The value of S_{satd}(liq.) from Table XI, and values of the entropy of graphite,[10] hydrogen[10] and fluorine[11] were used to compute values of the entropy, free energy and logarithm of the equilibrium constant of formation of liquid fluorobenzene.

$$6C(graphite) + 5/2H_2(g) + 1/2F_2(g) = C_6H_5F(liq)$$

$$\Delta Hf°_{298.16} = -34.7_5 \text{ kcal. mole}^{-1}$$

$$\Delta Sf°_{298.16} = -61.19 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta Ff°_{298.16} = -16.5_1 \text{ kcal. mole}^{-1} \qquad \log_{10} Kf = +12.1_0$$

BARTLESVILLE, OKLA.

[CONTRIBUTION NO. 59 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Benzenethiol: Thermodynamic Properties in the Solid, Liquid and Vapor States; Internal Rotation of the Thiol Group[1]

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Studies of benzenethiol by low temperature calorimetry, comparative ebulliometry, flow calorimetry and combustion calorimetry led to values of the standard entropy, heat capacity and heat of formation of the vapor. The calorimetric results were used with molecular structure information to evaluate the contributions of internal rotation and anharmonicity to the thermodynamic functions. Internal rotation of the thiol group is essentially free, and the contributions of anharmonicity are significant even at ordinary temperatures. Thermodynamic functions were computed by the methods of statistical mechanics for selected temperatures between 0 and 1000°K. Values of the heat, free energy and logarithm of the equilibrium constant of formation were computed for the same temperatures. The experimental studies provided the following information: Values of the heat capacity for the solid (12–258°K.), the liquid [$C_{satd} = 34.985 + 2.175 \times 10^{-3} T + 6.500 \times 10^{-5} T^2$ cal. deg.$^{-1}$ mole^{-1} (258–375°K.)] and the vapor [$C_p^\circ = -5.541 + 0.12212 T - 6.577 \times 10^{-5} T^2$ cal. deg.$^{-1}$ mole^{-1} (427–500°K.)]; the heat of fusion [2736 cal. mole^{-1}] at the triple point [258.27 ± 0.05°K.]; the entropy of the liquid at 298.16°K. [$S_{satd} = 53.25$ cal. deg.$^{-1}$ mole^{-1}]; the heat of vaporization [$\Delta H\text{v} = 15808.5 - 13.620 T - 1.586 \times 10^{-3} T^2$ cal. mole^{-1} (375–417°K.)]; the second virial coefficient in the equation of state, $PV = RT(1 + B/V)$, [$B = -588 - 28.50 \exp(1500/T)$ cc. mole^{-1} (375–500°K.)]; the vapor pressure [$\log_{10} p(\text{mm.}) = 6.99019 - 1529.454/(t + 203.048)$ (114–212°)]; and the standard heat of formation [$6C(graphite) + 3H_2(g) + S(rhombic) = C_6H_5SH$ (liq), $\Delta Hf°_{298.16} = +15.02 \pm 0.27$ kcal. mole^{-1}]. The heat capacity of solid benzenethiol has a λ-like anomaly near 128°K.

Introduction

An integrated experimental and computational program is conducted in this Laboratory to obtain thermodynamic data for organic sulfur compounds of interest in petroleum technology. As part of this program a comprehensive investigation was made of the thermodynamic properties of benzenethiol (thiophenol). Experimental studies were made by the methods of low temperature calorimetry, comparative ebulliometry, flow calorimetry and combustion calorimetry. The detailed results of these studies are given later in the Experimental section. The most significant results were values of the entropy, heat capacity and heat of formation of benzenethiol vapor, as given in Table I. The values of entropy and heat capacity were used with an assignment of the fundamental vibrational frequencies of the molecule to evaluate the contributions of internal rotation and anharmonicity to the thermodynamic functions. The functions $(F° - H_0^\circ)/T$, $(H° - H_0^\circ)/T$, $H° - H_0^\circ$, $S°$ and C_p° were computed by the methods of statistical mechanics for selected temperatures between 0 and 1000°K. Values of the appropriate thermodynamic functions were used with the experimental value of the heat of formation to compute the heat, free energy and logarithm of the equilibrium constant of formation for the same selected temperatures. These calculations of the thermodynamic properties are discussed in detail in the next section.

TABLE I

OBSERVED AND CALCULATED THERMODYNAMIC PROPERTIES OF BENZENETHIOL VAPOR

T, °K.	Entropy, $S°$, cal. deg.$^{-1}$ mole^{-1} Obsd.	Calcd.	T, °K.	Heat capacity, C_p°, cal. deg.$^{-1}$ mole^{-1} Obsd.	Calcd.
375.24	86.98	86.96	427.20	34.63	34.62
394.74	88.57	88.56	448.20	35.97	35.98
407.34	89.59	89.59	473.20	37.53	37.52
416.90	90.36	90.37	500.20	39.08	39.08

$$6C(graphite) + 3H_2(g) + {}^1/_2 S_2(g) = C_6H_5SH(g)$$
$$\Delta Hf°_{298.16}(\text{obsd.}) = +11.24 \pm 0.29 \text{ kcal. mole}^{-1}$$

Calculation of Thermodynamic Properties

The Vibrational Assignment.—The calculation of thermodynamic functions by the methods of statistical mechanics required an assignment of the fundamental vibrational frequencies of the benzenethiol molecule. The assignment used for that purpose was based on the spectroscopic data in Table II.[2–4] The data of ref. 2 and 4 were obtained from samples of the same highly purified benzenethiol that was used in this research. The vibrational assignment is given in Table III. The benzenethiol molecule has approximately C_{2v} symmetry, and the vibrations, exclusive of the two associated with the S–H group, are classified according to C_{2v} symmetry in Table III. In the

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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) American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology, Catalog of Raman Spectral Data, Serial No. 228.

