

Pitzer's method for unsymmetrical tops attached to a rigid frame¹⁹ 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 CH₃ 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 chloride²⁰ 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, $(F^\circ - H_0^\circ)/T$, $(H^\circ - H_0^\circ)$, 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. Giaque, *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

$T, ^\circ\text{K.}$	$-(F^\circ - H_0^\circ)/T,$ cal. deg. ⁻¹	$H^\circ - H_0^\circ,$ kcal.	$S^\circ,$ cal. deg. ⁻¹	$C_p^\circ,$ 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	31.59
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 Pitzer²¹ computed thermodynamic functions for ethanethiol using the vibrational assignment of Trotter and Thompson²² 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).

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[CONTRIBUTION NO. 26 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

The Entropy and Vapor Pressure of 1-Pentanethiol^{1a}

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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., $t^\circ\text{C.}$); (2) $\log P = A(1 - 399.797/T)$, (P atm., $T^\circ\text{K.}$), 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 paper² 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

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.

(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).

Material.—The 1-pentanethiol was an API-BM "Sample of Organic Sulfur Compounds" prepared and purified by API Research Project 48A at the Laramie, Wyo., Station of the Bureau of Mines. The sample had the following physical properties: n_D^{20} 1.44692, n_D^{25} 1.44439; d_4^{20} 0.84209 g./ml., d_4^{25} 0.83763 g./ml. The Laramie laboratory, which supplied the foregoing data, also determined the purity of the sample to be 99.92 \pm 0.05 mole % by the time-temperature freezing point method. This value may be compared with a value of 99.944 \pm 0.015 mole % obtained from calorimetric studies in this Laboratory.

Low Temperature Measurements.—The low temperature measurements covering the range 12 to 320°K. were made in the apparatus described in a previous paper.² The results of the low temperature heat capacity measurements are given in Table I. The temperature increment employed in each measurement was approximately 10% of the absolute temperature up to about 50°K., 6–7° up to the melting point, and 10° in the liquid range. The quantity measured is C_{satd} , the heat capacity of the condensed phase under its own vapor pressure. Over the temperature range of the experimental work C_{satd} does not differ significantly from C_p . The precision of the measurements was generally better than 0.1% and above 30°K. it is judged that the accuracy uncertainty is 0.2% or less.

TABLE I^a

1-PENTANETHIOL MOLAL HEAT CAPACITY, CAL. DEG. ⁻¹					
T , °K. ^b	C_{satd}	T , °K. ^b	C_{satd}	T , °K. ^b	C_{satd}
Crystals		73.69	15.547	Liquid	
		76.21	15.994	200.34	44.675
12.84	0.788	80.85	16.814	202.70	44.734
14.38	1.095	84.04	17.363	206.01	44.739
15.98	1.440	86.23	17.674	208.67	44.775
16.63	1.587	88.36	18.049	211.70	44.886
17.97	1.918	91.87	18.555	214.68	44.838
20.48	2.584	92.72	18.707	215.22	44.875
21.66	2.920	96.32	19.234	220.04	45.031
23.40	3.408	99.82	19.689	222.32	45.025
24.63	3.762	102.63	20.117	226.29	45.081
26.68	4.352	104.51	20.349	229.38	45.193
27.63	4.618	108.60	20.892	231.20	45.272
30.13	5.346	112.78	21.454	236.38	45.413
30.88	5.567	113.06	21.479	237.77	45.415
34.33	6.579	117.71	22.070	241.91	45.572
38.22	7.637	121.76	22.589	249.11	45.794
42.61	8.818	123.99	22.871	252.50	45.933
47.93	10.150	127.82	23.334	260.31	46.214
54.13	11.642	136.22	24.358	262.99	46.337
55.08	11.871	139.45	24.751	271.35	46.716
57.95	12.541	148.24	25.841	273.87	46.834
60.05	12.975	151.45	26.229	282.24	47.286
63.08	13.558	163.43	27.754	285.11	47.404
66.76	14.271	175.38	29.398	292.97	47.906
69.09	14.752	186.65	31.957	296.21	48.076
				301.89	48.396
				310.53	48.905
				321.00	49.518

^a All data in this paper are based on a molecular weight of 104.212 for 1-pentanethiol 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.

Duplicate determinations of the heat of fusion at the triple point yielded the values 4190.5 and 4189.8 cal. mole⁻¹. The value selected for ΔH_{fusion} is 4190 cal. mole⁻¹.

Equilibrium melting temperatures, as a function of the fraction melted, were determined by the method described in an earlier publication.³ The results are listed in Table II. From a plot of the reciprocal of fraction melted vs. equilibrium melting temperature the triple point was determined to be 197.46°K. by extrapolation of a straight line through all the points to zero value of $1/F$. The cryoscopic constant ($\Delta H_{\text{fusion}}/RT^2_{\text{T.P.}}$) is 0.0541 deg.⁻¹.

