TABLE II

THE LATENT HEAT OF THE SURFACE AND THE c AND d FACTORS FOR THE SERIES OF 1-ALKENES AND FOR n-DECYLCYCLOPENTANE, n-DECYLCYLOHEXANE AND n-DECYCLBENZENE

Compound	Temperature, °C. 0	10	20	30	40	50	60	70	80	90	100	c	d
1-Hexene	28.14	29.18	30.21	31.23	32.26	33.29	34.32	...	...	...	...	28.15	0.1030
1-Heptene	27.03	28.01	29.00	30.00	30.99	31.97	32.96	33.95	34.94	...	...	27.03	.09888
1-Octene	26.20	27.15	28.11	29.08	30.04	31.00	31.95	32.91	33.87	34.83	35.79	26.20	.0959
1-Nonene	25.41	26.34	27.27	28.20	29.13	30.06	30.99	31.92	32.85	33.78	34.71	25.41	.0930
1-Decene	25.04	25.96	26.87	27.79	28.71	29.62	30.54	31.45	32.37	33.28	34.20	25.04	.0916
1-Undecene	24.66	25.11	26.46	27.36	28.27	29.17	30.07	30.97	31.88	32.78	33.68	24.66	.0902
1-Dodecene	24.19	25.08	25.96	26.84	27.73	28.61	29.50	30.38	31.27	32.16	33.04	24.19	.0885
1-Tetradecene	23.74	24.61	25.48	26.35	27.22	28.09	28.96	29.83	30.70	31.57	32.44	23.74	.0870
1-Hexadecene	...	...	...	25.85	26.70	27.55	28.41	29.26	30.11	30.97	31.82	23.29	.08529
n-Decylcyclopentane	24.31	25.20	26.09	26.98	27.87	28.76	29.65	30.54	31.43	32.32	33.21	24.31	.0890
n-Decylcyclohexane	23.48	23.34	25.20	26.06	26.92	27.78	28.64	29.50	30.36	31.22	32.08	23.48	.0860
n-Decylbenzene	21.77	22.57	23.36	24.16	24.96	25.76	26.55	27.35	28.15	28.94	29.74	21.77	.0797

lished by the American Petroleum Institute, Project 44. The probable error of the derived values of the surface tensions were calculated and found to be no greater than 0.01 dyne cm.$^{-1}$. The principle of least squares was applied to the surface tension data, and the resulting equation was of the linear form, $\gamma = a - bt$. The surface tension data, together with the a and b factors of the linear equation, are tabulated in Table I.

Discussion

By applying the two-dimensional form of the thermodynamic equation of Clapeyron[3] it is possible to calculate the entropy of surface formation. This is found to be the negative temperature coefficient of the surface tension and is tabulated as the b factor in Table I. These values in turn enable the calculation of the enthalpy h and the latent heat of the surface Q. The temperature–latent heat relations for the compounds take the form of the linear equation, $Q = c + dt$. The Q values together with the c and d factors of the least squares equations, are recorded in Table II. The enthalpy of the surface is given by the relation, $h = \gamma + Q$, and from reference to the tables it is seen that h has a constant value over the temperature range employed. The entropy of the surface, represented by the b factor of Table I, is measured by the slope of the surface tension $vs.$ temperature curve. This has a constant value, and, therefore, it is evident that both the enthalpy and the entropy of the surface are independent of the temperature.

DETROIT, MICHIGAN

[CONTRIBUTION NO. 40 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

The Chemical Thermodynamic Properties of Thiacyclohexane from 0 to 1000°K.[1]

BY J. P. MCCULLOUGH, H. L. FINKE, W. N. HUBBARD, W. D. GOOD, R. E. PENNINGTON, J. F. MESSERLY AND GUY WADDINGTON

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As part of a program of investigations of the thermodynamic properties of organic sulfur compounds, an experimental and computational study was made of the properties of thiacyclohexane. The entropy of the liquid at saturation pressure at 298.16°K., 52.16 cal. deg.$^{-1}$ mole^{-1}, was computed from measured values of the heat capacity in the solid and liquid states (13 to 341°K.) and the heats of transition (262.4 and 1858.3 cal. mole^{-1} at 201.4 and 240.02°K., respectively) and fusion (585.2 cal. mole^{-1} at the triple point, 292.25°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 accurately represented by the empirical equations: [1] $C_{\mathrm{satd}}(\mathrm{liq.}) = 112.057 - 0.8324\,T + 2.865 \times 10^{-3}T^2 - 3.0 \times 10^{-6}T^3$, cal. deg.$^{-1}$ mole^{-1} (292–342°K.); [2] $\Delta H_{\mathrm{v}} = 14{,}355 - 13.871\,T$, cal. mole^{-1} (350–415°K.); [3] $C_{\mathrm{p}}^{\circ} = -13.82 + 0.15037\,T - 6.648 \times 10^{-5}T^2$, cal. deg.$^{-1}$ mole^{-1} (399–483°K.); and [4] $B = -1040 - 2.25 \exp(2000/T)$, cc. mole^{-1} (350–483°K.). From determinations of the heat of combustion, the standard heat of formation [$\Delta H_{\mathrm{f}}^{\circ}$(liq.)] of thiacyclohexane from graphite, hydrogen and rhombic sulfur was found to be -25.18 kcal. mole^{-1} at 298.16°K. Calorimetric, spectroscopic and molecular structure information 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 to 1000°K. One spectroscopically unobserved vibrational frequency was selected to fit the calorimetric entropy datum. Parameters required to compute the contributions of anharmonicity and "chair-boat" tautomerism were evaluated from the experimental 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 thiacyclohexane in the ideal gaseous state from graphite, hydrogen and gaseous diatomic sulfur, were computed from the calculated thermodynamic functions and appropriate calorimetric data.

A comprehensive series of investigations of the thermodynamic properties of organic sulfur compounds is being conducted in this Laboratory to provide relatively complete data for those compounds important in petroleum production and refining processes. Thorough studies are made of

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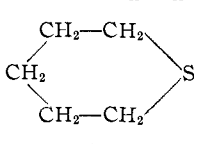
(1) This investigation was part of American Petroleum Institute Research Project 48A on the "Production, Isolation and Purification of Sulfur Compounds and Measurement of Their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

the properties of key members of the various homologous series of organic sulfur compounds. The results of these studies will serve as a basis for construction by approximate methods[2] of tables of thermodynamic properties for entire families of compounds.[3] One of the types of sulfur compounds known to occur in crude petroleum and petroleum distillates is the family of cyclic sulfides and their derivatives.[4] The results of thermodynamic investigations of the first three members of this family, thiacyclopropane,[5] thiacyclobutane[6] and thiacyclopentane,[7] have already been presented in publications from this Laboratory.

