Ethanethiol (Ethyl Mercaptan): Thermodynamic Properties in the Solid, Liquid and Vapor States. Thermodynamic Functions to 1000°K.[1]

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The thermodynamic properties of ethanethiol have been measured in the solid, liquid and vapor states over the temperature range 14 to 450°K. The entropy of the saturated liquid at 298.16°K. was derived from measurements of the heat capacity of the solid and liquid and the heat of fusion (1189 cal. mole^{-1} at the triple point, 125.26 ± 0.05°K.) Results obtained for the vapor pressure, heat of vaporization ($\Delta H_{vap.}$), vapor heat capacity in the ideal gaseous state (C), and second virial coefficient (B, in the equation of state, $PV = RT + BP$) are accurately represented by the empirical equations (1) $\log P = 6.95206 - 1084.531/(t + 231.385)$, ($P$, mm.; t, °C.); (2) $\Delta H_{vap.} = 8151 + 1.369T - 0.02288T^2$, cal. mole^{-1} (280–308°K.); (3) $C_p^0 = 4.45 + 4.836 \times 10^{-2} - 1.695 \times 10^{-5}T^2$, cal. deg.$^{-1}$ mole^{-1} (315–450°K.); (4) $B = -27 - 60.1 \exp(800/T)$, cc. mole^{-1} (280–450°K.). The entropy of the ideal gas at one atmosphere pressure and 298.16°K. (70.77 ± 0.15 cal. deg.$^{-1}$ mole^{-1}) was computed from these data. A vibrational assignment was made for ethanethiol, based upon information from similar molecules. The heights of the potential barriers to internal rotation selected to fit the experimental thermal data were 3310 cal. mole^{-1} for the methyl barrier and 1640 cal. mole^{-1} for the thiol barrier. Values of the free energy function, heat content, entropy and heat capacity were computed on the basis of an harmonic-oscillator, rigid-rotator approximation at selected temperatures up to 1000°K.

The thermodynamic properties of thiophene,[3] 2,3-dithiabutane[4] and 2-thiabutane[5] have been determined previously in this Laboratory. The present paper describes the results of studies of the thermodynamic properties of ethanethiol. Listed in the order of their presentation are the several topics to be discussed: (1) low temperature calorimetric studies; (2) vapor pressure; (3) heat of vaporization, vapor heat capacity and gas imperfection; (4) entropy of the ideal gas; (5) the heights of the potential barriers to internal rotation of the methyl and thiol groups as determined from the entropy and vapor heat capacity data; (6) thermodynamic functions from spectroscopic and molecular structure data.

A primary purpose of these investigations is to make available accurate thermodynamic functions for structurally simple members of families of sulfur compounds which are important to the petroleum industry. It will then be possible to construct systematically tables of thermodynamic functions for homologous series of sulfur compounds by approximate statistical mechanical methods.[6]

Experimental

Material.—The ethanethiol used for the low temperature investigation and the vapor pressure measurements was one of the samples of API-BM Certified Sulfur Compounds prepared and purified by API Research Project 48A at the Laramie Station of the Bureau of Mines. The following physical properties of this sample were measured at the Laramie Station: refractive index, $n^{25}D$ 1.42779; density, d_{25} 0.83316 g. ml.$^{-1}$. The amount of impurity in the ethanethiol as determined at Laramie by the time–temperature

(1) This investigation was performed as part of the work 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. Article not copyrighted.

(2) Deceased.

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

(4) D. W. Scott, H. L. Finke, M. E. Gross, G. B. Guthrie and H. M. Huffman, ibid., 72, 2424 (1950).

(5) D. W. Scott, H. L. Finke, J. P. McCullough, M. E. Gross, K. D. Williamson, G. Waddington and H. M. Huffman, ibid., 73, 261 (1951).

(6) The compilation and tabulation of selected values of the properties of sulfur containing compounds will be a part of the program of American Petroleum Institute Research Project 44.

freezing point method was 0.05 ± 0.04 mole %, while that determined in the calorimetric study to be discussed in a later section was 0.022 ± 0.005 mole %. For use in the heat of vaporization and vapor heat capacity investigations, a second sample of ethanethiol with a purity of 99.88 ± 0.03 mole % was obtained from the same source.