(3) K. W. F. Kohlrausch, "Ramanspektren," Akademische Verlagsgesellschaft, Becker & Erler, Leipzig, 1943, p. 280.

(4) American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology, Catalog of Infrared Spectral Data, Serial Nos. 1680 and 1681.

preceding paper[5] a vibrational assignment confirmed by accurate calorimetric values of vapor heat capacity is reported for the structurally related molecule, fluorobenzene. Most of the assignment for benzenethiol follows directly from simple analogy with that for fluorobenzene. Only vibrations 6a, 12, 7a, 18b, 11 and 16b undergo important changes in frequency with increasing mass of the substituent group on the benzene ring. These six frequencies are readily identified in the observed spectra by the Raman polarization, intensity and expected change of frequency with mass of the substituent. For two pairs of vibrations, 6a-16a and 8a-8b, the frequencies are not resolved in the observed spectra. The two vibrations associated with the S–H group have about the frequencies to be expected by analogy with the simple alkane thiols. The weak Raman lines and infrared bands of benzenethiol that are not assigned as fundamentals have plausible interpretations as binary sum or difference combinations.

TABLE II

THE VIBRATIONAL SPECTRA OF BENZENETHIOL, CM.$^{-1}$

Raman, liquid[a]	Infrared, liquid[b]	Interpretation
185 (2, 0.73)		b_2 fundamental
278 (2, 0.80)		b_1 fundamental
412 (4, 0.34)		a_1 & a_2 fundamentals
462 ($^1/_2$)	466 s	b_2 fundamental
516 (0)		$698 - 185 = 513$ A_2
615 (4, 0.69)	617 m	b_1 fundamental
662 (0?)		$1072 - 412 = 660$ B_1 or B_2
	689 s	b_2 fundamental
697 (5, 0.22)	699 m	a_1 fundamental
737 (2)	735 s	b_2 fundamental
	786 vw	$1480 - 698 = 782$ A_1
	796 vw	$185 + 616 = 801$ A_2
836 (1)	833 m	a_2 fundamental
844 (0)		$1026 - 185 = 841$ B_2
	872 vw	$412 + 464 = 876$ B_1 or B_2
904 (3)	898 s	b_2 fundamental
914 (5, 0.38)	915 s	C–S–H bending fundamental
	960 vw	$1582 - 616 = 966$ A_1 or B_1
	981 vw	$278 + 698 = 976$ B_1
991 (2)		b_2 fundamental
1000 (10) } 0.07	1003 m	a_1 fundamental
1024 (7) }	1027 s	a_1 fundamental
1070 (0)	1072 m	b_1 fundamental
1092 (7) } 0.20	1094 s	a_1 fundamental
1116 (6) }	1120 m	$412 + 698 = 1110$ A_1
1157 (6, dp)	1159 m	b_1 fundamental
1180 (4, p)	1185 m	a_1 fundamental
	1202 sh	$464 + 736 = 1200$ A_1
	1236 w	$2 \times 616 = 1232$ A_1
1272 (2, 0.47)	1272 w	b_1 fundamental
	1305 m	$278 + 1026 = 1304$ B_1
1328 (3)	1330 w	b_1 fundamental
	1370 sh	$278 + 1093 = 1371$ B_1
1381 (1)	1383 w	$2 \times 689 = 1378$
1441 (2)	1445 s	b_1 fundamental
1481 (2)	1479 s	a_1 fundamental
1527 (1)	1522 vw	$689 + 834 = 1523$ B_1
	1546 vw	$278 + 1272 = 1550$ A_1
1581 (10, 0.68)	1582 s	a_1 & b_1 fundamentals
[1600–2500 cm.$^{-1}$ region omitted]		
2566 (9)	2584 s	S–H stretching fundamental
	2778 w	$1329 + 1443 = 2772$ A_1
	2899 w	$1329 + 1582 = 2911$ A_1 or B_1
2954 (2)		$2 \times 1480 = 2960$ A_1
2996 (2)		$412 + 2575 = 2986$
3037 (4)		a_1 fundamental
3048 (12) } 0.37		b_1 fundamental
3056 (10) }		a_1 fundamental
	3086 s	b_1 fundamental
3150 (2)		a_1 fundamental
[3200–5000 cm.$^{-1}$ region omitted]		

[a] In parentheses are listed the relative intensity and depolarization factor. [b] Intensity designated by: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder

TABLE III

THE FUNDAMENTAL VIBRATIONAL FREQUENCIES OF BENZENETHIOL, CM.$^{-1}$

Species a_1		Species b_1		Species a_2		Species b_2	
6a	412	18b	278	16a	412[a]	11	185
12	698	6b	616	10a	834	16b	464
1	1002	15	1072	17a	970[b]	4	689
18a	1026	9b	1158			10b	736
7a	1093	3	1272			17b	901
9a	1182	14	1329			5	991
19a	1480	19b	1443				
8a	1582	8b	1582[a]				
13	3037	7b	3048	C–S–H bending	914		
2	3056	20b	3086				
20a	3150			S–H stretching	2575		

[a] Frequency used a second time. [b] Assumed same as in benzene.