The present paper, a continuation of the above series, describes an experimental and computational investigation of the thermodynamic properties of thiacyclohexane.[8] The experimental phase of this investigation included studies that provided values of the heat capacity in the solid, liquid and vapor states and of the heats of transition, fusion, vaporization and combustion. By use of standard thermodynamic procedures, values of the entropy, $S°$, heat capacity, C_p°, and heat of formation, ΔH_f°, all for the ideal gaseous state, were derived from the experimental data. The calorimetric data were then used with spectroscopic and molecular structure information to compute the thermodynamic properties of thiacyclohexane by the methods of statistical mechanics. Values of the following thermodynamic properties were computed at selected temperatures from 0 to 1000°K.: $(F° - H_0^\circ)/T$, $(H° - H_0^\circ)/T$, $H° - H_0^\circ$, $S°$, C_p°, ΔH_f°, ΔF_f° and $\log_{10} K_f$.



Experimental

Physical Constants.—The 1951 International Atomic Weights[9] and the 1951 values of the fundamental physical constants[10] were used for all computations described in this paper. The calorimetric data are based on a molecular weight of 102.196 for thiacyclohexane and the following definitions: 0° = 273.16°K.; and 1 cal. = 4.1840 abs. joules = 4.1833 int. joules.

The Material.—The sample of thiacyclohexane used for the low temperature thermal studies and for the combustion calorimetry was part of the Standard Sample of Sulfur Compound, API-USBM serial No. 17, 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 0.014 ± 0.005 mole % liquid-soluble, solid-insoluble impurity. A sample of slightly lower purity (99.9 mole %) was provided by the Laramie Station for use in measurements of the heat of vaporization and vapor heat capacity. The samples of thiacyclohexane were received in red-glass, 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 Low Temperature Heat Capacity Measurements.—The thermal properties of thiacyclohexane in the solid and liquid states were studied in the temperature range 13 to 342°K. with an adiabatic calorimeter similar to that described by Ruehrwein and Huffman.[11] Approximately 0.52 mole of thiacyclohexane was sealed in a platinum calorimeter equipped with horizontal, perforated heat-distributing disks of gold. A small amount of helium (30 mm. pressure at room temperature) was left in the calorimeter to promote thermal equilibration at low temperatures.

The observed values of the heat capacity at saturation pressure, C_{satd}, of solid and liquid thiacyclohexane 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.; suitably smaller increments were used in the temperature regions in which solid–solid transitions or fusion occurred.) The precision of the heat capacity measurements was usually within ±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 thiacyclohexane within 0.03 cal. deg.$^{-1}$ mole^{-1} in the temperature range, 292 to 342°K.

$$C_{\text{satd}}(\text{liq.}) = 112.057 - 0.8324\,T + 2.865 \times 10^{-3}T^2 - 3.0 \times 10^{-6}T^3 \quad (1)$$

The thermal behavior of solid thiacyclohexane was unusually complex. From about 150 to 200°K., the heat capacity curve (C_{satd} *vs.* T) showed abnormal positive curvature. Isothermal transitions were found to occur at 201.4 and 240.02°K., and a small "lambda-type" transition was found in the region between 201.4 and 210°K. The shape of the heat capacity curve from 125 to 320°K. is shown in Fig. 1. At least two series of heat capacity measurements were made over most of this temperature region. In the region of the "lambda," three series of heat capacity measurements were made as follows: (1) the sample was cooled slowly from 230 to 203.2°K., and measurements were made to 233.8°K. (the temperature increments employed in all measurements in the "lambda" region were 1 to 2°); (2) the sample was then melted, recrystallized and cooled slowly to 215.0°K., and measurements were made to

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[2] *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).

[3] 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.

[4] S. F. Birch, *J. Inst. Petroleum*, **39**, 185 (1953).

[5] G. B. Guthrie, Jr., D. W. Scott and Guy Waddington, This Journal, **74**, 2795 (1952).

[6] D. W. Scott, H. L. Finke, W. N. Hubbard, J. P. McCullough, C. Katz, M. E. Gross, J. F. Messerly, R. E. Pennington and Guy Waddington, *ibid.*, **75**, 2795 (1953).

[7] W. N. Hubbard, H. L. Finke, D. W. Scott, J. P. McCullough, C. Katz, M. E. Gross, J. F. Messerly, R. E. Pennington and Guy Waddington, *ibid.*, **74**, 6025 (1952).

[8] For a discussion of the nomenclature of sulfur compounds, see J. S. Ball and W. E. Haines, *Chem. Eng. News*, **24**, 2765 (1946).

[9] Edward Wichers, This Journal, **74**, 2447 (1952).

[10] F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, *ibid.*, **74**, 2699 (1952).

[11] (a) R. A. Ruehrwein and H. M. Huffman, *ibid.*, **65**, 1620 (1943); (b) G. D. Oliver, M. Eaton and H. M. Huffman, *ibid.*, **70**, 1502 (1948).

TABLE I

THE MOLAL HEAT CAPACITY OF THIACYCLOHEXANE IN CAL. DEG.$^{-1}$

T, °K.[a]	C_{satd}[b]	T, °K.	C_{satd}	T, °K.	C_{satd}
Crystals I		123.49	16.715	213.26	30.19
		130.04	17.398	213.65	30.26
13.08	0.751	132.62	17.678	216.97	30.70
14.90	1.123	136.76	18.125	217.64	30.78
15.20	1.191	139.62	18.405	218.19	30.95
16.57	1.517	143.85	18.846	221.40	31.38
17.13	1.659	147.45	19.222	222.91	31.64
18.29	1.951	151.38	19.660	223.27	31.73
18.88	2.114	159.14	20.563	226.18	32.22
20.17	2.465	167.07	21.603	226.54	32.31
20.64	2.607	170.95	22.133	231.27	33.30
22.11	3.014	175.57	22.860	231.86	33.47
22.49	3.123	178.94	23.454	232.90	33.68
24.36	3.658	184.09	24.489		
24.66	3.741	185.51	24.790	Crystals III	
26.89	4.372	189.01	25.739		
27.28	4.466	190.20	26.092	243.14	33.29
30.19	5.256	194.16	27.608	247.31	33.48
33.37	6.031	197.91	29.916	253.04	33.77
36.73	6.749			256.97	33.98
40.26	7.434	Crystals II		258.78	34.08
44.10	8.103			260.31	34.19
48.35	8.796	202.43	34.40	264.52	34.41
52.94	9.440	203.46	34.69	268.51	34.67
55.56	9.797	204.01	34.71	270.72	34.82
57.81	10.081	204.48	35.07	277.37	35.24
61.58	10.559	205.48	35.50	284.45	35.75[c]
67.39	11.207	205.60	35.64		
73.25	11.883	206.48	36.46	Liquid	
79.16	12.489	207.35	34.62		
85.14	13.130	207.47	34.99	295.63	38.84
85.47	13.156	207.61	33.94	300.23	39.18
90.20	13.623	208.70	30.07	300.58	39.21
91.07	13.705	209.38	30.14	306.13	39.63
96.14	14.164	209 85	30.00	306.82	39.73
102.81	14.781	210.99	30.04	314.33	40.32
109.67	15.418	211.52	30.09	322.72	40.94
116.71	16.071	212.13	30.07	331.95	41.71
				341.52	42.44

[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] The heat capacity data immediately below the triple point have not been corrected for the effects of premelting.

