Thermochemical Calculations.—The vapor pressure measurements of Smith, Line and Bell[3] on rhenium heptoxide and perrhenic acid make possible the calculation of the following entropy changes at 298.16°K.

$$Re_2O_7(c) = Re_2O_7(g) \qquad \Delta S° = 55.5 \pm 0.2 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (1)$$

$$2HReO_4(c) = Re_2O_7(c) + H_2O(g) \qquad \Delta S° = 22.0 \pm 0.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (2)$$

These data combined with the above value for the entropy of rhenium heptoxide (49.54 cal. deg.$^{-1}$ mole^{-1}) and the entropy of $H_2O(g)$ (45.13 cal. deg.$^{-1}$ mole^{-1})[10] give

$$S°_{298.16} \ (Re_2O_7(g), \text{ ideal gas at 1 atm.}) = 105.0 \pm 0.3 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$S°_{298.16} \ (HReO_4(c)) = 36.4 \pm 0.2 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Two separate determinations of the heat of formation of rhenium heptoxide have been made; Roth and Becker[11] obtained −297.5 ± 2.0 kcal. mole^{-1}, and Boyd,[12] *et al.*, obtained −295.9 ± 2.0 kcal. mole^{-1}. The average of the two values, −296.7 ± 2.0 kcal. mole^{-1}, combined with the entropy of formation, −139.78 cal. deg.$^{-1}$ mole^{-1},[13] gives −255.0 ± 2.0 kcal. mole^{-1} for the free energy of formation of rhenium heptoxide. The free energy of formation of crystalline perrhenic acid, −157.0 ± 1.0 kcal. mole^{-1}, may be obtained from the free energies of formation of $H_2O(g)$ (−54.64 kcal. mole^{-1})[14] and $Re_2O_7(c)$ (−255.0 kcal. mole^{-1}) combined with the standard free energy change of reaction (2), 4.5 kcal. mole^{-1}, computed from the vapor pressure equation of Smith,[3] *et al.*

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[14] F. D. Rossini, *et al.*, Bureau of Standards Circular 500, "Selected Values of Chemical Thermodynamic Properties," 1952.

OAK RIDGE, TENNESSEE

[CONTRIBUTION NO. 55 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

The Chemical Thermodynamic Properties and Rotational Tautomerism of 1-Propanethiol[1]

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Experimental and computational studies were made of the thermodynamic properties of 1-propanethiol in the temperature range 0 to 1000°K. The experimental studies provided the following information: values of heat capacity for the solid, the liquid [$C_{satd} = 45.862 - 0.15070\ T + 5.0219 \times 10^{-4}\ T^2 - 4.167 \times 10^{-7}\ T^3$, cal. deg.$^{-1}$ mole^{-1} (180 to 320°K.)], and the vapor [$C_p^\circ = 3.733 + 7.123 \times 10^{-2}\ T - 2.721 \times 10^{-5}\ T^2$, cal. deg.$^{-1}$ mole^{-1} (331 to 500°K.)]; the heat of transition [949.1 cal. mole^{-1}] at 142.10°K.; the heat of fusion [1309 cal. mole^{-1}] at the triple point [160.00 ± 0.05°K.]; the entropy in the saturated liquid state at 298.16°K. [57.96 cal. deg.$^{-1}$ mole^{-1}]; the heat of vaporization [$\Delta H_v = 9855 - 2.551T - 1.658 \times 10^{-2}T^2$ cal. mole^{-1} (303 to 341°K.)]; the second virial coefficient, B, in the equation of state, $PV = RT(1 + B/V)$, [$B = -32 - 94.7 \exp(800/T)$, cc. mole^{-1} (303 to 500°K.)]; the standard heat of formation of liquid 1-propanethiol from graphite, hydrogen and rhombic sulfur at 298.16°K. [−23.69 ± 0.16 kcal. mole^{-1}]; and the vapor pressure [$\log_{10} p\,(\text{mm.}) = 6.92846 - 1183.307/(t + 224.624)$, (24 to 102°)]. Tables of the thermodynamic properties in the solid and liquid states (10 to 320°K.) were computed. Experimentally determined properties of the vapor (S^0 and C_p^0) were used with spectroscopic and molecular structure information to evaluate barriers to internal rotation and the energy difference between the rotational tautomers of 1-propanethiol (the *trans* skeletal configuration is more stable by about 400 cal. mole^{-1}). Tables of the chemical thermodynamic properties in the ideal gaseous state at selected temperatures from 0 to 1000°K. were computed.

As part of American Petroleum Institute Research Project 48A, this Laboratory is conducting investigations of the chemical thermodynamic properties of organic sulfur compounds that occur in petroleum or petroleum products. Comprehensive studies are made of "key" members of various homologous series of sulfur compounds. The data obtained in these detailed studies will form the basis for calculating, by approximate statistical mechanical methods,[2] thermodynamic information for many other members of each series studied. The family of alkanethiols is one of the important classes of sulfur compounds found in petroleum, and reports on thermodynamic properties of methanethiol,[3] ethanethiol,[4] 2-propanethiol,[5,6] 2-methyl-2-propanethiol[7] and pentanethiol[8] have been pub-

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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] *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] H. Russel, D. W. Osborne and D. M. Yost, THIS JOURNAL, **64**, 165 (1942).

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[6] W. N. Hubbard and Guy Waddington, *Rec. trav. chim.*, **73**, 910 (1954).

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lished previously. As a member of this family, 1-propanethiol is of particular interest because it is the simplest alkanethiol for which rotational tautomerism affects the thermodynamic properties. Detailed investigations made of the thermodynamic properties of 1-propanethiol will be discussed in the following order: Calorimetric study of the low temperature thermal properties in the solid and liquid states; measurement of vapor pressures; investigation of the heat of vaporization and vapor heat capacity; determination of the heat of formation; and calculations of the chemical thermodynamic properties in the ideal gaseous state at selected temperatures from 0 to 1000°K.

