Low-Temperature Thermal Properties of Cyclohexanethiol and 2,4-Dimethyl-3-thiapentane

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The low-temperature thermal properties of cyclohexanethiol and 2,4-dimethyl-3-thiapentane were measured by adiabatic calorimetry over the ranges 12° to 370° K. and 12° to 380° K., respectively. Values of the molal heat capacity at saturation pressure were obtained for the solid and liquid for each compound. For cyclohexanethiol the heat of fusion, ΔHm, triple-point temperature for zero impurity, T_{tp}, and sample purity were 2390 cal., 189.64° ± 0.05° K., and 99.978 ± 0.010 mole %. For 2,4-dimethyl-3-thiapentane these values were 2489 cal., 195.07° ± 0.02° K., and 99.992 ± 0.002 mole %. From the above data, the following molal chemical thermodynamic properties were calculated for the condensed phases (values shown are for cyclohexanethiol and 2,4-dimethyl-3-thiapentane at 298.15° K.) at selected temperatures from 0° to 390° K.: Gibbs energy function, 28.61 and 35.05 cal. per degree; enthalpy function, 33.19 and 39.77 cal. per degree; enthalpy, 9896 and 11,856 cal.; entropy, 61.80 and 74.82 cal. per degree; and heat capacity, 46.04 and 55.45 cal. per degree.

THE LOW-TEMPERATURE thermal studies on cyclohexanethiol and 2,4-dimethyl-3-thiapentane (diisopropyl sulfide) were made as a part of a continuing program of thermodynamics research on hydrocarbons and related substances (*1*). The measurements were made to provide experimental values of the thermodynamic functions for these compounds in the condensed state. The values of the entropy in the liquid state have been combined (*11*) with values of the heat of vaporization (*16*) and vapor pressure (*9*) to provide measured values for the entropy of each compound in the ideal gas state. These have served in part as a basis for calculation of the chemical thermodynamic properties of cyclohexanethiol and 2,4-dimethyl-3-thiapentane in the ideal gas state from spectral and molecular structure data by Scott and Crowder (*11*).

EXPERIMENTAL

Apparatus and Physical Constants. The low-temperature calorimetric measurements were made with apparatus described by Huffman and coworkers (*6, 7, 12*). The "1961 International Atomic Weights" (*2*) and values of the 1963 physical constants (*10*) were used. Measurements of temperature were made with platinum resistance thermometers calibrated in terms of the International Practical Temperature Scale of 1948, text revision of 1960 (*14*), from 90° to 400° K., and in terms of the provisional scale of the National Bureau of Standards (*5*) from 11° to 90° K. Celsius temperatures were converted to Kelvin by the relation, 0° C. = 273.15° K. (*13*). Measurements of mass, electrical potential, and resistance were made in terms of standard devices calibrated at the National Bureau of Standards. Energy was measured in joules and converted to calories by the relation, 1 cal. = 4.184 joules.

Materials. The samples of cyclohexanethiol and 2,4-dimethyl-3-thiapentane used in this research were standard samples of organic sulfur compounds API-USBM 48-34 and 48-38, having purities of 99.978 and 99.992 mole %, respectively. These compounds were synthesized and purified at the Laramie, Wyo., Petroleum Research Center of the Bureau of Mines. The samples, about 55 ml. each, were received sealed in internal breakoff-tip glass ampoules and were transferred to the calorimeter without exposure to air or water. The 2,4-dimethyl-3-thiapentane showed only a very small amount of water, as evidenced by floaters when partially melted, and was used as received. The cyclohexanethiol was dried by a vapor phase transfer through magnesium perchlorate. In each case pure helium at 40-torr pressure and 23° C. was added to the calorimeter to promote thermal equilibration at low temperatures. Helium at this pressure will have a negligible effect on the melting-point temperatures.