225°K.; (3) the sample was cooled rapidly from 225 to 201.9°K., and measurements were made to 214°K. The results of these three series of measurements were in good agreement and showed no effects attributable to the thermal treatment of the sample.

The Transition Temperatures and Heats of Transition.—Each isothermal transition was studied by observing the equilibrium temperatures as a function of the fraction of the sample transposed. The temperatures that corresponded to complete transposition of the solid, the transition temperatures, were determined by plotting the equilibrium temperatures against the fraction transposed and extrapolating these data to 100% transposed. Duplicate determinations were made of the energy absorbed in the region of each isothermal transition. In each case measurements were made of the total enthalpy increase over a finite temperature interval that included the transition temperature. The isothermal heats of transition were calculated from these results by subtraction of the energy absorbed non-isothermally, as determined from the heat capacity data of Table I. The observed transition temperatures and heats of transition are summarized in Table II.

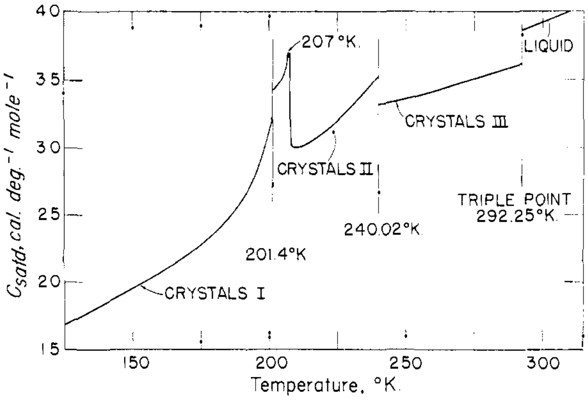

Fig. 1.—The heat capacity curve for thiacyclohexane.

TABLE II

THE MOLAL HEATS OF TRANSITION AND FUSION OF THIACYCLOHEXANE

T, °K.	Phase change	ΔH, cal.	ΔS, cal. deg.$^{-1}$
201.4 ± 0.1[a]	Transition I–II	262.4 ± 0.2[b]	1.303
240.02 ± .05[a]	Transition II–III	1858.3 ± .1[b]	7.742
292.25 ± .05[a]	Fusion	585.2 ± .1[b]	2.002

[a] Estimated accuracy uncertainty. [b] Maximum deviation from the mean of two results.

The lambda-type transition shown in Fig. 1 occurred in the region between 201.4 and 210°K., with a sharp peak at approximately 207°K. The energy absorbed in the region of the lambda-type transition was approximately 40 cal. mole^{-1} greater than that which would be calculated by extrapolation of the "normal" heat capacity curve for crystals II.

An unambiguous physical interpretation of these solid-state phenomena cannot be made on the basis of the thermal data alone. Detailed studies of the crystal structures of thiacyclohexane and cyclohexane would be valuable for obtaining an understanding of these phenomena.

The Triple Point, Sample Purity and Heat of Fusion.—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.[12] The results of these observations are presented in Table III. The equilibrium melting temperatures, T_{obsd}, were plotted against the reciprocal of fraction melted, $1/F$. The temperature at the triple point, $T_{T.P.}$, was determined by linear extrapolation of these data to $1/F = 0$. The mole fraction of total impurity, N_2^*, was calculated by the relationship $N_2^*/F = A(T_{T.P.} - T_{obsd})$, where A is the cryo-

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(12) S. S. Todd, G. D. Oliver and H. M. Huffman, THIS JOURNAL, **69**, 1519 (1947).

scopic constant, $\Delta H_{\text{fusion}}/RT^2_{\text{T.P.}}$. This procedure is based on the assumptions that ideal solutions are formed in the liquid phase and the impurity is insoluble in the solid phase.

Table III

Thiacyclohexane: Melting Point Summary

Triple point $T_{\text{T.P.}} = 292.25$°K.; cryoscopic constant, $A = 0.003448$ deg.$^{-1}$; impurity $= 0.014 \pm 0.005$ mole %.

Melted, %	$1/F$	T, °K. Obsd.	T, °K. Graph[b]
15.11	6.618	291.9850	291.9787
31.45	3.180	292.1106	292.1189
51.80	1.931[a]	.1698	.1698
72.42	1.381	.1941	.1922
93.13	1.074[a]	.2047	.2047
100.00	1.000		.2077
Pure	0.0		292.2484[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 of thiacyclohexane was determined in the manner described for the heats of transition. The results of duplicate measurements of the heat of fusion are included in Table II.

The Thermodynamic Properties of Thiacyclohexane in the Solid and Liquid States.—The low temperature calorimetric data discussed in previous sections were used in calculation of the entropy, heat content and free energy of thiacyclohexane in the solid and liquid states at saturation pressure. These data were determined by appropriate numerical integration of values of C_{satd} read from a large scale plot of the data of Table I. In Table IV, values of the important thermodynamic properties are tabulated at selected temperatures from 10 to 340°K.

The Heat of Vaporization.—Measurements of the heat of vaporization and vapor heat capacity of thiacyclohexane were made with the flow calorimeter system described in previous publications from this Laboratory.[13] The vaporizer described in reference 13a 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.

Table IV

The Molal Thermodynamic Properties of Thiacyclohexane in the Solid and Liquid States[a]

