.51
159.81	14.69
160.89	15.08
161.97	14.85
163.06	14.77
164.13	15.01
165.20	15.10
167.06	15.22
169.72	15.38
Series XVII	
145.32	13.42
ΔHt detns. *F*	
169.96	15.38
Series XVIII	
5.84	0.0727
6.28	0.0905
6.74	0.1118
7.28	0.1400
10.03	0.3485
12.80	0.7526
13.68	0.8892
14.53	1.0257
16.13	1.321
Series XIX	
15.63	1.226
17.40	1.577
18.81	1.883
20.42	2.237
22.59	2.737
25.28	3.370
27.99	3.989
30.68	4.595
33.78	5.260
37.56	6.002
41.45	6.671
45.49	7.297
50.49	7.944
56.17	9.223
61.87	9.151
67.08	9.569
ΔH detns. *G*	
142.71	13.31
ΔHt detns. *H*	
ΔH detns. *I*	
207.12	17.60
217.35	18.52
ΔHm detns. *J*	
245.31	27.29

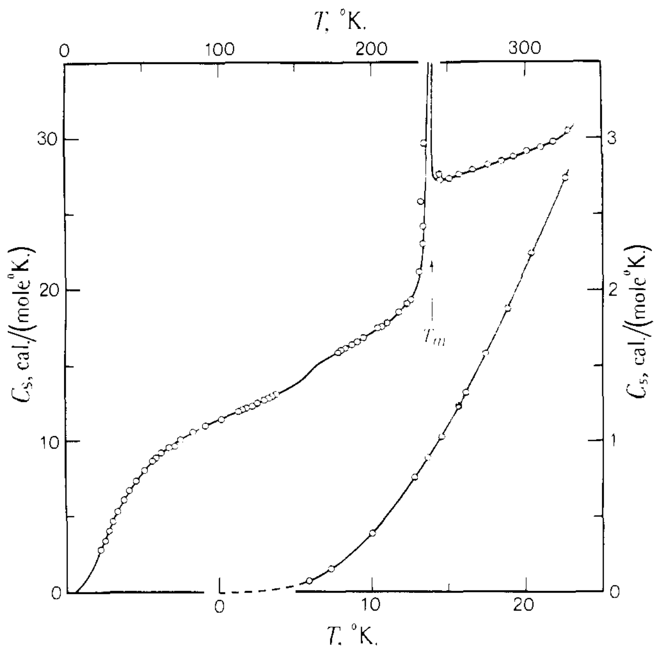


Figure 1. Heat capacity of thiazole

Experimental determinations indicated by circles except in the region of thermal anomaly, where they have been omitted for clarity in presenting inflections

Purity Determination. The amount of liquid-soluble, solid-insoluble impurity was estimated from the variation of the apparent melting temperature, T, against the reciprocal of the fraction melted, $1/F$, using the data given in Table I. The mole fraction of the impurity, N_2, is given by $N_2 = \Delta Hm\ (T_0 - T_1)/RT_0^2$. ΔHm is the enthalpy of melting, and T_0 and T_1 are triple point temperatures for the pure substance and for the sample—i.e., for values of $1/F$ = 0 and 1. The values found for T_0, T_1, and N_2 are 239.53° K., 239.48° K., and 0.0009_8. Meyer reported (*11*) T_0 = 239.58° K. from thermal analysis data.

RESULTS AND DISCUSSION

Heat Capacity and Thermodynamic Functions. The heat capacities at the mean temperature of the determination are listed in Table II and depicted in Figure 1. These data have been adjusted for curvature and are given in terms of the defined thermochemical calorie of 4.1840 joules, an ice point of 273.15° K., and a gram formula weight of 85.1314. The probable errors of the heat capacity measurements are considered to be 0.2% above 25° K. but increase gradually to 5% at 5° K. Heat capacities at selected temperatures listed in Table III were taken from a smooth curve obtained by a least squares fit polynomial function through experimental points and extrapolated below 6° K. by a Debye T^3 limiting law. The thermodynamic functions given in Table III were obtained by integrating the thermal data using a high speed computer program (*8*) and are considered to have a probable error of 0.1% above 100° K.