Experimental

Physical Constants.—The 1951 International Atomic Weights[9] and the 1951 values of the fundamental physical constants[10] were used in all calculations described in this paper. The data are based on a molecular weight of 76.160 for 1-propanethiol and the following relations: 0° = 273.16°K.; and 1 cal. = 4.1840 abs. j. = 4.1833 int. j. Measurements of temperature were made with platinum resistance thermometers calibrated in terms of the International Temperature Scale[11] between 90 and 500°K. and the provisional scale[12] of the National Bureau of Standards between 11 and 90°K. Measurements of mass, energy and temperature were made in terms of standard devices calibrated at the National Bureau of Standards.

The Material.—The sample of 1-propanethiol used in the low temperature thermal studies, vapor pressure measurements and heat of combustion experiments was part of the Standard Sample of Sulfur Compound, API-USBM serial no. 22, prepared and purified by American Petroleum Institute Research Project 48A at the Laramie, Wyoming, Station of the Bureau of Mines. In a calorimetric study of the melting point to be discussed subsequently, the amount of liquid-soluble, solid-insoluble impurity in the sample was found to be 0.015 ± 0.005 mole %. A second sample of 99.8 mole % purity was used in studies of the heat of vaporization and vapor heat capacity.

The Heat Capacity in the Solid and Liquid States.—The low temperature thermal studies (12 to 320°K.) were made in an adiabatic calorimeter system similar to that described in previous publications.[13] A platinum calorimeter with internal heat-distributing disks of gold was used. The calorimeter contained 0.59085 mole of the compound. About 30 mm. helium 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}, are recorded in Table I. No adjustment for the effects of hetero-phase premelting has been applied to these data. The temperature increments used in the measurements were small enough that corrections for non-linear variation of heat capacity with temperature were unnecessary. Generally, the precision of the results was within ±0.1%; and it is estimated that above 30°K., the accuracy uncertainty is not greater than 0.2%. An empirical equation that represents the observed heat capacity data for liquid 1-propanethiol between 180 and 320°K. with an average deviation of 0.01 cal. deg.$^{-1}$ mole^{-1} is

$$C_{\text{satd}}\text{ (liq.)} = 45.862 - 0.15070\,T + 5.0219 \times 10^{-4}T^2 - 4.167 \times 10^{-7}T^3,\ \text{cal. deg.}^{-1}\ \text{mole}^{-1} \quad (1)$$

TABLE I

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

T, °K.[a]	ΔT[b]	C_{satd}[c]
	Crystals I	
12.70	1.608	0.621
13.29	1.412	.719
14.23	1.407	.865
14.74	1.487	.956
15.67	1.448	1.120
16.30	1.625	1.246
17.12	1.440	1.412
17.89	1.573	1.579
18.62	1.558	1.731
19.67	2.003	1.970
20.22	1.643	2.094
21.78	2.220	2.471
22.01	1.937	2.518
24.00	2.061	3.002
24.16	2.541	3.046
26.32	2.572	3.574
26.82	2.783	3.698
29.75	3.075	4.414
32.91	3.242	5.159
36.49	3.930	5.934
40.58	4.240	6.773
45.02	4.645	7.619
49.91	5.147	8.511
53.99	3.030	9.204
55.26	5.538	9.405
57.72	4.431	9.798
62.79	5.707	10.600
68.65	6.020	11.441
74.69	6.053	12.245
81.02	6.603	13.088
83.22	2.075	13.369
86.15	3.788	13.745
87.43	6.222	13.909
90.67	5.249	14.269
96.24	5.877	14.863
102.40	6.447	15.520
108.72	6.194	16.178
114.81	5.989	16.781
120.70	5.794	17.382
126.41	5.626	17.945
127.44	4.193	18.010
131.95	5.474	18.509
132.25	5.443	18.526
136.69	4.008	19.015
	Crystals II	
143.02	3.712	24.735
143.72	3.702	24.862
145.06	3.704	24.869
145.73	5.113	24.964
146.70	3.659	25.049
147.38	3.654	25.115
147.46	3.713	25.123
148.74	3.661	25.155
148.77	3.646	25.181
149.41	4.368	25.291
150.67	4.336	25.350
150.80	5.038	25.314
151.51	4.403	25.426
152.78	3.620	25.463
153.74	4.304	25.661
156.37	3.535	26.120[d]
	Liquid	
167.58	4.639	32.697
170.85	9.686	32.660
172.21	4.634	32.638
180.52	9.670	32.555
190.66	10.608	32.497
201.25	10.574	32.485
211.79	10.522	32.516
220.36	10.485	32.595
230.81	10.416	32.704
241.19	10.341	32.890
251.49	10.263	33.101
261.71	10.170	33.352
271.84	10.071	33.641
281.86	9.973	33.963
291.78	9.867	34.339
301.61	9.776	34.676
304.07	10.578	34.751
312.51	5.572	35.082
314.58	10.461	25.185

[a] T is the mean temperature of each heat capacity measurement. [b] ΔT is the temperature increment used in each heat capacity measurement. [c] C_{satd} is the heat capacity of the condensed phase under its own vapor pressure. [d] The heat capacity data immediately below the melting point have *not* been corrected for the effects of premelting caused by impurities.

The Isothermal Transition and the Heat of Fusion.—An isothermal transition in crystalline 1-propanethiol was observed at 142.10°K. Thermal equilibration in the two phase region was slow, but the transition was shown to be of first order. The temperatures observed when 25 and 75% of the sample were transposed were 142.07 and 142.09°K., respectively, and 142.10 ± 0.05°K. was chosen as the transition temperature.

Measurements were made of the enthalpy change over a finite temperature interval that included the transition temperature. Subtraction of the energy absorbed non-isothermally by the crystals gave the heat of transition. Three determinations yielded an average value for the heat of transition of 949.1 ± 0.3 cal. mole^{-1}; the indicated uncertainty is the maximum deviation from the mean of the three determinations.

