dynamic properties at high temperature are listed below.

$H_T - H_{298.16}$

β: $54.90T + 6.452 \times 10^{-3}T^2 + 12.73 \times 10^5T^{-1} - 21{,}210$ ($\pm 0.2\%$; 298.16 to 1413.16°K.)

α: $76.111\ T - 35{,}700$ ($\pm 0.1\%$; 1413.16 to 1626.16°K.)

Liq: $96.854T - 45{,}330$ ($\pm 0.1\%$; 1626.16 to 1700°K.)

$S_T - S_{298.16}$

β: $126.412 \log T + 12.904 \times 10^{-3}T + 6.365 \times 10^5T^{-2} - 323.808$ (298.16 to 1413.16°K.)

α: $175.25 \log T - 457.97$ (1413.16 to 1626.16°K.)

Liq: $223.02 \log T - 596.52$ (1626.16 to 1700°K.)

C_p

β: $54.90 + 12.904 \times 10^{-3}T - 12.73 \times 10^5T^{-2}$ (298.16 to 1413.16°K.)

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[CONTRIBUTION NO. 61 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR]

Ethanethiol and 2-Thiapropane: Heats of Formation and Isomerization; The Chemical Thermodynamic Properties from 0 to 1000°K.[1]

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Experimental and computational investigations of ethanethiol and 2-thiapropane were made to supply previously lacking information needed for complete tables of chemical thermodynamic properties. Experimental results included values of heat of formation, $\Delta Hf°_{298.16}$ (liq.), for ethanethiol (-17.61 kcal. mole^{-1}) and 2-thiapropane (-15.64 kcal. mole^{-1}); heat of vaporization of 2-thiapropane, $\Delta Hv = 9087 - 4.1794\ T - 1.3860 \times 10^{-2}\ T^2$, cal. mole^{-1} (275 − 310°K.); vapor heat capacity of 2-thiapropane, $Cp° = 5.628 + 4.9990 \times 10^{-2}\ T - 1.5535 \times 10^{-5}\ T^2$, cal. deg.$^{-1}$ mole^{-1} (318–500°K.); and second virial coefficient of 2-thiapropane, $B = V(PV/RT - 1) = -264 - 21.70 \exp(1000/T)$, cc. mole^{-1} (275–500°K.). These results and previously published data provide experimental values of $\Delta Hf°$, $S°$ and $Cp°$ in the ideal gaseous state for both ethanethiol and 2-thiapropane. A revised vibrational assignment was made for 2-thiapropane, and thermodynamic properties of this compound were calculated from calorimetric, spectroscopic and molecular structure information. The height of the barrier to internal rotation in 2-thiapropane (2100 cal. mole^{-1}) was determined from the calorimetric value of $S°$; and empirical anharmonicity corrections were determined from the experimental values of $Cp°$. For consistency, previously published thermodynamic properties of ethanethiol were revised to include anharmonicity corrections. Values of the following thermodynamic functions of ethanethiol and 2-thiapropane were calculated at selected temperatures to 1000°K.: $(F° - H°_0)/T$, $(H° - H°_0)/T$, $H° - H°_0$, $S°$, $Cp°$, $\Delta Hf°$, $\Delta Ff°$ and $\log_{10} Kf$. Values of $\Delta Hi°$, $\Delta Fi°$ and $\log_{10} Ki$ for the isomerization of ethanethiol to 2-thiapropane also are reported.

Ethanethiol and 2-thiapropane are among the important sulfur-bearing constituents of the low-boiling fractions of petroleum.[2] The thermodynamic properties of these substances have been the subject of several calorimetric and computational investigations.[3–7] This paper reports additional calorimetric data that permit calculation of the chemical thermodynamic properties over a wide range of temperatures. The new experimental data presented include values of the heats of combustion and formation of ethanethiol and 2-thiapropane and values of the heat of vaporization and vapor heat capacity of 2-thiapropane. The calculated thermodynamic properties of ethanethiol given in an earlier paper from this Laboratory[7] were revised to include anharmonicity corrections and extended to include values of the heat, free energy and logarithm of the equilibrium constant of formation. The entropy datum of Osborne, Doescher and Yost[4] and the vapor heat capacity and heat of formation data from this investigation were used with spectroscopic and molecular structure information in new calculations of the thermodynamic properties of 2-thiapropane. Values of the following thermodynamic functions are reported at selected temperatures between 0 and 1000°K. for both ethanethiol and 2-thiapropane: $(F° - H°_0)/T$, $(H° - H°_0)/T$, $H° - H°_0$, $S°$, $Cp°$, $\Delta Hf°$, $\Delta Ff°$ and $\log_{10} Kf$.

Experimental

Physical Constants.—The 1951 International Atomic Weights[8] and, where practicable, the 1951 values of the fundamental physical constants[9] were used. The results are based on a molecular weight of 62.134 for the C_2H_6S isomers 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.[10] Measurements of mass, energy and resistance were made in terms of standard devices calibrated at the National Bureau of Standards.