T, °K.	$-(F_{\text{satd}} - H_0^\circ)/T$, cal. deg.$^{-1}$	$(H_{\text{satd}} - H_0^\circ)/T$, cal. deg.$^{-1}$	$H_{\text{satd}} - H_0^\circ$, cal.	S_{satd} cal. deg.$^{-1}$	C_{satd} cal. deg.$^{-1}$
			Crystals I		
10	0.03	0.09	0.89	0.12	0.36
15	.10	.29	4.37	.39	1.15
20	.23	.66	13.2	.89	2.42
25	.43	1.15	28.8	1.58	3.84
30	.68	1.72	51.5	2.40	5.20
35	1.00	2.30	80.5	3.30	6.39
40	1.34	2.88	115.0	4.22	7.38
45	1.72	3.42	154.1	5.14	8.25
50	2.10	3.95	197.4	6.05	9.04
60	2.91	4.91	294.5	7.82	10.35
70	3.73	5.77	404.0	9.50	11.52
80	4.55	6.56	524.5	11.11	12.58
90	5.37	7.28	655.6	12.65	13.60
100	6.17	7.96	796.2	14.13	14.52
110	6.96	8.60	946.1	15.56	15.45
120	7.73	9.21	1105	16.94	16.38
130	8.49	9.80	1274	18.29	17.39
140	9.24	10.38	1453	19.62	18.44
150	9.98	10.95	1643	20.93	19.50
160	10.71	11.52	1844	22.23	20.67
170	11.43	12.09	2056	23.52	21.98
180	12.13	12.69	2284	24.82	23.64
190	12.83	13.33	2532	26.16	26.02
200	13.52	14.08	2815	27.60	31.36
201.4	13.63	14.20	2859	27.83	32.38
			Crystals II		
201.4	13.63	15.50	3122	29.13	34.16
210	14.28	16.26	3415	30.54	30.00
220	15.05	16.91	3720	31.96	31.15
230	15.81	17.57	4040	33.38	33.02
240	16.58	18.26	4382	34.84	35.50
240.02	16.58	18.26	4383	34.84	35.50
			Crystals III		
240.02	16.58	26.00	6241	42.58	33.16
250	17.64	26.30	6575	43.94	33.62
260	18.68	26.59	6914	45.27	34.16
270	19.69	26.88	7258	46.57	34.77
273.16	20.00	26.98	7369	46.97	34.97
280	20.67	27.18	7609	47.85	35.42
290	21.63	27.47	7967	49.10	36.12
292.25	21.84	27.54	8048	49.38	36.30
			Liquid		
292.25	21.84	29.54	8633	51.38	38.60
298.16	22.43	29.73	8863	52.16	39.03
300	22.62	29.78	8935	52.40	39.17
310	23.60	30.10	9330	53.70	39.97
320	24.56	30.42	9734	54.98	40.76
330	25.49	30.76	10,150	56.25	41.53
340	26.41	31.09	10,570	57.50	42.32

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

The heat of vaporization of thiacyclohexane was measured at each of five temperatures from 351 to 414°K. The results are recorded in Table V, where the values of the heat of vaporization tabulated represent the average of data from two to five experiments, and the uncertainties given denote the maximum deviation of the experimental results from the mean. Considerable experimental difficulty, probably attributable to the high boiling point of thiacyclohexane, was encountered in the measurements of the heat of vaporization and vapor heat capacity. For this reason, the results of this investigation are not so reliable as those usually determined in this Laboratory. The estimated accuracy uncertainty of the heat of vaporization data in Table V is ±0.2%. The following empirical equation represents the experimental data within 1 cal. mole^{-1}:

$$\Delta H_v = 14{,}355 - 13.871T,\ \text{cal. mole}^{-1}\ (351\text{–}415^\circ\text{K.}) \quad (2)$$

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

TABLE V

THE MOLAL HEAT OF VAPORIZATION AND SECOND VIRIAL COEFFICIENT OF THIACYCLOHEXANE

T, °K.	p, mm.	ΔH_v, cal.	$-B$(obsd.), cc.	$-B$(calcd.),[a] cc.
351.44	100.0	9480 ± 5[b]	1700	1710
368.91	190.0	9238 ± 4	1600	1550
390.31	380.0	8942 ± 3	1460	1420
404.26	570.0	8747 ± 3	1370	1360
414.91	760.0	8599 ± 1	1290	1320

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

The Vapor Heat Capacity.—The vapor heat capacity of thiacyclohexane was measured at two or more pressures at each of four temperatures from 399 to 483°K.; the results are summarized in Table VI. Values of the heat capacity in the ideal gaseous state, C_p°, were determined from the data at finite pressure by linear extrapolations to zero pressure.[13a] Measurements were not made at pressures above 570 mm., since soft-soldered joints in the vaporizer apparently lost strength at the normal boiling point (142°), and leaks developed when experiments were attempted at 760 mm. It is estimated that the accuracy uncertainty of these values of C_p° is less than 0.4%. The following empirical equation represents the "observed" values of C_p° within 0.03 cal. deg.$^{-1}$ mole^{-1}.

TABLE VI

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

T, °K.	399.20	423.20	453.20	483.20
C_p (570.0 mm.)		38.276	40.836	43.415
C_p (380.0 mm.)	36.009	38.118		
C_p (190.0 mm.)	35.817	38.020	40.746	43.342
C_p° (obsd.)	35.63	37.88	40.70	43.31
$(\partial C_p/\partial P)_T$ (obsd.)	0.77	0.51	0.18	0.15
$(\partial C_p/\partial P)_T$ (calcd.)[a]	0.72	0.46	0.28	0.18

[a] Calculated by use of eq. 4; units of $(\partial C_p/\partial P)_T$ are cal. deg.$^{-1}$ mole^{-1} atm.$^{-1}$.

$$C_p^\circ = -13.82 + 0.15037T - 6.648 \times 10^{-5}T^2, \text{ cal. deg.}^{-1} \text{ mole}^{-1} \ (399\text{–}483\text{°K.}) \quad (3)$$

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[14] were used to compute values of the second virial coefficient, $B = (PV - RT)/P$, from the Clapeyron equation in the form, $B = [\Delta H_v/T(\mathrm{d}P/\mathrm{d}T)] - RT/P + V_L$, where V_L is the molal volume of the liquid. Values of $(\mathrm{d}^2B/\mathrm{d}T^2)$ were calculated from the observed pressure dependence of the vapor heat capacity by use of the relationship $(\partial C_p/\partial P)_T = -T(\partial^2V/\partial T^2)_P = -T(\mathrm{d}^2B/\mathrm{d}T^2)$. These results for B and its second derivative were correlated by means of the empirical equation

$$B = -1040 - 2.25 \exp(2000/T), \text{ cc. mole}^{-1} \ (350\text{–}483\text{°K.}) \quad (4)$$

in which T is in °K.; the numerical constants were evaluated by methods outlined in an earlier paper.[15] The values of B calculated by the Clapeyron equation and with eq. 4 are included in Table V.

The Entropy.—The entropy of the liquid at saturation pressure, S_{satd}, was computed from the low temperature calorimetric data. The entropy in the ideal gaseous state at 1 atm., S°, was calculated from the value of S_{satd}, the data of Table V, and vapor pressure data.[14] Table VII contains a summary of these calculations.