The Moments of Inertia, Internal Rotation and Anharmonicity.—As the bond distances and angles of the benzenethiol molecule have not been determined experimentally, they were assumed to be the same as in the related molecules benzene[6] and methanethiol,[7] namely, C–C, 1.397 Å.; C–H, 1.084 Å.; C–S, 1.818 Å.; S–H, 1.329 Å.; C–S–H angle, 100° 16′; all other angles, 120°. For this model the product of the principal moments of inertia is 5.692×10^{-113} g.^{3} cm.^{6}, and the reduced moment of inertia for internal rotation is 2.741×10^{-40} g. cm.^{2} The calculation of moments of inertia was done by the general method of Kilpatrick and Pitzer.[8] The symmetry numbers are 1 for over-all rotation and 2 for internal rotation.

To compute the contributions of internal rotation and anharmonicity to the thermodynamic functions it was necessary to evaluate three parameters from the calorimetric values of entropy and heat capacity: V_0, the height of the potential barrier hindering internal rotation and the two parameters, ν and z, of the empirical anharmonicity function described in a previous publication.[9] The values selected were: $V_0 = 0$ (free internal rotation), $\nu = 490$ cm.$^{-1}$ and $z = 0.346$ cal. deg.$^{-1}$ mole^{-1}.

The conclusion that internal rotation is essentially unhindered in benzenethiol is not sur-

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(5) D. W. Scott, J. P. McCullough, W. D. Good, J. F. Messerly, R. E. Pennington, T. C. Kincheloe, I. A. Hossenlopp, D. R. Douslin and Guy Waddington, THIS JOURNAL, **78**, 5457 (1956).

(6) B. P. Stoicheff, *Can. J. Phys.*, **32**, 339 (1954).

(7) R. W. Kilb, *J. Chem. Phys.*, **23**, 1736 (1955).

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

(9) 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).

TABLE IV

THE MOLAL THERMODYNAMIC PROPERTIES OF BENZENETHIOL[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	15.44	15.44	$-\infty$
273.16	−64.33	14.08	3.845	78.41	23.08	11.54	24.51	−19.61
298.16	−65.60	14.91	4.447	80.51	25.07	11.24	25.71	−18.85
300	−65.70	14.98	4.493	80.68	25.22	11.22	25.80	−18.79
400	−70.49	18.50	7.400	88.99	32.76	10.16	30.83	−16.84
500	−75.00	22.01	11.00	97.00	39.07	9.34	36.09	−15.78
600	−79.30	25.29	15.17	104.59	44.13	8.72	41.50	−15.12
700	−83.43	28.28	19.80	111.71	48.23	8.27	47.00	−14.68
800	−87.39	30.99	24.79	118.38	51.59	7.95	52.55	−14.36
900	−91.17	33.44	30.10	124.61	54.41	7.76	58.15	−14.12
1000	−94.82	35.66	35.66	130.48	56.79	7.70	63.75	−13.93

[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 benzenethiol by the reaction: $6C(\text{graphite}) + 3H_2(g) + {}^1/_2S_2(g) = C_6H_5SH(g)$.

prising. The barrier to internal rotation of the methyl group in toluene is very low (V_0 about 500 cal. mole^{-1}),[10] and replacement of the methyl group with a thiol group would be expected to result in an even lower barrier. The contributions of anharmonicity to the thermodynamic functions of benzenethiol are significant even at the lower temperatures, 0.05 and 0.16 cal. deg.$^{-1}$ mole^{-1} in $S°$ and $C_p°$ at 298.16°K., and increase to 0.65 and 0.96 cal. deg.$^{-1}$ mole^{-1} in $S°$ and $C_p°$ at 1000°K.

The Thermodynamic Function.—The molecular structure parameters described in the preceding paragraphs were used to compute the values of the thermodynamic functions listed in columns 2–6 of Table IV.[11] Calculated values of $S°$ and $C_p°$ are compared with the experimental values in Table I. It is seen that the agreement is within 0.03% at each of the temperatures at which either $S°$ or $C_p°$ was determined experimentally.

The Heat, Free Energy and Equilibrium Constant of Formation.—The calculated values of the thermodynamic functions, the experimental value of $\Delta Hf°_{298.16}$ (Table I) and values of the thermodynamic functions of C(graphite)[12] $H_2(g)$[12] and $S_2(g)$[13] were used to compute values of $\Delta Hf°$, $\Delta Ff°$ and $\log_{10} Kf$ at selected temperatures from 0 to 1000°K. The computed values are listed in columns 7–9 of Table IV.

Experimental

In general, the experimental methods and manner of correlating the data were the same as described in the preceding paper on fluorobenzene.[5] Also the same definitions of units and values of the fundamental physical constants and atomic weights were used. The results for benzenethiol are reported here, with a discussion of only those experimental details unique to this investigation. Molal values are based on a molecular weight of 110.174 for benzenethiol.