The Materials.—The samples of ethanethiol and 2-thiapropane used in the combustion calorimetric studies were portions of the Standard Samples of Sulfur Compounds, NBS serial no. 904 and API-USBM serial no. 13, respectively, which were prepared and purified at the Laramie,

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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] C. J. Thompson, H. J. Coleman, H. T. Rall and H. M. Smith, *Anal. Chem.*, **27**, 175 (1955).

[3] J. Thomsen, *Thermochemische Untersuchungen*, Vol. 4, Leipzig, 1886.

[4] D. W. Osborne, R. N. Doescher and D. M. Yost, THIS JOURNAL, **64**, 169 (1942).

[5] J. L. Binder, *J. Chem. Phys.*, **17**, 499 (1949); **18**, 77 (1950).

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

[7] 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).

[8] Edward Wichers, *ibid.*, **74**, 2447 (1952).

[9] F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, *ibid.*, **74**, 2699 (1952).

[10] H. F. Stimson, *J. Research Natl. Bur. Standards*, **42**, 209 (1949).

Wyo., Station of the Bureau of Mines. In a calorimetric melting point study described elsewhere,[7] the purity of the Standard Sample of ethanethiol was found to be 99.978 ± 0.005 mole %. The purity of the Standard Sample of 2-thiapropane was determined at the Laramie Station by the time–temperature freezing point method and found to be 99.99 ± 0.01 mole %. A sample of 2-thiapropane of 99.5 mole % purity was supplied by the Laramie Station for measuring the heat of vaporization and vapor heat capacity. Both compounds were dried by passing the vapors through $Mg(ClO_4)_2$. At no time in handling the materials or in the experiments were the samples in contact with gases other than dry helium.

The Heat of Vaporization of 2-Thiapropane.—Measurements of the heat of vaporization and vapor heat capacity of 2-thiapropane were made in the flow calorimeter system described in previous publications from this Laboratory.[11] The modified apparatus and procedure described in ref. 11b were used in this investigation.

The heat of vaporization of 2-thiapropane was measured at 275.85, 292.03 and 310.50°K., and the results of three determinations at each temperature are given in Table I. It is believed that the accuracy uncertainty of the tabulated data should not exceed ±0.1%. The following equation may be used for interpolation in the temperature range of the experiments, 275 to 310°K.

$$\Delta Hv = 9087 - 4.1794T - 1.3860 \times 10^{-2}T^2, \text{ cal. mole}^{-1} \qquad (1)$$

Osborne, *et al.*,[4] measured the heat of vaporization of 2-thiapropane at 291.06°K., and their result, 6688 ± 7 cal. mole^{-1}, is in good agreement with the value calculated with eq. 1, 6696 cal. mole^{-1}.

From eq. 1, the heat of vaporization of 2-thiapropane is calculated to be 6608 cal. mole^{-1} at 298.16°K. This datum, eq. 3 of a subsequent section and vapor pressure data[12] were used in calculating the *standard* heat, entropy and free energy of vaporization at 298.16°K., 6655 cal. mole^{-1}, 21.38 cal. deg.$^{-1}$ mole^{-1} and 280 cal. mole^{-1}, respectively.

The Vapor Heat Capacity of 2-Thiapropane.—The vapor heat capacity of 2-thiapropane was measured at 2 or more pressures at each of 5 temperatures from 318 to 500°K.; the results are summarized in Table II. "Observed" values of the heat capacity in the ideal gaseous state, $Cp°$, listed in Table II, were determined from the data at finite pressures by the method discussed in the next section.

Table I

The Molal Heat of Vaporization and Second Virial Coefficient of 2-Thiapropane

T, °K.	p, mm.	ΔHv, cal.	B(obsd.), cc.	B(calcd.),[a] cc.
275.85	189.7	6879 ± 2[b]	−1101	−1078
292.03	381.0	6684 ± 2	− 917	− 930
310.50	761.8	6453 ± 1	− 796	− 808

[a] Calculated with the aid of eq. 3. [b] Maximum deviation of experimental results from the mean.

Table II

The Molal Vapor Heat Capacity of 2-Thiapropane in Cal. Deg.$^{-1}$

T, °K.	318.20	355.20	400.20	450.20	500.20
Cp(755 mm.)	19.030	20.000	21.328	22.844	24.284
Cp(377 mm.)	18.688				
Cp(187 mm.)	18.536	19.724	21.195	22.761	24.253
$Cp°$(obsd.)	18.38	19.64	21.15	22.74	24.24
$Cp°$(calcd.)[a]	18.38	19.64	21.14	22.74	24.24
[Cp(1 atm.) − $Cp°$] (obsd.)	0.65	0.36	0.18	0.10	0.04
[Cp(1 atm.) − $Cp°$] (calcd.)[b]	.65	.35	.19	.10	.06

[a] Calculated from spectroscopic and molecular structure data. [b] Calculated by use of eq. 2 and 3.