The heat of fusion was evaluated in the same manner as the heat of transition. Five determinations yielded an average value for the heat of fusion of 1309 ± 0.6 cal. mole^{-1}; the indicated uncertainty is the maximum deviation from the mean of the five determinations. Corrections for the

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effects of premelting were applied in computing the heat of fusion.

The Triple Point Temperature, Cryoscopic Constants and Sample Purity.—For determination of the triple point temperature and sample purity, a study of the equilibrium melting temperature, T_{obsd}, as a function of fraction of total sample melted, F, was made by the procedure outlined in an earlier publication.[14] The results are summarized in Table II. The values of T_{obsd} were plotted as a function of $1/F$; and the triple point temperature, $T_{\text{T.P.}} = 160.00 \pm 0.05°\text{K.}$, was obtained by linear extrapolation to zero value of $1/F$. If the impurities present form ideal solutions in the liquid phase and are insoluble in the solid phase, the relation between mole fraction of total impurity, N_2^*, and melting point depression, $\Delta T = T_{\text{T.P.}} - T_{\text{obsd}}$ is[15]

$$-\ln(1 - N_2) = A\Delta T(1 + B\Delta T + \ldots..) \quad (2)$$

where $N_2 = N_2^*/F$. The cryoscopic constants, $A = \Delta H_{\text{fusion}}/RT^2_{\text{T.P.}} = 0.02573$ deg.$^{-1}$ and $B = 1/T_{\text{T.P.}} - \Delta C_{\text{fusion}}/2\Delta H_{\text{fusion}} = 0.00368$ deg.$^{-1}$ were evaluated from the values for $T_{\text{T.P.}}$ and ΔH_{fusion} (Table II) and from $\Delta C_{\text{fusion}} = 6.72$ cal.deg.$^{-1}$ mole^{-1} (Table III). Application of eq. 2 in its simplified form (for $N_2^* << 1$), $N_2^* = AF\Delta T$, yielded a value of 0.015 ± 0.005 mole % for the liquid-soluble, solid-insoluble impurity in the Standard Sample of 1-propanethiol.

TABLE II

1-PROPANETHIOL: MELTING POINT SUMMARY

Triple point temperature, $T_{\text{T.P.}} = 160.00 \pm 0.05°$ K.; cryoscopic constant, $A = 0.02573$ deg.$^{-1}$; impurity = 0.015 ± 0.005 mole %

Melted, %	$1/F$	T, °K. Obsd.	Graph.[a]
10.26	9.743	159.9411	159.9415
24.61	4.063	159.9747	159.9726
48.63	2.056	159.9832	159.9838
51.37[b]	1.947[b]	159.9830[b]	159.9844
70.26	1.423	159.9867	159.9874
80.12[b]	1.248[b]	159.9900[b]	159.9884
89.47	1.118	159.9889	159.9893
100.00	1.000		159.9898
Pure	*0.0*		*159.9955*[c]

[a] Temperatures read from a straight line through a plot of T_{obsd} *vs.* $1/F$. [b] Results obtained in a repeat melting point study. [c] The triple point temperature.

The Thermodynamic Properties in the Solid and Liquid States.—Values of the entropy, free energy function, heat content function, heat content and heat capacity at selected temperatures between 10 and 320°K. were computed from the low-temperature calorimetric data for 1-propanethiol. The values at 10°K. were calculated from a Debye function for 5 degrees of freedom with $\theta = 135.4°$; these parameters were evaluated from the heat capacity data between 12 and 20°K. The thermodynamic properties above 10°K. were computed from the heats and temperatures of transition and fusion and by numerical integration of values of C_{satd} read from a large scale plot of the data in Table I. The results are given in Table III. Corrections for the effects of premelting have been applied to the "smoothed" data recorded in Table III.

The Vapor Pressure.—The vapor pressure of 1-propanethiol at temperatures between 24 and 102° was measured with the twin ebulliometer system described in an earlier publication.[16] The heating element of the apparatus described in ref. 16 has been encased in a glass re-entrant well so that samples come into contact with glass surfaces only. Observations were made of the boiling and condensation temperatures of 1-propanethiol and water as the two compounds boiled simultaneously at a common pressure. The pressures corresponding to the observed boiling points of the water were obtained from the data of Osborne, Stimson and Ginnings.[17] The results are presented in Table IV. The difference between the boiling and condensation temperatures of the sample was observed to be 0.004° or less; this observation indicates that the material was essentially free of impurities of different volatility. The constants in an Antoine equation

$$\log_{10} p\,(\text{mm.}) = 6.92846 - 1183.307/(t + 224.624) \quad (3a)$$

were obtained from the data in Table IV by a least squares treatment.[18] Also, to provide a more accurate means of ex-

TABLE III

THE MOLAL THERMODYNAMIC PROPERTIES OF 1-PROPANETHIOL 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	0.026	0.078	0.778	0.104	0.311
15	.087	.258	3.863	.345	1.003
20	.201	.570	11.392	.771	2.048
25	.371	.984	24.607	1.355	3.250
30	.593	1.464	43.93	2.057	4.478
35	.857	1.978	69.23	2.835	5.618
40	1.155	2.499	99.96	3.654	6.659
45	1.478	3.015	135.66	4.493	7.618
50	1.823	3.521	176.07	5.344	8.531
60	2.551	4.495	269.67	7.046	10.164
70	3.314	5.412	378.8	8.726	11.624
80	4.094	6.271	501.6	10.365	12.948
90	4.880	7.084	637.6	11.964	14.196
100	5.666	7.849	784.9	13.515	15.265
110	6.448	8.571	942.8	15.019	16.304
120	7.224	9.257	1110.8	16.481	17.306
130	7.991	9.915	1288.9	17.906	18.313
140	8.749	10.551	1477.1	19.300	19.324
142 10	8.907	10.682	1517.9	19.589	19.540
			Crystals II		
142.10	8.907	17.362	2467.0	26.269	24.648
150	9.857	17.762	2664.2	27.619	25.280
160.00	11.019	18.257	2921.0	29.276	26.076
			Liquid		
160.00	11.019	26.438	4230.0	37.457	32.795
170	12.63	26.808	4557	39.44	32.66
180	14.17	27.130	4883	41.30	32.55
190	15.65	27.414	5208	43.06	32.50
200	17.06	27.668	5533	44.73	32.48
210	18.41	27.898	5858	46.31	32.50
220	19.72	28.109	6183	47.83	32.58
230	20.97	28.306	6510	49.28	32.69
240	22.18	28.492	6838	50.67	32.86
250	23 35	28.671	7167	52.02	33.07
260	24.47	28.845	7499	53.32	33.30
270	25.57	29.015	7834	54.58	33.58
273.16	25.90	29.068	7940	54.97	33.67
280	26.62	29.184	8171	55.81	33.90
290	27.65	29.352	8512	57.00	34.24
298.16	28.47	29.490	8792	57.96	34.55
300	28.65	29.522	8856	58.17	34.61
310	29.62	29.692	9204	59.31	34.99
320	30.56	29.864	9556	60.43	35.38

