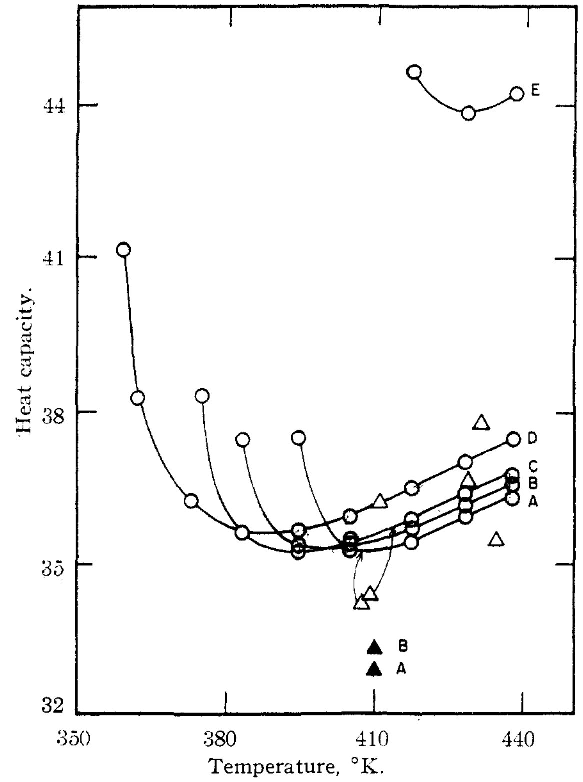

Fig. 2.—Heat capacity of *n*-butyl (A), isobutyl (B), *s*-butyl (C), *t*-butyl (D) and *n*-amyl (E) alcohols at 750 mm.: ○, this research; △, Reynolds and De Vries; ▲, Bennewitz and Rossner.

mole^{-1} deg.$^{-1}$, can be compared with data given by Weltner and Pitzer[13] for methyl alcohol. By using their expression for the second virial coefficient, β, the difference between C_p of the unassociated vapor at one atmosphere and C^0_p was calculated to be 1.06 by the relationship $(\partial C_p/\partial p)_T = -T(d^2\beta/dT^2)$. Adding this to Weltner and Pitzer's value for C^0_p (11.57) gives 12.6 to be compared with the value 12.5 of this research.

Table III

Heat Capacity of Benzene–Carbon Tetrachloride Mixtures at 750 Mm. and 373°K.

Mole % CCl_4	C_p(exptl.)	C_p(calcd.)	Deviation
0.00	25.80	...	....
24.48	25.02	24.92	−0.10
50.80	24.02	23.97	− .05
74.80	23.06	23.10	− .04
100.00	22.19	...	....

Table IV

Heat Capacity of Alcohol–Carbon Tetrachloride Mixtures

	C_p in cal. mole^{-1} deg.$^{-1}$		
Mole % alcohol	CH_3OH (352°K.)	C_2H_5OH (355°K.)	C_2H_5OH (437°K.)
0	22.02	22.10	22.78
10	21.22	21.69	
20	20.38	21.36	
25			22.20
30	19.52	20.89	
40		20.82	
50		20.84	21.66
60	17.64	20.99	
75			21.12
80	16.83	22.26	
100	16.30	25.50	21.00

For ethyl alcohol the values 16.01 and 20.54 were calculated for C_p of the unassociated vapor at one atmosphere at 355 and 437°K., respectively. There are no C^0_p values with which these can be compared.

Lafayette, Indiana

[Contribution No. 33 from the Thermodynamics Laboratory, Petroleum Experiment Station, Bureau of Mines]

The Thermodynamic Properties of 2-Methyl-2-propanethiol from 0 to 1000°K.[1]

By J. P. McCullough, D. W. Scott, H. L. Finke, W. N. Hubbard, M. E. Gross, C. Katz, R. E. Pennington, J. F. Messerly and Guy Waddington

Received December 5, 1952

Various thermodynamic properties of solid, liquid and gaseous 2-methyl-2-propanethiol were measured from 12 to 450°K. The data that were obtained are: heat capacity of the solid (12–274°K.); heats of transition, 972.0, 154.9 and 232.0 cal. mole^{-1} at 151.6, 157.0 and 199.4°K., respectively; heat of fusion, 593.2 cal. mole^{-1} at the triple point, 274.42°K.; heat capacity of the liquid, $C_{\text{satd}} = 28.57 + 4.005 \times 10^{-2}\ T + 1.500 \times 10^{-5}\ T^2$, cal. deg.$^{-1}$ mole^{-1} (274–330°K.); entropy of the saturated liquid at 298.16°K., 58.90 cal. deg.$^{-1}$ mole^{-1}; entropy of the ideal gas at 298.16°K. and unit fugacity, 80.79 cal. deg.$^{-1}$ mole^{-1}; vapor pressure from 22 to 99°, $\log_{10}p$ (mm.) $= 6.78781 - 1115.565/(t + 221.314)$; heat of vaporization, $\Delta H_v = 9699 - 2.224\ T - 0.01891\ T^2$, cal. mole^{-1} (298–337°K.); heat capacity of the ideal gas, $C_p^\circ = 2.38 + 0.10229\ T - 4.516 \times 10^{-5}\ T^2$, cal. deg.$^{-1}$ mole^{-1} (325–450°K.); the second virial coefficient, $B = (PV - RT)/P = -592 - 16.6 \exp(1200/T)$, cc. mole^{-1} (298–450°K.); and the standard heat of formation of the liquid from graphite, hydrogen and rhombic sulfur, $\Delta H_f = -33.78$ kcal. mole^{-1} (298.16°K.). These thermodynamic data were used with available spectroscopic and molecular-structure information to compute the following chemical thermodynamic properties at selected temperatures from 0 to 1000°K.: $(F^\circ - H_0^\circ)/T$, $(H^\circ - H_0^\circ)/T$, $(H^\circ - H_0^\circ)$, S°, C_p°, ΔH_f°, ΔF_f° and $\log_{10}K_f$.