RESULTS

Heat Capacities in the Solid and Liquid States. The heat capacities of cyclohexanethiol and 2,4-dimethyl-3-thiapentane were measured for the solid and liquid states over the ranges 12° to 365° K. and 12° to 383° K., respectively. The observed values of molal heat capacity at saturation pressure, C_s, are given in Table I. The temperature increments used in the measurements were small enough to eliminate the need for corrections to the heat capacity for curvature. The temperature increments, ΔT, used in the regions just below the melting point, are given as footnotes in Table I to permit calculation of corrections to C_s for the effects of premelting. The precision uncertainty of the results, as measured by the average deviation from the smooth curve, was less than 0.1%. Below 30° K. the accuracy uncertainty of the individual measurements is as much as 1% near 12° K., although smoothed values should be better than this. From 30° to 250° K., the accuracy uncertainty is less than 0.2%, except in the premelting region. In the premelting region the accuracy uncertainty is 0.5% owing to the imprecision in the assignment of premelting correction. This higher uncertainty will have a

Table I. Gram-Molal Heat Capacity, Cal. per Degree

T^a	C_s^b	T^a	C_s^b	T^a	C_s^b
Cyclohexanethiol					
Crystal					
11.45	0.913	29.04	5.872	107.64	17.243
11.62	0.953	32.29	6.679	112.77	17.843
12.93	1.256	35.75	7.442	119.63	18.650
12.98	1.269	39.38	8.154	126.24	19.409
14.35	1.630	43.35	8.844	132.63	20.151
14.73	1.752	47.74	9.559	138.82	20.878[c]
15.76	2.023	52.71	10.319	145.33	21.627[c]
16.52	2.263	53.77	10.467	152.14	22.444[c]
17.33	2.503	58.38	11.124	158.74	23.272[c]
18.47	2.848	59.18	11.228	161.76	23.490[c]
19.11	3.044	65.07	12.046	162.23	23.675[c]
20.58	3.488	71.06	12.787	165.16	24.076[c]
21.10	3.650	76.78	13.503	167.32	24.255[c]
22.87	4.175	82.70	14.279	168.76	24.507[c]
23.41	4.335	88.84	15.038	172.73	24.980[c]
25.50	4.941	94.69	15.721	174.65	25.303[c]
26.06	5.093	96.24	15.910		
28.57	5.758	101.82	16.560		
Liquid					
196.61	41.182	247.67	42.980	299.40	46.129
198.70	41.240	258.30	43.521	310.10	46.881
204.43	41.398	268.80	44.119	322.01	47.747
204.72	41.387	279.16	44.743	333.71	48.636
215.02	41.692	286.72	45.268	344.72	49.497
226.02	42.058	289.35	45.416	355.07	50.337
236.90	42.488	297.99	46.042	365.27	51.114
2,4-Dimethyl-3-thiapentane					
Crystal					
11.59	1.263	27.00	6.280	102.92	22.589
11.92	1.361	27.21	6.342	110.20	23.856
12.83	1.612	30.34	7.309	118.19	25.190
13.18	1.730	33.54	8.276	122.18	25.836
14.24	2.060	36.82	9.162	128.69	26.899
14.68	2.207	40.72	10.153	135.47	27.976
15.84	2.568	45.20	11.213	142.43	29.076
16.40	2.748	50.26	12.387	150.11	30.271
17.60	3.148	53.46	13.087	158.12	31.532
18.30	3.384	58.52	14.144	165.86	32.748[d]
19.60	3.817	64.28	15.347	175.72	34.329[d]
20.29	4.048	70.41	16.541	178.81	34.850[d]
21.79	4.554	76.73	17.764	182.01	35.365[d]
22.37	4.747	82.87	18.989	185.40	35.995[d]
24.20	5.365	89.11	20.173		
24.57	5.491	95.93	21.382		
Liquid					
203.70	49.801	267.25	53.324	330.26	57.936
206.61	49.982	270.07	53.540	337.83	58.520
210.58	50.156	279.31	54.173	338.49	58.565
214.58	50.343	280.19	54.222	340.84	58.746
219.35	50.570	290.18	54.914	349.86	59.437
228.95	51.062	291.18	55.019	351.78	59.611
238.96	51.601	302.88	55.854	361.71	60.374
249.46	52.198	314.42	56.722	362.55	60.478
255.57	52.589	325.58	57.569	373.19	61.282
259.83	52.858	326.29	57.629	383.21	62.026

[a] T is the mean temperature (in ° K.) of each heat capacity measurement. [b] C_s is the heat capacity of the condensed phase at saturation pressure. Values of C_s are not corrected for the effects of premelting caused by impurities. [c,d] The temperature increments of these measurements are in order of increasing T, ° K.: [c] 6.106, 6.916, 6.703, 6.506, 5.623, 7.555, 6.338, 5.484, 5.512, 5.347, 6.277; [d] 7.628, 6.370, 6.172, 6.218, 7.018.