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

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trapolation to temperatures beyond the range of the experiments, the following Cox equation[19] was derived

$$\log_{10}P \text{ (atm.)} = \text{A}(1 - 340.879/T) \qquad (3b)$$

$$\log_{10}\text{A} = 0.832843 - 7.1858 \times 10^{-4}T + 7.3990 \times 10^{-7}T^2$$

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 IV. The normal boiling point of 1-propanethiol, calculated from either equation, is 67.72° (340.88°K.).

TABLE IV

THE VAPOR PRESSURE OF 1-PROPANETHIOL

Boiling point, °C. Water	Boiling point, °C. 1-Propanethiol	p(obsd.),[a] mm.	p(obsd.) − p(calcd.) Eq. 3a	p(obsd.) − p(calcd.) Eq. 3b
60.000	24.275	149.41	+0.03	+0.02
65	29.563	187.57	− .02	− .01
70	34.891	233.72	− .04	− .03
75	40.254	289.13	.00	+ .01
80	45.663	355.22	.00	.00
85	51.113	433.56	+ .02	+ .01
90	56.605	525.86	+ .05	+ .01
95	62.139	633.99	+ .08	+ .03
100	67.719	760.00	+ .04	.00
105	73.341	906.06	− .01	− .05
110	79.004	1074.6	.0	.0
115	84.710	1268.0	.0	.0
120	90.464	1489.2	− .1	− .1
125	96.255	1740.8	.0	.0
130	102.088	2026.0	+ .2	.0

[a] From vapor pressure data for water given in ref. 17.

The Heat of Vaporization.—The heat of vaporization and vapor heat capacity of 1-propanethiol were studied in the flow calorimeter system described in previous publications.[20] The results of measurements of the heat of vaporization at boiling points corresponding to 1/4, 1/2 and 1 atm. pressure are summarized in Table V. The estimated accuracy uncertainty of the values of the heat of vaporization reported in Table V is ±0.1%. The following empirical equation was derived for interpolation in the temperature range of the measurements (303 to 341° K.).

$$\Delta H_v = 9855 - 2.551\,T - 1.658 \times 10^{-2}T^2, \text{ cal. mole}^{-1} \qquad (4)$$

TABLE V

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

T, °K.	P, atm.	ΔH_v, cal.	$B_{\text{obsd.}}$, cc.	$B_{\text{calcd.}}$, cc.[a]
303.03	0.250	7559 ± 1[b]	−1387	−1360
320.64	.500	7332 ± 0[b]	−1186	−1180
340.88	1.000	7059 ± 5[b]	−1012	−1022

[a] Calculated with eq. 6. [b] Maximum deviation of experimental results from the mean of three or more determinations.

The Vapor Heat Capacity and the Effects of Gas Imperfection.—The vapor heat capacity of 1-propanethiol was measured at two or more pressures at each of five temperatures between 331 and 500°K. The results are summarized in Table VI.

To correlate the thermal data an equation of state for 1-propanethiol was obtained from data for the vapor pressure, heat of vaporization and vapor heat capacity. Values of the second virial coefficient, B, in the equation of state, $PV = RT(1 + B/V)$ were computed by use of the exact Clapeyron equation. Values of $\mathrm{d}^2B/\mathrm{d}T^2$ were determined from the thermodynamic relationship, $(\partial^2 V/\partial T^2)_P = -1/T(\partial C_p/\partial P)_T$, in terms of which the variation of vapor heat capacity with pressure is represented, with slight approximations,[20b] by

TABLE VI

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

T, °K.	331.20	351.20	401.20	453.20	500.20
C_p((1.000 atm.)		26.052	28.272	30.650	32.684
C_p(0.500 atm.)	24.779	25.700			
C_p(0.250 atm.)	24.561	25.536	28.009	30.492	32.581
C_p°(obsd.)	24.35	25.38	27.93	30.44	32.55
C_p°(calcd.)[a]	24.35	25.38	27.92	30.43	32.57
[C_p(1 atm.) − C_p°](obsd.)		0.67	0.35	0.21	0.13
[C_p(1 atm.) − C_p°](calcd.)[b]		.67	.35	.20	.13

[a] Calculated from spectroscopic and molecular structure data. [b] Calculated from eq. 5 and 6.

$$C_p = C_p^\circ - T\left(\frac{\mathrm{d}^2B}{\mathrm{d}T^2}\right)P + 2\left(\frac{B}{R}\right)\left(\frac{\mathrm{d}^2B}{\mathrm{d}T^2}\right)\left(1 - \frac{3BP}{RT}\right)P^2 \qquad (5)$$

The numerical constants of the following empirical equation for B were determined by the method described in ref. 20b.

$$B = -32 - 94.7 \exp(800/T) \text{ cc. mole}^{-1} \text{ (303–500°K.)} \qquad (6)$$

Values of B, computed by use of eq. 6, and values of C_p (1 atm.) − C_p°, computed from eq. 5 and 6, are compared with experimental data in Tables V and VI, respectively.