Vapor Pressure Measurements.—The vapor pressure of 1-pentanethiol was measured from 76 to 166° by an ebulliometric method which has been described in a previous publication from this Laboratory.⁴ In preliminary experi-

TABLE II

1-PENTANETHIOL MELTING POINT SUMMARY

Triple point ($T_{\text{T.P.}}$) = 197.46 \pm 0.05°K.; impurity = 0.056 \pm 0.015 mole %; N_2/F = 0.0541 ΔT . N_2 = mole fraction impurity in sample; F = fraction of sample melted; ΔT = $T_{\text{T.P.}}$ - $T_{\text{obs.}}$; 0°C. = 273.16°K. The agreement of columns 3 and 4 implies fulfillment of the underlying assumptions of this method of determining impurity, namely: (a) ideality of the solution and (b) that the impurities are liquid-soluble, solid-insoluble.

Melted, %	1/F	Obsd. T , °K.	Graph
8.28	12.08	197.3310	197.3311
25.94	3.855	.4174	.4170
51.13	1.956	.4378	.4371
70.38	1.421	.4427	.4424
91.11	1.098	.4458	.4458
100	1.000		.4468
Pure	0.000		.4573

ments employing an ebulliometer with a manganin wire heater in direct contact with the sample, it was found that the difference between the boiling and condensation temperatures increased quite rapidly during the course of measurements, even at the lowest temperature studied. This difficulty was attributed to reaction of the sample with the metal heater or to decomposition catalyzed by the metal surface. The ebulliometer was therefore modified so that the sample came into contact with nothing but glass. The heater was enclosed in a re-entrant well, the outside of which was wrapped with "Fiberglas" thread in order to have a rough surface to promote even boiling and prevent bumping. After the ebulliometer was modified in this manner, a final series of measurements was made with a fresh sample of 1-pentanethiol that showed no evidence of decomposition, even at the highest temperatures studied. At the conclusions of these measurements, the difference in the boiling and condensation temperatures of the sample at a pressure of 149.4 mm. was found to be only 0.007°.

The results of the final series of measurements are tabulated in Table III. Two empirical equations have been selected to represent these data, an Antoine equation

$$\log_{10} p = 6.93311 - 1369.479/(t + 211.314) \quad (1)$$

and an equation of the form suggested by Cox⁵

$$\log_{10} P = A(1 - 399.797/T) \quad (2)$$

where

$$\log_{10} A = 0.85780 - 6.8478 \times 10^{-4}T + 6.0427 \times 10^{-7}T^2$$

In these equations, p is the vapor pressure in mm., P the vapor pressure in atmospheres, t the temperature in °C, and T the temperature in °K. The Antoine equation, with three empirical constants, is of a form convenient for numerical computation and is satisfactory for most purposes. The Cox equation, with four empirical constants, is of a form less convenient for numerical computation, but has the advantage of giving a more reliable extrapolation outside the range of experimental measurements. The differences between the observed values of the vapor pressure and those calculated from equations 1 and 2 are listed in the fourth and fifth columns of Table III. The normal boiling point given by either equation is 126.64°.

The heat of vaporization at 298.16°K. was computed from the vapor pressure data, using equation 2 and the exact form of the Clapeyron equation. The equation of state, $PV = RT + BP$, was assumed for the vapor; the second virial coefficient, B , was estimated to be -3.61 at 298.16°K. by a correlation similar to that given in a recent publication⁶ from this Laboratory, but revised in the light of additional data for sulfur compounds. The value obtained for the heat of vaporization at 298.16°K. was 9825 cal. mole⁻¹ with an estimated uncertainty of ± 50 cal. mole⁻¹ which includes the uncertainty arising from extrapolation of the vapor pressure equation outside the temperature range of the data from which it was derived.

S. S. Todd, W. N. Hubbard, J. C. Smith and H. M. Huffman, *ibid.*, **71**, 797 (1949).

(5) E. R. Cox, *Ind. Eng. Chem.*, **28**, 613 (1936).

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

(4) Guy Waddington, J. W. Knowlton, D. W. Scott, G. D. Oliver,

(6) D. W. Scott, H. L. Finkle, M. E. Gross, G. B. Guthrie and H. M. Huffman, *THIS JOURNAL*, **72**, 2424 (1950).

TABLE III

VAPOR PRESSURE OF 1-PENTANETHIOL				
Boiling point, °C.		Vapor pressure mm.	$p^{\text{obsd}} - p^{\text{calcd}}$	
Water	Pentanethiol		Eq. 1	Eq. 2
60.000	76.470	149.41	-0.01	-0.01
65	82.569	187.57	.00	+ .01
70	88.721	233.72	- .01	+ .01
75	94.918	289.13	+ .01	+ .02
80	101.167	355.22	- .01	- .01
85	107.457	433.56	+ .06	+ .06
90	113.802	525.86	+ .05	+ .02
95	120.193	633.99	+ .06	+ .05
100	126.638	760.00	- .01	- .03
105	133.131	906.06	- .11	- .09
110	139.671	1074.6	- .1	.0
115	146.255	1268.0	- .1	+ .1
120	152.896	1489.1	- .2	.0
125	159.580	1740.8	.0	+ .2
130	166.314	2026.0	+ .3	+ .3

The Entropy in the Liquid and Ideal Gas States.—The calorimetric and vapor pressure data have been used to calculate the entropy of 1-pentanethiol in the liquid and ideal gas states at 298.16°K. Table IV summarizes the results.

