tion between these two groups and explains why this compound lies on curve A. One is left with the conclusion that since mesityl oxide has a lower IP and $\nu_{C=O}$ than, for example, acetone (21), the $(CH_3)_2C{=}CH$ group must be classed with, but stronger than, CH_3 in its capacity as an electron releasing group.

In conclusion, it should be noted that only compounds with the same functional group, namely, the carbonyl group, can be considered in the present correlations. It would be impossible to include ethers or amines, etc., because the lone pair electrons are in a different configuration. Among themselves, however, ethers or amines, etc., should give the same sort of correlation of donor strength with IP. Lack of experimental data prohibits such a test at the moment.

Experimental

All the spectra were recorded on a double beam spectrometer employing NaCl optics.[12] Immediately after each run the spectrum was calibrated with the 2851 cm.$^{-1}$ and the 1603 cm.$^{-1}$ bands of a thin film of polystyrene. Spectral bands were reproducible to about ±5 cm.$^{-1}$ at 3,000 cm.$^{-1}$ and to about ±2 cm.$^{-1}$ at 1700 cm.$^{-1}$. Some runs where a strong solvent band interfered with the measurement were performed differentially using a variable thickness cell.

The great majority of the compounds were Eastman Kodak white label products which were used without further purification. Other reagents were prepared and distilled here.

Hydrochloric acid solutions were prepared by bubbling anhydrous HCl through the appropriate mixture for about 5 minutes. No attempt was made to analyze the mixtures for HCl since its concentration was known to be small. Solutions of C_6H_5CCH in the carbonyl compound were prepared so that the concentration of the former was about 0.5 *M*.

The carbonyl stretching frequencies were measured by making up a solution of the carbonyl compound in CCl_4 to a strength of about 0.01 *M*, and using a cell 0.5 mm. in thickness. Gas phase values of the carbonyl stretching frequencies were measured using a 10 cm. cell at low pressures.

Acknowledgments.—Thanks are due to Professor K. Watanabe for permitting me to see his paper on ionization potentials before publication and for several other unpublished values of IP, to Dr. K. U. Ingold for his unpublished value for benzophenone, and to Dr. W. C. Steele for the measurements he kindly made in these laboratories. The encouragement of Dr. Norman Wright is gratefully acknowledged.

MIDLAND, MICHIGAN

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[CONTRIBUTION NO. 66 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

2-Methyl-1-propanethiol: Chemical Thermodynamic Properties and Rotational Isomerism[1]

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The chemical thermodynamic properties of 2-methyl-1-propanethiol in the vapor state (0 to 1000°K.) were calculated by methods of statistical mechanics utilizing observed values of the standard entropy, heat capacity and heat of formation. The thermodynamic results are consistent with spectroscopic evidence for a small energy difference between rotational isomers. Experimental studies provided the following information: Values of heat capacity for the solid (12°K. to the triple point), the liquid (triple point to 350°K.) and the vapor (350 to 500°K.); the triple point temperature; the heat of fusion; thermodynamic functions for the solid and liquid (0 to 350°K.); heat of vaporization (321 to 362°K.); second virial coefficient, *B*, in the equation of state, $PV = RT(1 + B/V)$; vapor pressure; and standard heat of formation.

Comprehensive thermodynamic studies of 2-methyl-1-propanethiol (isobutyl mercaptan) were made as part of studies of all seven isomeric thiols and sulfides, $C_4H_{10}S$.[2] The experimental part of this investigation consisted of studies by low temperature calorimetry, vapor-flow calorimetry, comparative ebulliometry and combustion calorimetry. The detailed results are given later in the Experimental section. However, the more pertinent results that are needed for the calculation of thermodynamic properties, as discussed in the next section, are collected in Table I.