Thermal Anomaly between 145° and 175° K. The variation of the heat capacity as a function of temperature for crystalline thiazole between 145° and 175° K. reveals a marked inflection point as shown in Figure 1, the location and shape of which may be at least partially dependent on the thermal history of the sample. Heat capacity determinations across this region show an average reproducibility of 0.5%, in contrast to the 0.1% usually obtained. Presumably this might have been occasioned by the slow thermal equilibration and/or possible poor thermal conductivity of the sample in the inflection-temperature range, causing variable loss of heat to the shield. However, over the entire anomalous region, the average enthalpy increment, $H_{145} - H_{125}$ = 439 cal. per mole, was observed to have a nearly normal precision of 0.2% as shown in Table IV.

Table III. Thermodynamic Functions of Thiazole[a]

T	C_s	$S°$	$H° - H_0°$	$-(G° - H_0°)/T$
		CRYSTAL		
5	0.058	0.015	0.057	0.004
10	0.365	0.122	0.910	0.031
15	1.110	0.398	4.444	0.102
20	2.145	0.854	12.50	0.230
25	3.301	1.456	26.10	0.413
30	4.444	2160	45.49	0.644
35	5.503	2.926	70.40	0.915
40	6.439	3.724	100.31	1.216
45	7.221	4.529	134.5	1.539
50	7.879	5.324	172.3	1.878
60	8.980	6.865	257.0	2.582
70	9.779	8.312	350.9	3.298
80	10.409	9.660	452.0	4.010
90	10.937	10.918	558.8	4.709
100	11.385	12.094	670.5	5.389
110	11.791	13.198	786.3	6.049
120	12.216	14.242	906.3	6.689
130	12.686	15.238	1030.8	7.308
140	13.165	16.196	1160.1	7.909
145	13.418	16.662	1226.5	8.203
		THERMAL ANOMALY REGION, 145° TO 175° K.		
150	13.72	17.12	1294.3	8.49
155	14.16	17.58	1364	8.78
160	14.70	18.04	1436	9.06
165	15.11	18.50	1511	9.34
170	15.45	18.95	1587	9.62
175	15.61	19.40	1666	9.88
180	15.98	19.85	1745	10.16
190	16.53	20.73	1907	10.69
200	17.18	21.59	2076	11.21
210	17.77	22.44	2251	11.73
220	19.07	23.29	2433	12.23
225	20.96	23.74	2533	12.48
239.48[b]	(4776)	24.93	2810	13.20
		LIQUID		
239.48[b]	(4776)	34.49	5097	13.20
245	26.99	35.11	5247	13.69
250	27.29	35.66	5382	14.13
260	27.76	36.74	5658	14.98
270	28.10	37.79	5937	15.80
273.15	28.20	38.12	6026	16.06
280	28.38	38.82	6220	16.61
290	28.66	39.82	6505	17.39
298.15	28.92	40.62	6739	18.01
300	28.98	40.80	6793	18.15
310	29.42	41.75	7085	18.90
320	30.03	42.70	7382	19.63
330	30.87	43.63	7686	20.34
340	32.00	44.57	8000	21.04

[a] Units. Cal., mole, ° K. [b] Assuming melting completely isothermal.

Thermal anomalies with a similar dependence on temperature have been reported for methylamine (*1*), 2-methylthiophene (*2, 12*), 3-methylthiophene (*10*), and benzothiophene (*4*). These, together with the increase in the slope of the heat capacity curve above the transition temperature, have been attributed to a gain in molecular freedom.

Enthalpy and Entropy of Melting. In the course of the heat capacity measurements, four enthalpy increment determinations were made through the melting region (cf. Table V). The average enthalpy of fusion calculated from the excess enthalpy over extrapolated curves drawn to represent the crystalline and liquid heat capacities is 2292 cal. per mole, including the premelting contribution. The corresponding entropy increment is 9.57 cal./(mole °K.).

Liquid Phase. The following empirical equation represents the heat capacity of the liquid phase within 0.1% of the experimental values over the entire range of measurement.

$$C_s = 28.7287 + 1.2641T + 0.4989T^2 + 0.7638T^3$$

C_s varies nearly linearly with temperature to 310° K., at which temperature it rises more rapidly. Similar liquid-state thermal behavior for pyrrolidine (*9*) (the heat capacity of which is, however, slightly more convex), pyrrole (*16*), and mono- and trimethylamines (*1*) has been attributed to weak intermolecular association occurring in these nitrogen compounds.

