Heat Capacity and Thermodynamic Properties of 2-Methylthiazole from 5° to 350° K.

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The low temperature heat capacity of 2-methylthiazole was determined by adiabatic calorimetry. The stable form was characterized by a temperature of melting of 248.42° K. and an entropy of melting (ΔSm) of 11.70 cal./(mole ° K.). A metastable form melting at 246.50° K. was also investigated. For this phase ΔSm = 11.00 cal./(mole ° K.). The heat capacity (C_s), entropy (S°), enthalpy function $[(H^\circ - H^\circ_0)/T]$, and Gibbs energy function $[-G^\circ\ H^\circ_0)/T]$ in cal./(mole ° K.) for the liquid at 298.15° K. are: 36.01, 50.64, 28.13, and 22.50.

LOW TEMPERATURE HEAT CAPACITY measurements on 2-methylthiazole have been made in conjunction with the thermodynamic investigation of the properties of thiazole and its derivatives initiated by Metzger and his associates at Marseilles (*3*, *10*). In addition to providing values of thermodynamic functions and the melting behavior of both stable and metastable forms, the work is of special interest because, in contrast to several other compounds with a methyl group on an aromatic ring—e.g., 2-methylthiophene (*1*) and 3-methylthiophene (*6*)—this one does not show a point of inflection in the heat capacity characteristic of a glass-type transition.

EXPERIMENTAL

Preparation and Characterization of Sample. 2-Methylthiazole was synthesized by action of dibromoether on a mixture of acetamide and P_2S_5 in dioxane, purified by distillation through a spinning band column, characterized by its infrared spectrum, and stored in evacuated, sealed glass ampoules.

Determination of Purity. The amount of liquid-soluble, solid-insoluble impurity was estimated from a plot of the apparent melting temperature, T, against the reciprocal of the fraction melted, $1/F$, as presented in Table I. The mole fraction, N_2, of the impurity is given by (*14*):

$$N_2 = \Delta Hm(T_0 - T_1)/RT_0^2$$

ΔHm is the enthalpy of melting of the stable phase; T_0 and T_1 are the temperatures corresponding to $1/F = 0$ and 1, respectively. The values of T_0, T_1, and N_2 found are 248.42° K., 248.20° K., and 0.0040.

Cryostat and Calorimeter. Measurements were made in the Mark III vacuum cryostat (*12*) by the quasi-adiabatic technique (*13*). The gold-plated copper calorimeter used (laboratory designation W-24A) had horizontal radial vanes and a volume of 90.4 cc. The heat capacity of the calorimeter-heater-thermometer assembly was determined in a separate series of measurements. Only minor adjustments were needed for the difference between these determinations and those on the loaded calorimeter for the slight differences in amount of Cerroseal (indium-tin) solder for sealing the calorimeter, Apiezon T grease for thermal contact with the heater-thermometer assembly, and helium gas in the sample space. The mass of the calorimetric sample was 61.3387 grams in vacuo, and its heat capacity ranged from 92% of the total at 5° K. to 62% at 350° K. Buoyancy corrections were made using a sample density of 1.1106 grams per cc. (*11*). A helium pressure of 120 torr at 300° K. was used to facilitate thermal equilibration in the sample space. A capsule-type, strain-free platinum resistance thermometer (laboratory designation A-3) located within the entrant well of the calorimeter was used to determine termperature. Above the oxygen point, the scale is believed to accord with the thermodynamic temperature scale to within 0.03° K. All measurements of mass, temperature, resistance, voltage, and time are referred to calibrations or standardizations made by the National Bureau of Standards.

Table I. Fractional Melting of 2-Methylthiazole[a]

T	ΔT	C_s	$\Sigma\Delta H_{\text{excess}}$	T_{final}	$1/F$
246.03	2.781	225	540.8	247.42	5.396
247.54	0.232	1280	1010.7	247.66	2.887
247.73	0.162	1830	1303.8	247.81	2.238
247.85	0.069	4360	1601.1	247.88	1.823
247.91	0.059	5290	1909.8	247.94	1.528
247.96	0.048	10040	2386.4	247.99	1.223
248.07	0.158	3030	2860.8	248.15	1.020
Triple point of pure compound				= 248.42	
Triple point of sample				= 248.20	
Mole fraction impurity				= 0.0040	

[a] Units. Cal., mole, ° K. Based upon melting detns. *B*. Data are for stable crystalline phase.