Calculation of Thermodynamic Properties

Thermodynamic functions were calculated by standard methods of statistical mechanics. Most of the parameters needed were obtained from available spectroscopic and molecular-structure information; the few remaining were selected to fit the observed values of entropy and heat capacity in Table I. Finally, the calculated thermodynamic functions and the observed value of the heat of formation in Table I were used to calculate the standard heat, standard free energy and common loga-

TABLE I

OBSERVED AND CALCULATED THERMODYNAMIC PROPERTIES OF 2-METHYL-1-PROPANETHIOL VAPOR

T, °K.	Entropy, *S*°, cal. deg.$^{-1}$ mole^{-1} Obsd.	Calcd.	*T*, °K.	Heat capacity, *Cp*°, cal. deg.$^{-1}$ mole^{-1} Obsd.	Calcd.
321.31	88.91	88.91	351.20	32.04	32.02
340.07	90.64	90.65	373.20	33.49	33.52
361.65	92.61	92.61	413.20	36.12	36.16
			453.20	38.64	38.63
			500.20	41.33	41.31

$$4C(c,\ \text{graphite}) + 5H_2(g) + {}^1/_2S_2(g) = C_4H_{10}S(g)$$

$$\Delta Hf^\circ_{298.16}(\text{obsd.}) = -38.48 \pm 0.22 \text{ kcal. mole}^{-1}$$

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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.

[2] D. W. Scott, H. L. Finke, J. P. McCullough, J. F. Messerly, R. E. Pennington, I. A. Hossenlopp and Guy Waddington, THIS JOURNAL, **79**, 1062 (1957), and earlier publications cited therein.

rithm of the equilibrium constant of formation at selected temperatures between 0 and 1000°K.

Vibrational Assignment.—The harmonic oscillator contributions to the thermodynamic functions were computed from a vibrational assignment based on the spectroscopic data in Table II.[3-5] The data of ref. 4 and 5 were obtained from samples of the same highly purified material used in this research. Two spectroscopically distinguishable rotational isomers are possible for 2-methyl-1-propanethiol, as shown in Fig. 1. The appearance of two moderately intense frequencies (671 and 711 cm.$^{-1}$) in the region of C–S stretching frequencies is evidence that both isomers are present in significant concentration in the liquid at room temperature. Arguments for assigning the higher of the two frequencies to the C_1 isomer have been given by Brown and Sheppard for the analogous isobutyl chloride.[6] Surprisingly, no other features of the spectrum show the presence of a second isomer. In fact, all the observed frequencies below 500 cm.$^{-1}$ and between 750 and 1400 cm.$^{-1}$ are needed to account for the frequencies expected in these regions from a single isomer. The designations for the vibrational modes in Table II are somewhat schematic and are intended merely to show that the expected number of frequencies are assigned in the several regions of the spectrum. For the unsymmetrical CH_3 bending and C–H stretching frequencies, which are not all resolved in the observed spectra, average values of 1460 and 2950 cm.$^{-1}$ were selected. The complete set of frequencies selected for the C_1 rotational isomer is: 224, 339, 402, 429, 711, 772, 807, 827, 924, 955, 1050, 1102, 1116, 1169, 1227, 1257, 1320, 1336, 1370, 1388, 1428, 1460(4), 2575 and 2950(9) cm.$^{-1}$.

TABLE II

VIBRATIONAL SPECTRA OF 2-METHYL-1-PROPANETHIOL, CM.$^{-1}$

Raman, liquid[a] K. & K.[3]	Raman, liquid[a] API[4]	Infrared, liquid[b] API[5]	Interpretation
224(1)			Skeletal bending
339(4)	339(4)		Skeletal bending
402(2)	402(1)		Skeletal bending
427(3)	429(4)	*ca.* 433 vw	Skeletal bending
522(0)	518(1/2?)	*ca.* 517 vw	924 − 402 = 522
668(3)	671(4)	671 w	C—S str., C_s isomer
708(5)	711(7)	711 m	C—S str., C_1 isomer
		743 vw	339 + 402 = 741
770(2)	772(3)	779 vw	C–S–H bend
801(2)	805(2)	809 w	CH_2 rock
824(2)	827(2)	828 m	CH_3 rock
924(1)	927(3)	922 m	CH_3 rock
955(3)	957(4)	953 w	CH_3 rock
		ca. 1050 sh	C—C str.
1108(2)	1105(3)	1100 m	CH_3 rock
	1116(3)	*ca.* 1115 sh	C—C str.
	1169(2)	1169 m	C—C str.
1216(2)	1226(2)	1228 m	CH_2 twist.
1250(1)	1255(1)	1259 s	CH_2 wag
1319(1)	1319(3)	1326 m	CH wag
1336(1)	1336(3)		CH wag
1370(1/2)		1371 s	CH_3 sym. bend
		1388 s	
1423(2b)	1429(3)	1428 m	CH_2 bend
1452(4b)	1454(6)	1468 s	CH_3 unsym. bend(4)
[1500–2500 cm.$^{-1}$ region omitted]			
2573(8b)	2577(8)	2564 w	S—H str.
[2600–5000 cm.$^{-1}$ region omitted]			