To determine the "observed" values of C_p° listed in Table V, the last term in eq. 5 was evaluated for each experimental point by use of eq. 6, and the result[21] was subtracted from C_p(obsd.). The adjusted values of C_p at each temperature were then extrapolated linearly to zero pressure to obtain C_p°(obsd.).[22] The accuracy uncertainty of the values of C_p°(obsd.) listed in Table V should not exceed 0.2%. The following empirical equation represents these data within ±0.05% from 331 to 500°K.

$$C_p^\circ = 3.733 + 7.123 \times 10^{-2}T - 2.721 \times 10^{-5}T^2, \text{ cal. deg.}^{-1}\text{ mole}^{-1} \qquad (7)$$

The Entropy in the Ideal Gaseous State.—The experimental and derived data given in the foregoing sections were used to compute "observed" values of the entropy in the ideal gaseous state at one atmosphere pressure. These calculations are summarized in Table VII.

The Heat of Formation and Related Properties.—In a recent paper from this Laboratory[6] on heat of combustion studies of the C_3H_8S isomers, the standard heat of formation of liquid 1-propanethiol from graphite, hydrogen and rhombic sulfur was reported to be −23.69 ± 0.16 kcal. mole^{-1} at 298.16°K. The standard heat, free energy and entropy of vaporization of 1-propanethiol calculated from eq. 3b, 4 and 6 were found to be 7.645 kcal. mole^{-1}, 0.952 kcal. mole^{-1} and 22.45 cal. deg.$^{-1}$ mole^{-1}, respectively, at 298.16°K. These vaporization data, the experimental values of heat formation and entropy of liquid 1-propanethiol and values of the thermodynamic functions of graphite,[23] hydrogen[23] and rhombic sulfur[24] were used to compute the standard heat, $\Delta Hf^\circ_{298.16}$, free energy, $\Delta Ff^\circ_{298.16}$, and logarithm of the equilibrium constant, $\log_{10} Kf^\circ_{298.16}$, of formation of 1-propanethiol in the liquid and ideal gaseous states. Values of the heat and free energy of formation of $S_{2(g)}$[25] were used to calculate these same properties for the formation of 1-propanethiol in the ideal gaseous state from graphite, hydrogen and $S_{2(g)}$. The results are given in Table VIII.

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[19] E. R. Cox, *Ind. Eng. Chem.*, **28**, 613 (1936).

[20] (a) Guy Waddington, S. S. Todd and H. M. Huffman, THIS JOURNAL, **69**, 22 (1947); (b) J. P. McCullough, D. W. Scott, R. E. Pennington, I. A. Hossenlopp and Guy Waddington, *ibid.*, **76**, 4791 (1954).

[21] The maximum value of the last term in eq. 5 was 0.05 cal. deg.$^{-1}$ mole^{-1}.

[22] For a discussion of the reasons for using this procedure, see: J. P. McCullough, H. L. Finke, J. F. Messerly, R. E. Pennington, I. A. Hossenlopp and Guy Waddington, THIS JOURNAL, **77**, 6119 (1955).

[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] "Selected Values of Chemical Thermodynamic Properties," Circular 500 of the National Bureau of Standards, Washington, D. C., 1952; Series I, Table 14-1.

[25] W. H. Evans and D. D. Wagman, *J. Research Natl. Bur. Standards*, **34**, 141 (1952).

TABLE VII

THE MOLAL ENTROPY OF 1-PROPANETHIOL, CAL. DEG.$^{-1}$

0–10°K.	Debye extrapolation[a]	0.104
10–142.10°	Crystals I, $\int C_{satd}$ d ln T	19.485
142.10°	Transition, 949.1/142.10	6.679
142.10–160.00°	Crystals II, $\int C_{satd}$ d ln T	3.007
160.00°	Fusion, 1309/160.00	8.181
160.00–298.16°	Liquid, $\int C_{satd}$ d ln T	20.505
S_{satd} (liq.), 298.16°K. (±0.10)[b]		57.96

T, °K.	303.03	320.64	340.88
S_{satd} (liq.)	58.52[c]	60.50[c]	62.70[d]
$\Delta H_v/T$[e]	24.95	22.87	20.71
S(ideal) − S(real)[f]	0.07	0.11	0.18
R ln P[g]	−2.76	−1.38	0.00
$S°$(obsd.)(±0.15)[b]	80.78	82.10	83.59
$S°$(calcd.)[h]	80.77	82.09	83.58

[a] A Debye function for 5 degrees of freedom with θ = 135.4°K. was used for this extrapolation. [b] Estimated accuracy uncertainty. [c] Interpolated from Table III. [d] Extrapolation by use of eq. 1. [e] Entropy of vaporization; from data of Table V. [f] Entropy of gas imperfection; from eq. 6. [g] Entropy of compression; from eq. 3b. [h] Calculated from spectroscopic and molecular structure data.

TABLE VIII

THE MOLAL HEAT AND FREE ENERGY AND THE LOGARITHM OF THE EQUILIBRIUM CONSTANT FOR THE FORMATION OF 1-PROPANETHIOL

State[a]	Reference state[b]	$\Delta Hf_{298.16}$, kcal.	$\Delta F°f_{298.16}$, kcal.	$\log_{10} Kf_{298.16}$
Liquid	S(rhombic)	−23.69 ± 0.16[c]	−0.26	+0.19
Gas	S(rhombic)	−16.04 ± 0.16[c]	+0.70	−0.51
Gas	S_2(g)	−31.46	−8.87	+6.50

[a] Standard state of 1-propanethiol. [b] Reference state for elemental sulfur in the reactions: 3 C(graphite) + 4 H_2(g) + S(rhombic) → C_3H_8S (l or g); 3C(Graphite) + 4H_2(g) + $^1/_2S_2$(g) → C_3H_8S(g). [c] The uncertainty given is the interval equal to twice the "over-all" standard deviation. See F. D. Rossini and W. E. Deming, *J. Wash. Acad. Sci.*, 29, 416 (1939).