Solid and Liquid Heat Capacities.—The low temperature thermal studies were made in an apparatus similar to that of Ruehrwein and Huffman.[7] The sample (ca. 0.76 mole) was sealed in a platinum calorimeter which has horizontal, perforated discs of gold to facilitate attainment of thermal equilibrium. The calorimeter was contained in a cryostat designed to minimize the interchange of energy between the calorimeter and its surroundings. During heat capacity determinations, a measured quantity of energy was imparted to the calorimeter and contents by means of an electrical heater, and the resulting temperature rise was observed with a strain free platinum resistance thermometer. Since adiabatic conditions were maintained throughout the period of each observation, the heat capacity at the mean temperature of a run and at the corresponding saturation pressure is given by the relationship, $C_{sat} = (1/m)(W/4.1833 \Delta T - C_{cal})$, where W is the energy supplied to the calorimeter in international joules, m is the number of moles of sample, ΔT is the temperature increment, and C_{cal} is the previously measured heat capacity of the empty calorimeter. The temperature increment employed in each measurement was approximately 10% of the absolute temperature below 50°K., 5 to 6° from 50°K. to the melting point and 10° in the liquid region. Table I presents the experimental results of the low temperature heat capacity studies. The precision of these measurements was, in general, better than 0.1%; and at temperatures above 30°K. it is believed that the accuracy uncertainty should not be greater than 0.2%.

Heat of Fusion, Triple Point and Sample Purity.—Duplicate measurements of the heat of fusion of ethanethiol, made in the course of the low temperature thermal studies, each yielded the value

$$\Delta H_{fusion} = 1189 \text{ cal. mole}^{-1}, \text{ at the triple point, } T_{T.P.} = 125.26 \pm 0.05°K.$$

The triple point was determined in a calorimetric study of the equilibrium melting temperature of the sample as a function of the fraction melted, as described in an earlier publication from this Laboratory.[8] The results of this study are given in Table II. The reciprocal of fraction melted, $1/F$, was plotted against T_{obsd}. From a straight line through the points at approximately 31, 50 and 70% melted, the melting point of the actual sample under its own vapor pressure and the triple point of the pure com-

(7) R. A. Ruehrwein and H. M. Huffman, THIS JOURNAL, 65, 1620 (1943).

(8) S. S. Todd, G. D. Oliver and H. M. Huffman, ibid., 69, 1519 (1947).

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Table I[a]

The Molal Heat Capacity of Ethanethiol, Cal. Deg.,$^{-1}$ Mole Sample = 0.75949

T, °K.[b]	C_{satd}	T, °K.[b]	C_{satd}	T, °K.[b]	C_{satd}
Crystals		64.21	10.149	146.04	27.069
		68.78	10.663	147.56	27.045
14.38	1.019	69.70	10.759	154.04	26.967
15.53	1.244	74.65	11.299	157.67	26.925
16.84	1.527	75.43	11.384	167.77	26.825
18.52	1.901	81.49	12.068	177.85	26.746
20.54	2.373	85.78	12.519	187.83	26.696
21.95	2.731	88.09	12.776	197.87	26.679
22.93	2.963	90.54	13.010	207.86	26.662
24.42	3.318	95.17	13.470	216.06	26.727
25.58	3.601	96.30	13.573	225.96	26.794
27.37	4.023	101.87	14.104	235.82	26.902
30.51	4.747	102.31	14.155	245.62	27.029
33.58	5.425	107.24	14.609	255.35	27.191
37.57	6.220	112.80	15.138	265.00	27.372
42.88	7.169	118.54	15.727	274.57	27.559
48.12	8.019			284.07	27.783
51.20	8.465	Liquid		293.48	28.033
53.22	8.763			299.06	28.198
53.63	8.822	130.05	27.298	303.26	28.316
56.86	9.239	135.12	27.218	306.30	28.398
58.70	9.471	137.43	27.194	313.40	28.622
62.86	9.983	138.97	27.149	315.26	28.685

[a] All data in this paper are based on a molecular weight of 62.134 for ethanethiol and the following definitions: 1 cal. = 4.1833 int. joules; 0°C. = 273.16°K. [b] T is the mean temperature of each heat capacity measurement.

pound were obtained by reading the temperature intercepts at values of $1/F$ of 1 and 0, respectively.