[a] In parentheses are listed the relative intensities on a scale of 10 for the most intense band. [b] Intensity designated by: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

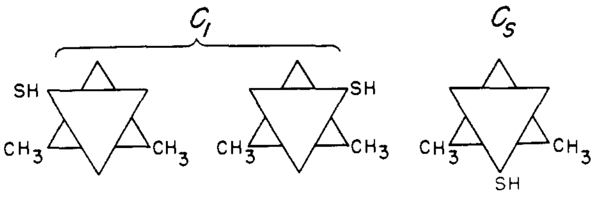

Fig. 1.—Rotational isomers of 2-methyl-1-propanethiol.

Moments of Inertia, Internal Rotation and Anharmonicity.—Moments of inertia were calculated for the C_1 rotational isomer with the thiol hydrogen atom *trans* to the CH group. Bond distances and angles were taken to be: C–C, 1.54 Å.; C–H, 1.09 Å.; C–S, 1.818 Å.; S–H, 1.329 Å.; C–S–H angle, 100° 16′; all other angles tetrahedral. These are partly the usual values for paraffin hydrocarbons; the rest are transferred from methanethiol.[7] The calculations were made by the general method of Kilpatrick and Pitzer.[8] The product of the principal moments of inertia is 1.946×10^{-113} g.^{3} cm.^{6} The diagonal elements of the internal rotational kinetic energy matrix were taken as the reduced moments of inertia, namely: 5.092 and 5.229×10^{-40} g. cm.^{2} for the methyl rotations, 2.709×10^{-40} g. cm.^{2} for the thiol rotation and 35.75×10^{-40} g. cm.^{2} for the skeletal rotation. Neglect of the off-diagonal elements was justified, because the square root of the determinant of the matrix differed by less than 1% from the square root of the product of the diagonal elements.

Simple threefold cosine-type barriers to internal rotation were assumed for the methyl and thiol groups. Values of the barrier height were taken to be 3620 cal. mole^{-1} for the methyl rotations, as in 2-methylpropane,[9] and 1500 cal. mole^{-1} for the thiol rotation, as in other alkanethiols.[10] The barrier for the skeletal rotation was selected to fit the observed values of entropy and heat capacity at the lower temperatures for which the effects of vibrational anharmonicity are small. A simple, threefold, cosine-type barrier with height 5750 cal. mole^{-1} was found to give a satisfactory fit. This barrier was used for calculation of thermodynamic functions.

The parameters, ν = 1100 cm.$^{-1}$ and Z = −1.30

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(4) American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology, Catalog of Raman Spectral Data, Serial No. 227.

(5) Ref. 4, Catalog of Infrared Spectral Data, Serial Nos. 1678 and 1679.

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TABLE III

THE MOLAL THERMODYNAMIC PROPERTIES OF 2-METHYL-1-PROPANETHIOL[a]