TABLE VII

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

0–13°K.	Debye extrapolation[a]	0.260
13–210.4°	Graphical, $\int C_{\text{satd}}\, \mathrm{d} \ln T$	27.570
201.4°	Transition, 262.4/201.4	1.303
201.4–240.02°	Graphical, $\int C_{\text{satd}}\, \mathrm{d} \ln T$	5.707
240.02°	Transition, 1858.3/240.02	7.742
240.02–292.25°	Graphical, $\int C_{\text{satd}}\, \mathrm{d} \ln T$	6.802
292.25°	Fusion, 585.2/292.25	2.002
292.25–298.16°	Graphical, $\int C_{\text{satd}}\, \mathrm{d} \ln T$	0.778
$S_{\text{satd.}}$, liq., 298.16°K.		52.16 ± 0.10[b]
298.16–351.44°	Graphical, $\int C_{\text{satd}}\, \mathrm{d} \ln T$[c]	6.753
351.44°	Vaporization, $\Delta H_v/T$[d]	26.975
351.44°	Gas imperfection, $P(\mathrm{d}B/\mathrm{d}T)$[e]	0.034
351.44°	Compression, $R \ln (p/760)$[f]	−4.030
S°, gas, 351.44°K.		81.90 ± 0.20[b]

[a] A Debye function for 6.5 degrees of freedom with $\theta = 141.3°$ was used for this extrapolation. [b] Estimated accuracy uncertainty. [c] Extrapolated by use of eq. 1. [d] From data of Table V. [e] Calculated by use of eq. 4. [f] From data of ref. 14.

The Heats of Combustion and Formation.—The heat of combustion of thiacyclohexane was determined in a rotating-bomb combustion calorimeter. The apparatus and method used for this investigation were described in detail in a recent publication.[16] The results of eight satisfactory combustion experiments are summarized in Table VIII. In the last column of the table are given the experimentally determined values of $\Delta U_c^\circ/M$, the change in internal energy per gram mass of thiacyclohexane for the idealized combustion reaction

$$C_5H_{10}S(\text{liq.}) + 9O_2(\text{gas}) + 71H_2O(\text{liq.}) \longrightarrow 5CO_2(\text{gas}) + H_2SO_4\cdot 75H_2O(\text{aq.}) \quad (I)$$

when each reactant and each product is in its appropriate standard reference state at 25°.[17]

All combustion experiments were made in a platinum-lined bomb (Pt-4).[16] The amount of water initially added to the bomb was 10 grams. The air originally present in the bomb was not removed before charging with O_2, since the small quantities of nitrogen oxides formed in the combustion reaction effectively catalyze the oxidation of sulfur to the +6 oxidation state. Each combustion experiment was initiated at 23.00°, and the quantities of sample and auxiliary oil were chosen to produce a 2° temperature increment in the calorimeter. After 60% of the expected temperature rise had occurred, the bomb was rotated simultaneously about 2 perpendicular axes for 90 sec. to rinse the interior parts with the bomb solution and ensure that the solution was homogeneous and in equilibrium with the gaseous phase.

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

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

(16) W. N. Hubbard, C. Katz and Guy Waddington, *J. Phys. Chem.*, **58**, 142 (1954).

(17) W. N. Hubbard, D. W. Scott and G. Waddington, *ibid.*, **58**, 152 (1954).

TABLE VIII[a,b,c]

SUMMARY OF THIACYCLOHEXANE COMBUSTION EXPERIMENTS

Comb. no.	C^{i}_{eff} (cont.), cal. deg.$^{-1}$	C^{f}_{eff} (cont.), cal. deg.$^{-1}$	ΔT_c, deg.	Corrections, cal.						m', g.	$\Delta U_c^\circ/M$, cal. g.$^{-1}$
				q_{fuse}	q_{oil}	q_{CO_2}	q_{N}[c]	$q_{\text{diln.}}$	$q_{\text{corr.}}$		
A_1	13.51	13.79	2.00972	−15.89	−1219.20	3.40	10.54	+0.16	−0.03	0.73054	−9080.46
A_8	13.83	14.10	2.06548	−15.81	− 990.79	3.46	9.89	+ .06	− .09	.77995	−9080.46
A_{10}	13.81	14.10	2.00207	−15.81	− 673.31	3.31	10.54	+ .04	− .16	.78741	−9081.14
A_{11}	13.76	14.05	2.00234	−15.85	− 488.67	3.28	9.54	+ .00	− .19	.80827	−9077.66
										Ave.	−9079.9 ± 0.76[d]
B_1	13.82	14.10	2.00068	−15.61	− 945.49	3.35	9.72	+ .10	− .09	.75719	−9078.00
B_3	13.82	14.11	1.99832	−16.08	− 788.86	3.32	9.36	+ .07	− .12	.77324	−9080.14
B_6	13.82	14.10	2.04684	−15.97	− 243.62	3.30	9.74	− .10	− .24	.85427	−9080.01
B_{12}	13.77	14.05	2.00238	−16.36	− 441.44	3.27	9.98	+ .00	− .20	.81336	−9078.00
										Ave.	−9079.0 ± .60[d]
										Ave. of both series	−9079.5 ± .50[d]

[a] Auxiliary data: C_{eff} (calor.) = 3909.5 cal. deg.$^{-1}$; volume of bomb = 0.3471 l.; initial total pressure = 30 atm.; electrical ignition energy = 1.35 cal.; ρ, density of thiacyclohexane = 0.98093 at 25°. [b] The column headings of this table correspond to the following computation item numbers of ref. 17: C^{i}_{eff}(cont.), item 75; C^{f}_{eff}(cont.), item 76; ΔT_c, items 79–78–80; q_{fuse}, item 97; q_{oil}, item 96; q_{CO_2}, item 87; q_{N}, item 92; q_{diln}, items 90 and 91; $q_{\text{corr.}}$, items 81 + 82 + 83 + 84 + 85 + 88 + 89 + 93 + 94; m', mass of compound, item 2; $\Delta U_c^\circ/M$, item 99. [c] The correction for nitrous acid alone was approximately −0.06 cal. and the total acid titrated after the experiments was 99.82 ± 0.07%[22] of that expected from the mass of sample and total nitrogen determined by Devarda's method. [d] See footnote 19.

The energy equivalent of the calorimetric system was determined by combustion experiments with benzoic acid, NBS Sample 39g, which was certified to evolve 26.4338 abs. kj. g.$^{-1}$ (weight in vacuum) under specified conditions.[18] For the calibration experiments, in which the conditions were essentially those specified in ref. 18, a value of 26.4343 abs. kj. g.$^{-1}$ (weight in vacuum) was used. From six determinations, the energy equivalent of the calorimetric system, C_{eff} (calor.), was found to be 3909.5 ± 0.2[19] cal. deg.$^{-1}$.