RESULTS AND DISCUSSION

Heat Capacities and Other Thermal Properties. The experimental heat capacities at the mean temperatures of the determinations are presented in Table II in chronological order 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 molecular weight of 99.1551.

The smoothed heat capacities and the thermodynamic functions derived from these data are given at selected temperatures in Table III. The heat capacity was extrapolated below 6° K. by a Debye T^3 limiting law. These values, obtained by means of a high-speed digital computer using programs previously described (*5*), have been checked by comparison with large scale plots of the data. The thermodynamic functions are believed to have a precision charac-

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Table II. Heat Capacities of 2-Methylthiazole[a]

T	C_s
Series I	
Melting detns. *A*	
266.72	34.79
280.05	35.35
Series II	
220.27	23.27
Melting detns. *B*	
265.34	34.74
Series III	
209.56	21.88
220.63	23.38
ΔHm detns. *C*	
Series IV	
ΔHm detns. *D*	
Series V	
112.44	14.75
188.98	20.11
208.57	21.81
Series VI	
ΔHm detns. *E*	
Series VII[b]	
5.52	0.054
6.31	0.118
7.94	0.274
8.92	0.391
9.94	0.530
10.96	0.705
12.04	0.900
13.11	1.112
14.26	1.393
18.00	2.340
19.38	2.687
20.92	3.123
22.65	3.610
24.82	4.225
27.15	4.893
29.35	5.518
31.75	6.176
34.30	6.871
37.24	7.574
40.85	8.409
45.37	8.960
50.74	9.888
64.16	11.765
71.71	12.648
80.95	13.549
91.46	14.343
101.27	15.04
111.01	15.72
120.59	16.25
129.95	16.76
139.00	17.32
151.26	17.98
Series VIII	
ΔHm detns. *F*	
268.08	34.81
Series IX[b]	
ΔHm detns. *G*	
259.92	34.50
Series X	
5.54	0.044
6.90	0.207
7.67	0.324
8.43	0.442
Series XI	
7.24	0.258
9.27	0.593
9.88	0.713
10.58	0.859
11.53	1.063
12.69	1.338
14.19	1.710
15.91	2.174
17.83	2.710
20.03	3.332
24.29	4.546
26.47	5.142
28.76	5.738
31.77	6.491
35.24	7.298
39.25	8.125
44.07	8.970
49.70	9.412
56.43	10.276
63.46	11.074
70.56	11.771
78.27	12.379
85.84	13.003
93.45	13.525
101.77	14.06
119.78	15.23
129.49	15.89
139.75	16.58
150.19	17.27
159.75	17.87
168.70	18.59
177.96	19.22
189.54	20.15
204.09	21.37
Series XII	
144.90	17.59
158.25	18.37
171.54	19.14
184.95	20.09
Series XIII	
194.17	20.77
ΔH detns. *H*	
Series XIV	
ΔHm detns. *I*	
Series XV[b]	
223.05	24.05
ΔHm detns. *J*	
Series XVI	
272.13	34.97
281.84	35.40
291.43	35.77
302.00	36.13
312.39	36.72
322.64	37.23
332.78	38.02
340.61	38.51

[a] Units. Cal., mole, °K. [b] Series VII, IX, and XV run on metastable crystalline form.