T, °K.	$(F° - H°_0)/T$, cal. deg.$^{-1}$	$(H° - H°_0)/T$, cal. deg.$^{-1}$	$H° - H°_0$, kcal.	$S°$, cal. deg.$^{-1}$	$Cp°$, cal. deg.$^{-1}$	$\Delta Hf°$,[b] kcal.	$\Delta Ff°$,[b] kcal.	$\log_{10} Kf$ [b]
0	0	0	0	0	0	−31.53	−31.53	Infinite
273.16	−67.64	16.69	4.559	84.33	26.50	−38.01	−10.59	8.47
298.16	−69.14	17.59	5.245	86.73	28.28	−38.48	− 8.06	5.91
300	−69.25	17.66	5.297	86.91	28.41	−38.51	− 7.87	5.74
400	−74.82	21.21	8.485	96.03	35.31	−40.19	2.60	− 1.42
500	−79.93	24.66	12.33	104.59	41.30	−41.52	13.45	− 5.88
600	−84.72	27.85	16.71	112.56	46.26	−42.57	24.55	− 8.94
700	−89.24	30.78	21.55	120.02	50.35	−43.37	35.80	−11.18
800	−93.53	33.44	26.75	126.97	53.77	−43.97	47.15	−12.88
900	−97.60	35.87	32.28	133.47	56.68	−44.38	58.58	−14.22
1000	−101.50	38.07	38.07	139.58	59.17	−44.64	70.03	−15.30

[a] To retain internal consistency, some values in this table are given to one more decimal place than is justified by the absolute accuracy. [b] The standard heat, standard free energy and common logarithm of the equilibrium constant for the formation of 2-methyl-1-propanethiol by the reaction: $4C(c, \text{graphite}) + 5H_2(g) + {}^1/_2S_2(g) = C_4H_{10}S(g)$.

cal. deg.$^{-1}$ mole^{-1}, of an empirical anharmonicity function[11] were evaluated from the heat capacity data at the higher temperatures. This function is barely significant at the lower temperatures and increases to −1.31 and −0.55 cal. deg.$^{-1}$ mole^{-1} in $C_p°$ and S° at 1000°K. Although this function has the temperature dependence of an anharmonicity contribution, it is also in part an empirical correction for inadequate treatment of all internal degrees of freedom. The negative values in this instance do not necessarily imply that negative anharmonicity coefficients are preponderant because other factors could outweigh the expected positive anharmonicity contribution.

Molal Thermodynamic Properties.—Calculated values of the thermodynamic functions are listed in columns 2–6 of Table III.[12] Comparison with observed values is made in Table I. Agreement within 0.04 cal. deg.$^{-1}$ mole^{-1} was obtained at each of the temperatures at which either $S°$ or $C_p°$ was determined.

Calculated values of $\Delta Hf°$, $\Delta Ff°$ and $\log_{10}Kf$ are listed in columns 7–9 of Table III. These are based on the experimental value of $\Delta Hf°_{298.16}$ (Table I) and values of the thermodynamic functions of C(c, graphite),[13] $H_2(g)$[13] and $S_2(g)$.[14]

Energy Difference between Rotational Isomers.—A simple, threefold, cosine-type barrier for skeletal rotation implies that there is no energy difference between the C_1 and Cs rotational isomers. Uncertainties in the treatment of other degrees of freedom make it impractical to set an upper limit to the energy difference. However, the thermodynamic results are consistent with the spectroscopic evidence that the energy difference is small.

Experimental

The reported values are based on a molecular weight of 90.186 for 2-methyl-1-propanethiol (1951 International Atomic Weights[15]) and the relations: 0° = 273.16°K. and 1 cal. = 4.1840 abs. j. = 4.1833 int. j. The 1951 values of the fundamental physical constants[16] were used in all calculations. Measurements of temperature were made with platinum resistance thermometers calibrated in terms of the International Temperature Scale[17] between 90 and 500°K. and the provisional scale[18] of the National Bureau of Standards between 11 and 90°K. All electrical and mass measurements were referred to standard devices calibrated at the National Bureau of Standards.

The apparatus and methods used in the continuing program of this Laboratory evolve as improvements suggested by experience or modifications required by different samples are made. Not all of these improvements have been described in the literature, but the basic experimental techniques used for 2-methyl-1-propanethiol are presented in published descriptions of apparatus and methods for low temperature calorimetry,[19] flow calorimetry[20] and comparative ebulliometry.[21]

The Material.—The 2-methyl-1-propanethiol used for low temperature calorimetry, comparative ebulliometry and combustion calorimetry was part of the Standard Sample of Sulfur Compound, API-USBM 24, prepared and purified at the Laramie, Wyo., Station of the Bureau of Mines. The purity, as determined by a calorimetric study of melting point as a function of fraction melted, was 99.99 mole %. For flow calorimetry, which required a larger volume of material, the Laramie Station furnished a second sample of somewhat lower purity (estimated from mass spectra to be 99.9 mole %).