Gas Imperfection and Correlation of the Heat Capacity Data for 2-Thiapropane.—An equation of state of 2-thiapropane vapor was obtained from the heat of vaporization and vapor heat capacity data of this investigation and the vapor pressure data of White, Barnard-Smith and Fidler.[12] 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.[13] Values of d^2B/dT^2 were determined by use of the thermodynamic relationship, $(\partial^2 V/\partial T^2)_P = -(1/T)(\partial Cp/\partial P)_T$, in terms of which the variation of vapor heat capacity with pressure is represented, with slight approximations,[11b] by

$$Cp = Cp° - T\left(\frac{d^2B}{dT^2}\right)P + \left(\frac{2B}{R}\right)\left(\frac{d^2B}{dT^2}\right)\left(1 - \frac{3BP}{RT}\right)P^2 \qquad (2)$$

The numerical constants of the following empirical equation for B were determined by the method described in ref. 11b.

$$B = -264 - 21.70 \exp(1000/T), \text{ cc. mole}^{-1} \text{ (275–500°K.)} \qquad (3)$$

Values of B, computed by use of eq. 3, and values of Cp(1 atm.) − $Cp°$, computed by use of eq. 2 and 3, are compared with experimental data in Tables I and II, respectively.

To determine the "observed" values of $Cp°$ listed in Table II, the last term in eq. 2 was evaluated for each experimental point by use of eq. 3, and the result[14] was subtracted from Cp (obsd.). The adjusted values of Cp at each temperature were then extrapolated linearly to zero pressure to obtain $Cp°$ (obsd.). The accuracy uncertainty of the values of $Cp°$ (obsd.) listed in Table II should not exceed ±0.2%. The following empirical equation represents these data within ±0.05% between 318 and 500°K.

$$Cp° = 5.628 + 4.4990 \times 10^{-2}T - 1.5535 \times 10^{-5}T^2, \text{ cal. deg.}^{-1} \text{ mole}^{-1} \qquad (4)$$

The Entropy of 2-Thiapropane in the Ideal Gaseous State.—From low temperature calorimetric measurements, Osborne, *et al.*,[4] found the entropy of 2-thiapropane in the saturated liquid state at 298.16°K. to be 46.94 ± 0.07 cal. deg.$^{-1}$ mole^{-1}. Addition of the standard entropy of vaporization presented in a previous section gives the entropy in the ideal gaseous state at 298.16°K., $S° = 68.32 \pm 0.09$ cal. deg.$^{-1}$ mole^{-1}. This value does not differ significantly from that calculated by Osborne, *et al.*,[4] 68.28 cal. deg.$^{-1}$ mole^{-1}.

The Heats of Combustion of Ethanethiol and 2-Thiapropane.—The heats of combustion of ethanethiol and 2-thiapropane were determined in a rotating-bomb combustion calorimeter by methods described in an earlier publication from this Laboratory.[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 to 30 atm. total pressure. Each combustion experiment was initiated at 296.16°K., and the quantities of sample 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 39 g). Combustion experiments with both isomers and calibration experiments with benzoic acid were made alternately under as nearly identical conditions as possible in order to minimize errors

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(11) (a) G. 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).

(12) P. T. White, D. G. Barnard-Smith and F. A. Fidler, *Ind. Eng. Chem.*, **44**, 1430 (1952).

(13) The vapor pressure data of White, Barnard-Smith and Fidler[12] are consistent with the heat of vaporization results of this research in that they yield reasonable values of the second virial coefficient, B. The vapor pressure data of Osborne, *et al.*[4] (and related values in "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds." American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology, table 107k, October 31, 1953) apparently contain small errors in dp/dT and could not be used in calculating values of B.

(14) The maximum value of the last term in eq. 2 was 0.03 cal. deg.$^{-1}$ mole^{-1} at 1 atm. and 318.20°K.

(15) W. N. Hubbard, C. Katz and Guy Waddington, *J. Phys. Chem.*, **58**, 152 (1954).

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

in the heat of isomerization. The calorimetric results for ethanethiol and 2-thiapropane are summarized in Table III. The experimental values of $\Delta Ec°/M$ apply to the idealized combustion reaction I at 298.16°K.

TABLE III

ENERGY OF IDEALIZED COMBUSTION REACTIONS[a,b]

Ethanethiol

m'(ethanethiol), g.	0.81009	0.82706	0.85774	0.88648	0.89139	0.89764
$\Delta t_c = t_f - t_i - \Delta t_{cor}$, deg.	2.00062	2.00053	2.00171	2.00092	2.00316	2.00542
$\mathcal{E}$(Calor.)($-\Delta t_c$), cal.	−7820.48	−7820.13	−7824.74	−7821.66	−7830.41	−7839.25
$\mathcal{E}$(Cont.)($-\Delta t_c$),[c] cal.	−27.77	−27.77	−27.68	−27.79	−27.72	−27.86
ΔE_{ign}, cal.	1.35	1.35	1.35	1.35	1.35	1.35
ΔE^f_{decomp} ($HNO_3 + HNO_2$), cal.	9.58	9.74	10.50	10.32	10.92	10.31
ΔE, cor. to st. states,[d] cal.	0.53	0.37	0.07	−0.24	−0.30	−0.34
$-n'' \Delta Ec°$(auxiliary oil), cal.	1074.33	934.83	684.18	443.20	407.61	365.65
$-n''' \Delta Ec°$(fuse), cal.	15.73	16.24	16.12	15.42	15.97	15.22
$n' \Delta Ec°$(ethanethiol), cal.	−6746.73	−6885.37	−7140.20	−7379.40	−7422.58	−7474.92
$\Delta Ec°/M$(ethanethiol), cal. g^{-1}	−8328.37	−8325.12	−8324.43	−8324.38	−8326.97	−8327.30

Av. value and standard dev. of the mean: −8326.10 ± 0.69 cal. g.$^{-1}$.