An integrated experimental and computational program is conducted in this Laboratory to obtain thermodynamic data for organic sulfur compounds important in petroleum production and refining. For structurally simple compounds, experimental thermodynamic data are used with spectroscopic and molecular-structure information to calculate the following thermodynamic properties at selected temperatures from 0 to 1000°K.: $(F^\circ - H_0^\circ)/T$, $(H^\circ - H_0^\circ)/T$, $(H^\circ - H_0^\circ)$, S°, C_p°, ΔH_f, ΔF_f° and

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[1] This investigation was performed as part of American Petroleum Institute Research Project 48A on the "Production, Isolation and Purification of Sulfur Compounds and Measurements of their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

log$_{10}K_f$. With such comprehensive data for key members of the various homologous series available as a basis, tables of the chemical thermodynamic properties of entire families of organic sulfur compounds will be constructed by methods previously employed in similar compilations of the properties of hydrocarbons.[2,3]

Studies of the important aliphatic thiols (mercaptans) were initiated with investigations of the thermodynamic properties of ethanethiol[4] and 1-pentanethiol.[5] The results of a relatively complete investigation of the thermodynamic properties of 2-methyl-2-propanethiol (*t*-butyl mercaptan) are reported in this paper. In the order of their presentation, the topics discussed are: (1) the results of low-temperature calorimetric studies; (2) the vapor pressure; (3) the heat of vaporization, vapor heat capacity and gas imperfection; (4) the entropy in the ideal gaseous state; (5) the heats of combustion and formation; (6) the vibrational assignment and moments of inertia; (7) the magnitudes of the potential barriers to internal rotation of the methyl and thiol groups, as determined from the calorimetric entropy and vapor heat capacity data; and (8) the chemical thermodynamic properties from 0 to 1000°K.

Experimental

All experimental data reported in this paper are based on a molecular weight of 90.186 for 2-methyl-2-propanethiol and the following definitions: 0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules = 4.1840 abs. joules. The 1951 International Atomic Weights[6] and the 1951 values of the fundamental physical constants[7] were used for all computations.

The Material.—The 2-methyl-2-propanethiol used in the low-temperature calorimetric studies and for measurements of the vapor pressure and heat of combustion was part of the Standard Sample of Sulfur Compound, NBS 905, prepared and purified by American Petroleum Institute Research Project 48A at the Laramie (Wyo.) Station of the Bureau of Mines. In calorimetric studies of its melting point, this sample was found to contain 0.011 ± 0.005 mole % of liquid-soluble, solid-insoluble impurity. A noncertified sample, with a reported purity of 99.96 mole %, was obtained from the Laramie Station for use in the heat of vaporization and vapor heat capacity investigations.

The following physical properties of the standard sample of 2-methyl-2-propanethiol were measured at the Laramie Station[8]; refractive index, $n^{25}\mathrm{D}$, 1.42007; density, d^{25}, 0.79472 g. ml.$^{-1}$.

Solid and Liquid Heat Capacities.—The thermal properties of 2-methyl-2-propanethiol were measured from 12 to 329°K. in an adiabatic cryostat similar to that described by Ruehrwein and Huffman.[9] The sample was contained in a platinum calorimeter, which is equipped with horizontal, perforated disks of gold to facilitate thermal equilibration and prevent settling of solid during fusion experiments.

Two series of measurements were made in the investigation of the low-temperature properties of 2-methyl-2-propanethiol. The thermometer employed in the first series developed an electrical short before measurements below 50°K. had been made. The second investigation was made with the same sample and calorimeter, but with a new

Table I

The Molal Heat Capacity of 2-Methyl-2-propanethiol in Cal. Deg.$^{-1}$

T, °K.^{a}	$C_{\mathrm{satd}}{}^b$	T, °K.^{a}	$C_{\mathrm{satd}}{}^b$	T, °K.^{a}	$C_{\mathrm{satd}}{}^b$
Series I (mole sample = 0.51599)					
Crystals I		Crystals II		211.02	33.669
				212.87	33.715
54.93	10.300	156.08	33.764	218.46	33.967
59.90	10.940			221.00	34.031
64.98	11.607	Crystals III		224.09	34.188
70.60	12.318			230.69	34.429
76.30	13.074	156.66	32.417	231.95	34.456
82.03	13.890	163.14	32.669	235.14	34.603
83.50	14.105	163.74	32.808	242.76	34.913
87.81	14.735	169.65	33.091	243.84	35.016
88.77	14.861	171.41	33.215	246.05	35.124
93.96	15.578	171.47	33.194	252.37	35.382
95.02	15.717	180.52	33.617	260.79	35.816
100.94	16.570	181.63	33.669	268.59	36.401
101.57	16.653	191.20	34.140		
108.21	17.644	192.81	34.225	Liquid	
115.37	18.744				
122.30	19.878	Crystals IV		283.95	41.146
129.91	21.242			285.78	41.255
137.41	22.837	203.18	33.386	295.15	41.693
144.74	24.913	208.10	33.566		
Series II (mole sample = 0.47934)					
Crystals I		89.74	15.000	164.11	32.845
		91.00	15.163	164.21	32.831
12.35	1.060	97.69	16.099	167.07	33.077
13.71	1.413	97.81	16.131	168.98	33.085
15.45	1.865	98.37	16.193	174.00	33.325
16.19	2.078	104.62	17.111	176.87	33.407
17.72	2.541	107.75	17.535	185.96	33.930
19.31	3.050	111.94	18.217		
20.30	3.369	119.57	19.435	Crystals IV	
23.53	4.329	127.07	20.718		
23.54	4.346	134.19	22.110	207.64	33.594
26.10	4.942	136.17	22.540	224.47	34.206
28.74	5.706	140.04	23.476	241.19	34.894
30.64	6.152	143.78	24.555	249.92	35.301
36.02	7.346	147.38	25.827	258.55	35.727
40.78	8.234	150.09	27.058	263.59	35.971
42.56	8.616			270.95	37.542
47.38	9.261	Crystals II			
49.01	9.503			Liquid	
54.75	10.260	153.42	33.878		
59.06	10.802	154.12	33.851	280.91	41.019
59.49	10.813	154.92	33.720	281.27	41.015
63.82	11.443	155.23	33.828	286.93	41.282
65.39	11.656	155.56	33.705	288.78	41.370
68.73	12.069	156.44	33.828	296.22	41.760
73.09	12.626			302.24	42.039
74.20	12.757	Crystals III		311.29	42.494
79.76	13.548			320.24	42.939
81.47	13.805	157.03	32.341	329.09	43.375
85.01	14.314	161.72	32.603		

[a] T is the mean temperature of each heat capacity measurement. [b] C_{satd} is the heat capacity of the condensed phase at saturation pressure.