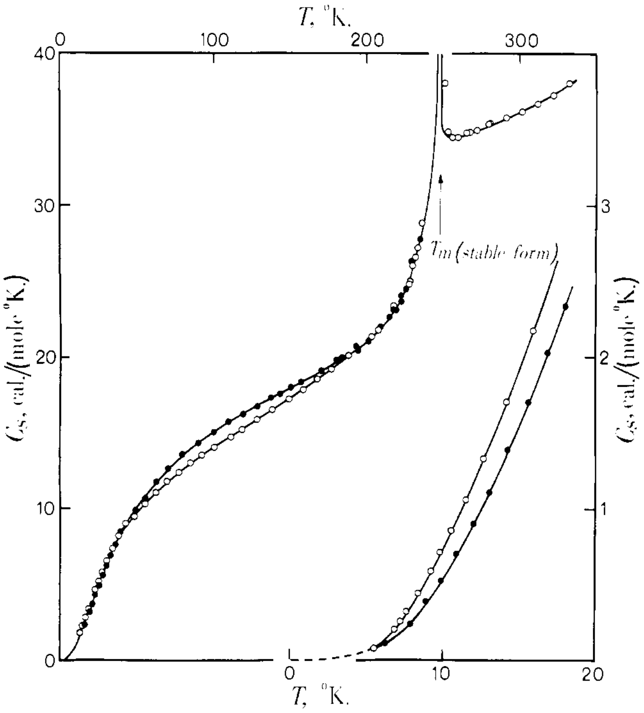

Figure 1. Heat capacity of 2-methylthiazole

○ Experimental determinations on stable phases

● Experimental data on metastable phase

terized by a probable error of less than 0.3% above 50° K. The entropy and the Gibbs energy function have not been adjusted for nuclear spin and isotopic mixing contributions and are hence practical values for use in chemical thermodynamic calculations.

Melting and Freezing Behavior of Stable and Metastable Forms. The phase equilibria and consequently the thermal behavior of 2-methylthiazole are complicated by the existence of both stable and metastable forms. From the summary in Table IV, the stable form is seen to have a melting temperature, *Tm*, of 248.42° K. and an enthalpy of melting, ΔHm, of 2907 cal. per mole. The variation of heat capacity with temperature, for the stable form, is depicted by the continuous curve in Figure 1 over the entire crystalline region.

This behavior is in marked contrast to that observed in thiazole (*3*), where an inflection in the temperature dependence of the heat capacity was observed between 145° and 175° K. It was noted (*1, 6*) in a similar series of compounds that introduction of a methyl group to a thiophene ring appears to lessen the probability of a transition in the crystalline phase, but occasions an inflection in the temperature dependence of the heat capacity for both 2- and 3-methylthiophene. These facts may support the hypothesis that the methyl group is more embedded in the thiazole ring than in the thiophene ring, and that, hence, no additional degree of freedom is obtained upon increasing the temperature, or alternatively, that inflections in the C_s *vs.* T curves noted for 2- and 3-methylthiophene and for thiazole may be attributed to librational motion of the ring. In that case, introduction of a methyl group or a heteroatom like nitrogen could preclude such librational motions at low temperatures. Introduction of a methyl group between sulfur and nitrogen may prevent these librational motions over the entire temperature range of the crystalline state by the loose packing caused by the steric effects of a methyl group or by a change in geometrical structure of the molecule. Diffractional and structural studies on this and related compounds are desiderata in providing a firmer understanding of this phenomenon.

Table III. Thermodynamic Functions of 2-Methylthiazole[a]