The Material.—The benzenethiol used for low temperature calorimetry, comparative ebulliometry and combustion calorimetry was part of the Standard Sample of Sulfur Compound, API-USBM 23-5S, prepared and purified at the Laramie (Wyo.) Station of the Bureau of Mines. The purity of this sample, as determined by a calorimetric study of melting point as a function of fraction melted, was 99.98 ± 0.01 mole %. This sample was dried by passage of the vapor through anhydrous magnesium perchlorate before use in any experimental determinations. For flow calorimetry, which required a larger volume of material, a second sample of somewhat lower purity was used. The purity of the second sample, as determined by the time–temperature freezing point method at the Laramie Station, was 99.9 mole %. The samples were received in sealed ampoules with internal breakoff tips. Transfers by vacuum distillation before use assured the removal of any phenyl disulfide that may have formed during storage by reaction with traces of oxygen in the ampoules.

The Heat Capacity in the Solid and Liquid States.—The observed values of the heat capacity at saturation pressure, C_{satd}, are listed in Table V. Solid benzenethiol has a λ-type transition in the temperature range 110 to 135°K. The heat capacity peaks sharply at about 128°K. and then falls off precipitously to "normal" values. Heat capacity measurements over the range of anomalous behavior were made with smaller than normal temperature increments (listed in Table V) and corrections for curvature were applied to the values obtained. At other temperatures the usual temperature increments were employed (about 10% of the absolute temperature below 50°K. and 5 to 12° above 50°K.), and no corrections for curvature were necessary. As there was no detectable hysteresis or influence of thermal history on the measured values of heat capacity, the chronological sequence of the measurements is not indicated in Table V. The heat capacity of liquid benzenethiol may be represented by the empirical equation,

$$C_{\text{satd}}(\text{liq}) = 34.985 + 2.175 \times 10^{-3}T + 6.500 \times 10^{-5}T^2 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (1)$$

which represents the observed values between the melting point and 375°K. with a maximum deviation of 0.09%.

Heat of Fusion, Triple Point, Cryoscopic Constants and Purity of Sample.—Three determinations of the heat of fusion each gave the value 2736 cal. mole^{-1}.

The results of the usual melting point study are given in Table VI. The triple point temperature is 258.27 ± 0.05°K. The cryoscopic constants, $A = \Delta H_{\text{fusion}}/RT_{\text{T.P.}}^2 = 0.02064$ deg.$^{-1}$ and $B = 1/T_{\text{T.P.}} - \Delta C_{\text{fusion}}/2\Delta H_{\text{fusion}} = 0.00255$ deg.$^{-1}$, were evaluated from the values of $T_{\text{T.P.}}$ (258.27°K.), ΔH_{fusion} (2736 cal. mole^{-1}) and ΔC_{fusion} (7.23 cal. deg.$^{-1}$ mole^{-1}). The concentration of liquid-soluble, solid-insoluble impurity in the benzenethiol sample was found to be 0.02 ± 0.01 mole %.

The Thermodynamic Properties in the Solid and Liquid States.—Values of the free energy function, heat content function, heat content, entropy and heat capacity at selected temperatures between 10 and 380°K. are given in Table VII. The thermodynamic properties at 10°K. were computed from a Debye function for 4.2 degrees of fredom with $\theta = 96.2°$; these parameters were evaluated from the heat capacity data between 13 and 20°K. Corrections for the effects

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[10] K. S. Pitzer and D. W. Scott, THIS JOURNAL, **65**, 803 (1943).

[11] The vibrational contributions were computed by use of the tables of H. L. Johnston, L. Savedoff and J. Belzer, "Contributions to the Thermodynamic Functions by a Planck-Einstein Oscillator in One Degree of Freedom," Office of Naval Research, Department of the Navy, Washington, D. C., July, 1949; the empirical anharmonicity contributions were computed by use of the tables of R. E. Pennington and K. A. Kobe, *J. Chem. Phys.*, **22**, 1442 (1954).

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

[13] W. H. Evans and D. D. Wagman, *ibid.*, **49**, 141 (1952).

of premelting have been applied to the "smoothed" data recorded in Table VII.

TABLE V

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

T, °K.[a]	C_{satd}[b]	T, °K.[a]	ΔT[c]	C_{satd}[b]	T, °K.[a]	C_{satd}[b]
Crystals		85.65		13.306	175.82	23.368
		91.29		13.949	182.43	23.946
12.87	1.349	91.50		13.968	188.25	24.415
13.41	1.501	96.46		14.542	195.01	25.030[e]
13.89	1.643	101.90		15.216	202.64	25.758[e]
14.65	1.856	107.53		16.005	210.58	26.553[e]
15.09	1.957	112.73	3.259	16.859[d]	218.31	27.405[e]
16.29	2.278	113.25	5.507	16.960[d]	225.85	28.276[e]
16.56	2.347	115.94	3.158	17.486[d]	233.64	29.282[e]
18.25	2.810	119.05	3.052	18.268[d]	239.97	30.024[e]
18.30	2.822	119.11	6.219	18.285[d]	241.66	30.405[e]
20.16	3.325	122.04	2.932	19.239[d]	244.40	30.804[e]
20.48	3.406	123.51	2.227	19.848[d]	249.41	31.782[e]
22.39	3.919	124.89	2.778	20.64[d]		
22.79	4.018	125.02	5.610	20.78[d]	Liquid	
24.97	4.574	125.68	2.118	21.19[d]		
25.30	4.652	127.30	1.135	23.00[d]	262.47	40.07
27.86	5.265	128.29	0.833	23.83[d]	267.83	40.25
28.14	5.329	129.05	0.703	20.18[d]	273.94	40.47
31.28	6.003	129.88	0.946	19.914[d]	274.92	40.51
34.91	6.739	129.94	0.950	19.851[d]	282.82	40.80
39.12	7.487	130.26	2.835	19.829[d]	284.60	40.86
43.74	8.223	130.89	0.949	19.842[d]	295.06	41.27
48.90	8.955	132.15	1.578	19.878[d]	302.74	41.60
53.46	9.559	133.09	2.828	19.922[d]	312.21	41.99
54.11	9.642	134.40	2.937	20.007[d]	322.05	42.43
57.44	10.049	136.60		20.172	332.26	42.90
62.46	10.670	141.03		20.532	342.35	43.35
67.99	11.304	146.13		20.957	352.35	43.82
73.60	11.919	152.48		21.472	363.13	44.34
79.49	12.581	159.58		22.049	374.50	44.90
		167.00		22.649		