Heat Capacity in the Solid and Liquid States.—Low temperature calorimetry was done with 43.691 g. of sample in a platinum calorimeter with helium (4 cm. pressure at room temperature) added to promote thermal equilibration. The observed values of heat capacity, C_{satd} are listed in Table IV. Above 30°K. the accuracy uncertainty is estimated to be no greater than 0.2%. The heat-capacity curve for the solid (C_{satd} *vs.* T) has the normal sigmoid shape. The heat-capacity curve for the liquid between 190 and 350°K.

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may be represented by the empirical equation

$$C_{\text{satd}}(\text{liq}) = 51.121 - 0.16774\ T + 6.1980 \times 10^{-4}T^2 - 5.7067 \times 10^{-7}\ T^3 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (1)$$

The Heat of Fusion, The Triple Point, Cryoscopic Constants and Purity of Sample.—Three determinations of the heat of fusion, ΔH_{fusion}, gave the values 1191.7, 1191.5 and 1189.3 cal. mole^{-1}. The average value with the uncertainty taken as the maximum deviation is 1190.8 ± 1.5 cal. mole^{-1}.

The results of a study of melting temperature, T_{obsd}, as a function of fraction of total sample melted, F, are listed in Table V. Also listed in Table V are the values obtained for the triple point temperature, $T_{\text{T.P.}}$, the mole fraction of impurity in the sample, N_2^*, and the cryoscopic constants,[22] $A = \Delta H_{\text{fusion}}/RT_{\text{T.P.}}^2$ and $B = 1/T_{\text{T.P.}} - \Delta C_{\text{fusion}}/2\Delta H_{\text{fusion}}$, calculated from the observed values of $T_{\text{T.P.}}$, ΔH_{fusion} and ΔC_{fusion} (15.38 cal. deg.$^{-1}$ mole^{-1}).

TABLE IV

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

T, °K.[a]	$C_{\text{satd.}}$[b]	T, °K.[a]	$C_{\text{satd.}}$[b]	T, °K.[a]	$C_{\text{satd.}}$[b]
Crystals		73.96	14.076	96.43	37.34
12.41	1.185	79.83	14.996	104.52	37.44
12.86	1.294	82.40	15.430	115.61	37.45
13.46	1.459	85.34	15.944	126.56	37.50
14.19	1.643	87.74	16.293		
14.81	1.816	92.68	17.027	Liquid	
15.56	2.011	93.74	17.178	137.42	37.49
16.48	2.283	98.40	17.876	147.94	37.50
17.09	2.452	99.48	18.018	158.65	37.50
18.34	2.824	100.33	18.138	169.29	37.54
18.83	2.960	103.68	18.644	179.87	37.61
20.24	3.383	104.29	18.776	190.38	37.70
20.68	3.511	106.32	19.059	194.15	37.71
22.25	3.978	107.03	19.127[c]	200.82	37.82
22.88	4.157	109.76	19.558[c]	204.39	37.85
24.42	4.616	112.84	20.008[c]	214.54	38.02
25.37	4.900	113.43	20.082[c]	224.61	38.26
26.68	5.268	116.14	20.508[c]	235.10	38.53
28.19	5.695	118.83	20.892[c]	245.99	38.88
31.44	6.579	123.30	21.569[c]	256.76	39.26
34.84	7.390			267.90	39.70
38.39	8.158	Glass and		279.38	40.21
42.24	8.921	undercooled liquid		290.73	40.72
46.48	9.687	56.01	11.37	294.86	40.93
51.03	10.482	61.96	12.40	301.93	41.27
53.67	10.915	68.24	13.45	305.93	41.48
55.84	11.266	75.16	14.68	316.87	42.07
57.68	11.564	82.72	16.32	327.66	42.62
62.69	12.387	85.22	16.94	338.31	43.23
68.12	13.219	90.74	21.10	348.80	43.81

[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] Not corrected for the effects of premelting caused by impurities.