T	C_s	S°	$H^\circ - H_0^\circ$	$-(G^\circ - H_0^\circ)/T$
		STABLE CRYSTAL		
5	0.090	0.030	0.113	0.008
10	0.735	0.230	1.748	0.055
15	1.927	0.742	8.273	0.191
20	3.327	1.486	21.36	0.418
25	4.741	2.382	41.56	0.719
30	6.055	3.364	68.60	1.077
35	7.245	4.388	101.90	1.477
40	8.265	5.425	140.77	1.906
45	9.051	6.445	184.12	2.353
50	9.687	7.433	231.02	2.812
60	10.710	9.292	333.2	3.739
70	11.622	11.012	444.9	4.657
80	12.499	12.622	565.5	5.553
90	13.306	14.142	694.6	6.424
100	14.013	15.581	831.3	7.268
110	14.641	16.947	974.6	8.086
120	15.245	18.246	1124.0	8.879
130	15.877	19.491	1279.6	9.648
140	16.552	20.692	1441.7	10.394
150	17.251	21.858	1610.7	11.120
160	17.95	22.994	1787	11.827
170	18.64	24.103	1970	12.516
180	19.38	25.189	2160	13.190
190	20.19	26.258	2358	13.850
200	21.04	27.315	2564	14.497
210	21.92	28.36	2778	15.13
220	23.25	29.41	3003	15.76
230	24.96	30.48	3245	16.37
240	26.55	31.58	3502	16.98
248.42[b]	(27.90)	32.52	3732	17.49
		LIQUID		
248.42[b]	(34.03)	44.22	6639	17.49
255	34.24	45.15	6872	18.20
260	34.49	45.81	7043	18.72
270	34.92	47.12	7391	19.75
273.15	35.04	47.53	7501	20.07
280	35.30	48.40	7742	20.75
		LIQUID		
290	35.68	49.65	8097	21.73
298.15	36.01	50.64	8389	22.50
300	36.09	50.86	8455	22.68
		METASTABLE CRYSTAL		
5	0.067	0.022	0.084	0.006
10	0.543	0.171	1.305	0.041
15	1.557	0.568	6.368	0.143
20	2.872	1.192	17.38	0.323
25	4.274	1.983	35.22	0.574
30	5.699	2.888	60.16	0.883
35	7.041	3.870	92.08	1.239
40	8.203	4.887	130.23	1.631
45	9.023	5.897	173.2	2.049
50	9.832	6.890	220.3	2.484
55	10.568	7.862	271.4	2.928
60	11.240	8.811	325.9	3.379
70	12.413	10.634	444.3	4.287
80	13.403	12.358	573.5	5.189
90	14.249	13.987	711.9	6.077
100	14.99	15.527	858.2	6.946
110	15.64	16.987	1011.4	7.793
120	16.24	18.374	1170.8	8.617
130	16.80	19.697	1336.1	9.419
140	17.35	20.962	1506.9	10.199
150	17.89	22.18	1683	10.96
160	18.45	23.35	1865	11.70
170	19.05	24.49	2052	12.41
180	19.71	25.59	2246	13.12
190	20.45	26.68	2447	13.80
200	21.33	27.75	2655	14.47
210	22.37	28.81	2874	15.13
220	23.62	29.88	3103	15.78
225	24.35	30.42	3223	16.09
246.50[b]	(26.85)	32.75	3772	17.45
246.50[b]	(34.30)	43.75	6485	17.45
260	34.49	[45.58][c]	[6947][c]	[18.86][c]

[a] Units. Cal., mole, ° K. [b] Assuming melting completely isothermal. [c] Exclusively from thermal data on metastable solid phase.

Table IV. Enthalpy of Melting of 2-Methylthiazole[a]

Detn. Designation	No. of Detns.	T_1	T_2	$H_{T_2} - H_{T_1}$	$H_{255} - H_{225}$
		STABLE CRYSTAL			
A	11	230.21	254.58	3599.89	3745.5
B	11	224.60	256.54	3813.01	3751.7
C	2	226.03	259.38	3874.31	3749.3
D	1	255.97	252.80	3648.19	3751.1
E	2	229.17	258.42	3759.75	3745.7
F	3	222.54	261.38	4027.20	3749.6
Av. value,				$H_{255} - H_{225} =$	3748.8
Lattice contribution,				$H_{255} - H_{225} =$	841.9
$Tm = 248.42$				$\Delta Hm =$	2907
				$\Delta Sm =$	11.70
		METASTABLE CRYSTAL			
G	5	226.92	257.00	3577.62	3557.7
H	4	226.82	262.86	3773.65	3546.0
Av. value,				$H_{255} - H_{225} =$	3551.9
Lattice contribution,				$H_{255} - H_{225} =$	839.5
$Tm = 246.50$				$\Delta Hm =$	2712
				$\Delta Sm =$	11.00

[a] Units. Cal., mole, ° K.