[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] ΔT is the temperature increment of each heat capacity measurement. [d] Corrected for curvature. [e] Not corrected for the effects of premelting caused by impurities.

TABLE VI

BENZENETHIOL: MELTING POINT SUMMARY

Triple point temperature: 258.27 ± 0.05°K.; cryoscopic constant, $A = 0.02064$ deg.$^{-1}$; impurity = 0.02 ± 0.01 mole %.

Melted, %	$1/F$[a]	T, °K. Obsd.	T, °K. Graph.[c]
11.83	8.451	258.2066	258.1932
26.46	3.780	258.2391	258.2359
50.94	1.963[b]	258.2525[b]	258.2525
70.55	1.417	258.2575	258.2575
90.11	1.110[b]	258.2603[b]	258.2603
100.00	1.000		258.2613
Pure	0.000		258.2704

[a] Reciprocal of fraction melted. [b] A straight line through these points was extrapolated to $1/F = 0$ to obtain the triple point temperature. [c] Temperatures read from the straight line of footnote b.

TABLE VII

THE MOLAL THERMODYNAMIC PROPERTIES OF BENZENETHIOL IN THE SOLID AND LIQUID STATES[a]

T, °K.	$(F_{satd} - H_0^0)/T$, cal. deg.$^{-1}$	$(H_{satd} - H_0^0)/T$, cal. deg.$^{-1}$	$H_{satd} - H_0^0$, cal.	S_{satd}, cal. deg.$^{-1}$	C_{satd} cal. deg.$^{-1}$
			Crystals		
10	0.061	0.180	1.802	0.241	0.704
15	.197	.549	8.241	.746	1.942
20	.424	1.064	21.287	1.488	3.278
25	.722	1.640	40.99	2.362	4.579
30	1.074	2.228	66.85	3.302	5.730
35	1.460	2.803	98.09	4.263	6.753
40	1.871	3.354	134.15	5.225	7.644
45	2.296	3.874	174.34	6.170	8.414
50	2.730	4.363	218.15	7.093	9.102
60	3.606	5.261	315.6	8.867	10.369
70	4.479	6.075	425.2	10.554	11.525
80	5.340	6.825	546.0	12.165	12.642
90	6.185	7.536	678.2	13.721	13.800
100	7.015	8.220	822.0	15.235	14.973
110	7.830	8.896	978.5	16.726	16.396
115	8.233	9.241	1062.7	17.474	17.298
120	8.633	9.601	1152.1	18.234	18.543
122	8.793	9.753	1189.8	18.546	19.220
124	8.954	9.912	1229.1	18.866	20.104
126	9.113	10.084	1270.6	19.197	21.508
128	9.274	10.284	1316.3	19.558	25.594
130	9.435	10.450	1358.5	19.885	19.867
132	9.595	10.593	1398.2	20.188	19.872
140	10.235	11.138	1559.3	21.373	20.446
150	11.026	11.786	1767.9	22.812	21.267
160	11.805	12.405	1984.7	24.210	22.081
170	12.575	12.998	2209.6	25.573	22.893
180	13.335	13.570	2442.6	26.905	23.710
190	14.083	14.126	2683.9	28.209	24.565
200	14.822	14.671	2934.1	29.493	25.491
210	15.55	15.210	3194	30.76	26.486
220	16.27	15.747	3464	32.01	27.579
230	16.98	16.286	3745	33.26	28.760
240	17.68	16.833	4040	34.52	30.08
250	18.38	17.391	4347	35.77	31.47
258.27	18.95	17.862	4613	36.82	32.68
			Liquid		
258.27	18.95	28.456	7349	47.41	39.91
260	19.14	28.533	7418	47.68	39.97
270	20.23	28.963	7820	49.19	40.32
273.16	20.57	29.095	7947	49.66	40.44
280	21.29	29.376	8225	50.67	40.69
290	22.33	29.772	8633	52.10	41.06
298.16	23.16	30.08	8970	53.25	41.40
300	23.34	30.15	9046	53.50	41.47
310	24.34	30.52	9463	54.87	41.89
320	25.31	30.89	9884	56.20	42.33
330	26.27	31.24	10310	57.51	42.78
340	27.21	31.59	10740	58.80	43.24
350	28.13	31.92	11175	60.06	43.70
360	29.03	32.26	11614	61.30	44.19
370	29.92	32.59	12059	62.51	44.67
380	30.79	32.91	12508	63.71	45.15

[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.