Calculation of Thermodynamic Properties

Internal rotation about the central carbon–carbon bond in 1-propanethiol results in *trans* and *skew* rotational tautomers, depicted in Fig. 1, which possess significantly different moments of inertia and fundamental vibrational frequencies. There are two optical isomers with the *skew* structure, but their moments of inertia and spectra are identical. For calculation of the thermodynamic functions, it is necessary to determine the moments of inertia and vibrational assignment for only one of these tautomers, since it has been shown that to a good approximation the thermodynamic functions of each tautomer may be expected to be the same.[26]

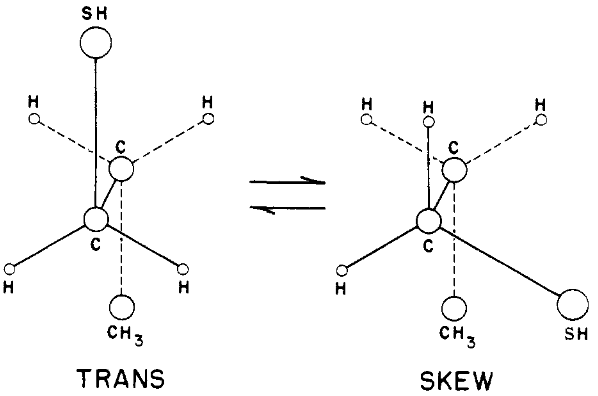

Fig. 1.—The rotational tautomers of 1-propanethiol. Only one of the optical isomers with the *skew* conformation is shown.

The Vibrational Assignment.—The concentrations of the *trans* and *skew* tautomers depend on the energy difference between the two structures. It will be shown later that in the gas phase the potential energy of the *trans* form is only about 400 cal. mole^{-1} lower than that of the *skew* forms; therefore, the observed spectra[27,28] summarized in Table IX should contain frequencies of both rotational tautomers. At lower temperatures, the energy difference would become more significant, and upon crystallization it is probable that only the lower energy *trans* tautomer would be present. Because spectra of crystalline 1-propanethiol were not available, the observed frequencies were sorted by comparison with the spectra of 1-bromopropane in the solid and liquid states.[29] That region of the spectra of

TABLE IX

ASSIGNMENT OF VIBRATIONAL SPECTRA OF 1-PROPANETHIOL[a]

Raman,[b] liq. $\Delta\nu$, cm.$^{-1}$	Infrared,[c] liq. ν, cm.$^{-1}$	*trans* Fundamental, ν, cm.$^{-1}$	Description
233 (0)			CH_3 torsion
290 ($^1/_2$)		290	CCS bend, both tautomers
363 (5)		363	CCC bend, *trans*
417 (0)			CCC bend, *skew*
651 (6)	655 s		CS stretch, *skew*
701 (3)	706 m	719	CS stretch, *trans*, in resonance with 2 × 363 = 726
736 (4)	733 ms		
767 ($^1/_2$b)	763 w	765	CH_2 rock, *trans*
805 ($^1/_2$b)	793 ms		CH_2 rock, *skew*
	815 sh		CSH bend, *skew*
880 (1b)	883 s	882	CSH bend, *trans*
905 ($^1/_2$b)	897 s	901	CC stretch *trans*
	925 m		CC stretch, *skew*
964 (0)	961 mw	962	CH_3 rock, both tautomers
1032 (5)	1032 w	1032	CC stretch, *trans*
	1060 sh	1060	CH_3 rock, both tautomers
	1088 s		CC stretch, *skew*
1103 (2)	1105 s	1104	CH_2 rock, both tautomers
1205 ($^1/_2$)			233 + 962 = 1195
	1225 m	1225	CH_2 twist, both tautomers
1256 ($^1/_2$)	1246 s	1250	CH_2 wag, both tautomers
1294 ($^1/_2$)	1298 s	1296	CH_2 wag, both tautomers
1330 (0)	1339 m	1335	CH_2 twist, both tautomers
	1380 s	1380	CH_2 bend, both tautomers
1440 (5b)		1440 [2]	2 CH_2 bend and 2 CH_3 bend, both tautomers
	1458 s	1458 [2]	
2570 (8b)	2564 s	2568	SH stretch, both tautomers
(Average value used)		2950 [7]	7 CH stretch, both tautomers

[a] Above 1500 cm.$^{-1}$ only those frequencies assigned as fundamentals are tabulated. [b] Ref. 27: numbers in parentheses indicate relative intensity values. [c] Ref. 28: relative intensities are indicated by w = weak, mw = medium weak, m = medium, s = strong and sh = shoulder.

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(26) K. S. Pitzer, *J. Chem. Phys.*, **14**, 239 (1946).

(27) Raman data: (a) S. Venkateswaren, *Indian J. Phys.*, **5**, 219 (1930); (b) G. Radinger and H. Wittek, *Z. physik. Chem.*, **B45**, 329 (1940).

(28) Infrared data: (a) I. F. Trotter and H. W. Thompson, *J. Chem. Soc.*, 481 (1946); (b) American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology, "Catalog of Infrared Spectral Data," spectra numbered 1676 and 1677.

(29) (a) J. K. Brown and N. Sheppard, *Trans. Faraday Soc.*, **50**, 1164 (1954); (b) J. K. Brown and N. Sheppard, *Disc. Faraday Soc.*, **9**, 144 (1950); (c) B. M. Bishui, *Indian J. Phys.*, **22**, 333 (1948); (d) S. Nakamura, *J. Chem. Soc. Japan*, **60**, 1010 (1939).

these two compounds for which analogy was most useful is presented in Table X.