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[2] (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 a part of the program of American Petroleum Institute Research Project 44.

[4] J. P. McCullough, D. W. Scott, H. L. Finke, M. E. Gross, K. D. Williamson, R. E. Pennington, Guy Waddington and H. M. Huffman, This Journal, **74**, 2801 (1952).

[5] H. L. Finke, D. W. Scott, M. E. Gross, Guy Waddington and H. M. Huffman, *ibid.*, **74**, 2804 (1952).

[6] Edward Wichers, *ibid.*, **74**, 2447 (1952).

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

[8] W. E. Haines, R. V. Helm and J. S. Ball, unpublished data from American Petroleum Institute Research Project 48A, Bureau of Mines, Laramie, Wyo.

[9] R. A. Ruehrwein and H. M. Huffman, This Journal, **65**, 1620 (1943).

platinum resistance thermometer. Since the results of the two studies were essentially indistinguishable, all the data were considered together.

The experimental heat capacities at saturation pressure (C_{satd}) of the four crystalline modifications and of the liquid are presented in Table I. The temperatures listed are the mean temperatures of the individual measurements. The temperature increment employed in each measurement was approximately 10% of the absolute temperature below 50°K., 5 to 6° from 50 to 150°K. and 8 to 10° above 150°K. Near the transitions, however, increments of less than 5° were used. The precision of the heat capacity results was usually better than 0.1%; at temperatures above 30°K. the accuracy uncertainty should not be greater than 0.2%.

The thermal behavior of 2-methyl-2-propanethiol was normal, except in the temperature region 15 to 40°K. At these temperatures, the time required after each heating period for the calorimeter and its contents to reach thermal equilibrium was approximately 1 hour instead of the customary 5 to 10 minutes. No unusual heat effect was found in this temperature region, but it is possible that the anomalous behavior was due to the fact that the measurements were made on supercooled crystals, *i.e.*, that a solid–solid transition was not detected. However, this possibility seems unlikely, not only because of the regularity of the heat-capacity data, but also because of the good agreement between the experimental entropy and that computed from spectroscopic and molecular-structure information (see discussion below and Table VII). It is more probable that the slow thermal equilibration was due to poor heat transfer caused by shrinkage of the crystals away from the calorimeter walls and heat-distributing disks.[10]

The long equilibration periods required in the measurements made from 15 to 40°K. were responsible for a small but significant heat leak. During a heating period, the temperature of the calorimeter became higher than that of the sample; in the following equilibration period, the temperature of the calorimeter decreased as heat was transferred to its contents. In this temperature region, the thermal shield did not cool so rapidly as did the surface of the calorimeter. The resulting calorimeter to shield temperature difference gave rise to an appreciable heat leak because of the long equilibration periods. Heat-exchange coefficients, determined in separate experiments, were used to correct the observed values of the heat capacity. The effect of these corrections on the entropy at 298.16°K. was 0.04 cal. deg.$^{-1}$ mole^{-1}.

The combined heat capacity data of the two series were plotted against temperature, and a smooth curve was drawn through the experimental points. The curve was extended visually to the transition temperatures and melting point. Only the two results obtained immediately below the melting point (at 268.59°K. in series I and 270.95°K. in series II) showed an appreciable effect of premelting phenomena. To eliminate the effect of premelting, these two points were disregarded in the extrapolation of the heat capacity data to the melting point. The resulting curve was used in the calculation of the heats of transition and fusion; values of C_{satd} taken from the smooth curve were used to evaluate graphically the integrals, $\int C_{\mathrm{satd}}\, \mathrm{d} \ln T$, required for calculation of the entropy (Table VII).

The experimental data for the heat capacity of liquid 2-methyl-2-propanethiol are represented within 0.01 cal. deg.$^{-1}$ mole^{-1} by the empirical equation

$$C_{\mathrm{satd}}\,(\mathrm{liq.}) = 28.57 + 4.005 \times 10^{-2}T + 1.500 \times 10^{-5}T^2,$$
$$\mathrm{cal.\ deg.^{-1}\ mole^{-1}}\ (280\text{–}330\,°\mathrm{K.}) \quad (1)$$

The Heats of Transition and Fusion.—In the low-temperature thermal studies, three isothermal transitions were found to occur in crystalline 2-methyl-2-propanethiol. The results of replicate measurements of the heats of transition, $\Delta H_{\mathrm{trans}}$, and of the heat of fusion, $\Delta H_{\mathrm{fusion}}$, are recorded in Table II. The transition temperatures listed were determined by observing the equilibrium temperatures when about 20, 50 and 80% of the sample had been transposed, and extrapolating these temperatures to 100% transposed. An uncertainty of ±0.1° is assigned to the transition temperatures.

TABLE II

THE MOLAL HEATS OF TRANSITION AND FUSION OF 2-METHYL-2-PROPANETHIOL

T, °K.	ΔH, cal. Series I	Series II	Mean
151.6 (trans)	971.7	971.2	
	973.0		972.0 ± 1.0[a]
157.0 (trans)	155.3	154.9	
	154.6	154.6	154.9 ± 0.4[a]
199.4 (trans)	232.0	231.1	
		231.9	232.0 ± .1[a]
274.42 (fusion)	593.4	593.0	
	592.8	593.6	593.2 ± .4[a]

[a] Maximum deviation of experimental results from the mean.

The Triple Point and Sample Purity.—Calorimetric studies of the equilibrium melting temperature as a function of the fraction of sample melted were made by the method described in an earlier publication from this Laboratory.[11] The results of these experiments are recorded in Table III. The equilibrium melting temperatures, T_{obsd}, were plotted against the reciprocal of the fraction melted, $1/F$. The triple point, $T_{\mathrm{T.P.}}$, was determined by linear extrapolations of these data to $1/F = 0$. The mole fraction of total impurity in the sample, N^*_2, was calculated by the relationship, $N^*_2/F = A(T_{\mathrm{T.P.}} - T_{\mathrm{obsd}})$, where A is the cryoscopic constant, $\Delta H_{\mathrm{fusion}}/RT^2_{\mathrm{T.P.}}$. This procedure is based on the assumptions that ideal solutions are formed in the liquid phase and that the impurities are insoluble in the solid phase. The slight deviations from linearity of plots of T_{obsd} *vs.* $1/F$ indicate that some of the impurities formed solid solutions with 2-methyl-2-propanethiol.