TABLE V

2-METHYL-1-PROPANETHIOL: MELTING POINT SUMMARY

Triple point temperature, $T_{\text{T.P.}} = 128.31 \pm 0.05$°K.; mole fraction of impurity $= N_2^* = AF(T_{\text{T.P.}} - T_{\text{obsd}}) = 0.00007$; cryoscopic constants, $A = 0.03640$ deg.$^{-1}$ and $B = 0.00134$ deg.$^{-1}$.

Melted, %	$1/F$	$T_{\text{obsd.}}$ °K.	$T_{\text{graph,}}$ °K.[a]
11.62	8.602	128.2856	128.2873
26.83	3.727	128.2992	128.2992
47.13	2.122	128.3026	128.3022
67.43	1.483	128.3041	128.3035
92.80	1.078	128.3043	128.3043
100.00	1.000		128.3044
Pure	0.000		128.3063

[a] Temperatures read from a straight line through a plot of T_{obsd} vs. $1/F$.

Thermodynamic Properties in the Solid and Liquid States.—Values of thermodynamic properties for the condensed phases were computed from the calorimetric data for selected temperatures between 10 and 350°K. The results are given in Table VI. The values at 10°K. were computed from a Debye function for 4.5 degrees of freedom with $\theta = 100.9°$; these parameters were evaluated from the heat

TABLE VI

THE MOLAL THERMODYNAMIC PROPERTIES OF 2-METHYL-1-PROPANETHIOL IN THE SOLID AND LIQUID STATES[a]

T, °K.	$-(F_{\text{satd.}} - H°_0)/T$, cal. deg.$^{-1}$	$(H_{\text{satd.}} - H°_0)/T$, cal. deg.$^{-1}$	$H_{\text{satd.}} - H°_0$, cal.	$S_{\text{satd.}}$, cal. deg.$^{-1}$	$C_{\text{satd.}}$, cal. deg.$^{-1}$
			Crystals		
10	0.056	0.168	1.68	0.224	0.661
15	.183	.520	7.80	.703	1.860
20	.401	1.034	20.68	1.435	3.310
25	.695	1.637	40.93	2.332	4.792
30	1.050	2.281	68.42	3.331	6.195
35	1.451	2.931	102.59	4.382	7.428
40	1.883	3.561	142.42	5.444	8.488
45	2.338	4.161	187.25	6.499	9.423
50	2.805	4.732	236.59	7.537	10.302
60	3.763	5.798	347.8	9.561	11.945
70	4.733	6.788	475.2	11.521	13.492
80	5.700	7.720	617.6	13.420	15.023
90	6.662	8.623	776.0	15.285	16.631
100	7.616	9.497	949.7	17.113	18.099
110	8.561	10.346	1,138.0	18.907	19.586
120	9.498	11.176	1,341.2	20.674	21.017
128.31	10.268	11.848	1,520.2	22.116	22.105
			Liquid		
128.31	10.268	21.131	2,711.2	31.40	37.48
130	10.55	21.345	2,774.9	31.89	37.49
140	12.17	22.499	3,150	34.67	37.50
150	13.76	23.499	3,525	37.26	37.50
160	15.31	24.374	3,900	39.68	37.52
170	16.80	25.148	4,275	41.95	37.55
180	18.26	25.839	4,651	44.10	37.61
190	19.68	26.460	5,028	46.14	37.69
200	21.05	27.025	5,405	48.07	37.80
210	22.38	27.541	5,784	49.92	37.94
220	23.67	28.018	6,164	51.69	38.14
230	24.93	28.464	6,547	53.39	38.39
240	26.15	28.883	6,932	55.03	38.68
250	27.34	29.282	7,320	56.62	39.01
260	28.49	29.663	7,712	58.15	39.38
270	29.62	30.03	8,108	59.65	39.79
273.16	29.97	30.14	8,234	60.11	39.93
280	30.71	30.39	8,508	61.10	40.24
290	31.79	30.73	8,913	62.52	40.69
298.16	32.65	31.01	9,247	63.66	41.08
300	32.84	31.07	9,322	63.91	41.17
310	33.86	31.41	9,737	65.27	41.68
320	34.86	31.74	10,156	66.60	42.22
330	35.85	32.06	10,581	67.91	42.76
340	36.80	32.39	11,011	69.19	43.32
350	37.75	32.71	11,448	70.46	43.87

[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.