Table II

Ethanethiol Melting Point Summary

Heat of fusion, ΔH_{fusion} = 1189 cal. mole^{-1}; triple point, $T_{T.P.}$ = 125.26 ± 0.05°K.; cryoscopic constant, A = 0.0381 deg.$^{-1}$; impurity = 0.022 ± 0.005 mole %.

Melted, %	$1/F$	Obsd.	T, °K. Graph[a]
8.47	11.81	125.2100	125.2154
30.81	3.25	.2455	.2454
49.84	2.01	.2525	.2525
69.99	1.43	.2558	.2558
90.14	1.11	.2560	.2576
100.00	1.00		.2583
Pure	0.00		.2640

[a] Deviations from T_{obsd} indicate departure from assumed conditions.

The amount of impurity in the low temperature calorimetric sample was computed from these data by means of the relationship $N_2/F = A\Delta T$, where N_2 is the mole fraction of impurity, F is the fraction of sample in the liquid state, $A = \Delta H_{fusion}/RT^2_{T.P.}$ is the cryoscopic constant and $\Delta T = T_{T.P.} - T_{obsd}$.

Vapor Pressure.—The vapor pressure of ethanethiol was measured from 0.4 to 66.1° by an ebulliometric method, using the apparatus that has been described in a previous publication from this Laboratory.[3] Water and ethanethiol were placed in twin ebulliometers where both compounds were boiled at the same pressure. The boiling and condensation temperatures of ethanethiol and the boiling point of water were observed with the same calibrated platinum resistance thermometer. The pressure under which the two substances boiled was determined from the vapor pressure data for water tabulated by Osborne, Stimson and Ginnings.[9] The results of this study are given in Table III. The following Antoine equation was obtained from the experimental data by a least-squares adjustment[10]

$$\log_{10} P \text{ (mm.)} = 6.95206 - 1084.531/(t + 231.385) \quad (1)$$

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

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

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where t is in °C. The normal boiling point of ethanethiol given by equation (1) is 35.00°. For comparison with the observed data, values of the vapor pressure computed by means of this equation are listed in the last column of Table III.

Table III

The Vapor Pressure of Ethanethiol

Boiling point, °C. Water	Ethanethiol	Pressures, mm. Obsd.	Calcd.
65.000	0.405	187.57	187.55
70	5.236	233.72	233.70
75	10.111	289.13	289.18
80	15.017	355.22	355.30
85	19.954	433.56	433.56
90	24.933	525.86	525.86
95	29.944	633.99	633.87
100	35.000	760.00	759.92
105	40.092	906.06	906.00
110	45.221	1074.6	1074.5
115	50.390	1268.0	1268.0
120	55.604	1489.1	1489.6
125	60.838	1740.8	1740.8
130	66.115	2026.0	2025.7

Heat of Vaporization.—Measurements of the heat of vaporization and vapor heat capacity of ethanethiol were made in the flow calorimeter system which has been described in detail elsewhere.[11] The steady flow of vapor required for vapor heat capacity measurements was maintained by boiling the liquid in a cycling vaporizer; the vapor was passed through the calorimeter, condensed and returned to the vaporizer. A relationship between the power input of the electrical boiler heater and the vapor flow rate was obtained by collecting and weighing the material vaporized in a measured time interval by a measured quantity of energy. By applying suitable small corrections to the proportionality thus obtained, heats of vaporization were computed[11a] which are believed to have an accuracy uncertainty of 0.1%.

Ethanethiol was found to react with some of the metals present in the vaporizers previously employed in this Laboratory. Consequently, for use with this compound and other corrosive materials a glass vaporizer was constructed which is similar to that described in ref. (11a) except that the heating element and leads are completely enclosed in glass tubing. Results obtained with this vaporizer for the heat of vaporization and vapor heat capacity of benzene were within the accuracy uncertainty of previously accepted values.[12]

The results of triplicate determinations of the heat of vaporization of ethanethiol at each of three temperatures are recorded in Table IV, where the uncertainties given denote the maximum deviation of experimental results from the mean. The following equation may be used for interpolation within the range of temperature of the experiments

$$\Delta H_{vap.} = 8151 + 1.369T - 0.02288T^2, \text{ cal. mole}^{-1}$$
$$(280-308°K.) \quad (2)$$