negligible effect on the over-all enthalpy and entropy as the heat of fusion calculations largely compensate for inaccuracy in the heat capacity in the premelting region. From data obtained on other compounds in the range 250° to 370° K., the authors believe that the heat capacities obtained using a platinum sample container are too large. The deviation increases steadily from 0.1% at 250° K. to 0.7% at 370° K. This progressive decline in accuracy with increasing temperature is thought to be related to variations in the temperature profile of the sample container during heating periods and will be discussed in detail in a forthcoming paper (*3*).

The heat capacity of cyclohexanethiol and 2,4-dimethyl-3-thiapentane in the liquid state is represented by Equations 1 and 2 below, respectively, with maximum deviations of 0.06 and 0.07% and average deviations of 0.02 and 0.03% for the temperature ranges indicated.

$$C_s = 58.804 - 0.22268T + 8.2813 \times 10^{-4}T^2 - 7.5521 \times 10^{-7}T^3 \quad 215°\text{–}365° \text{ K.} \qquad (1)$$

$$C_s = 55.912 - 0.12300T + 5.6586 \times 10^{-4}T^2 - 5.2975 \times 10^{-7}T^3 \quad 206°\text{–}383° \text{ K.} \qquad (2)$$

Heat of Fusion, Triple-Point Temperature, and Sample Purity. The heat of fusion, ΔHm, for each compound was calculated from the heat capacity data and enthalpy measurements made over temperature intervals that included the triple-point temperature. Correction to the heat of fusion for the effects of premelting owing to impurities was made in each case. For cyclohexanethiol, four measurements of the heat of fusion were made which gave values of 2389.1, 2389.5, 2389.5, and 2392.3 cal. The average value, 2390, was chosen. For 2,4-dimethyl-3-thiapentane, three measurements were made giving values of 2489.0, 2487.9, and 2489.6 cal., and again the average value of 2489 was chosen and used in calculation of the thermodynamic functions.

The triple-point temperature and sample purity for cyclohexanethiol and 2,4-dimethyl-3-thiapentane were determined from a study of the equilibrium melting temperature as a function of the fraction of the sample melted (*8*, *15*). The resulting melting-point summaries are given in Table II. In each case the equilibrium temperature, T_F, was plotted as a function of $1/F$, the reciprocal of the fraction of the sample in the liquid state. The triple-point temperature, T_{tp}, was determined by linear extrapolation of T_F to zero value of $1/F$.

If impurities form an ideal solution in the liquid phase and are insoluble in the solid phase, the relation between mole fraction of total impurity, N_2^*, and melting-point depression, $\Delta T = T_{tp} - T_F$, is (*4*)

$$-\ln (1 - N_2) = A\Delta T(1 + B\Delta T + \dots) \qquad (3)$$

Table II. Melting Point Summaries

F	$1/F$	T_F	$T_{\text{Calcd.}}$
Cyclohexanethiol			
$A = 0.03345$ deg.$^{-1}$, $B = 0.00291$ deg.$^{-1}$, impurity = 0.022 mole %			
0.09961	10.039	189.6008	189.5760
0.25403	3.937	189.6193	189.6142
0.49676	2.013	189.6274	189.6263
0.69534	1.438	189.6299[a]	189.6299
0.89385	1.119	189.6319[a]	189.6319
1.00000	1.000		189.6326
Pure	0		189.6389
2,4,-Dimethyl-3-thiapentane			
$A = 0.03291$ deg.$^{-1}$, $B = 0.00273$ deg.$^{-1}$, impurity = 0.008 mole %			
0.11993	8.338	195.0520	195.0524
0.27425	3.646	195.0630	195.0630
0.50594	1.977	195.0668[a]	195.0668
0.71183	1.405	195.0679	195.0681
0.91770	1.090	195.0688[a]	195.0688
1.00000	1.000		195.0690
Pure	0		195.0713

[a] A straight line through these points was extrapolated to $1/F$ = 0 to obtain triple-point temperature, T_{tp}.