TABLE III

2-METHYL-2-PROPANETHIOL: MELTING POINT SUMMARY

Triple point, $T_{\mathrm{T.P.}} = 274.42 \pm 0.05$°K.; cryoscopic constant, $A = 0.00396$ deg.$^{-1}$; impurity = 0.011 ± 0.005 mole %

Melted, %	$1/F$	T, °K. Obsd.	Graph[b]
		Series I	
10.53	9.50	274.2440	274.1767
24.45	4.09	.3213	.3174
49.56	2.02	.3712[a]	.3712
68.90	1.45	.3897	.3860
88.38	1.13	.3943[a]	.3943
100.00	1.00		.3977
Pure	0.00		.4237[c]
		Series II	
24.07	4.16	274.3194	274.2901
69.45	1.44	.3729[a]	.3729
89.68	1.12	:3828[a]	.3828
100.00	1.00		.3859
Pure	0.00		.4164[c]

[a] Straight lines through these points were extrapolated to $1/F = 0$ to obtain the triple point, $T_{\mathrm{T.P.}}$. [b] Temperatures read from the straight lines of footnote *a*. [c] Triple point.

The Vapor Pressure.—The vapor pressure of 2-methyl-2-propanethiol was measured from 20 to 99° with the twin-ebulliometer system described in an earlier publication from this Laboratory.[12] The ebulliometer described in ref. 12 has been modified by enclosing the heater in a glass re-entrant well so that samples of corrosive compounds come

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[10] A similar region of slow approach to thermal equilibrium was found in a subsequent study of the heat capacity of tetramethyllead (to be published). In this instance, the rate of thermal equilibration was greatly increased when a small amount of helium was added to the calorimeter to improve the rate of heat transfer.

[11] S. S. Todd, G. D. Oliver and H. M. Huffman, This Journal, **69**, 1519 (1947).

[12] 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).

into contact with glass only. The boiling and condensation temperatures of both 2-methyl-2-propanethiol and water were measured when they were boiling at a common pressure. The "observed" vapor pressures, presented in Table IV, were obtained from the vapor pressure data for water given by Osborne, Stimson and Ginnings.[13] That the difference between the boiling and condensation temperatures of the sulfur compound at 760 mm. was only 0.002° indicates that impurities with volatilities different from 2-methyl-2-propanethiol were not present in significant quantities. The Antoine equation was obtained from the data of Table IV by a least-squares adjustment[14]

$$\log_{10} p = 6.78781 - 1115.565/(t + 221.314) \quad (2)$$

where p is in mm. and t is in °C. Values of the vapor pressure computed by means of eq. (2) are tabulated in the last column of Table IV. The normal boiling point given by eq. (2) is 64.22°.

TABLE IV

THE VAPOR PRESSURE OF 2-METHYL-2-PROPANETHIOL

Boiling point, °C. Water	2-Methyl-2-propanethiol	Pressures, mm. Obsd.^{a}	Eq. (2)
60.000	20.496	149.41	149.42
65	25.785	187.57	187.57
70	31.127	233.72	233.72
75	36.519	289.13	289.14
80	41.959	355.22	355.24
85	47.446	433.56	433.54
90	52.983	525.86	525.79
95	58.573	633.99	633.93
100	64.217	760.00	760.03
105	69.908	906.06	906.11
110	75.654	1074.6	1074.7
115	81.449	1268.0	1268.2
120	87.294	1489.1	1489.3
125	93.188	1740.8	1740.7
130	99.138	2026.0	2025.8

^{a} From vapor pressure data for water given in ref. 13.

The Heat of Vaporization.—The heat of vaporization and vapor heat capacity of 2-methyl-2-propanethiol were measured with the flow calorimeter system described in previous papers.[15] Two series of measurements were conducted because a slight irregularity was detected in correlating the results of the first investigation. A glass vaporizer with a glass-sheathed heating element[4] and the flow calorimeter described in ref. 15a were employed in the first study; both a new vaporizer and a new calorimeter were used in the second. The new vaporizer, also made of glass, is equipped with a heating element that consists of glass-insulated manganin wire sheathed by small platinum tubing (see Fig. 1). In the construction of the heater assembly, the straight heating element was wrapped with glass thread to promote smooth boiling, and then wound in three concentric helices, which were spaced and supported by a Mycalex[16] framework (not shown). The ends of the platinum sheath were gold-welded to larger platinum tubes, which, in turn, were joined through graded glass seals to Pyrex tubes. The heater leads (not shown) were brought through the platinum and glass tubes and out of the vaporizer through a ring seal. With this arrangement, corrosive compounds come into contact with inert materials only. The platinum-sheathed heating element produces much steadier ebullition than that encased in glass tubing.[4]

The new flow calorimeter is of essentially the same design as that described previously.[15a] However, platinum-tungsten soldered joints in the thermometer circuit were placed out of the direct flow of effluent vapor so as to eliminate thermal e.m.f.'s, such as those encountered in the thermometer circuit of the earlier calorimeter.

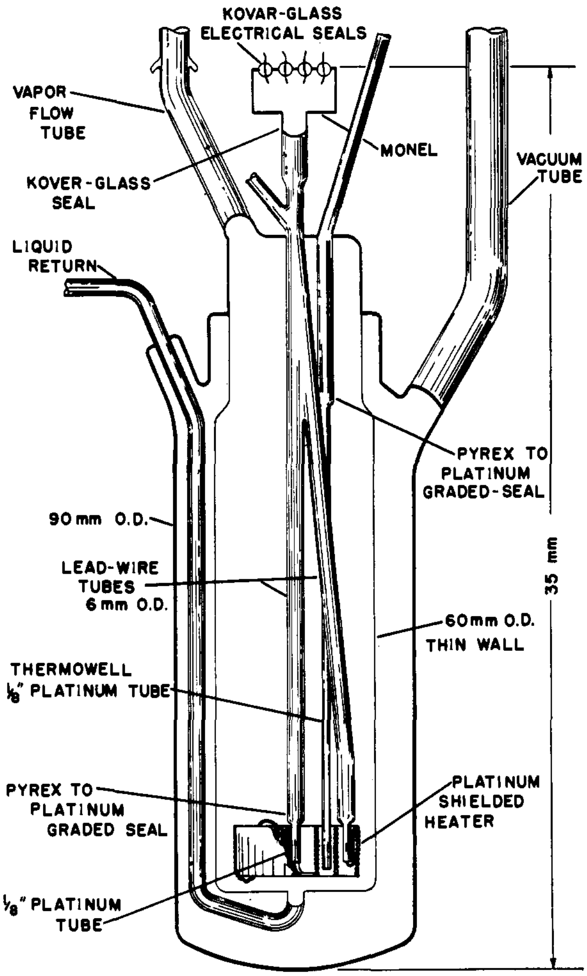

Fig. 1.—Glass vaporizer with platinum-sheathed heater.