TABLE X

COMPARISON OF THE SPECTRA OF 1-PROPANETHIOL AND 1-BROMOPROPANE

1-Propanethiol		1-Bromopropane		
Raman, liq., cm.$^{-1}$	Infrared, liq., cm.$^{-1}$	Raman, liq., cm.$^{-1}$	Infrared, liq., cm.$^{-1}$	Assignment
651 (6)	655 s	563 (10)	(567 s)[a]	CX stretch, *skew*
719 (3)[b]	719 m[b]	647 (7)	647 s	CX stretch, *trans*
767 (1/2b)	763 w		740 m	CH_2 rock, *trans*
805 (1/2b)	793 ms	776 (3)	(777 s)[a]	CH_2 rock, *skew*
	815 sh			CSH bend, *skew*
880 (1b)	883 s			CSH bend, *trans*
905 (1/2b)	897 s	842 (2)	839 s	CC stretch, *trans*
	925 m		(884 m)[a]	CC stretch, *skew*
964 (0)	961 mw	886 (2)	892 s	CH_3 rock, both tautomers
1032 (5)	1032 w	1024 (5)	1030 m	CC stretch, *trans*
	1088 s	1086 (1/2b)	(1084 m)[a]	CC stretch, *skew*

[a] Those frequencies in parentheses disappear in the spectra of crystalline 1-bromopropane. [b] The doublet 701–733 cm.$^{-1}$ was interpreted as Fermi resonance between a fundamental at 719 cm.$^{-1}$ and 2 × 363 = 726 cm.$^{-1}$; see Table IX.

The observed spectra of crystalline 1-bromopropane do not include the region of the skeletal bending frequencies. For this reason, the assignment of the skeletal bending frequencies of 1-propanethiol was based on the results of approximate normal coördinate calculations. Both tautomeric structures were treated as four-atomic molecules consisting of a CH_3 group, two CH_2 groups, and an SH group. The effective force constants used (in atomic weight-ångström units) were 4.0 for C–C stretching, 3.0 for C–S stretching and 1.0 for C–C–C and C–C–S angle bending. The results of these calculations and an assignment of observed frequencies are given in Table XI. As should be expected, the numerical agreement is not close, but the results provide a satisfactory basis for the assignment of the skeletal bending and C–S stretching modes. The results for the C–C stretching modes are not of much significance because interaction with methyl and methylene rocking modes was neglected.

TABLE XI

SKELETAL FREQUENCIES OF 1-PROPANETHIOL IN CM.$^{-1}$

Trans		*Skew*	
Calcd.	Obsd.	Calcd.	Obsd.
259	290	266	290
329	363	441	417
776	719	731	653
964	901	944	925
1064	1032	1071	1088

The higher hydrogen vibration frequencies of the rotational tautomers are not expected to differ enough that they may be resolved in the spectra, and the frequencies above 1100 cm.$^{-1}$ have been assigned in a conventional manner (Table IX).

To complete the assignment of the observed frequencies, the weak Raman line at 1205 cm.$^{-1}$ was interpreted as the sum combination 233 + 962 = 1195 cm.$^{-1}$, and the Raman line at 233 cm.$^{-1}$ was assumed to arise from torsional oscillation of the methyl group. It will be shown in a later section that best agreement with the calorimetric data was obtained by assuming the barrier to internal rotation of the methyl group to be 3100 cal. mole^{-1}; this corresponds to a torsional frequency of 230 cm.$^{-1}$.

Some confirmation of the assignment presented in Table IX may be obtained by applying the approximate sum rule for rotational tautomers,[30] $\Sigma\nu^2(trans) = \Sigma\nu^2(skew)$. Only six vibrational frequencies are split enough that they are resolved in the observed spectra, and the sum rule terms corresponding to these are $\Sigma\nu^2(trans) = 3.89 \times 10^6$ and $\Sigma\nu^2(\text{skew}) = 3.94 \times 10^6$. Also, from the approximations mentioned above concerning the thermodynamic functions of rotational tautomers[25] and the treatment to be discussed for the barrier to internal rotation about the central C–C bond, it follows that the vibrational heat capacity contributions of the tautomers should be the same. For the six frequencies for which the assignment differs, the heat capacity contributions are 5.16 and 5.17 cal. deg.$^{-1}$ mole^{-1} at 331.2°K. and 7.93 and 7.92 cal. deg.$^{-1}$ mole^{-1} at 500.2°K. for the *trans* and *skew* tautomers, respectively.

The Moments and Reduced Moments of Inertia.—The product of the principal moments of inertia and the reduced moments of inertia for internal rotation were calculated for the *trans* skeletal structure by the formalized procedure of Kilpatrick and Pitzer.[31] Conventional values of bond distances and angles were used: C–C bond distance, 1.54 Å.; C–H bond distance, 1.09 Å.; C–S bond distance, 1.815 Å.; C–S–H bond angle, 100°; and all other bond angles tetrahedral. With these structural parameters, the calculated product of the principal moments of inertia is 4.542×10^{-114} g.^{3} cm.^{6}, and the reduced moments of inertia of the SH, CH_3 and C_2H_5 groups are 2.648×10^{-40}, 4.580×10^{-40} and 22.153×10^{-40} g. cm.^{2}, respectively.

The Barriers to Internal Rotation, Rotational Tautomerism and Anharmonicity Corrections.—Simple threefold, cosine-type potential barriers were assumed for internal rotation of the CH_3 and SH groups. A potential function of the following form was assumed for internal rotation about the central

$$V(\phi) = (V_0/2)(1 - \cos 3\phi),\ 0 < \phi < \pi/3 \text{ and } 5\pi/3 < \phi < 2\pi$$
$$V(\phi) = (V_0/2)(1 - \cos 3\,\phi) + \Delta E_t,\ \pi/3 < \phi < 5\pi/3 \quad (8)$$

C–C bond where V_0 is the barrier height, ϕ is the angle of rotation measured from the *trans* configuration, and ΔE_t is the energy difference between the *trans* and *skew* tautomers. The contribution of tautomerism to the thermodynamic functions was then calculated by considering the "equilibrium" between the rotational tautomers.[32] This equilibrium was described by two parameters: (1) ΔE_t, the energy of the reaction *trans* tautomer → *skew* tautomer; and, (2) the entropy change for this reaction, assumed to be $R \ln 2$.