TABLE IV

1-PENTANETHIOL MOLAL ENTROPY, CAL. DEG. ⁻¹		
0-12°K.	Debye, 6° freedom, $\theta = 134.9$	0.218
12-197.46°	Solid, graphical $\int C_{\text{satd}} d \ln T$	33.863
197.46°	Fusion, 4190/197.46	21.219
197.46-298.16°	Liquid, graphical $\int C_{\text{satd}} d \ln T$	18.882
Entropy (± 0.15) of liquid at 298.16°K.		74.18
Vaporization, 9825/298.16		32.95
Compression, $R \ln p/760$		- 7.95
Gas imperfection		0.00
Entropy (± 0.35) of ideal gas at 1 atm. and 298.16°K.		99.18

Discussion

The stated purpose of this investigation is to provide data that will guide the computations by incremental methods of the thermodynamic functions S° , $(H_T^\circ - H_0^\circ)$, $(H_0^\circ - F_T^\circ)/T$ and C_p° for the *n*-alkane thiols of interest. Reliable computation of such functions is not yet possible on the basis of existing data. However, it is of interest to compare the difference between ideal gas entropies for ethanethiol² and 1-pentanethiol with that between propane and *n*-hexane, which differ from the two thiols by the replacement of an SH group by a CH₃ group. The experimental ideal gas entropies at 298.16°K. for ethanethiol² and 1-pentanethiol (this paper) are 70.77 and 99.18 cal. deg.⁻¹ mole⁻¹, respectively. The corresponding values for propane⁷ and *n*-hexane⁸ are 64.51 and 92.93 cal. deg.⁻¹ mole⁻¹. The differences between the respective pairs are 28.41 and 28.42 cal. deg.⁻¹ mole⁻¹. This excellent agreement is undoubtedly partly fortuitous but suggests that similar incremental relationships exist between thiols as in hydrocarbons of related structure. Because of the extensive thermodynamic information already available for hydrocarbons, this circumstance will facilitate the compilation of tables of thermodynamic functions for the alkanethiols.

(7) (a) K. S. Pitzer, *Ind. Eng. Chem.*, **36**, 829 (1944); (b) Kemp and Egan, *THIS JOURNAL*, **60**, 1521 (1938).

(8) Liquid entropy 298.16°K. = 70.76 cal. deg.⁻¹ mole⁻¹, D. R. Douslin and H. M. Huffman, *ibid.*, **68**, 1704 (1946); entropy of vaporization 298.16°K. = 25.29 cal. deg.⁻¹ mole⁻¹, from data of N. S. Osborne and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **39**, 453 (1947); compression, $R \ln (p/760) = -3.21$ cal. deg.⁻¹ mole⁻¹; gas imperfection, $(\partial B/\partial T)_P = 0.09$ cal. deg.⁻¹ mole⁻¹, B (defined by $PV = RT + BP$) = -455 - 28.5 exp 1175/T cc. mole⁻¹, previously unpublished but based on $(\partial C_p/\partial p)_T$ and ΔH_{vap} data of G. Waddington and D. R. Douslin, *THIS JOURNAL*, **69**, 2275 (1947).

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Infrared Spectra of Organic Compounds Exhibiting Polymorphism

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It has been shown that infrared spectrometry is a new and useful tool for the study of polymorphism. Examples of its use have been cited, including a series of five phthalocyanines and three other crystalline organic compounds. The polymorphic forms of the latter, while giving identical spectra in solution, showed as crystals marked differences in infrared absorption.

Little has been published about infrared absorption by polymorphic modifications of the same compound. If infrared spectra of a compound's crystal modifications were found to be identical, one could confidently conclude that transition from one form to the other does not involve intramolecular changes. If, on the other hand, the spectra of polymorphic crystal modifications were found to be not the same, one could not entirely dismiss the possibility of a transition, accompanied by intramolecular shifts of linkages in the latticed molecules. Dissimilarity of vibrations in crystal modifications of the same compound could be caused by mere difference in latticing, but it could also be due to a

combination of two causes, different latticing together with different linkages inside the latticed molecules.

Actually, we discovered appreciable differences between infrared absorption spectra of diverse crystal modifications of the same compound. Indeed, the spectra could be thought to be those of separate compounds. This was the case with phthalocyanines, 2-chloro-4-nitrobenzoic acid, allylthiourea and anthranilic acid. Hence, it is difficult to identify a compound in its crystalline phase by reference to known spectra, if the latter do not include the spectra of all polymorphic forms of the compound.