The results of the heat of vaporization experiments are summarized in Table V. Replicate measurements were made with both vaporizers at each of three temperatures. Although slightly greater precision was obtained in the second series of measurements, the average of the results obtained at 337.38 and 317.16°K. differed from those of the first series by less than 1 cal. mole^{-1}. At 298.16°K. the results of the second series were about 5 cal. mole^{-1} lower than those of the first. Since the new vaporizer produces vapor at a steadier flow rate (particularly at reduced pressures), the data of the second series are considered to be the more reliable. At 337.38 and 317.16°K., the data from both series of experiments were averaged to obtain the values listed in Table V, but only data from the second series of measurements were averaged for the result at 298.16°K.[16a]

TABLE V

THE MOLAL HEAT OF VAPORIZATION AND GAS IMPERFECTION OF 2-METHYL-2-PROPANETHIOL

T,°K.	ΔH_v, cal.	$-B$ (obsd.) cc.	$-B$ (calcd.)^a cc.	$V^{a,b}$ cc.	$(\partial V/\partial T)_P{}^{a,b}$ cc. deg.$^{-1}$	$-(\partial^2 V/\partial T^2)_P{}^{a,b}$ cc. deg.$^{-2}$
298.16	7355 ± 2^c	1588	1521	100,950	356.2	0.254
317.16	7092 ± 3^c	1316	1322	50,330	171.6	.159
337.38	6797 ± 2^c	1160	1174	26,510	87.79	.0944

^{a} Calculated with the aid of eq. (5). ^{b} At saturation pressures. ^{c} Maximum deviation of experimental results from the mean.

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[13] N. S. Osborne, H. F. Stimson and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 261 (1939).

[14] C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *ibid.*, **35**, 219 (1945).

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

[16] Mycalex, compression molded glass-bonded mica, is manufactured by the Mycalex Corp. of America.

[16a] The average of all the results obtained at 298.16°K. was 7358 ± 5 cal. mole^{-1}.

The accuracy uncertainty of these data should not be greater than 0.1%. The following empirical equation may be used for interpolation in the range of temperature of the measurements

$$\Delta H_v = 9699 - 2.224T - 0.01891T^2, \text{ cal. mole}^{-1} \cdot (298\text{–}337\,^\circ\text{K.}) \quad (3)$$

The Vapor Heat Capacity.—Measurements of the vapor heat capacity of 2-methyl-2-propanethiol were made at two or more pressures at each of four temperatures between 325 and 449°K. The results of these measurements are recorded in Table VI. As noted in Table VI, measurements were made in the second series at four experimental points (those referred to in footnotes *a* and *b*). At three of these points (in italics), the data from the two series agreed within 0.02%. However, the values obtained for the vapor heat capacity at 181 mm. and 325°K. was 0.2% lower in the second series than in the first. It is believed that the first result was in error for an unknown reason, since use of the value from the second series eliminated the irregularity noted in correlating the original data.

TABLE VI

THE MOLAL VAPOR HEAT CAPACITY OF 2-METHYL-2-PROPANETHIOL IN CAL. DEG.$^{-1}$

T, °K.	325.20	358.20	402.20	449.20
C_p (760.0 mm.)	.....	*33.810*[a]	36.527[c]	39.362[c]
C_p (382.9 mm.)	*31.393*[a]	*33.521*[a]	.....	.....
C_p (181.4 mm.)	31.122[b]	33.362[c]	36.299[c]	39.254[c]
C_p° (obsd.)	30.88	33.22	36.23	39.22
C_p° (calcd.)[d]	30.88	33.24	36.28	39.33
Δ (obsd. − calcd.)	0.00	−0.01	−0.05	−0.11
$(\partial C_p/\partial P)_T$ (obsd.)	1.02	0.59	0.30	0.14
$(\partial C_p/\partial P)_T$ (calcd.)[e]	1.04	0.57	0.29	0.16

[a] Results in italics are averages of data from both the first and second series of measurements. [b] Results of second series only. [c] Results of first series only. [d] Calculated from spectroscopic and molecular structure data. [e] Calculated by use of eq. (5); units of $(\partial C_p/\partial P)_T$ are cal. deg.$^{-1}$ mole^{-1} atm.$^{-1}$.

Experimental values of the heat capacity in the ideal gaseous state, C_p°, were obtained at each temperature by linear extrapolation to zero pressure of plots of heat capacity *vs.* pressure.[17] The accuracy uncertainty of these values of C_p° is estimated to be 0.2%. Equation (4) represents the observed values of C_p° within 0.01 cal. deg.$^{-1}$ mole^{-1}

$$C_p^\circ = 2.38 + 0.10229T - 4.516 \times 10^{-5}T^2, \text{ cal. deg.}^{-1} \text{ mole}^{-1} \, (325\text{–}450\,^\circ\text{K.}) \quad (4)$$

Gas Imperfection and the Second Virial Coefficient.—The results of the measurements of the vapor pressure, heat of vaporization and vapor heat capacity, as presented in previous sections, were utilized to obtain a representation for the second virial coefficient, B, in the equation of state $PV = RT + BP$. Values of B were calculated by use of 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 molar volume of the liquid. The relationship, $(\partial C_p/\partial P)_T = -T(\partial^2 V/\partial T^2)_P = -T(\mathrm{d}^2B/\mathrm{d}T^2)$, was used to calculate values of $(\mathrm{d}^2B/\mathrm{d}T^2)$ from the observed values of $(\partial C_p/\partial P)_T$. These results were correlated with the empirical equation

$$B = -592 - 16.61 \exp(1200/T), \text{ cc. mole}^{-1} \, (298\text{–}450\,^\circ\text{K.}) \quad (5)$$

where T is in °K. The constants of eq. (5) were evaluated by the method outlined in an earlier paper.[17] Equation (5) is not expected to be valid much beyond the range of temperature and pressure of the experimental measurements.