The λ-type transition of solid benzenethiol corresponds to an "excess" enthalpy of about 40 cal. mole^{-1} above the "normal" heat capacity curve; the associated entropy change is therefore about 0.3 cal. deg.$^{-1}$ mole^{-1}. The transition may result from non-isothermal disordering of the SH groups in the crystal. For complete disordering, the entropy would increase by $R \ln 2 = 1.38$ cal. deg.$^{-1}$ mole^{-1}. However, the process responsible for the transition may occur over a wide range of temperature, so that only part of the total enthalpy and entropy change occurs at temperatures near the lambda point.

Low temperature studies of benzenethiol were made between 90 and 300°K. by Parks, Todd and Moore.[14] The average deviation of these workers' heat capacity data from

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(14) G. S. Parks, S. S. Todd and W. K. Moore, THIS JOURNAL, **58**, 398 (1936).

the results of this research is 0.8% and the maximum deviation is 1.9% at 300°K. The observation by Parks, *et al.*, of a heat capacity anomaly between 120 and 130°K. and their reported values of the triple point temperature (258.2°K.), heat of fusion (2743 cal. mole^{-1}) and entropy of the liquid at 298.16°K. (52.6 cal. deg.$^{-1}$ mole^{-1}) are all in reasonable accord with the results of this research.

The Vapor Pressure.—The vapor pressure data for benzenethiol are listed in Table VIII. The Antoine and Cox equations selected to represent these results are

$$\log_{10} p(\text{mm}). = 6.99019 - 1529.454/(t + 203.048) \quad (2)$$

$$\log_{10} P(\text{mm.}) = \text{A}(1 - 442.298/T) \quad (3)$$

$$\log_{10} \text{A} = 0.873700 - 6.4975 \times 10^{-4}\, T + 5.2309 \times 10^{-7}\, T^2$$

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 VIII. The normal boiling point, calculated from either equation, is 169.14° (442.30°K.).

TABLE VIII

THE VAPOR PRESSURE OF BENZENETHIOL

Boiling point, °C. Water	Benzenethiol	p (obsd), mm.	p (obsd) − p (calcd), mm. Eq. 2	Eq. 3
60.000	114.543	149.41	0.00	0.00
65	121.191	187.57	+ .01	+ .02
70	127.897	233.72	− .01	.00
75	134.649	289.13	− .02	− .01
80	141.447	355.22	+ .01	.00
85	148.294	433.56	+ .04	+ .02
90	155.194	525.86	+ .01	− .01
95	162.140	633.99	+ .03	.00
100	169.137	760.00	+ .02	+ .02
105	176.188	906.06	− .09	− .07
110	183.278	1074.6	+ .1	+ .1
115	190.426	1268.0	− .1	+ .1
120	197.623	1489.1	− .1	.0
125	204.867	1740.8	.0	+ .1
130	212.160	2026.0	+ .2	.0

The Heat of Vaporization, Vapor Heat Capacity and Effects of Gas Imperfection.—In the studies by flow calorimetry, unusual precautions were taken to exclude air from the system because benzenethiol is oxidized to phenyl disulfide by oxygen. Despite these precautions, when the system was washed out with carbon disulfide at the conclusion of the experiments with benzenethiol about 0.6 g. of nonvolatile material was recovered. Part of this appeared to be phenyl disulfide and the rest may have been mercaptide from corrosion of metal parts with which the sample came into contact. Contamination of the sample with 0.6 g. of *non-volatile* impurity would have produced a negligible effect on the heat of vaporization and vapor heat capacity data. Determination of the heat of vaporization at $^1/_4$ atm. at the conclusion of the experiments gave results insignificantly different from those obtained at the beginning of the study when the sample was presumably uncontaminated.

The experimental values of the heat of vaporization are given in Table IX and the experimental values of vapor heat capacity in Table X. No measurements were made at pressures greater than $^1/_2$ atm. (boiling point 416.90°K.), as soft-soldered connections on the vaporizer might have been damaged by higher temperatures. The estimated accuracy uncertainties in ΔHv and C_p° are 0.1 and 0.2%, respectively. Equation 4, which represents the experimental values of ΔHv within 1 cal. mole^{-1}, was derived for interpolation in the temperature range of the measurements (375 to 417°K.)

$$\Delta H\text{v} = 15808.5 - 13.620T - 1.586 \times 10^{-3}\, T^2, \quad \text{cal. mole}^{-1} \quad (4)$$

Equation 5 represents the experimental values of C_p° within 0.01 cal. deg.$^{-1}$ mole^{-1}.

$$C_p^\circ = -5.541 + 0.12212\, T - 6.577 \times 10^{-5}\, T^2 \quad \text{cal. deg.}^{-1}\ \text{mole}^{-1} \quad (5)$$

The effects of gas imperfection were correlated by the procedure described in the preceding paper,[5] and the results of the correlation were used to obtain the "observed" values of C_p° from the experimental values of C_p at finite pressures. The empirical equation obtained for B, the second virial coefficient in the equation of state, $PV = RT(1 + B/V)$, is

$$B = -588 - 28.50 \exp(1500/T) \quad \text{cc. mole}^{-1}\ (375\text{–}500\,°\text{K.}) \quad (6)$$

This equation for B is probably less reliable than usual because of the more limited pressure range over which data were obtained. Comparisons of "observed" values of B and C_p(0.500 atm.) − C_p° with those calculated from eq. 6 are given in Tables IX and X, respectively.