Vapor Heat Capacity.—The heat capacity of ethanethiol vapor was determined by observing its temperature rise, ΔT, when it was passed over an electrical heater at a constant, known rate of flow. The calorimeter which contains the heater and two platinum resistance thermometers is so designed that the vapor heat capacity is given by

$$C_p = W/F\Delta T - k/F = C_{p(app)} - k/F$$

where W is the measured power input of the calorimeter heater, F is the vapor flow rate obtained from measurement of the power input of the vaporizer heater and k is proportional to the heat loss from the calorimeter. Since k was constant for a particular set of conditions, C_p was evaluated by measuring $C_{p(app)}$ at several rates of flow, plotting

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

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

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TABLE IV

THE MOLAL HEAT OF VAPORIZATION AND GAS IMPERFECTION OF ETHANETHIOL

T, °K.	$\Delta H_{vap.},$ 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.$^{-2}$
281.16	6728 ± 1	1066	1061	65,361	246.7	0.1804
298.16	6526 ± 2	897	907	34,363	126.2	.1243
308.16	6401 ± 2	839	833	24,454	88.84	.1013

[a] Calculated with the aid of equation (4). [b] At saturation pressure.

$C_{p(app.)}$ vs. $1/F$ and extrapolating the resulting straight line to $1/F = 0$.[11a]

The results of measurements of the vapor heat capacity of ethanethiol at two or more pressures at each of four temperatures from 317 to 449°K. are summarized in Table V. The heat capacity in the ideal gaseous state, C_p°, was obtained at each temperature by linear extrapolation to zero pressure of plots of heat capacity vs. pressure.[11,12] An accuracy uncertainty of 0.2% is assigned to the experimental values of C_p°. Equation 3 accurately represents the observed values of C_p° within the temperature range of the experimental measurements.

$$C_p^\circ = 4.45 + 4.836 \times 10^{-2}T - 1.695 \times 10^{-5}T^2$$
$$\text{cal. deg.}^{-1}\text{mole}^{-1} \ (315\text{-}450°\text{K.}) \quad (3)$$

TABLE V

THE MOLAL VAPOR HEAT CAPACITY OF ETHANETHIOL, CAL. DEG.$^{-1}$

T, °K.	317.20	358.25	402.20	449.20
C_p (760 mm.)	18.740	19.944	21.356	22.894
C_p (527 mm.)	18.538	....	....	....
C_p (264 mm.)	18.312	19.716	21.228	22.800
C_p° (obsd.)	18.08	19.59	21.16	22.75
C_p° (calcd.)[a]	18.07	19.56	21.11	22.68
$(\partial C_p/\partial P)_T$ (obsd.)	0.66	0.35	0.20	0.14
$(\partial C_p/\partial P)_T$ (calcd.)[b]	0.65	0.36	0.21	0.13

[a] Calculated from spectroscopic and molecular structure data. [b] Calculated by use of equation (4); units of $(\partial C_p/\partial P)_T$ are cal. deg.$^{-1}$ mole^{-1} atm.$^{-1}$.

Gas Imperfection and Second Virial Coefficient.—By using the exact form of the Clapeyron equation, the second virial coefficient, B, in the equation of state, $PV = RT + BP$, may be evaluated from the experimental heat of vaporization and vapor pressure data. The relationship employed is

$$B = [\Delta H_{vap}/T(dP/dT)] - RT/P + V_L$$

where V_L is the molal volume of the liquid. Since $(\partial C_p/\partial P)_T = -T(d^2B/dT^2)$, the observed variation of C_p with pressure was used to obtain values of the second derivative of B with respect to temperature. These data were correlated by means of the empirical equation

$$B = -27 - 60.1 \exp(800/T), \text{ cc. mole}^{-1} \quad (4)$$

where T is in °K. The constants of equation (4) were evaluated by methods outlined in an earlier paper.[12] The values of the second virial coefficient derived from experimental data and those computed from equation (4) are included in Table IV. Values of the molal volume and its first and second derivatives with respect to temperature are also recorded in Table IV. In the last two lines of Table V the observed values of $(\partial C_p/\partial P)_T$ are compared with those computed by use of equation (4).

Entropy.—The calorimetric data presented above were utilized to compute the entropy of ethanethiol in both the liquid and vapor states. These calculations are summarized in Table VI. Equation (4) was employed to calculate the entropy of gas imperfection, which is given by $P(dB/dT)$ in terms of the second virial coefficient.