Values of B calculated by use of the Clapeyron equation and values of B, $(\partial V/\partial T)_P$ and $(\partial^2 V/\partial T)^2_P$ obtained with the aid of eq. (5) are included in Table V. In the last two lines of Table VI, values of $(\partial C_p/\partial P)_T$ obtained by use of eq. (5) are compared with the experimental results.

The Entropy.—The experimental data presented in previous sections were used to compute the entropy of 2-methyl-2-propanethiol in the liquid and vapor states. Table VII contains a summary of these calculations.

TABLE VII

THE MOLAL ENTROPY OF 2-METHYL-2-PROPANETHIOL IN CAL. DEG.$^{-1}$

0–12°K.	Debye extrapolation[a]	0.340
12–151.6°	Graphical, $\int C_{satd}\,\mathrm{d}\ln T$	24.150
151.6°	Transition, 972.0/151.6	6.412
151.6–157.0°	Graphical, $\int C_{satd}\,\mathrm{d}\ln T$	1.185
157.0°	Transition, 154.9/157.0	0.987
157.0–199.4°	Graphical, $\int C_{satd}\,\mathrm{d}\ln T$	8.000
199.4°	Transition, 232.0/199.4	1.163
199.4–274.42°	Graphical, $\int C_{satd}\,\mathrm{d}\ln T$	11.073
274.42°	Fusion, 593.2/274.42	2.162
274.42–298.16°	Graphical, $\int C_{satd}\,\mathrm{d}\ln T$	3.426
S_{satd}(liq.) 298.16°K.		58.90 ± 0.15

T, °K.	298.16	317.16	337.38
S_{satd}(liq.)	58.898	61.512	64.186
$\Delta H_v/T$[b]	24.669	22.361	20.146
$P(\mathrm{d}B/\mathrm{d}T)$[c]	0.073	0.106	0.149
$R \ln (p/760)$[d]	−2.846	−1.362	.000
S°, gas (obsd.)	80.79	82.62	84.48
S°, gas (calcd.)[e]	80.79	82.62	84.54

[a] A Debye function for 5 degrees of freedom with θ = 108.9° was used for this extrapolation. [b] Entropy of vaporization; from data of Table V. [c] Entropy of gas imperfection; from eq. (5). [d] Entropy of compression; from eq. (2). [e] Calculated from spectroscopic and molecular structure data.

The Heats of Combustion and Formation.—The heat of combustion of 2-methyl-2-propanethiol was determined in a rotating-bomb calorimeter recently constructed in this Laboratory. A description of the apparatus and method and the complete experimental details of the studies of 2-methyl-2-propanethiol and other organic sulfur compounds will be presented in a forthcoming publication.[18] Consequently, only the pertinent results will be given here. The heat of combustion of 2-methyl-2-propanethiol, ΔH_c°, for the reaction given by eq. (6) is -827.5_9 kcal. mole^{-1} at 298.16°K.

$$C_4H_{10}S(l) + 8O_2(g) \longrightarrow 4CO_2(g) + H_2SO_4\cdot 70H_2O(aq) - 66H_2O(l) \quad (6)$$

Determinations were made of the heat of combustion of a mixture of paraffin oil and rhombic sulfur, the composition of which was adjusted to result in the same concentration of products as given in eq. (6). The heat of combustion of the paraffin oil was also measured. These data and the heats of formation of carbon dioxide[19] and water[19] were used with the above value for ΔH_c° to calculate the standard heat of formation of liquid 2-methyl-2-propanethiol, ΔH_f° (l). The standard heat of formation in the ideal gaseous state, ΔH_f° (g), was calculated by adding the standard heat of vaporization, computed from data of Table V, to ΔH_f° (l). The standard free energies, ΔF_f°, and the equilibrium constants, K_f, for the formation of both liquid and gaseous 2-methyl-2-propanethiol were calculated from these heats of formation, the entropy values from Table VII, and the thermodynamic functions of graphite,[19] hydrogen[19] and rhombic sulfur.[20] The heat of formation of S_2(g) from rhombic sulfur and the thermodynamic functions of S_2(g)[21] were used to compute the same properties (ΔH_f°, ΔF_f° and K_f) for the

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

(18) "A Rotating Combustion-Bomb for Precision Calorimetry. The Heats of Combustion of Some Sulfur-Containing Compounds," by W. N. Hubbard, Charles Katz and Guy Waddington.

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

(20) "Selected Values of Chemical Thermodynamic Properties," Circular of the National Bureau of Standards, 500, Washington, D. C., 1952: Series I, Table 14-1.

(21) National Bureau of Standards Report No. 1037, by W. H. Evans and D. D. Wagman.

formation of gaseous 2-methyl-2-propanethiol from graphite, $H_2(g)$ and $S_2(g)$. The results of these calculations are given in Table VIII.

TABLE VIII

THE MOLAL HEAT AND FREE ENERGY AND THE LOGARITHM OF EQUILIBRIUM CONSTANT FOR THE FORMATION OF 2-METHYL-2-PROPANETHIOL AT 298.16°K.

State[a]	Reference state[b]	ΔH_f°, kcal.	ΔF_f°, kcal.	$\log_{10} K_f$
Liquid	S(rhombic)	−33.78 ± 0.29[c]	−0.92	0.67
Gas	S(rhombic)	−26.39 ± 0.30[c]	−0.06	+0.04
	$S_2(g)$	−41.79	−9.60	+7.04

[a] Standard state of 2-methyl-2-propanethiol. [b] Reference state for elemental sulfur in the equations: (1) $4C(\text{graphite}) + 5H_2(g) + S(\text{rhombic}) \rightarrow C_4H_{10}S(l \text{ or } g)$ and (2) $4C(\text{graphite}) + 5H_2(g) + {}^1/_2S_2(g) \rightarrow C_4H_{10}S(g)$. [c] Uncertainties are twice the "over-all" standard deviation (F. D. Rossini and W. E. Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939)).