The effects of anharmonicity of normal vibrational modes were calculated by the empirical pro-

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(30) S. Mizushima, T. Shimanouchi, I. Nakagawa and A. Miyake, *J. Chem. Phys.*, **21**, 215 (1953).

(31) J. E. Kilpatrick and K. S. Pitzer, *ibid.*, **17**, 1064 (1949).

(32) K. S. Pitzer, *ibid.*, **5**, 473 (1937).

TABLE XII

THE MOLAL THEMODYNAMIC PROPERTIES OF 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.$^{-1}$	$C_p°$, cal. deg.$^{-1}$	$\Delta Hf°$,[b] kcal.	$\Delta Ff°$,[b] kcal.	$\log_{10} Kf°$[b]
0	0	0	0	0	0	−26.17	−26.17	Infinite
273.16	−63.52	14.95	4.084	78.47	21.39	−31.08	−10.74	+ 8.59
298.16	−64.86	15.54	4.633	80.40	22.65	−31.46	− 8.87	+ 6.50
300.00	−64.95	15.59	4.677	80.54	22.75	−31.49	− 8.73	+ 6.36
400	−69.76	18.03	7.212	87.79	27.86	−32.87	− 0.92	+ 0.50
500	−74.05	20.47	10.235	94.52	32.56	−34.01	+ 7.21	− 3.15
600	−78.00	22.83	13.70	100.83	36.72	−34.90	15.53	− 5.66
700	−81.69	25.08	17.56	106.77	40.37	−35.56	23.98	− 7.49
800	−85.18	27.19	21.75	112.37	43.60	−35.99	32.53	− 8.89
900	−88.51	29.18	26.26	117.69	46.47	−36.23	41.10	− 9.98
1000	−91.67	31.04	31.04	122.71	49.01	−36.28	49.70	−10.86

[a] To form an internally consistent set of values 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 1-propanethiol by the reaction: $3C\ (\text{graphite}) + 4H_2(g) + {}^1/_2\ S_2(g) \rightarrow C_3H_8S(g)$.

cedure outlined in a previous publication.[33] This procedure required evaluation of two parameters, ν and Z (defined in ref. 33), from the experimental vapor heat capacity data.

The following values of the parameters used to compute the contributions of internal rotation, rotational tautomerism and anharmonicity were chosen simultaneously to give agreement between calculated and experimental values of $S°$ and $C_p°$: methyl barrier, 3100 cal. mole^{-1}; thiol barrier, 1650 cal. mole^{-1}; ethyl barrier, 2900 cal. mole^{-1}; energy of the reaction *trans* tautomer → *skew* tautomer, ΔE_t = 400 cal. mole^{-1}; and anharmonicity parameters, ν = 1300 cm.$^{-1}$ and Z = 2.50 cal. deg.$^{-1}$ mole^{-1}. Comparisons of the calculated and experimental values of $C_p°$ and $S°$ are given in Tables VI and VII, respectively. Agreement within 0.1% was obtained over the 200° range of temperature for which experimental data are available.

The values given above for the potential barriers to internal rotation and the energy difference between rotational tautomers are consistent with results found in studies of related hydrocarbons and sulfur compounds. Reported thiol barrier heights for four compounds[3-5,7] range from 1360 to 1640 cal. mole^{-1}. Methyl barriers for straight chain hydrocarbons[34,35] are about 3400 cal. mole^{-1}, and the methyl barrier in ethanethiol[4] is 3310 cal. mole^{-1}. A value of about 3300 cal. mole^{-1} has been used for the barrier to rotation about internal C–C bonds in straight chain hydrocarbons.[34,35] The energy difference between rotational tautomers of *n*-paraffins has been found to be between 500 and 800 cal. mole^{-1} from both calorimetric[34,35] and spectroscopic[36] data. The slightly lower value found for the energy difference between the *trans* and *skew* tautomers of 1-propanethiol is probably due to the fact that the C–S bond distance is appreciably greater than the C–C bond distance.

The Thermodynamic Properties in the Ideal Gaseous State.—The vibrational assignment, product of principal moments of inertia, reduced moments of inertia, barriers to internal rotation, energy difference between rotational tautomers, and anharmonicity parameters discussed above were used to compute values of the thermodynamic functions of 1-propanethiol in the ideal gaseous state at selected temperatures from 0 to 1000°K.[37] The results are given in Table XII.

The heat of formation of gaseous 1-propanethiol at 298.16°K. (Table VIII) was used with the thermodynamic properties in Table XII and the thermodynamic properties for C(graphite),[24] $H_2(g)$[24] and $S_2(g)$[26] to compute values of $\Delta Hf°$, $\Delta Ff°$ and $\log_{10}Kf°$, the heat, free energy, and common logarithm of the equilibrium constant of formation, at selected temperatures from 0 to 1000°K. These values are included in Table XII.

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(33) J. P. McCullough, H. L. Finke, W. N. Hubbard, W. D. Good, R. E. Pennington, J. F. Messerly and Guy Waddington, THIS JOURNAL, **76**, 2661 (1954).

(34) K. S. Pitzer, *Ind. Eng. Chem.*, **36**, 829 (1944).

(35) W. B. Person and G. C. Pimentel, THIS JOURNAL, **75**, 532 (1953).

(36) N. Sheppard and G. J. Szasz, *J. Chem. Phys.*, **17**, 86 (1949).

(37) The harmonic oscillator contributions to the thermodynamic functions were taken from H. L. Johnston, L. Savedoff and J. Belzer, "Contributions to the Thermodynamic Functions by a Planck-Einstein Oscillator in One Degree of Freedom," NAVEXOS P-646, Office of Naval Research, Department of the Navy, Washington, D. C., July, 1949. Restricted rotation contributions were calculated from the tables of K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942). Anharmonicity contributions were computed from the tables of R. E. Pennington and K. A. Kobe, *ibid.*, **22**, 1442 (1954).