2-Thiapropane

m'(2-thiapropane), g.	0.83452	0.87622	0.87681	0.87691	0.88815	0.90539	0.90601	0.89377
$\Delta t_c = t_f - t_i - \Delta t_{cor}$, deg.	2.00105	2.00128	2.00234	2.00025	2.00028	2.00082	1.99923	1.99938
$\mathcal{E}$(Calor.)($-\Delta t_c$), cal.	−7822.16	−7823.06	−7827.21	−7819.04	−7819.15	−7821.27	−7815.05	−7815.64
$\mathcal{E}$(Cont.)($-\Delta t_c$),[c] cal.	−27.67	−27.80	−27.69	−27.68	−27.68	−27.79	−27.77	−27.67
ΔE_{ign}, cal.	1.35	1.35	1.35	1.35	1.35	1.35	1.35	1.35
ΔE^f_{decomp}($HNO_3 + HNO_2$), cal.	10.70	10.56	10.34	10.46	9.56	10.52	11.61	10.45
ΔE, cor. to st. states,[d] cal.	0.31	−0.13	−0.13	−0.18	−0.26	−0.48	−0.49	−0.37
$-n'' \Delta Ec°$(auxiliary oil), cal.	845.75	500.97	498.01	491.20	398.82	254.82	242.41	346.32
$-n''' \Delta Ec°$(fuse), cal.	15.54	15.50	15.22	16.12	15.38	14.99	15.97	15.61
$n' \Delta Ec°$(2-thiapropane), cal.	−6976.18	−7322.61	−7330.11	−7327.77	−7421.98	−7567.86	−7571.97	−7469.95
$\Delta Ec°/M$(2-thiapropane), cal. g.$^{-1}$	−8359.51	−8357.05	−8359.98	−8356.35	−8356.67	−8358.67	−8357.49	−8357.80

Av. value and standard dev. of the mean: −8357.94 ± 0.47 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.) = 3909.03 cal. deg.$^{-1}$; V(Bomb) = 0.347 l.; physical properties at 25° of ethanethiol and 2-thiapropane, respectively—ρ = 0.833 and 0.842 g. ml.$^{-1}$, $(\partial E/\partial P)_T = -0.012$ and -0.012 cal. g.$^{-1}$ atm.$^{-1}$, c_p = 0.453 and 0.455 cal. deg.$^{-1}$ g.$^{-1}$. [c] $\mathcal{E}^i$(Cont.)(t_i − 25°) + $\mathcal{E}^f$(Cont.)(25° − t_f + Δt_{cor}). [d] Items 81–85, incl., 87–91, incl., 93 and 94 of the computation form of ref. 16.

$$C_2H_6S(liq) + 5O_2(g) + 43H_2O(liq) \longrightarrow 2CO_2(g) + H_2SO_4{\cdot}45H_2O(liq) \quad (I)$$

For this reaction, the standard changes in internal energy, $\Delta Ec°_{298.16}$ are −517.33 ± 0.10[17] and −519.31 ± 0.08[17] kcal. mole^{-1} and the standard heats of combustion, $\Delta Hc°_{298.16}$, are −519.11 ± 0.10[17] and −521.09 ± 0.08[17] kcal. mole^{-1} for ethanethiol and 2-thiapropane, respectively.

Combustion experiments were made[18] with mixtures of rhombic sulfur and auxiliary oil chosen to give nearly the same final state of the bomb process as the experiments with the C_2H_6S isomers. From these experiments, the heat of combustion of rhombic sulfur according to reaction II was determined.

$$S(rhombic) + 3/2O_2(g) + 46H_2O(liq) \longrightarrow H_2SO_4{\cdot}45H_2O(liq) \quad (II)$$

$$\Delta Hc°_{298.16} = -143.67 \pm 0.11^{17} \text{ kcal. mole}^{-1}$$

The Heats of Formation and Related Properties of Ethanethiol and 2-Thiapropane.—The values of $\Delta Hc°_{298.16}$ for ethanethiol, 2-thiapropane and rhombic sulfur, and values of the heat of formation of carbon dioxide and water[19] were used to compute values of the heat of formation, $\Delta Hf°_{298.16}$, of ethanethiol and 2-thiapropane in the liquid state. Values of the heat of formation of ethanethiol and 2-thiapropane in the ideal gaseous state were computed from the values for the liquid state by addition of the standard heats of vaporization, 6.58_1[20] and 6.65_5 kcal. mole^{-1}, respectively.