Calculation of Thermodynamic Functions

Vibrational Assignment.—A complete vibrational assignment was needed to compute the thermodynamic properties of ethanethiol from spectroscopic and molecular structure data. The follow-

TABLE VI

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

0-14°K.	Debye, 5° freedom, $\theta = 129.4$			0.322
14-125.26°	Crystals. graphical, $\int C_{satd}\,d\ln T$			16.212
125.26°	Fusion, 1189/125.26			9.492
125.26-298.16°	Liquid. graphical, $\int C_{satd}\,d\ln T$			23.449
S_{satd} (liq.), 298.16° K.				49.48 ± 0.10

T, °K.	281.16	298.16	308.16
S_{satd} (liq.)	47.835	49.475	50.410
Vaporization, $\Delta H_{vap}./T$	23.929	21.888	20.772
Compression, $R \ln (P/760)$	-2.101	-0.727	0.000
Gas imperfection, $P(dB/dT)$[a]	0.088	.133	.164
S°, gas (obsd.)	69.75 ± 0.15	70.77 ± 0.15	71.35 ± 0.15
S°, gas (calcd.)[b]	69.76	70.77	71.35

[a] Computed with the aid of equation (4). [b] Calculated from spectroscopic and molecular structure data.

ing assignment of fundamental frequencies is that of Sheppard[13] as revised by the present authors with the use of information gained in their study of 2-thiabutane[14]: C–C–S bending, 332; C–S stretching, 660; CH_2 rocking, 745; C–S–H bending, 870; C–C stretching, 978; CH_3 rocking, 1049 and 1097; CH_2 wagging, 1269; CH_2 twisting, 1309; CH_3 bending, 1385 and 1450 (2); CH_2 bending, 1450; S–H stretching, 2575; and average C–H stretching, 2950 (5) cm.$^{-1}$.

Only those Raman shifts observed by both Wagner[15] and Vogel-Högler[16] were assigned as fundamentals. The weak lines reported by Wagner[15] at 440 and 838 cm.$^{-1}$ and that observed by Vogel-Högler[16] at 1246 cm.$^{-1}$ probably are not actual Raman displacements of ethanethiol.

Moments of Inertia and Barriers to Internal Rotation.—As the molecular structure of ethanethiol has not been studied, the bond distances and angles were estimated to be the same as those in closely related molecules. The values used were: C–C bond distance, 1.54 Å.; C–H distance, 1.09 Å.; C–S distance, 1.83 Å.[17]; S–H distance, 1.35 Å.[17]; C–S–H bond angle, 100°[17]; and all other angles, 109°28'.

The 1949 atomic weights and the values of the fundamental constants given by Wagman, et al.,[18] were used in all computations described in this paper. Using these parameters the product of the three principal moments of inertia was calculated to be 7.928×10^{-115} g.^{3} cm.^{6}. For calculating the reduced moments of inertia for internal rotation,

(13) N. Sheppard, J. Chem. Phys., 17, 79 (1949).

(14) See footnote 11, ref. 5.

(15) J. Wagner, Z. physik. Chem., B40, 439 (1938).

(16) Ruth Vogel-Högler, Acta Phys. Austriaca, 1, 311 (1948).

(17) These figures are the same as those for methanethiol; see H. Russell, D. W. Osborne and D. M. Yost, THIS JOURNAL, 64, 165 (1942).

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

Pitzer's method for unsymmetrical tops attached to a rigid frame[19] was applicable, and the reduced moments obtained by that method are 4.695 × 10⁻⁴⁰ and 2.660 × 10⁻⁴⁰ g. cm.² for the methyl and thiol rotations, respectively.

Simple cosine-type potential barriers were assumed for the internal rotation of both the CH_3 and the SH groups. The heights of these barriers required to fit the experimental entropy and vapor heat capacity at 300°K., where anharmonicity effects are small, are 3310 cal. mole⁻¹ for the motion about the C–C bond and 1640 cal. mole⁻¹ for that about the C–S bond. These values may be compared with 3700 cal. mole⁻¹ determined for the methyl barrier in ethyl chloride[20] and 1460 cal. mole⁻¹ for the thiol barrier in methanethiol.[17]

Thermodynamic Functions.—Using the vibrational assignment, the moments and reduced moments of inertia, and the barriers to internal rotation discussed in previous sections, values of the functions, $(F° - H_0°)/T$, $(H° - H_0°)$, $S°$ and $C_p°$, were computed on the basis of an harmonic-oscillator, rigid-rotator approximation at selected temperatures from 298.16 to 1000°K. Values of the entropy calculated for the temperatures at which experimental data were obtained are included in Table VI, and a similar comparison of computed and experimental vapor heat capacity results is presented in Table V. The small differences between the calculated and observed values of $C_p°$ are to be expected since the effect of anharmonicity cannot be computed on the basis of available data.