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[22] A. R. Glasgow, A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

capacity data between 12 and 18°K. Corrections for the effects of premelting have been applied to the "smoothed" data recorded in Table VI.

Vapor Pressure.—Observed values of vapor pressure, determined by comparative ebulliometry with water as the reference substance, are listed in Table VII. The difference between the boiling and condensation temperatures of the sample was less than 0.002° at 1 atm. pressure. The Antoine and Cox equations selected to represent the results are

$$\log_{10} p(\text{mm.}) = 6.88746 - 1237.282/(t + 220.313) \quad (2)$$

$$\log_{10} P(\text{atm.}) = \text{A}(1 - 361.654/T) \quad (3)$$

$$\log_{10} \text{A} = 0.841479 - 7.3368 \times 10^{-4}\, T + 7.2741 \times 10^{-7}\, T^2$$

In these equations, t is in °C. and T is in °K. Comparisons of the observed and calculated vapor pressure for both the Antoine and Cox equations are given in Table VII. The normal boiling point, calculated from either equation, is 88.49° (361.65°K.).

TABLE VII

THE VAPOR PRESSURE OF 2-METHYL-1-PROPANETHIOL

Boiling point, °C.		p (obsd.),[a] mm.	p (obsd.) − p (calcd.), mm.	
Water	2-Methyl-1-propanethiol		Eq. 2	Eq. 3
60.000	42.207	149.41	+0.01	+0.01
65	47.830	187.57	− .02	− .01
70	53.498	233.72	− .01	− .01
75	59.211	289.13	+ .02	+ .01
80	64.974	355.22	+ .01	− .01
85	70.780	433.56	+ .06	+ .03
90	76.641	525.86	− .01	− .05
95	82.542	633.99	+ .02	− .01
100	88.493	760.00	+ .02	+ .02
105	94.493	906.06	− .01	+ .04
110	100.539	1074.6	+ .1	+ .1
115	106.640	1268.0	− .2	− .1
120	112.785	1489.1	− .2	− .1
125	118.972	1740.8	+ .1	+ .1
130	125.212	2026.0	+ .3	.0

[a] From the vapor-pressure data for water given by N. S. Osborne, H. F. Stimson and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 261 (1939)

Heat of Vaporization, Vapor Heat Capacity and Effects of Gas Imperfection.—The experimental values of heat of vaporization and vapor heat capacity are given in Tables VIII and IX. The estimated accuracy uncertainty of the values of ΔHv and $C_p°$ are 0.1 and 0.2%, respectively. The empirical equations selected to represent the results are

$$\Delta Hv = 11595 - 9.010\, T - 0.00707\, T^2 \text{ cal. mole}^{-1} \ (321\text{–}362°\text{K.}) \quad (4)$$

$$C_p° = 2.427 + 9.949 \times 10^{-2}\, T - 4.337 \times 10^{-5}\, T^2 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \ (351\text{–}500°\text{K.}) \quad (5)$$

Equation 5 represents the experimental values of $C_p°$ within 0.1%. The effects of gas imperfection were correlated by the procedure described in an earlier publication from this Laboratory.[23] The empirical equation obtained for B, the second virial coefficient in the equation of state, $PV = RT(1 + B/V)$, is

$$B = 350 - 223.7 \exp(700/T) \text{ cc. mole}^{-1} \ (321\text{–}500°\text{K.}) \quad (6)$$

Comparisons of "observed" values of B and $-T(\text{d}^2B/\text{d}T^2) = \lim\limits_{P \to 0} (\partial C_p/\partial P)_T$ with those calculated from eq. 6 are given in Tables VIII and IX.

The Entropy in the Ideal Gaseous State.—The entropy in the ideal gaseous state at 1 atm. pressure was calculated as indicated in Table X.

TABLE VIII

THE MOLAL HEAT OF VAPORIZATION AND SECOND VIRIAL COEFFICIENT OF 2-METHYL-1-PROPANETHIOL

T, °K.	P, atm.	ΔHv, cal.	$B_{\text{obsd.}}$, cc.	$B_{\text{calcd.}}$,[a] cc.
321.31	0.250	7970 ± 2[b]	−1707	−1626
340.07	0.500	7714 ± 1[b]	−1418	−1402
361.65	1.000	7412 ± 1[b]	−1172	−1200

[a] Calculated from eq. 6. [b] Maximum deviation from the mean of three determinations.