Experiments described in recent publications from this Laboratory[16,20] have shown that Vycor-glass ampoules are more satisfactory than soft-glass ampoules for containing samples in combustion experiments with organic sulfur compounds. The preference for Vycor ampoules was based on the greater chemical resistance of the material, but the possibility that thermal decomposition of the sample occurred as a result of the high temperature required to seal Vycor ampoules was not investigated. To determine if decomposition occurred with significant effect on the results, two series of combustion experiments were made in this investigation. In the A series of experiments, unsealed fine-capillary[21] Vycor ampoules were used to contain the sample. In the B series, sealed Vycor ampoules were used. The fact that the values of $\Delta U_c^\circ/M$ obtained in the B series of experiments are within the range of values obtained in the A series indicates that errors due to decomposition in the process of sealing a sample in Vycor ampoules are within the precision of the heat-of-combustion experiments.

The value selected for $\Delta U_c^\circ/M$ was −9079.5 ± 0.5[19] cal. g.$^{-1}$, the average of all eight satisfactory combustion experiments. From this value for $\Delta U_c^\circ/M$ the value of the heat of combustion, ΔH_c°, for reaction I was found to be −930.26 kcal. mole^{-1} at 25°.

The standard heat of combustion of rhombic sulfur, ΔH_c°, according to reaction II was determined

$$\text{S(rh.)} + 3/2\text{O}_2\text{(gas)} + 76\text{H}_2\text{O(liq.)} \longrightarrow \text{H}_2\text{SO}_4\cdot 75\text{H}_2\text{O(aq.)} \quad \text{(II)}$$

and found to be −143.59 ± 0.09[22] kcal. mole^{-1}. Subtraction of the heat of reaction II from the heat of reaction I gives −786.67 kcal. mole^{-1} for the heat of combustion of thiacyclohexane according to reaction III

$$\text{C}_5\text{H}_{10}\text{S(liq.)} + 15/2\text{O}_2\text{(gas)} \longrightarrow 5\text{CO}_2\text{(gas)} + \text{S(rh.)} + 5\text{H}_2\text{O(liq.)} \quad \text{(III)}$$

From the value for the heat of reaction III and values of the heats of formation of carbon dioxide[23] and water,[23] the standard heat of formation, ΔH_f°(liq.), of liquid thiacyclohexane, according to reaction IV, was computed to be −25.18 ± 0.20[22] kcal. mole^{-1} at 25°

$$5\text{C(graphite)} + 5\text{H}_2\text{(gas)} + \text{S(rh.)} \longrightarrow \text{C}_5\text{H}_{10}\text{S(liq.)} \quad \text{(IV)}$$

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° (10.22 ± 0.05 kcal. mole^{-1}), as calculated by use of eq. 2[24] 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 thiacyclohexane were calculated from the values for the heat of formation, the entropy at 25° (Tables VII and XII), and thermodynamic

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(18) National Bureau of Standards Certificate for Standard Sample 39g.

(19) The uncertainty given is the standard deviation of the mean.

(20) J. P. McCullough, S. Sunner, H. L. Finke, W. N. Hubbard, M. E. Gross, R. E. Pennington, J. F. Messerly and Guy Waddington, THIS JOURNAL, **75**, 5075 (1953).

(21) G. Waddington, J. W. Knowlton, D. W. Scott, G. D. Oliver, S. S. Todd, W. N. Hubbard, J. C. Smith and H. M. Huffman, *ibid.*, **71**, 797 (1949).

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

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

(24) This calculation involved a long extrapolation of the experimental data. However, the same value of the heat of vaporization at 25°, 10,220 cal. mole^{-1}, results from use of either eq. 2 or the vapor pressure data of White, *et al.* (ref. 14).

functions for graphite,[23] hydrogen[23] 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 thiacyclohexane from C(graphite), S_2(gas) and H_2(gas). These data are presented in Table IX.

TABLE IX

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

State[a]	Reference state[b]	ΔH_f°, kcal.	ΔF_f°, kcal.	$\log_{10} K_f$
Liquid	S(rhombic)	-25.18 ± 0.20^c	$+10.10$	-7.40
Gas	S(rhombic)	-14.96 ± 0.25^c	$+12.83$	-9.40
	S_2(gas)	-30.38	$+3.27$	-2.40

[a] Standard state of thiacyclohexane. [b] Reference state for elemental sulfur in the reactions

$$\text{(A)}\quad 5\text{C(graphite)} + 5H_2\text{(gas)} + \text{S(rhombic)} \longrightarrow C_5H_{10}S\text{(liq. or gas)}$$

$$\text{(B)}\quad 5\text{C(graphite)} + 5H_2\text{(gas)} + 1/2S_2\text{(gas)} \longrightarrow C_5H_{10}S\text{(gas)}.$$

See footnote 22.

Sunner[27] reported the heat of formation of liquid thiacyclohexane at 20° to be −25.60 ± 0.20 kcal. mole^{-1}. Adjustment of Sunner's datum to 25° yields −25.54 ± 0.20 kcal. mole^{-1}, in agreement with the value reported in this paper within the sum of the uncertainties of the two sets of measurements.

Calculation of Thermodynamic Properties

The Vibrational Assignment.—To compute the thermodynamic functions of thiacyclohexane from calorimetric, spectroscopic and molecular-structure information, an assignment of the fundamental vibrational frequencies was made. The Raman[28] and infrared[29] spectral data used for this purpose were determined from measurements made on the standard sample of thiacyclohexane, API-USBM serial No. 17. These data are included in Table X and will be published in the appropriate American Petroleum Institute Research Project 44 catalogs of spectral data. A schematic assignment of these data to particular vibrational modes also is given in Table X.

In general, the frequencies attributed to fundamental vibrational modes are in the expected regions of the spectra, and the assignment agrees well with that proposed for cyclohexane,[30] except for expected effects of the heteroatom. However, examination of the spectra indicated that one low skeletal frequency had not been observed. To obtain agreement between the calculated and observed values of the entropy, a value of 214 cm.$^{-1}$ was used for this unobserved frequency. (The corresponding frequency of cyclohexane was also unobserved, and a value of 231 cm.$^{-1}$ was used to fit the experimental entropy.[30])

TABLE X

THE VIBRATIONAL SPECTRA AND ASSIGNMENT FOR THIACYCLOHEXANE[a]

Raman,[b] liq. cm.$^{-1}$	Infrared,[c] liq. cm.$^{-1}$	Assignment
188 (20)		Skeletal deform.
(Unobserved frequency near 214 cm.$^{-1}$; see text)		Skeletal deform.
341 (50)		Skeletal deform.
356 (20)		Skeletal deform.
394 (50)		Skeletal deform.
504 (20)	506	Skeletal deform.
655 (100)	658	C–S stretch.
686 (60)	688	C–S stretch.
792 (1)	790	2 × 394 = 788
812 (60)	813	CH_2 rock. or C–C stretch.
823 (5)	826	CH_2 rock. or C–C stretch.
	897	CH_2 rock. or C–C stretch.
902 (20)	903	CH_2 rock. or C–C stretch.
928 (50)	928	CH_2 rock. or C–C stretch.
964 (30)	964	CH_2 rock. or C–C stretch.
	ca. 998	341 + 655 = 996
1011 (60)	1012	CH_2 rock. or C–C stretch.
	ca. 1031	341 + 686 = 1027
1061 (40)	1060	CH_2 rock. or C–C stretch.
1089 (30)	1088	CH_2 rock. or C–C stretch.
1140 (30)	1140	CH_2 wagging
1216 (30)	1217	CH_2 wagging
1237 (60)	1238	CH_2 wagging
1260 (40)	1266	CH_2 wagging
1299 (10)	1300	CH_2 wagging
	ca. 1310	CH_2 twist.
1349 (10)	1339	CH_2 twist.
1420 (80)	1429	CH_2 bend.
1435 (50)	1437	CH_2 bend.

