2-Methylfuran—Heat Capacity and Thermodynamic Properties from 5° to 310° K.

H. GARY CARLSON and EDGAR F. WESTRUM, Jr.
Department of Chemistry, University of Michigan, Ann Arbor, Mich.

The heat capacity of 2-methylfuran has been measured over the low temperature range by adiabatic calorimetry. A fractional melting study applied over the premelting region indicated an enthalpy of melting (ΔH_m) of 2044 cal. per mole and temperature of melting (T_m) of 181.90° K. Values of the heat capacity at saturation (C_s), the entropy ($S°$), and the Gibbs function $[-(G° - H°_0)/T]$ are 34.35, 51.12, and 24.26 cal. per (mole ° K.), respectively, at 298.15° K.

AS PART of a continuing investigation of the glass-type transformation occurring in 2-methylthiophene (*1*) and in 2,5-dimethylthiophene (*2*), an investigation was made of the thermal properties of 2-methylfuran. Inability to obtain a sample of as high purity as is desirable for calorimetric investigation precludes definitive results. However, the by-product thermal and chemical thermodynamic data may be of considerable interest for scientific and technological purposes. No evidence for a glass-type transformation was found in the sample. Because this furan derivative melted some 30° K. below the analogous thiophene, it is probable that both the over-all and internal molecular freedom of the two molecules are quite different.

EXPERIMENTAL

Cryostat and Calorimeter. Measurements were made in an adiabatic, vacuum cryostat, similar to one previously described (*5*) equipped with automatic regulation of the adiabatic shield but without a helium economizer. Copper-constantan two-element thermopiles sense the temperature difference between the calorimeter and adiabatic shield. The cylindrical silver calorimeter with entrant thermometer-heater well and demountable valve (W-14) which was used for this investigation is similar to one described elsewhere (*1*). The eight (5-mm. thick) circular vanes along the heater-thermometer well were machined with the well from solid silver rod. Closure of the calorimeter was made possible by a valve sealed by a small gold disk pressed against a sharp orifice by a demountable valve assembly.

Sample Preparation and Loading. The 2-methylfuran was prepared by repeated fractionation (under purified helium gas) of a commercial sample. After 2 months' storage in vacuo at 70° K., a final distillation in the vacuum-loading line gave a clear, colorless product which was collected in a graduated receiver and transferred as liquid into the outgassed calorimeter by a small helium pressure in the vacuum line. The calorimeter was then closed to maintain a vacuum-tight seal. After completion of calorimetric measurements, two separate portions of the sample were analyzed. The following values were obtained: 72.81 ± 0.05 and 72.74% of carbon; 7.52 and 7.61% of hydrogen (theoretical values: 73.15% and 7.37%, respectively). A purity determined by fractional melting (discussed below) indicated 99.16 mole % of 2-methylfuran. The weight of the sample was 57.634 grams (in vacuo). Its heat capacity represented 60 to 70% of the total over most of the temperature range.

RESULTS

Heat Capacity. The thermal history of the sample may be inferred from Table I. In these tables, the experimental heat capacities are presented in chronological sequence at the mean temperatures of the determinations. These data are given in terms of the defined thermochemical calorie equal to 4.1840 j., an ice point of 273.15° K., and a mole equal to 82.103 grams. The data have been adjusted for curvature and for the vaporization of the sample into the vapor space in the calorimeter. Static determination of the vapor pressure of the sample gave the following results: | *t*, ° C.; *p*, mm. | 19.5, 132 | 0, 51 | -22, 13 | -60, 0 |. These results and a literature value | 63,737| (*3*) may be represented by the equation:

$$\log p_{(\text{mm.})} = 8.0557 - 1739.13/T$$

A value for ΔH_v of 7959 cal. per mole, calculated from the vapor pressure data, was used as a temperature independent constant in the correction of the liquid heat capacity. A gaseous heat capacity of 38 cal. per (mole ° K.) was assumed. These heat capacity values for the condensed phases are considered to have a probable error of less than 0.5% above 10° K.

The liquid phase was observed to undercool as much as 30° below the freezing point. Equilibrium was reached within two hours at all temperatures below 170° K. However, in the region where the sample was more than 10% melted, a static temperature (rate of change no greater than a few ten-thousandths of a degree per hour) was attained only upon a 10-hour wait after an energy addition.

Fractional Melting. Assuming that the solution of liquid 2-methylfuran and liquid-soluble, solid-insoluble impurity is ideal, the calculated value for the mole fraction of impurity is 0.0084, and the melting point for the pure compound is 181.90° K. Adjustment of the apparent enthalpy of melting (ΔH_m), 2044 cal. per mole, and the apparent entropy of melting (ΔS_m), 11.24 cal. per (mole ° K.), for the impurity present yields a ΔH_m of 2061 and a ΔS_m of 11.33 per mole of pure compound. However, if any impurity present dissolves in the liquid as it forms and is completely dissolved by the end of the fractional melting, its enthalpy of solution will approximate the enthalpy of melting of the 0.0084 mole of 2-methylfuran which is unaccounted for. It is also possible that the solubility of impurity in the liquid is a function of temperature in the liquid range and causes the measured liquid heat capacity to be higher than it should be for a pure compound. For the evaluation of the molal thermodynamic functions given in Table II, the measured apparent enthalpy and entropy of melting have been used.