TABLE IX

THE MOLAL HEAT OF VAPORIZATION AND SECOND VIRIAL COEFFICIENT OF BENZENETHIOL

T, °K.	P, atm.	ΔHv, cal.	$B_{\text{obsd.}}$, cc.	$B_{\text{calcd.}}$, cc.[a]
375.24	0.125	10475[b]	−2100	−2140
394.74	.250	10184 ± 4[c]	−1905	−1862
407.34	.375	9997 ± 5[c]	−1730	−1720
416.90	.500	9855 ± 3[c]	−1609	−1629

[a] Calculated with eq. 6. [b] Single determination. [c] Maximum deviation from the mean of three or more deterns.

TABLE X

THE MOLAL HEAT CAPACITY OF BENZENETHIOL IN CAL. MOLE^{-1}

T, °K.	427.20	448.20	473.20	500.20
C_p (0.500 atm.)	35.176	36.393	37.805	39.295
C_p (0.250 atm.)	34.899	36.176	37.667	39.188
C_p° (obsd.)	34.63	35.97	37.53	39.08
[C_p (0.500 atm.) − C_p°] (obsd.)	0.55	0.42	0.27	0.22
[C_p (0.500 atm.) − C_p°] (calcd.)[a]	0.55	0.41	0.29	0.21

[a] Calculated with eq. 6.

The Entropy in the Ideal Gaseous State.—The entropy in the ideal gaseous state at 1 atm. pressure was calculated from results given in the foregoing sections. The calculations are summarized in Table XI.

TABLE XI

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

0–10°K.	Debye extrapolation[a]	0.241
10–258.27°	Crystals, numerical $\int C_{\text{satd}}\, d \ln T$	36.581
258.27°	Fusion, 2736/258.27	10.594
258.27–298.16°	Liquid, numerical $\int C_{\text{satd}}\, d \ln T$	5.834
S_{satd}(liq.), 298.16°K. (±0.10)[b]		53.25

T, °K.	375.24	394.74	407.34	416.90
S_{satd}(liq.)	63.15[c]	65.45[d]	66.91[d]	67.99[d]
$\Delta H\text{v}/T$[e]	27.91	25.80	24.54	23.64
S(ideal) − S(real)[f]	0.05	0.07	0.09	0.11
$R \ln (p/760)$[g]	−4.13	−2.75	−1.95	−1.38
S° (obsd.) (±0.15)[b]	86.98	88.57	89.59	90.36

[a] 1.4 $D(96.2/T)$. [b] Estimated accuracy uncertainty. [c] Interpolated from Table VII. [d] Extrapolated by use of eq. 1. [e] Entropy of vaporization. [f] Entropy of gas imperfection from eq. 3 and 6. [g] Entropy of compression from eq. 3.

The Heats of Combustion and Formation and Related Properties.—The heats of combustion and formation of benzenethiol were determined by the rotating-bomb method of combustion calorimetry.[15] The samples were contained in Pyrex ampoules. Ten grams of water was initially added to the bomb, and the air originally present in the bomb was not removed when the bomb was charged with oxygen. Each combustion was initiated at 23.00°, and the quantities of

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(15) W. N. Hubbard, C. Katz and G. Waddington, *J. Phys. Chem.*, **58**, 142 (1954).

TABLE XII

BENZENETHIOL: THE ENERGY OF THE IDEALIZED COMBUSTION REACTIONS[a,b]

m' (Benzenethiol), g.	0.86950	0.81765	0.81634	0.84014	0.84853	0.87084	0.87096	0.88145	0.88475
$\Delta t_c = t_f - t_i - \Delta t_{cor}$, deg.	1.99957	1.99895	1.99936	2.00015	1.99738	1.99990	1.99967	2.00056	1.99864
$\mathcal{E}$ (calor.) $(-\Delta t_c)$, cal.	−7816.5	−7814.1	−7815.7	−7818.8	−7808.0	−7817.8	−7816.9	−7820.4	−7812.9
$\mathcal{E}$ (cont.)$(-\Delta t_c)$,[c] cal.	−27.5	−27.5	−27.5	−27.5	−27.5	−27.5	−27.5	−27.5	−27.5
ΔE_{ign}, cal.	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
ΔE^f_{dec} ($HNO_3 + HNO_2$), cal.	7.8	9.6	7.6	8.8	6.6	7.7	8.7	9.2	6.6
ΔE, cor. to st. states,[d] cal.	4.8	5.0	5.0	4.9	4.9	4.8	4.8	4.8	4.8
$-n'' \Delta Ec°$ (auxiliary oil), cal.	503.4	934.7	947.7	751.7	673.4	491.5	488.8	403.1	371.8
$-n''' \Delta Ec°$ (fuse), cal.	15.9	15.5	15.3	15.4	15.3	15.7	16.1	15.4	15.7
$n' \Delta Ec°$ (benzenethiol), cal.	−7310.7	−6875.4	−6866.2	−7064.1	−7133.9	−7324.2	−7324.6	−7414.0	−7440.1
$\Delta Ec°/M$ (benzenethiol), cal. g.$^{-1}$	−8407.9	−8408.7	−8411.0	−8408.2	−8407.3	−8410.5	−8409.8	−8411.1	−8409.3

Average value and standard deviation of the mean: 8409.3 ± 0.5 cal. g.$^{-1}$.