Table III. Gram-Molal Thermodynamic Functions for Condensed Phases[a]

T, °K.	$-(G_s - H_0^\circ)/T$, Cal./° K.	$(H_s - H_0^\circ)/T$, Cal./° K.	$H_s - H_0^\circ$, Cal.	S_s, Cal./° K.	C_s, Cal./° K.
Cyclohexanethiol					
Crystal					
10	0.052	0.156	1.556	0.208	0.616
12	0.090	0.265	3.181	0.355	1.028
14	0.141	0.410	5.734	0.551	1.535
16	0.207	0.585	9.354	0.792	2.095
18	0.287	0.786	14.155	1.074	2.706
20	0.381	1.009	20.176	1.390	3.316
25	0.671	1.620	40.49	2.291	4.794
30	1.023	2.261	67.84	3.284	6.118
35	1.420	2.898	101.43	4.318	7.284
40	1.847	3.509	140.38	5.356	8.266
45	2.294	4.086	183.87	6.380	9.119
50	2.753	4.629	231.47	7.382	9.911
60	3.687	5.632	337.9	9.319	11.355
70	4.625	6.545	458.1	11.170	12.658
80	5.554	7.387	591.0	12.942	13.926
90	6.471	8.184	736.6	14.655	15.175
100	7.373	8.942	894.2	16.315	16.346
110	8.259	9.668	1063.5	17.928	17.519
120	9.131	10.371	1244.6	19.502	18.691
130	9.988	11.056	1437.3	21.044	19.845
140	10.832	11.725	1641.5	22.557	21.008
150	11.663	12.383	1857.4	24.046	22.177
160	12.483	13.033	2085.3	25.517	23.416
170	13.293	13.681	2325.7	26.974	24.667
180	14.093	14.326	2578.7	28.419	25.929
189.640	14.857	14.947	2834.5	29.803	27.125
Liquid					
189.64	14.857	27.550	5224.5	42.407	41.020
190	14.909	27.575	5239	42.484	41.030
200	16.341	28.254	5651	44.595	41.271
210	17.735	28.880	6065	46.615	41.536
220	19.092	29.463	6482	48.554	41.851
230	20.414	30.009	6902	50.422	42.208
240	21.702	30.525	7326	52.227	42.623
250	22.958	31.019	7755	53.977	43.093
260	24.184	31.493	8188	55.677	43.615
270	25.381	31.952	8627	57.333	44.188
273.15	25.753	32.094	8767	57.847	44.376
280	26.551	32.400	9072	58.951	44.798
290	27.696	32.839	9523	60.535	45.463
298.15	28.611	33.192	9896	61.803	46.038
300	28.816	33.271	9981	62.088	46.169
310	29.914	33.699	10447	63.613	46.874
320	30.991	34.122	10919	65.113	47.599
330	32.047	34.542	11399	66.589	48.351
340	33.085	34.959	11886	68.044	49.125
350	34.104	35.375	12381	69.479	49.925
360	35.107	35.791	12885	70.897	50.733
370	36.093	36.205	13396	72.298	51.500
2,4-Dimethyl-3-thiapentane					
Crystal					
10	0.073	0.216	2.160	0.289	0.844
12	0.125	0.363	4.360	0.488	1.373
14	0.195	0.550	7.700	0.745	1.981
16	0.282	0.769	12.300	1.051	2.619
18	0.386	1.011	18.200	1.397	3.283
20	0.506	1.272	25.430	1.778	3.951
25	0.864	1.976	49.390	2.840	5.630
30	1.290	2.718	81.530	4.008	7.207
35	1.765	3.467	121.33	5.232	8.680
40	2.276	4.200	168.01	6.476	9.975
45	2.812	4.909	220.90	7.721	11.170
50	3.365	5.593	279.66	8.958	12.327
60	4.501	6.895	413.7	11.396	14.458
70	5.657	8.121	568.5	13.778	16.463
80	6.818	9.285	742.8	16.103	18.418
90	7.976	10.409	936.8	18.385	20.333
100	9.130	11.489	1148.9	20.619	22.086
110	10.273	12.532	1378.5	22.805	23.820
120	11.407	13.543	1625.1	24.950	25.483
130	12.531	14.523	1888.0	27.054	27.107
140	13.642	15.479	2167.0	29.121	28.693
150	14.742	16.412	2461.8	31.150	30.260
160	15.831	17.326	2772.2	33.160	31.830