TABLE IX

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

T, °K.	351.20	373.20	413.20	453.20	500.20
C_p (1.000 atm.)		34.269	36.576	38.939	41.555
C_p (0.500 atm.)	32.494	33.856			
C_p (0.250 atm.)	32.260	33.679	36.227	38.712	41.385
$C_p°$ (obsd.)	32.04	33.49	36.12	38.64	41.33
$-T(\text{d}^2B/\text{d}T^2)$, obsd.[a]	0.87	0.71	0.44	0.29	0.22
$-T(\text{d}^2B/\text{d}T^2)$, calcd.[b]	0.90	0.69	0.45	0.31	0.21

[a] Units: cal. deg.$^{-1}$ mole^{-1} atm.$^{-1}$. [b] Calculated from eq. 6.

TABLE X

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

T, °K.	321.31	340.07	361.65
$S_{\text{satd.}}$ (liq.)	66.77[a]	69.20[a]	71.90[b]
$\Delta Hv/T$	24.81	22.68	20.50
S(ideal) − S(real)[c]	0.08	0.14	0.21
Compression, $R \ln P$[c]	−2.75	−1.38	0.00
$S°$(obsd.)(±0.20)	88.91	90.64	92.61

[a] Interpolated from Table VI. [b] Extrapolated by use of eq. 1. [c] Calculated by use of eq. 6 and 3.

The Heat of Formation and Related Properties.—The heat of formation was determined by a rotating-bomb method of combustion calorimetry.[24] Detailed description of the experiments is planned for inclusion in another publication, and only the pertinent results are reported here. The standard heat of formation of the liquid was found to be $\Delta Hf°_{298.16} = -31.36 \pm 0.21$ kcal. mole^{-1} for the reaction

$$4\text{C(c, graphite)} + 5\text{H}_2\text{(g)} + \text{S(c, rhombic)} = \text{C}_4\text{H}_{10}\text{S(liq)}$$

From this result and entropy data for C(c, graphite),[13] H_2(g)[13] and S(c, rhombic),[14] the following values of the standard entropy, standard free energy and logarithm of the equilibrium constant of formation were calculated.

$$\Delta Sf°_{298.16} = -105.46 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta Ff°_{298.16} = +0.08 \text{ kcal. mole}^{-1}; \ \log_{10}Kf = -0.06$$

The standard heat of vaporization at 298.16°K. was calculated to be 8.30 kcal. mole^{-1} by use of eq. 3, 4 and 6 and the relationship $\Delta Hv° = \Delta Hv - BRT/V + (\text{d}B/\text{d}T)RT^2/V$. This value was used to obtain the standard heat of formation of the vapor, $\Delta Hf°_{298.16} = -23.06 \pm 0.21$ kcal. mole^{-1} for the reaction

$$4\text{C(c, graphite)} + 5\text{H}_2\text{(g)} + \text{S(c, rhombic)} = \text{C}_4\text{H}_{10}\text{S(g)}$$

The following values of related properties were calculated as before.

$$\Delta Sf°_{298.16} = -82.38 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta Ff°_{298.16} = +1.50 \text{ kcal. mole}^{-1}; \ \log_{10}Kf = -1.10$$

Finally, the heat of formation of S_2(g) from rhombic sulfur[14] was used to obtain the standard heat of formation of the vapor from S_2(g), $\Delta Hf°_{298.16} = -38.48 \pm 0.22$ kcal. mole^{-1} for the reaction

$$4\text{C(c, graphite)} + 5\text{H}_2\text{(g)} + {}^1/_2\text{S}_2\text{(g)} = \text{C}_4\text{H}_{10}\text{S(g)}$$

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[23] J. P. McCullough, H. L. Finke, J. F. Messerly, R. E. Pennington, I. A. Hossenlopp and Guy Waddington, THIS JOURNAL, **77**, 6119 (1955).

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