A metastable form melting at $T = 246.50°$ K. and involving a ΔHm of 2712 cal. per mole and a corresponding ΔSm of 11.00 cal. per mole ° K. was also noted. The thermal data are summarized in Table IV. Observation of the cooling curves showed that the sample invariably crystallized in the metastable form under the experimental cooling rate after an undercooling of about 15° K. below its melting temperature. Upon heating the metastable form from low temperatures to about 170° K., transformation to the stable form occurred spontaneously but sometimes after a delay as long as 40 hours in this region. This hysteresis phenomenon represented typical behavior. However, by cooling fairly rapidly (about 0.3° K. per minute) down through the 170° to 200° K. region, this metastable form could be cooled to 5° K. and heat capacity measurements performed. On making heat capacity measurements through the temperature range 170° to 200° K., we invariably transformed the metastable form to the stable form. The enthalpy increment (ΔHt) accompanying the conversion from the metastable form to the stable crystalline form was sufficient to heat the calorimeter assembly approximately 4.2° K. in a 1.5-hour period under adiabatic conditions. This corresponds to a $\Delta Ht = -198$ cal. per mole for the transformation of metastable crystals to stable crystals at about 204° K. It accords with an enthalpy increment of 208 cal. per mole deduced from values cited in Table III. The metastable form exhibits a lower heat capacity than the stable form up to 40° K. (Figure 1). Above this temperature the positions of the curves are inverted. The lower entropy of melting and higher heat capacity through the higher temperature range suggest that the metastable form is more disordered than the stable form. Metastable forms have 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 $S_{0^\circ \mathrm{K.}}$ (stable) $-S_{0^\circ \mathrm{K.}}$ (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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LITERATURE CITED

(1) Carlson, H.G., Westrum, E.F., Jr., J. CHEM. ENG. DATA **13**, 273 (1968).

(2) Finke, H.L., Gross, M.E., Messerly, J.F., Waddington, G., *J. Am. Chem. Soc.* **76**, 854 (1954).

(3) Goursot, P., Westrum, E.F., Jr., J. CHEM. ENG. DATA **13**, 471 (1968).

(4) Hickman, J.B., *J. Am. Chem. Soc.* **75**, 4344 (1953).

(5) Justice, B.H., Ph.D. dissertation, University of Michigan, Ann Arbor, Mich., 1961, U. S. Atomic Energy Commission Rept. **T.I.D.-12722** (1961).

(6) McCullough, J.P., Sunner, S., Finke, H.L., Hubbard, W.N., Gross, M.E., Pennington, R.R., Messerly, J.F., Good, W.D., Waddington, G., *J. Am. Chem. Soc.* **75**, 5075 (1953).

(7) Meyer, R., Metzger, J., *Compt. Rend.* **1967**, 1333.

(8) Putnam, W.E., Kilpatrick, J.E., *J. Chem. Phys.* **27**, 1075 (1957).

(9) Taylor, R.D., Johnson, B.H., Kilpatrick, J.E., *Ibid.*, **23**, 1225 (1955).

(10) Vincent, E.J., Phan Tan Luu, R., Metzger, J., *Bull. Soc. Chim. France* **1966**, 3567.

(11) Vincent, E.J., Phan Tan Luu, R., Metzger, J., Surzur, J.M., *Comp. Rend.* **1965**, 6345.

(12) Westrum, E.F., Jr., *J. Chem. Educ.* **39**, 443 (1962).

(13) Westrum, E.F., Jr., Furukawa, G.T., McCullough, J.P., "Adiabatic Low-Temperature Calorimetry," in "Experimental Thermodynamics," J.P. McCullough and D.W. Scott, eds., Butterworth's, London, 1968.

(14) Westrum, E.F., Jr., McCullough, J.P., "Thermodynamics of Crystals," in "Physics and Chemistry of the Organic Solid State," D. Fox, M.M. Labes, A. Weissberger, eds., Vol. 1, p. 32, Interscience, New York, 1963.

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

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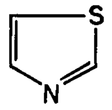
The heat capacity of thiazole was determined by adiabatic calorimetry from 5° to 340° K. A glass-type transition occurs between 145° and 175° K. Melting occurs at 239.53° K. with an entropy increment of 9.57 cal./(mole ° K.). At 298.15° K. the heat capacity, C_p, entropy, S°, and Gibbs energy function, $[(G^\circ - H^\circ_0)/T]$, 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

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