Table I. Heat Capacity of 2-Methylfuran[a]

T	C_s	T	C_s	T	C_s
Series I		7.79	0.165	Series IV	
		8.79	0.258		
Fusion Runs A		10.09	0.415	139.85	17.55
191.05	30.84	11.30	0.561	Fusion Runs B	
		12.46	0.731		
Series II		13.61	0.935	Series V	
		14.81	1.166		
63.027	10.61	16.15	1.444	196.32	30.87
69.56	11.30	17.71	1.789	204.76	30.98
76.28	11.90	19.60	2.226	213.94	31.13
82.90	12.60	21.95	2.795	223.51	31.35
89.66	13.34	24.42	3.399	233.16	31.61
96.98	13.97	23.99	3.296	242.71	31.93
104.74	14.64	26.93	4.012	252.17	32.25
112.67	15.27	29.96	4.850	261.53	32.64
120.99	15.92	32.96	5.419	270.80	33.05
129.79	16.68	36.22	6.124	279.96	33.43
138.83	17.48	39.85	6.850	289.00	33.88
		43.91	7.595	297.98	34.34
Series III		48.61	8.404	306.89	34.82
		54.10	9.282		
7.29	0.144	59.84	10.194		

Melting Region

T	ΔT	C_s	$\Sigma\Delta H_{\text{excess}}$	$\frac{1}{F}$	T_2
		Series I, Runs A			
150.77	9.16	18.69	0.4		155.353
159.69	8.68	20.05	4.5		164.027
167.99	7.92	22.87	19.1	86.3	171.955
176.44	8.96	81.85	565.5	3.613	180.917
181.14	0.45	1123	1061.3	1.925	181.368
181.45	0.17	2773	1518.5	1.346	181.534
181.60	0.13	3670	1977.3	1.033	181.660
185.06	6.81	40.48	2043.2	(1.000)	181.627
		Series IV, Runs B			
149.65	9.57	18.55	0.2		
173.39	37.92	77.29	2044.3	(1.000)	

[a] Units: cal., mole, ° K.

Table II. Thermodynamic Properties of 2-Methylfuran[a]

T	C_p	$S°$	$H° - H°_0$	$-(G° - H°_0)/T$
10	0.39	0.125	0.942	0.031
15	1.20	0.424	4.76	0.106
20	2.32	0.919	13.49	0.244
25	3.55	1.567	28.14	0.441
30	4.74	2.320	48.91	0.690
35	5.85	3.137	75.42	0.981
40	6.88	3.986	107.31	1.303
45	7.82	4.852	144.10	1.650
50	8.67	5.721	185.36	2.013
60	10.13	7.436	279.67	2.774
70	11.34	9.092	387.24	3.559
80	12.38	10.676	506.0	4.351
90	13.33	12.189	634.5	5.139
100	14.20	13.639	772.2	5.917
110	15.04	15.032	918.5	6.682
120	15.87	16.38	1073.2	7.43
130	16.70	17.68	1236.0	8.17
140	17.59	18.95	1407.4	8.90
150	18.55	20.20	1588.0	9.61
160	19.60	21.43	1778.7	10.31
170	20.69	22.65	1980.2	11.00
180	21.77	23.86	2192.4	11.68
190	30.82	36.68	4529.5	12.84
200	30.92	38.26	4838.1	14.07
210	31.07	39.78	5148.1	15.26
220	31.28	41.22	5459.8	16.41
230	31.53	42.62	5773.7	17.52
240	31.83	43.97	6090.5	18.59
250	32.18	45.28	6410.6	19.63
260	32.57	46.54	6734.3	20.64
270	32.99	47.78	7062.1	21.63
280	33.45	48.99	7394.2	22.57
290	33.93	50.17	7731.1	23.51
300	34.45	51.33	8072.9	24.42
273.15	33.13	48.17	7166.2	21.93
298.15	34.35	51.12	8009.3	24.26

[a] Units: cal., mole, ° K.

Thermodynamic Properties. The heat capacities and thermodynamic properties at selected temperatures are presented in Table II. The values for heat capacity were obtained from a curve fitted through the experimental points by the least squares method and carefully compared with a large scale plot of the data. The thermodynamic functions were obtained by the integration of the computer curve. The precision of the heat capacity measurements (Table I) is characterized by a probable error of less than 0.1%, and the fit of the smoothed values (Table II) with the computer curve bears out this estimate. The thermodynamic functions, however, are considered to have a reliability characterized by a probable error of about 0.2% above 100° K. This conservative estimate is conditioned by the lower than characteristic purity of the sample. An additional digit beyond those significant is given in Table II for internal consistency and to permit interpolation and differentiation. The entropies and Gibbs energies have not been adjusted for nuclear spin and isotopic mixing contributions and are hence practical values for use in chemical thermodynamic calculations.

Discussion. Although Hickman (*4*) observed transitory formation of a metastable crystalline form of 2-methylfuran after considerable undercooling (i.e., upon relatively slower cooling), this phase was not found during an intensive search for it within the variation of cooling parameters possible in the cryostat. Because small differences in ring composition geometry should be largely obscured by spatial considerations involving the methyl group, 2-methylfuran would not be expected to differ appreciably from 2-methylthiophene in its thermophysical properties; it would hardly resemble furan. However, examination of the ring parameters (*3*) suggests that it is not unlikely that 2-methylfuran would have to sweep out a smaller volume on rotation than 2-methylthiophene and would thus be expected to melt at a lower temperature than the thiophene derivative. It is possible that observation of a glass-type transformation (e.g., similar to that in 2-methylthiophene) may have been precluded by a gradual "pretransitional" increment in the heat capacity occasioned by contaminant.

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