The calculated thermodynamic functions for

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

(20) J. Gordon and W. F. Giauque. This Journal, **70**, 1506, 4277 (1948).

ethanethiol are recorded in Table VII. In order to form an internally consistent set of values, the entries in this table are given to more significant figures than are warranted by their absolute accuracy.

TABLE VII

THE MOLAL THERMODYNAMIC FUNCTIONS OF ETHANETHIOL

T, °K.	$-(F° - H_0°)/T$, cal. deg.⁻¹	$H° - H_0°$, kcal.	$S°$, cal. deg.⁻¹	$C_p°$, cal. deg.⁻¹
298.16	58.64	3.617	70.77	17.36
300	58.72	3.648	70.88	17.43
400	62.46	5.572	76.39	21.03
500	65.75	7.840	81.43	24.25
600	68.77	10.40	86.11	27.03
700	71.56	13.23	90.46	29.42
800	74.17	16.28	94.52	31.50
900	76.65	19.52	98.34	33.32
1000	79.01	22.93	101.94	34.91

Before experimental thermal data were available, Barrow and Pitzer[21] computed thermodynamic functions for ethanethiol using the vibrational assignment of Trotter and Thompson[22] and heights of potential barriers for internal rotation transferred from propane and methanethiol. Their values for the thermodynamic functions differ by no more than 2% from those given in Table VII. The differences in the two tabulations may be ascribed to the facts that a new vibrational assignment, based on more recent information, and barrier heights chosen to fit the experimental thermal data were used in the present work.

(21) G. M. Barrow and K. S. Pitzer, Ind. Eng. Chem., **41**, 2737 (1949).

(22) I. F. Trotter and H. W. Thompson, J. Chem. Soc., 481 (1946).

The Entropy and Vapor Pressure of 1-Pentanethiol[1a]

By H. L. Finke, D. W. Scott, M. E. Gross, Guy Waddington and H. M. Huffman[1b]

The low temperature thermal properties and the vapor pressure of 1-pentanethiol have been measured. From the heat capacities of the solid and liquid states and the heat of fusion (4190 cal. mole⁻¹) at the triple point (197.46°K.), the entropy of the saturated liquid at 298.16°K. was found to be 74.18 cal. deg.⁻¹ mole⁻¹. Over the temperature range of the experiments the vapor pressure is accurately represented by the equations (1) $\log p = 6.93311 - 1369.479/(t + 211.314)$, ($p$ mm., t°C.); (2) $\log P = A(1 - 399.797/T)$, ($P$ atm., T°K.), where $\log A = 0.85780 - 6.8478 \times 10^{-4}T + 6.0427 \times 10^{-7}T^2$. The entropy of the ideal gas at 298.16°K. was computed to be 99.18 cal. deg.⁻¹ mole⁻¹.

In a previous paper[2] it is pointed out that this Laboratory, under the sponsorship of American Petroleum Institute Research Project 48A, is conducting a program of detailed calorimetric and theoretical investigations of structurally simple sulfur compounds occurring in or derivable from petroleum. A primary purpose of these studies is to

(1) (a) This investigation was performed as part of the work 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. Article not copyrighted. (b) Deceased.

(2) 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).

obtain accurate thermodynamic information that will serve as a sound basis for the computation, by semi-empirical methods, of thermodynamic functions for the more complex homologs of the simple molecules which have been studied in detail. An acceptable application of this plan requires that experimental values of thermodynamic properties be provided for a few selected higher homologs in each family to provide checks on the values of thermodynamic functions that have been obtained essentially by computational extrapolation. The experimentally determined entropy of 1-pentanethiol at 298.16°K. presented in this paper will provide a guidepost in the construction of tables of thermodynamic functions for the n-alkanethiols.