(*Continued on page 429*)

Table III. Gram-Molal Thermodynamic Functions for Condensed Phases[a] (*Continued*)

T, ° K.	$-(G_s - H_0^\circ)/T$, Cal./° K.	$(H_s - H_0^\circ)/T$, Cal./° K.	$H_s - H_0^\circ$, Cal.	S_s, Cal./° K.	C_s, Cal./° K.
		2,4-Dimethyl-3-thiapentane			
		Crystal			
170	16.909	18.224	3098	35.13	33.39
180	17.976	19.111	3440	37.09	35.01
190	19.031	19.995	3799	39.03	36.76
195.07	19.566	20.439	3987	40.01	37.54
		Liquid			
195.07	19.566	33.20	6476	52.77	49.45
200	20.391	33.61	6721	54.00	49.66
210	22.055	34.38	7220	56.44	50.13
220	23.678	35.10	7723	58.78	50.60
230	25.248	35.79	8232	61.04	51.12
240	26.785	36.44	8746	63.23	51.66
250	28.285	37.06	9265	65.35	52.23
260	29.756	37.65	9790	67.41	52.87
270	31.18	38.23	10322	69.41	53.51
273.15	31.62	38.41	10491	70.03	53.73
280	32.58	38.79	10861	71.37	54.21
290	33.96	39.33	11407	73.29	54.91
298.15	35.05	39.77	11856	74.82	55.45
300	35.30	39.86	11959	75.16	55.57
310	36.61	40.38	12518	76.99	56.35
320	37.90	40.89	13086	78.79	57.14
330	39.17	41.40	13661	80.57	57.92
340	40.42	41.89	14244	82.31	58.68
350	41.63	42.39	14835	84.02	59.46
360	42.83	42.87	15433	85.70	60.25
370	44.02	43.35	16040	87.37	61.03
380	45.17	43.83	16654	89.00	61.81
390	46.32	44.30	17276	9.062	62.61

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

where $N_2 = N_2^*/F$. The cryoscopic constants, $A = \Delta Hm/RT_{tp}^2$ and $B = 1/T_{tp} - \Delta Cm/2\Delta Hm$, were calculated from the mean value of ΔHm, given above, the triple-point temperature, T_{tp}, given in Table II, and the value of ΔCm, the difference between the heat capacity of the compound in the solid and liquid states at the triple point, obtained from data in Table III. Values of A and B for cyclohexanethiol and 2,4-dimethyl-3-thiapentane are given in Table II. The impurity value given in Table II was calculated using Equation 3 in its simplified form (for $N_2^* < < 1$), $N_2^* = AF\Delta T$.

Chemical Thermodynamic Properties in the Solid and Liquid States. The low-temperature data for cyclohexanethiol and 2,4-dimethyl-3-thiapentane were used in calculating the values of the Gibbs energy function, enthalpy function, enthalpy, entropy, and heat capacity for the liquid and solid states at selected temperatures from 10° to 390° K. The values at 10° K. were calculated from Debye functions whose parameters (for cyclohexanethiol, $\theta = 108.79°$ C. and 5.2 degrees of freedom, and for 2,4-dimethyl-3-thiapentane, $\theta = 96.01°$ C. and 5.0 degrees of freedom) were calculated from the values of the heat capacity between 11° and 20° K. The values of the thermodynamic properties above 10° K. were calculated from the observed values of the heat and temperature of melting and appropriate numerical integration of smoothed values of C_s at regular intervals. The results, shown in Table III, were corrected for the effects of heterophase premelting. Although the values of impurity of 0.015 mole % for cyclohexanethiol and 0.0075 mole % for 2,4-dimethyl-3-thiapentane used in the corrections for premelting deviated from the impurities calculated from the melting-point studies (Table II), these lower values represented the effective concentrations in the premelting region.

ACKNOWLEDGMENT

The assistance of Robert C. Hartman with some of the measurements is gratefully acknowledged.

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RECEIVED for review January 3, 1967. Accepted April 13, 1967. Contribution No. 149 from the thermodynamics laboratory of the Bartlesville Petroleum Research Center, Bureau of Mines, U. S. Department of the Interior, Bartlesville, Okla. 74003.