[a] The region above 1500 cm.$^{-1}$ has been omitted. [b] Ref. 28; the numbers in parentheses indicate relative intensities. [c] Ref. 29.

The weak Raman line and infrared bands not assigned as fundamentals are readily explained as the overtone and sum-combination tones given in Table X. Not all of the frequencies above 1300 cm.$^{-1}$ were resolved and average values were used for the CH_2 twisting, CH_2 bending and C–H stretching modes. The assignment used in calculating the thermodynamic functions was as follows: skeletal deformation, 188, [214], 341, 356, 394, 504; C–S stretching, 655 and 685; CH_2 rocking and C–C stretching, 812, 825, 897, 902, 928, 964, 1011, 1061, 1089; CH_2 wagging, 1140, 1216, 1237, 1263, 1299; CH_2 twisting, 1310 (2) and 1344 (3); CH_2 bending, 1425 (2) and 1435 (3); C–H stretching, 2950 (10) cm.$^{-1}$

The Product of the Moments of Inertia.—Because the molecular structure of thiacyclohexane has not been investigated experimentally, it was necessary to assume a reasonable configuration for the molecule. Thiacyclohexane may exist in a single "chair" form or in two "boat" forms, and one of the latter would exhibit optical isomerism. Since Beckett, Pitzer and Spitzer[30] have shown that cyclohexane exists predominantly in the "chair"

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(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) W. H. Evans and D. D. Wagman, *J. Research Natl. Bur. Standards*, **49**, 141 (1952).

(27) Stig Sunner, Thesis, University of Lund, Carl Bloms Boktryckeri, Lund, Sweden, 1949.

(28) Unpublished data from Gulf Research Fellowship, Mellon Institute, Pittsburgh, Pa.

(29) Unpublished data from American Petroleum Institute Research Project 48A, Bureau of Mines, Laramie, Wyo.

(30) C. W. Beckett, K. S. Pitzer and Ralph Spitzer, THIS JOURNAL, **69**, 2488 (1947).

form, it was assumed that the "chair" form of thiacyclohexane is also the most stable configuration. However, the heteroatom undoubtedly strains the thiacyclohexane molecule. Approximate calculations were made of the strain energy of several assumed models of the "chair" form. Since distortions of bond distances require significantly more energy than angular distortions, conventional bond distances were used for these calculations, and only angular strains were considered. The approximate calculations showed that the most stable configuration of the "chair" form of thiacyclohexane is that in which the conventional C–C–C, C–C–S and C–S–C bond angles are undistorted and in which all of the strain energy is due to distortion of the dihedral angles about the ring single bonds. The structural parameters for the model chosen are: C–S bond distance, 1.82 Å.; C–C bond distance, 1.54 Å.; C–H bond distance, 1.09 Å.; C–S–C bond angle, 105°; and all other bond angles, 109° 28′.

On the basis of these parameters the product of the principal moments of inertia of the "chair" form of thiacyclohexane was calculated to be 2.411 × 10^{-113} g.^{3} cm.^{6}

TABLE XI

COMPARISON OF CALCULATED AND CALORIMETRIC DATA

A. Entropy at 351.44°K. (cal. deg.$^{-1}$ mole^{-1})

Trans. + rot. + H.O.[a]	81.755
Anharm.[b]	0.034
Chair–Boat[c]	.118
S° (calcd.)	81.91
S° (obsd.)	81.90
Δ	+0.01

B. Vapor heat capacity (cal. deg.$^{-1}$ mole^{-1})

T, °K.	399.20	423.20	453.20	483.20
Trans. + rot. + H.O.[a]	34.283	36.266	38.671	40.951
Anharm.[b]	0.420	0.543	0.711	0.897
Chair–Boat[c]	.929	1.088	1.278	1.453
C_p° (calcd.)	35.63	37.90	40.66	43.30
C_p° (obsd.)	35.63	37.88	40.70	43.31
Δ	0.00	+0.02	−0.04	−0.01

[a] The sum of the translational, rotational and harmonic-oscillator contributions. [b] The contribution of anharmonicity. [c] The contribution of chair to boat tautomerism.

The Effects of Chair–Boat Tautomerism and Anharmonicity.—In their computation of the thermodynamic properties of cyclohexane, Beckett, Pitzer and Spitzer found it necessary to consider both the effects of "chair–boat" tautomerism and of anharmonicity of normal vibrations.[30] A somewhat similar treatment of these two effects was necessary for calculating the thermodynamic functions of the related molecule, thiacyclohexane.

The contribution of tautomerism to the thermodynamic functions of thiacyclohexane was treated in the manner described by Beckett, *et al.*[30] To simplify the calculations it was assumed that the energy difference between the two "boat" configurations of the sulfur compound is negligible. Thus, the equilibrium of the reaction, chair tautomer → boat tautomer, was described by two parameters: (1) the energy difference between the chair and boat tautomers, ΔH(chair → boat); and (2) the entropy change of the tautomeric reaction, assumed to be $R \ln 3$.

Anharmonicity coefficients could not be determined from the available spectroscopic data, but it was apparent from the calorimetric vapor heat capacity data that the normal vibrations of thiacyclohexane are quite anharmonic. For this reason, a semi-empirical method was developed to compute the effect of anharmonicity on the thermodynamic functions.

Expressions for the contribution of anharmonicity may be derived from the partition function for polyatomic molecules, such as that given by Wagman, *et al.*[23] Although these expressions could not be evaluated because of the lack of anharmonicity coefficient data, they were used to determine the form of the following semi-empirical equations for the *total* anharmonicity contributions

$$C^\circ(\text{anh.}) = Z\{C^\circ/R\}\{[3(C^\circ/R)/u] - [1 + 2/u][(H^\circ - H^\circ_0)/RT]\} \quad (5)$$

$$S^\circ(\text{anh.}) = [Z/u][C^\circ/R][(H^\circ - H\ )/RT] \quad (6)$$

$$(H^\circ - H^\circ_0)/T\,(\text{anh.}) = [Z/2u]\{(H^\circ - H^\circ_0)/RT]\ [2(C^\circ/R) - (H^\circ - H^\circ)/RT] \quad (7)$$

where $u = hc\nu/kT$ and the values of (C°/R) and $(H^\circ - H^\circ_0)/RT$ are those for anharmonic-oscillator of frequency ν. The adjustable parameters ν and Z are an arbitrary frequency and a term involving an arbitrary anharmonicity coefficient, respectively.