Third-Law and Spectroscopic Entropy. The standard entropy of ideal gaseous thiazole at 298.15° K. was computed from the thermal data of this investigation and the vapor pressure equation of Soulié (*17*) as indicated in Table VI. The spectroscopic entropy of ideal gaseous thiazole was computed by standard methods (*7*) using values for the principal moments of inertia (I_a = 59.269 a.m.u./sq. A., I_B = 91.818 a.m.u./sq.A., and I_c = 151.087 a.m.u./sq.A.) calculated by Vincent *et al.* (*19*), the infrared spectroscopic studies of Davidovics *et al.* (*3*), the Raman investigations of Scheinker *et al.* (*15*) on liquid thiazole, and the assignments of Davidovics as summarized in Table VII. The calculated value of $S^\circ_{298.15}$(g) = 66.41 ± 0.09 cal./(mole °K.) is in good accord with that derived from thermal measurements (cf. Table VI), indicating that thiazole has no zero point entropy.

Table IV. Enthalpy through Region of Thermal Anomaly for Thiazole[a]

Designation	No. of Detns.	$H_{175} - H_{145}$
Series XIII	15	436.9
Series XV	16	440.5
Series XVI	16	440.1
Series XVII	3	437.1
Series XIX	2	440.3
Av. value, $H_{175} - H_{145}$		439.0

[a] Units. Cal., mole, ° K.

Table V. Enthalpy of Melting for Thiazole[a]

Designation	No. of Detns.	$H_{245} - H_{225}$
Series II	7	2713.4
Series III	9	2712.5
Series IV	4	2714.5
Series XIX	1	2715.2
Av. value, $H_{245} - H_{225}$		2713.9
Lattice contribution, $H_{245} - H_{225}$		426.9
Premelting (below 225° K.)		4.5
ΔHm		2292

[a] Units. Cal., mole, ° K.

Table VI. Experimental Third-Law Entropy of Thiazole[a]

Temp., ° C.	Basis	ΔS° or S°
0-5	Debye extrapolation	0.01
5-239.48	Crystal, $\int C_s d \log T$	25.03
239.48	Melting, 2292/239.48	9.57
239.48 – 298.15	Liquid, $\int C_s d \log T$	6.01
	Liquid	40.62 ± 0.04
	Vaporization, 9918/298.15[b]	33.26
298.15	Compression, $R \ln(P/760)$[b]	–7.48
	Adjustment to ideal gas[c]	0.06
	Gas	66.46 ± 0.20

[a] Units. Cal., mole, ° K. [b] Based on equation (*17*) log P (torr) = 7.1411 – 1424.80/(t + 216.694). [c] By comparison with values for pyridine, picoline, methylamine, and thiophene.

Table VII. Vibrational Spectrum and Assignment for Thiazole[a]

No.	$\tilde{\nu}$, Cm.$^{-1}$	Source (Phase)	Identification
1	3134	IR(g)	$\nu(C_5—H)$
2	3100	IR(g)	$\nu(C_4—H)$
3	3100	IR(g)	$\nu(C_4—H)$
4	1479	IR(soln)	Ω_1 A′
5	1380	IR(soln)	Ω_2 A′
6	1318	IR(soln)	Ω_3 A′
7	1240	IR(g)	$\delta(C—H)$
8	1124	IR(g)	$\delta(C—H)$
9	1043	IR(g)	$\delta(C—H)$
10	888	IR(g)	$\nu(C_4—H)$
11	864	IR(soln)	Ω_4 A′
12	811	Raman(l)	Ω_5 A′
13	797	IR(g)	$\nu(C_2—H)$
14	756	IR(shldr)	Ω_6 A′
15	716	IR(g)	$\nu(C—H)$
16	610	Raman(l)	Ω_7 A′
17	606	IR(soln)	Γ_1 A″
18	463	Raman(l)	Γ_2 A″

[a] Based upon assignments of Davidovics *et al.* (*3*).