[a] The symbols and abbreviations in this table are those used in ref. 16, except as noted. The values of $\Delta Ec°$ for the auxiliary oil and the fuse are those used in ref. 15. [b] Auxiliary data: $\mathcal{E}$(calor.) = 3909.11 cal. deg.$^{-1}$; V(bomb) = 0.347 l.; physical properties of benzenethiol at 25°—ρ = 1.073 g. ml.$^{-1}$, $(\partial E/\partial P)_T$ = −0.006 cal. g.$^{-1}$ atm.$^{-1}$, c = 0.376 cal. deg.$^{-1}$ g.$^{-1}$. [c] $\mathcal{E}^i$(cont.)$(t_i - 25°) + \mathcal{E}^f$(cont.)$(25° - t_f + \Delta t_{cor})$. [d] Items 81-85, incl., 87-91, incl., 93 and 94 of the computation form of ref. 16.

benzenethiol and auxiliary oil (Sample USBM-P3a) were chosen to produce a temperature rise of about 2°. Corrections to standard states[16] were applied to the results of all calorimetric experiments. The energy equivalent of the calorimetric system, $\mathcal{E}$(calor.), was determined by combustion of benzoic acid (National Bureau of Standards Sample 39g). The calorimetric results are summarized in Table XII. The experimental value of $\Delta Ec°/M$ applies to the idealized combustion reaction (eq. 7) at 298.16°K.

$$C_6H_5SH(liq) + 9O_2(g) + 73H_2O(liq) = 6CO_2(g) + H_2SO_4{\cdot}75H_2O(liq) \quad (7)$$

$$\Delta Ec°_{298.16} = -926.49 \pm 0.15^{17} \text{ kcal. mole}^{-1}$$

$$\Delta Hc°_{298.16} = -928.27 \pm 0.15^{17} \text{ kcal. mole}^{-1}$$

Combustion experiments had previously been done with mixtures of rhombic sulfur and auxiliary oil chosen to give nearly the same final state of the bomb process as the experiments with benzenethiol. From these experiments, the heat of combustion of rhombic sulfur according to eq. 8 was determined.

$$S(rhombic) + 3/2O_2(g) + 76H_2O(liq) = H_2SO_4{\cdot}75H_2O(liq)$$

$$\Delta Hc°_{298.16} = -143.98 \pm 0.22^{17} \text{ kcal. mole}^{-1} \quad (8)$$

The values of $\Delta Hc°_{298.16}$ for benzenethiol and rhombic sulfur, and the values of the heat of formation of carbon dioxide and water,[12] were used to compute the heat of formation of benzenethiol. Determination of the heats of combustion of benzenethiol and rhombic sulfur under nearly identical conditions had the advantage that any systematic errors, if present, would largely cancel in the computation of the heat of formation. Values of the entropy of benzenethiol (Table XI), graphite,[12] hydrogen[12] and rhombic sulfur[18] were used to compute the entropy, free energy and logarithm of the equilibrium constant of formation of benzenethiol.

$$6C(graphite) + 3H_2(g) + S(rhombic) = C_6H_5SH(liq) \ (8)$$

$$\Delta Hf°_{298.16} = +15.02 \pm 0.27^{17} \text{ kcal. mole}^{-1}$$

$$\Delta Sf°_{298.16} = -56.17 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta Ff°_{298.16} = 31.77 \text{ kcal. mole}^{-1} \qquad \log_{10} Kf°_{298.16} = -23.23$$

The heat of vaporization of benzenethiol at 298.16°K. was estimated in three ways: (a) by extrapolation of eq. 4 for ΔHv, (b) from the Clapeyron equation by using eq. 3 and 6, and (c) from a thermodynamic network that utilized the thermodynamic functions of Table IV. The estimated values were 11.61, 11.59 and 11.64 kcal. mole^{-1}, respectively. The value from the thermodynamic network was selected as the most reliable. The standard heat of vaporization at 298.16°K., $\Delta Hv°$, does not differ significantly from the heat of vaporization to the real gas and was taken to be 11.64 ± 0.05 kcal. mole^{-1}. The foregoing value of $\Delta Hv°$ and the value of $S°$ for benzenethiol vapor from Table IV were used to compute the heat, free energy, entropy and logarithm of the equilibrium constant of formation of benzenethiol vapor.

$$6C(graphite) + 3H_2(g) + S(rhombic) = C_6H_5SH(g) \quad (9)$$

$$\Delta Hf°_{298.16} = 26.66 \pm 0.28^{17} \text{ kcal. mole}^{-1}$$

$$\Delta Sf°_{298.16} = -28.91 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta Ff°_{298.16} = 35.28 \text{ kcal. mole}^{-1} \qquad \log_{10} Kf°_{298.16} = -25.89$$

The heat of formation of $S_2(g)$ from rhombic sulfur[13] was used to compute the heat of formation of benzenethiol vapor from $S_2(g)$ according to the equation

$$6C(graphite) + 3H_2(g) + 1/2S_2(g) = C_6H_5SH(g)$$

$$\Delta Hf°_{298.16} = +11.24 \pm 0.29^{17} \text{ kcal. mole}^{-1}$$

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(16) W. N. Hubbard, D. W. Scott and G. Waddington, Chapter V, "Experimental Thermochemistry," F. D. Rossini editor, Interscience Publishers, Inc., New York, N. Y., 1956, pp. 75-128.

(17) "Uncertainty interval" equal to twice the final "over-all" standard deviation. See F. D. Rossini and W. E. Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

(18) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," N. B. S. Circular 500, 1952, Series 1, Table 14-1.