Calculation of Thermodynamic Functions

Vibrational Assignment.—A complete vibrational assignment for 2-methyl-2-propanethiol was made for use in computation of the thermodynamic functions. Table IX contains a summary of the available infrared[23] and Raman[23] spectral data. Unfortunately, the states of polarization of the Raman lines were not measured, and the infrared band contours for all normal modes of this molecule are nearly identical. Therefore, the assignment of the fundamental frequencies given in Table IX was made by analogy with the structurally similar molecules $(CH_3)_3CX$, where X = H, Cl, Br and I. Although 2-methyl-2-propanethiol does not have the symmetry of these molecules (point group C_{3v}), the asymmetry caused by the hydrogen of the thiol group is small. For this reason those vibrational modes that are analogous to the doubly degenerate modes of isobutane and the *t*-butyl halides were not split sufficiently to be resolved in the spectra of 2-methyl-2-propanethiol. The assignments to symmetry classes given in Table IX are those for the corresponding vibrations of molecules with the symmetry of point group C_{3v}. An assignment for *t*-butyl chloride (for which polarization data are available) is included in Table IX for comparison.[24] Vibrational assignments for isobutane,[2a] *t*-butyl bromide[24] and *t*-butyl iodide[24] form a consistent set with the assignments of Table IX if allowance is made for the different masses of the tertiary substituents.

TABLE IX

SPECTRA AND VIBRATIONAL ASSIGNMENT FOR 2-METHYL-2-PROPANETHIOL

2-Methyl-2-propanethiol Raman,[a] liq., cm.⁻¹	2-Methyl-2-propanethiol Infrared,[b] liq., cm.⁻¹	*t*-Butyl chloride Raman,[c] liq., cm.⁻¹	Assignment[d]
295 (3)		304 d	C–C–X bend. (*E*)
368 (5)		372 p	C–C–C bend. (A_1)
395 (1)		406	C–C–C bend. (*E*)
445 (1/2)			820 − 368 = 452
587 (10)		570 p	C–X str. (A_1)
	ca. 679		295 + 368 = 663
	ca. 737		2 × 368 = 736
819 (6)	820	812 p	C–C str. (A_1)
866 (2)	867		C–S–H bend.
930 (2)	933	925 d	CH_3 rock. (*E*)
	965	Inactive	CH_3 rock. (A_2)
1030 (1/2)	1035	1026 d	CH_3 rock. (*E*)
1103 (0)			295 + 819 = 1114
1160 (4)	1164	1147 p	CH_3 rock. (A_1)
1177 (3)			See text
1218 (3b)	*ca.* 1214	1234 d	C–C str. (*E*)
1369 (1/2)	1364	1361	CH_3 bend. (A_1, *E*)
	ca. 1391		368 + 1030 = 1398
1449 (5vb)	1458	1445	CH_3 bend. (A_2, *E*)
2570 (7)	2565		S–H str.
2960 (10vb)	2959	2950	C–H str.

[a] Reference 22. Above 1500 cm.⁻¹, only those lines assigned as fundamentals are given. [b] Ref. 23. See footnote *a*. [c] Ref. 24; d = depolarized, p = polarized. [d] X refers to S or Cl.

By analogy with data for related organic sulfur compounds, the frequencies at 587, 867 and 2570 cm.⁻¹ were assigned to the C–S stretching, C–S–H bending and S–H stretching vibrations, respectively.

The assignment of the weak infrared band at 965 cm.⁻¹ to the unsymmetrical CH_3 rocking mode (A_2 mode of point group C_{3v}) is uncertain. The corresponding mode is inactive in both the Raman and infrared spectra of molecules with C_{3v} symmetry, and it is reasonable to expect that it may not have sufficient intensity to appear in the spectra of 2-methyl-2-propanethiol. In a normal coordinate analysis of the lower frequencies of 2,2,-3,3-tetramethylbutane, Scott, *et al.*,[25] calculated a value of 971 cm.⁻¹ for an analogous CH_3 rocking frequency of the *t*-butyl group (classes A_{2g} and A_{1u}, point group D_{3d}). Since the vibration under consideration is, to a first approximation, independent of the group attached to the *t*-butyl group, the similar CH_3 rocking mode in 2-methyl-2-propanethiol should have approximately the same frequency as that calculated for 2,2,3,3-tetramethylbutane. Consequently, the infrared band at 956 cm.⁻¹ was assigned to this mode. However, a reasonable alternative assignment is the sum-combination, 368 + 587 = 955 cm.⁻¹.

The thermodynamically unimportant hydrogen vibrations above 1300 cm.⁻¹ were not all resolved, and average values were used for these modes.

The Raman doublet, 1160–1177 cm.⁻¹, was interpreted as the result of Fermi resonance between a fundamental at about 1165 cm.⁻¹ (CH_3 rocking) and the first overtone of the fundamental at 587 cm.⁻¹ (C–S stretching), 2 × 587 = 1174 cm.⁻¹ The remaining lines and bands below 1500 cm.⁻¹ were assigned as the combinations and overtones given in Table IX.

The following vibrational assignment was employed to compute the thermodynamic properties

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(22) (a) Catalog of Infrared Spectral Data, American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Serial No. 1120 (1950); (b) I. F. Trotter and H. W. Thompson, *J. Chem. Soc.*, 418 (1946); (c) unpublished data obtained by Mr. N. G. Adams of this Station.

(23) K. W. F. Kohlrausch and F. Köppl, *Sitz. ber. Akad. Wiss. Wien*, **142**, 465 (1933).

(24) The assignments for the *t*-butyl halides were based on Raman data from: "Ramanspektren," K. W. F. Kohlrausch, Akademische Verlagsgesellschaft Becker & Erler, Leipzig, 1943, p. 243.

(25) D. W. Scott, D. R. Douslin, M. E. Gross, G. D. Oliver and H. M. Huffman, THIS JOURNAL, **74**, 883 (1952).