CONCLUSIONS

The crystal structure of thiazole has not yet been studied at low temperature. Interpretations based only on low-temperature calorimetric data must remain somewhat speculative. These data suggest that an ordered orientation exists in the crystal structure below 130° K., whereas beyond 175° K. thiazole molecules may be randomly distributed among different orientations. Comparisons of the thermal behavior of several five-membered rings indicate that between 120° and 190° K. most exhibit one or more anomalies in the temperature dependence of the heat capacity. First-order solid-solid transitions occur in thiophene (125° K.) (*20*) furan (150° K.) (*5*), and cyclopentane (138° K.) (*18*); a second-order solid-solid transition occurs in thiophene (138° K.) (*20*) inflections occur in thiazole 160° K.), 2-methylthiophene (160° K.) (*2, 12*), and 3-methylthiophene (*10*). Enthalpies of melting have been determined for furan (187.5° K.) (*5*), thiacyclopentane 129.7° K.) (*6*), and cyclopentane (176.4° K.) (*18*). Larger molecular repulsion envelopes or molecular sizes yield smaller thermal irregularities in this kind of compound. Probably small differences in the ring nuclear geometry are obliterated by spatial considerations. Addition of a heteroatom—e.g., sulfur or oxygen—to a cyclopentane ring has little effect on the crystalline behavior; but increasing geometrical molecular volume or repulsive molecular envelope by introduction of one more heteroatom—e.g., thiazole—or one methyl group—e.g., 2-methylthiophene—appears to eliminate the glass-crystalline behavior completely.

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Some Thermodynamic Properties of High Purity Dimethyl Terephthalate

JOHN H. ELLIOTT and MARJORIE D. CHRIS
Research Center, Hercules, Inc., Wilmington, Del. 19899

To use the freezing point as a criterion of purity of 99.9+ mole % dimethyl terephthalate (DMT), its freezing point with zero impurity (t_{f_0}) was determined by the method of Schwab and Wichers. t_{f_0} in equilibrium with 1 atm. of N_2 is 140.655° ± 0.002° C.; in equilibrium with 1 atm. of air, 140.648° ± 0.002° C. on the international practical temperature scale. Its heat of fusion is 7560 cal. per mole, giving a cryoscopic constant of 0.0228 mole fraction per degree C. These results enable the purity of DMT to be estimated to 0.005 mole % by platinum resistance thermometry. The heat capacity of DMT from 30° to 200° C. was determined using an adiabatic calorimeter. The triple point of DMT is estimated to be 140.636° ± 0.004° C., and the variation of its freezing point with pressure is 0.042° C. per atmosphere. Thermometric cells, based on freezing DMT, maintain a temperature which is constant to 0.002° C. for at least 2 hours and are stable after prolonged heating at 155° C. and after 11 years' aging.

DIMETHYL TEREPHTHALATE (DMT), a large volume industrial chemical, is an important intermediate in the manufacture of polyesters. For this use, high purity (99.9+ mole %) is essential. The freezing point, t_f, of DMT is a commonly used criterion of purity. For this criterion to be meaningful, however, it is necessary to know the freezing point with zero impurity t_{f_0}, and the cryoscopic constant.

The lack of literature data on t_{f_0} or the cryoscopic constant prompted the present report of an extensive investigation of some thermodynamic properties of DMT which was carried out in our laboratories some years ago. The major portion of this paper deals with the establishment of t_{f_0} and the auxiliary data necessary to use the freezing point of DMT as a quantitative measure of purity. Certain other thermodynamic properties of DMT which were measured during the course of this work are included.

These studies demonstrated that DMT is a useful secondary thermometric standard. The preparation, reproducibility, and stability of thermometric cells employing DMT are discussed.

EXPERIMENTAL

Temperatures, on the international practical temperature scale (*11*), were measured by means of platinum resistance thermometers in conjunction with a Mueller bridge, a d.c. amplifier, and a recording potentiometer. Details of the equipment and calibrations are given below.

The Mueller bridge was the Leeds & Northrup Model G-2, reading in absolute ohms. It was calibrated by the National Bureau of Standards and this calibration was checked frequently with a standard 10.0099-ohm resistor (Leeds & Northrup), certified by both Leeds & Northrup and the National Bureau of Standards. Within the range of interest, bridge corrections never exceeded 0.0002 ohm or 0.002° C.

The detection circuit, in lieu of the usual galvanometer, was a Liston-Becker Model 14 d.c. amplifier and a Brown electronic strip chart recorder. The output of the amplifier was connected to the recorder through a 50-ohm attenuator. The recorder (50-mv., full scale) was modified so that the null point was at mid-scale. This measuring arrangement was stable and not affected by mechanical vibration. By