The standard free energy, $\Delta Ff°_{298.16}$, and logarithm of the equilibrium constant, $\log_{10} Kf_{298.16}$, for the formation of both isomers in the liquid and gaseous states were calculated from the values of $\Delta Hf°_{298.16}$, values of the entropy of each compound,[21] and the thermodynamic properties of graphite,[19] hydrogen[19] and rhombic sulfur.[22] The heat of formation of $S_2(g)$ from rhombic sulfur and other thermodynamic properties of $S_2(g)$[23] were used to compute $\Delta Hf°_{298.16}$, $\Delta Ff°_{298.16}$ and $\log_{10} Kf_{298.16}$ for the formation of ethanethiol and 2-thiapropane in the ideal gaseous state from C(graphite), $H_2(g)$ and $S_2(g)$. The results of these calculations are summarized in Table IV.

Calculation of Thermodynamic Properties

The calorimetric investigations described in this and earlier[4,7] papers provide values of the important chemical thermodynamic functions of ethanethiol and 2-thiapropane between 0 and 500°K. These thermodynamic data were extended to higher temperatures by methods of statistical mechanics based on calorimetric, spectroscopic and molecular struc-

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[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] Unpublished results, this Laboratory.

[19] (a) E. J. Prosen, R. S. Jessup and F. D. Rossini, *J. Research Natl. Bur. Standards*, **33**, 447 (1944); (b) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *ibid.*, **34**, 143 (1945).

[20] Calculated from data of ref. 7.

[21] Values of the entropy of ethanethiol in the liquid and ideal gaseous states were taken from ref. 7. The entropy of liquid 2-thiapropane was taken from ref. 4 and that in the ideal gaseous state from a preceding section of this paper.

[22] 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 I, Table 14-1.

[23] W. H. Evans and D. D. Wagman, *J. Research Natl. Bur. Standards*, **49**, 141 (1951).

TABLE IV

THE STANDARD MOLAL HEAT AND FREE ENERGY AND THE LOGARITHM OF THE EQUILIBRIUM CONSTANT FOR THE FORMATION OF ETHANETHIOL AND 2-THIAPROPANE AT 298.16°K.

Compound	$\Delta Hf°_{298.16}$, kcal.	$\Delta Ff°_{298.16}$, kcal.	$\log_{10} Kf_{298.16}$
$2C(graphite) + 3H_2(g) + S(rhombic) \rightarrow C_2H_6S(liq)$			
Ethanethiol	−17.61	−1.36	1.00
2-Thiapropane	−15.64	+1.37	−1.00
$2C(graphite) + 3H_2(g) + S(rhombic) \rightarrow C_2H_6S(g)$			
Ethanethiol	−11.03	−1.13	0.83
2-Thiapropane	− 8.98	+1.65	−1.21
$2C(graphite) + 3H_2(g) + {}^1/_2S_2(g) \rightarrow C_2H_6S(g)$			
Ethanethiol	−26.45	−10.70	7.84
2-Thiapropane	−24.40	−7.91	5.80

TABLE V

THE VIBRATIONAL SPECTRA AND ASSIGNMENT FOR 2-THIAPROPANE, C_{2v} SYMMETRY

Raman,[a] Liq. $\Delta\nu$, cm.$^{-1}$	Infrared,[a] Liq. ν, cm.$^{-1}$	Infrared,[a] Gas ν, cm.$^{-1}$	Assignment
282 m, p			C–S–C bending, a_1
480 vw			$282 + [200]^b = 482\ A_1$ or A_2
691 vs, p	691 s	683 s 704 s	C–S stretching, a_1
741 m, d	741 m		C–S stretching, b_2
804 vw			$1028 - [200]^b = 828\ A_1$ or A_2
919 vw	906 m	905 w	CH_3 rocking, b_2
	972 s	975 m	CH_3 rocking, b_1
(Unobsd. frequency near 1000)[b]			CH_3 rocking, a_2
	1028 s	1024 vs 1037 vs	CH_3 rocking, a_1
1043 vw			$1334 - 282 = 1052\ A_1$
1235 vw	1240 sh	1242 vw	$282 + 972 = 1254\ B_1$
		1270 vw	$1460 - [200]^b = 1260\ B_1$ or B_2
		1295 vw	$282 + 1028 = 1310\ A_1$
	1309 s	1304 s 1325 s	Sym. CH_3 bending, b_2
1334 w, p		1335 s	Sym. CH_3 bending, a_1
1420 m + 1442 m, d	1429 vs	1420 vs 1441 vs	Unsym. CH_3 bending, a_2 Unsym. CH_3 bending, b_2 Unsym. CH_3 bending, a_1
		1460 vs	Unsym. CH_3 bending, b_1

[a] Intensities are indicated by: vw = very weak; w = weak; m = medium; s = strong; and vs = very strong. Raman polarization is indicated by p = polarized and d = depolarized. [b] See text.

ture information. The method of calculation for 2-thiapropane and the revision and extension of previous calculations for ethanethiol[7] are described in the following paragraphs.