TABLE X

THE MOLAL THERMODYNAMIC PROPERTIES OF 2-METHYL-2-PROPANETHIOL[a]

	$-(F^\circ - H^\circ_0)/(H^\circ - H^\circ_0)$							
T, °K.	T, cal. deg.$^{-1}$	T, cal. deg.$^{-1}$	$H^\circ - H^\circ_0$, kcal.	S°, cal. deg.$^{-1}$	C°_p, cal. deg.$^{-1}$	$-\Delta H^\circ_f$,[b] kcal.	ΔF°_f,[b] kcal.	$\log_{10} K_f$[b]
0	0	0	0	0	0	34.77	−34.77	Infinite
273.16	61.92	16.41	4.482	78.33	27.08	41.32	−12.29	9.83
298.16	63.41	17.38	5.182	80.79	28.91	41.79	− 9.60	7.04
300	63.52	17.45	5.235	80.97	29.04	41.82	− 9.40	6.85
400	69.08	21.24	8.498	90.32	36.13	43.42	+ 1.65	− 0.90
500	74.19	24.88	12.44	99.07	42.39	44.66	13.08	− 5.72
600	79.04	28.23	16.94	107.3	47.60	45.59	24.71	− 9.00
700	83.62	31.33	21.93	115.0	51.92	46.23	36.49	−11.39
800	88.00	34.12	27.30	122.1	55.53	46.67	48.32	−13.20
900	92.16	36.68	33.01	128.8	58.61	46.90	60.23	−14.63
1000	96.14	39.02	39.02	135.2	61.24	46.94	72.15	−15.77

[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 2-methyl-2-propanethiol by the reaction: 4C(graphite) + $5H_2$(g) + $^1/_2S_2$(g) → $C_4H_{10}S$(g).

of 2-methyl-2-propanethiol: C–C–S bending, 295 (2); C–C–C bending, 368 and 395 (2); C–S stretching, 587; C–C stretching, 820 and 1218 (2); C–S–H bending, 867; CH_3 rocking, 932 (2), 965, 1033 (2) and 1165; CH_3 bending 1370 (3) and 1450 (6); S–H stretching, 2570; C–H stretching, 2950 (9) cm.$^{-1}$

The Moments of Inertia and Barriers to Internal Rotation.—Since the molecular structure of 2-methyl-2-propanethiol has not been studied experimentally, the bond distances and angles were assumed to be the same as those in related molecules. Conventional values were used for the C–C bond distance, 1.54 Å., the C–H bond distance, 1.09 Å., and the C–C–C, C–C–H and H–C–H bond angles, 109° 28′. The following parameters involving the sulfur atom are the same as those selected for methanethiol[26]: C–S bond distance, 1.83 Å.; S–H bond distance, 1.35 Å.; and C–S–H bond angle, 100°.

On the basis of the above parameters, the product of the three principal moments of inertia was calculated to be 1.492×10^{-113} g.^{3} cm.^{6}. The general method of Kilpatrick and Pitzer[27] was used to compute the reduced moments of inertia of the methyl and thiol groups, 5.197×10^{-40} and 2.829×10^{-40} g. cm.^{2}, respectively.

Simple cosine-type potential barriers, $V(\phi) = {}^1/_2 V_0(1 + \cos 3\phi)$, were used to describe the restricted internal rotation of both the thiol group and the methyl groups (the latter groups were assumed to be equivalent). The heights of the potential barriers required to fit the calorimetric entropy at 300°K. and the vapor heat capacity at 325°K. are 5100 cal. mole^{-1} for the rotation about a C–C bond and 1360 cal. mole^{-1} for that about the C–S bond. These values may be compared with the following: thiol barriers, 1460 cal. mole^{-1} in methanethiol[26] and 1640 cal. mole^{-1} in ethanethiol[4]; methyl barriers, 3310 cal. mole^{-1} in ethanethiol,[4] 3620 cal. mole^{-1} in 2-methylpropane[2a] and 4300 cal. mole^{-1} in 2,2-dimethylpropane.[2a]

Thermodynamic Functions.—The vibrational assignment, the moments and reduced moments of inertia, and the barriers to internal rotation discussed in previous sections were used to compute the thermodynamic functions, $(F^\circ - H^\circ_0)/T$, $(H^\circ - H^\circ_0)/T$, $(H^\circ - H^\circ_0)$, S° and C°_p, at selected temperatures from 273.16 to 1000°K. For these calculations, it was necessary to make the usual approximations involved in treating a molecule as an harmonic oscillator, rigid rotator with independent internal rotations. The experimental and calculated values of the entropy and vapor heat capacity are compared in Tables VII and VI, respectively.[28]

The values of the thermodynamic functions listed in Table X were used with the experimental value of the heat of formation at 298.16°K. to compute the heat, ΔH°_f, free energy, ΔF°_f, and common logarithm of the equilibrium constant, $\log_{10} K_f$, for the formation of gaseous 2-methyl-2-propanethiol from the elements. Gaseous diatomic sulfur, S_2(g), was adopted as the reference state for calculating the thermodynamic properties of gaseous 2-methyl-2-propanethiol from 0 to 1000°K. The thermodynamic properties for graphite and hydrogen given by Wagman, *et al.*,[19] and those for sulfur given in ref. 21 were used for these calculations.

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(26) H. Russell, D. W. Osborne and D. M. Yost, *ibid.*, **64**, 165 (1942).

(27) J. E. Kilpatrick and K. S. Pitzer, *J. Chem. Phys.*, **17**, 1064 (1949).

(28) The signs of the values of C°_p (obsd.) − C°_p(calcd.) shown in Table VI are the opposite of those obtained in a similar manner for related compounds. By using 1250 cm.$^{-1}$ instead of 965 cm.$^{-1}$ for the uncertain CH_3 rocking frequency (see discussion), the following more nearly "normal" values of C°_p(obsd.) − C°_p(calcd.) were obtained: +0.01, 0.05 and 0.06 cal. deg.$^{-1}$ mole^{-1} at 325.20, 358.20 and 449.20° K., respectively. The heights of the methyl and thiol barriers were changed to 4760 and 1610 cal. mole^{-1}, respectively. However, the use of the high value for the CH_3 rocking frequency does not seem reasonable in view of the results obtained by Scott, *et al.*,[24] for 2,2,3,3-tetramethylbutane. That the calculated values of C°_p are higher than the observed is more likely due to the approximations employed in the computations or to a negative contribution of anharmonicity to the heat capacity. The effect of anharmonicity on the heat capacity cannot be estimated on the basis of available spectroscopic data.