TABLE XII

THE MOLAL THERMODYNAMIC PROPERTIES OF THIACYCLOHEXANE[a]

T, °K.	$(F^\circ - H^\circ_0)/T$, cal. deg.$^{-1}$	$(H^\circ - H^\circ_0)/T$, cal. deg.$^{-1}$	$H^\circ - H^\circ_0$, kcal.	S°, cal. deg.$^{-1}$	C°_p, cal. deg.$^{-1}$	ΔHf°,[b] kcal.	ΔFf°,[b] kcal.	$\log_{10}K$,[b]
0	0	0	0	0	0	−22.35	−22.35	+ ∞
273.16	−61.20	13.89	3.794	75.09	23.54	−29.78	+ 0.47	− 0.38
298.16	−62.46	14.80	4.413	77.26	25.86	−30.38	3.27	− 2.40
300	−62.56	14.86	4.458	77.42	26.03	−30.43	3.47	− 2.53
400	−67.37	18.86	7.544	86.23	35.71	−32.45	15.09	− 8.24
500	−72.03	23.16	11.58	95.19	44.73	−33.91	27.16	−11.87
600	−76.63	27.41	16.45	104.04	52.37	−34.85	39.47	−14.38
700	−81.16	31.44	22.01	112.60	58.71	−35.35	51.90	−16.20
800	−85.61	35.19	28.15	120.80	64.00	−35.47	64.37	−17.58
900	−89.95	38.65	34.78	128.60	68.49	−35.28	76.84	−18.66
1000	−94.20	41.83	41.83	136.03	72.34	−34.78	89.28	−19.51

[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 thiacyclohexane by the reaction: 5 C(graphite) + 5 H_2(gas) + $^1/_2$ S_2(gas) → $C_5H_{10}S$(gas).

To compute the contributions to the thermodynamic functions of tautomerism and anharmonicity, it was necessary to evaluate three parameters from experimental values of C_p° at four temperatures. The parameters selected simultaneously to fit the calorimetric data were: ΔH(chair → boat) = 4020 cal. mole^{-1}, ν = 1025 cm.$^{-1}$ and Z = 8.17 cal. deg.$^{-1}$ mole^{-1}. Comparisons of the experimental and calculated values of S° and C_p° are made in Table XI. Because the calculated values of C_p° were not sensitive to simultaneous variations of the adjustable parameters, the division of the total contribution of anharmonicity and tautomerism into the individual contributions listed in Table XI was somewhat arbitrary. However, the value used for ΔH(chair → boat) is of the same order of magnitude as that used for cyclohexane, 5600 cal. mole^{-1}.[30] Also, if the effect of anharmonicity was neglected, no choice of ΔH (chair → boat) gave satisfactory agreement between the calculated and experimental values of C_p°.

The Chemical Thermodynamic Properties.—The vibrational assignment, product of principal moments of inertia and other parameters discussed in the preceding sections were used to compute values of the thermodynamic functions of thiacyclohexane at selected temperatures to 1000°K. The results of these calculations are given in Table XII.

The data of Tables IX and XII were used with thermodynamic data for C(graphite),[23] H_2(gas)[23] and S_2(gas)[26] to compute values of the standard heat, ΔH_f°, standard free energy, ΔF_f°, and common logarithm of the equilibrium constant, $\log_{10} K_f$, for the formation of thiacyclohexane from the elements. Values of these functions at selected temperatures to 1000°K. are included in Table XII.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF FLORIDA]

Physical and Thermodynamic Properties of Terpenes. II. The Heats of Combustion of Some Terpene Hydrocarbons

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The heats of combustion of α-pinene, β-pinene, dipentene, *d*-limonene, *cis*-alloöcimene and myrcene, in the liquid state, were measured in a bomb calorimeter. The samples, of known purity, were enclosed in thin glass bulbs, placed in a platinum crucible in an illium bomb together with 30 atmospheres of oxygen, and ignited by means of an iron fuse wire. The amount of reaction was based on the weight of carbon dixoide formed in the combustion. Tests were made for incomplete combustion by analyzing for carbon monoxide. The calorimeter was calibrated with benzoic acid. The heats of combustion were reported in kcal./mole at 25° for the reactants and products in their standard states. The following values were obtained: α-pinene, 1483.0 ± 0.25 kcal./mole; β-pinene, 1485.1 ± 0.34 kcal./mole; *d*-limonene, 1473.9 ± 0.27 kcal./mole; dipentene, 1474.7 ± 0.24 kcal./mole; *cis*-alloöcimene, 1481.2 ± 0.60 kcal./mole; myrcene, 1490.4 ± 0.24 kcal./mole.

Introduction

A search of the literature revealed only a few references dealing with the experimentally determined heats of combustion of terpene hydrocarbons. This work was done in the early part of this century[2] before thermochemical standards had been established and before many of the errors inherent in the combustion experiments had been analyzed. There is also a question of the purity of the compounds used in the measurements. In view of this, it appeared desirable to obtain the information presented herein. This paper presents the combustion data on six terpenes, of known purity, determined in a calorimeter capable of attaining a precision of a few hundredths of one per cent.

Method

The method used is a substitution one whereby the heat released in an unknown reaction is compared to that released in a known one, with the calorimeter serving as an absorber and comparator of the energies involved. The energy equivalent of the calorimeter was determined in a series of experiments using benzoic acid supplied by the Bureau of Standards (Standard sample 39f). Sufficient benzoic acid was used to give a temperature rise in the calorimeter of about 1.5°, and the unknown reactions were adjusted to produce substantially the same temperature change. The energy equivalent of the calorimeter and all the corrections were evaluated directly in terms of the resistance change of the platinum resistance thermometer used.

Unit of Energy and Molecular Weights

The unit of energy upon which the values of this investigation are based is the absolute joule in terms of which the heats of combustion of benzoic acid are known. The heat of combustion of benzoic acid was taken as 26433.8 ± 2.6 abs. j./g. under standard conditions of the bomb process.[3–5]

To convert to the conventional thermochemical calorie, the relation was used

$$4.1840 \text{ abs. j.} = 1 \text{ calorie}$$

The molecular weight of carbon dioxide, the mass of which was used to determine the amount of reaction, was taken to be 44.010, and the molecular weight of the $C_{10}H_{16}$ terpenes was taken to be 136.23.

(1) This paper is abstracted from a portion of a dissertation submitted by Warren T. Eriksen to the Graduate Council of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1952.

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