The Vibrational Assignment for 2-Thiapropane.—The vibrational spectra of 2-thiapropane have been studied by several investigators,[24,25] and a critical selection of the results is given in Table V. The assignment of fundamental frequencies in Table V is based on C_{2v} molecular symmetry. This assignment differs from that given earlier by Thompson[25b] in the designation of the four CH_3 rocking frequencies. Thompson assigned these frequencies as follows: a_1, 1040; a_2, 917; b_1, 1242; and b_2, 1274 cm.$^{-1}$. In connection with an analysis of the spectrum of 2-thiabutane, Scott, *et al.*,[26] calculated the following (unpublished) values of the CH_3 rocking frequencies of 2-thiapropane: a_1, 1025; a_2, 957; b_1, 966; and b_2, 900 cm.$^{-1}$. The assignment in Table V was based on these calculated results.

Thompson's assignment of the CH_3 rocking mode of species a_1 is in reasonable agreement with that of Table V, but in Table V, the doublet at 1024–1037 cm.$^{-1}$ in the vapor phase spectrum has been interpreted as the P and R branches expected for an a_1 mode, whereas Thompson made separate assignments for each frequency. The weak Raman displacement at 1043 cm.$^{-1}$ may correspond to the same mode, or it may arise from the difference combination, $1334 - 282 = 1052\ A_1$ (the corresponding sum combination, $1334 + 282 = 1616\ A_1$, appears at 1605[25c] cm.$^{-1}$ in the infrared spectrum of the vapor and at 1609[24c] cm.$^{-1}$ in the Raman spectrum).

The CH_3 rocking mode of species a_2 should be inactive in the infrared spectrum and weak or missing in the Raman spectrum. The frequency, 1000 cm.$^{-1}$, given in Table V was chosen to give agreement between calculated and observed values of $S°$ and $Cp°$. This assignment is in reasonable agreement with the calculated value of 957 cm.$^{-1}$ and is consistent with assignments for less symmetrical methylalkyl sulfides.[27]

The assignments for the b_1 and b_2 CH_3 rocking modes given in Table V are in good agreement with the results of the normal coördinate analysis. Thompson's choices for these vibrations cannot be reconciled with the calorimetric vapor heat capacity data and are inconsistent with more recent assignments for other alkyl sulfides.[26,27]

The assignment of the remaining fundamental frequencies is the same as that given by Thompson[25b] except for minor numerical changes. The weak Raman lines and infrared bonds not assigned as fundamentals may all be interpreted as sum or difference combinations, although some of these frequencies may be due to impurities (only one combination was reported in the spectrum of ref. 25a, which was determined on a portion of the Standard Sample of 2-thiapropane). If all of these weak frequencies are real, some must arise from combinations involving the torsional modes of vibration. As will be shown in a later section, the height of the potential barrier to internal rotation is

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[24] Raman data: (a) R. Vogel-Högler, *Acta phys. Austriaca*, **1**, 311 (1948); (b) S. C. Sirkar and B. M. Bishui, *Science and Culture*, **9**, 90 (1943); (c) R. Fonteyne, *J. Chem. Phys.*, **8**, 60 (1940); (d) L. Medard and F. Deguillon, *Compt. rend.*, **203**, 1518 (1936); K. W. F. Kohlrausch, *Monatsh.*, **68**, 349 (1936); C. S. Venkateswaren, *Indian J. Phys.*, **6**, 51 (1931).

[25] Infrared data: (a) American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology, "Catalog of Infrared Spectrograms," serial no. 1299 [liquid]; (b) H. W. Thompson, *Trans. Faraday Soc.*, **37**, 38 (1941) (gas); (c) ref. 24c (gas).

[26] D. W. Scott, H. L. Finke, J. P. McCullough, M. E. Gross, K. D. Williamson, Guy Waddington and H. M. Huffman, THIS JOURNAL, **73**, 261 (1951).

[27] See, for example, ref. 26; and J. P. McCullough, H. L. Finke, J. F. Messerly, R. E. Pennington, I. A. Hossenlopp and Guy Waddington, *ibid.*, **77**, 6119 (1955).

2100 cal. mole^{-1}, corresponding to a torsional frequency of 180 cm.$^{-1}$.[28] Pitzer has shown that the torsional frequencies of methyl ether are split 140 cm.$^{-1}$,[29] and a similar, but smaller, splitting can be expected for 2-thiapropane. Several of the doubtful frequencies listed in Table V can be explained as combinations if it is assumed that one of the torsional frequencies appears near 200 cm.$^{-1}$.

The following fundamental frequencies were used in calculations of the thermodynamic functions of 2-thiapropane: C–S–C bending, 282; C–S stretching, 691 and 741; CH_3 rocking, 906, 972, [1000] and 1028; sym. CH_3 bending, 1309 and 1334; unsym. CH_3 bending, 1430 (4); C–H stretching, 2900 (6) cm.$^{-1}$. Average values were used for the thermodynamically unimportant frequencies above 1400 cm.$^{-1}$.

The Moments and Reduced Moments of Inertia of 2-Thiapropane.—The C–S bond distance in 2-thiapropane was determined by Brockway and Jenkins[30] and found to be 1.82 ± 0.03 Å. This datum and the following estimated parameters were used in calculation of the moments of inertia: C–H bond distance, 1.09 Å.; C–S–C bond angle, 105°; all other bond angles 109°28′. The results are: $I_A = 43.24 \times 10^{-40}$, $I_B = 120.52 \times 10^{-40}$ and $I_C = 153.16 \times 10^{-40}$ g. cm.^{2}. The reduced moment of inertia for the equivalent methyl groups was calculated by the method of Pitzer and Gwinn[31] and found to be 4.795×10^{-40} g. cm.^{2}.

The Potential Barrier to Internal Rotation and the Effect of Anharmonicity for 2-Thiapropane.—For 2-thiapropane, the potential barrier to internal rotation, 2100 cal. mole^{-1}, and the unobserved CH_3 rocking frequency of species a_2, 1000 cm.$^{-1}$, were selected simultaneously to give agreement with the value of $S°$ at 298.16°K. and $Cp°$ at 318.20°K. This value for the barrier to internal rotation does not differ significantly from that reported by Osborne, *et al.*,[4] and used in later calculations for other alkyl sulfides.[26,27]

The differences between calculated and observed values of $Cp°$ at the higher temperatures were attributed to the neglect of anharmonicity of the normal vibrations. The effect of anharmonicity was computed by the empirical method outlined in an earlier paper.[32] The following values of the anharmonicity parameters defined in ref. 32 were required: $\nu = 1000$ cm.$^{-1}$; $Z = 0.400$ cal. deg.$^{-1}$ mole^{-1}.

Calculated and observed values of $Cp°$ are compared in Table II. Agreement within 0.01 cal. deg.$^{-1}$ mole^{-1} (0.05%) was obtained over the 180° temperature range in which experimental data were available. The calculated value of $S°$ at 298.16°K., 68.32 cal. deg.$^{-1}$ mole^{-1}, is in exact agreement with the experimental value reported in a previous section. Because good agreement with experimental data was obtained, the vibrational assignment, moments of inertia, barrier height and anharmonicity parameters given in foregoing sections were used to calculate values of the following thermodynamic functions at selected temperatures to 1000°K.: $(F° - H_0°)/T$, $(H° - H_0°)/T$, $H° - H_0°$, $S°$ and $Cp°$.

Revision of the Thermodynamic Properties of Ethanethiol.—The calculated thermodynamic properties of ethanethiol given in ref. 7 did not include corrections for the effects of anharmonicity. The deviations between calculated and observed values of $Cp°$[7] were used to obtain the following values of the empirical anharmonicity parameters defined in ref. 32: $\nu = 1000$ cm.$^{-1}$ and $Z = 0.400$ cal. deg.$^{-1}$ mole^{-1}. It is interesting to note that the same parameters were required for both ethanethiol and 2-thiapropane. These anharmonicity parameters were used to revise the calculated thermodynamic properties of ethanethiol. Calculated and observed values of $S°$ and $Cp°$, in cal. deg.$^{-1}$ mole^{-1}, are compared below:

T, °K.	281.16	298.16	308.16
$S°$(obsd.)	69.75	70.77	71.35
$S°$(calcd.)	69.76	70.77	71.35

T, °K.	317.20	358.20	402.20	449.20
$Cp°$(obsd.)	18.08	19.59	21.16	22.75
$Cp°$(calcd.)	18.08	19.59	21.16	22.75

The close agreement between calculated and experimental results shown in the foregoing table and in Table II is partly fortuitous. These comparisons show that the precision and internal consistency of the experimental results are good but do not necessarily prove the absence of small systematic errors. The empirical treatment of anharmonicity not only corrects for the neglect of anharmonicity, but also tends to compensate for errors in the various parameters used in calculating the thermodynamic properties. In addition, the calculated results are obviously subject to an uncertainty at least as great as the experimental data. Nevertheless, the nearly exact agreement obtained over the entire range of temperature for which experimental data were available gives added confidence in both the experimental and calculated results for ethanethiol and 2-thiapropane.

The Chemical Thermodynamic Properties of Ethanethiol and 2-Thiapropane.—Calculated values of the functions $(F° - H_0°)/T$, $(H° - H_0°)/T$, $H° - H_0$, $S°$ and $Cp°$ for 2-thiapropane and the revised values of these functions for ethanethiol are given in Table VI. These thermodynamic properties of the C_2H_6S compounds, the values of $\Delta Hf°_{298.16}$ given in Table IV, and the thermodynamic properties of C-(graphite),[19] H_2(g)[19] and S_2(g)[23] were used in computing values of $\Delta Hf°$, $\Delta Ff°$ and $\log_{10} Kf$ for both compounds at selected temperatures from 0 to 1000 °K. The results also are included in Table VI.

The thermodynamic properties listed in Table VI differ significantly from those published by earlier investigators.[5,6] Changes in the values of $\Delta Hf°$, $\Delta Ff°$ and $\log_{10} Kf$ are due primarily to use of the heat of formation data given in this paper in place of the early data of Thomsen.[3]

The differences in the other thermodynamic properties of 2-thiapropane are almost entirely due to the change in assignment of the CH_3 rocking fre-

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[28] E. B. Wilson, Jr., *Chem. Revs.*, **27**, 17 (1940).

[29] K. S. Pitzer, *J. Chem. Phys.*, **10**, 605 (1942).

[30] L. O. Brockway and H. O. Jenkins, THIS JOURNAL, **58**, 2036 (1936).

[31] K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

[32] 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 VI

The Molal Thermodynamic Properties of Ethanethiol and 2-Thiapropane[a]

T, °K.	$(F° - H°_0)/T$, cal. deg.$^{-1}$	$(H° - H°_0)/T$, cal. deg.$^{-1}$	$H° - H°$, kcal.	$S°$, cal. deg.$^{-1}$	$Cp°$, cal. deg.$^{-1}$	$\Delta Hf°$,[b] kcal.	$\Delta Ff°$,[b] kcal.	$\log_{10} Kf$[b]
				Ethanethiol				
0	0	0	0	0	0	−22.42	−22.42	Infinite
273.16	−57.60	11.69	3.193	69.29	16.46	−26.16	−12.00	+9.60
298.16	−58.64	12.13	3.617	70.77	17.37	−26.45	−10.70	7.84
300.00	−58.72	12.16	3.648	70.88	17.44	−26.47	−10.60	7.72
400	−62.46	13.94	5.576	76.40	21.08	−27.52	− 5.14	.81
500	−65.76	15.70	7.850	81.46	24.36	−28.39	+ 0.56	−0.24
600	−68.78	17.38	10.428	86.16	27.21	−29.09	6.41	−2.33
700	−71.58	18.96	13.27	90.54	29.68	−29.63	12.37	−3.86
800	−74.21	20.44	16.35	94.65	31.83	−30.03	18.39	−5.02
900	−76.69	21.81	19.63	98.50	33.71	−30.29	24.48	−5.94
1000	−79.07	23.08	23.08	102.15	35.38	−30.44	30.55	−6 68
				2-Thiapropane				
0	0	0	0	0	0	−20.52	−20.52	Infinite
273.16	−54.64	12.17	3.324	66.81	16.86	−24.13	− 9.29	+7.43
298.16	−55.71	12.61	3.760	68.32	17.71	−24.40	− 7.91	5.80
300.00	−55.79	12.64	3.792	68.43	17.77	−24.42	− 7.82	5.70
400	−59.66	14.33	5.732	73.99	21.12	−25.46	− 2.12	1.16
500	−63.04	16.01	8.005	79.05	24.24	−26.34	+ 3.81	−1.67
600	−66.11	17.61	10.566	83.72	27.01	−27.05	9.91	−3.61
700	−68.93	19.14	13.40	88.07	29.44	−27.60	16.13	−5.04
800	−71.60	20.54	16.43	92.14	31.59	−28.05	22.37	−6.11
900	−74.10	21.88	19.69	95.98	33.50	−28.33	28.70	−6.97
1000	−76.47	23.13	23.13	99.60	35.17	−28.49	35.05	−7.66

[a] To form an internally consistent set of values of the thermodynamic properties and to retain the higher accuracy of increments with temperature of a given property, some of the values in this table are given to one more significant figure than is justified by their absolute accuracy. [b] The standard heat, standard free energy and common logarithm of the equilibrium constant of formation according to the reaction: $2C(\text{graphite}) + 3H_2(g) + {}^1/_2S_2(g) \rightarrow C_2H_6S(g)$.

quencies. Binder[5] and Barrow and Pitzer[6] used Thompson's[25b] vibrational assignment for this compound and obtained good agreement with the experimental entropy datum at 298.16°K. However, the values of $Cp°$ calculated by these authors differed by as much as 4% from the experimental data of this investigation. These results show conclusively the value of experimental vapor heat capacity data in verifying the assignment of fundamental vibrational frequencies in the range 800–1200 cm.$^{-1}$.

Barrow and Pitzer's results for ethanethiol[6] are in relatively good agreement with the results of this investigation although these authors had no calorimetric data on which to base their calculations.

The Isomerization Equilibria between Ethanethiol and 2-Thiapropane.—Values of the standard heat, $\Delta Hi°$, free energy, $\Delta Fi°$, and logarithm of the equilibrium constant, $\log_{10} Ki$, for the isomerization reaction ethanethiol → 2-thiapropane were computed from the data in Table VI and are given in Table VII. The ratio of 2-thiapropane to ethanethiol, $C_t:C_e$, in an equilibrium mixture is listed for each temperature in the last column of Table VII. Thompson, *et al.*,[2] found that the value of this ratio in Wasson crude oil is about 1:6. Although the results in Table VII are not strictly applicable under the conditions in petroleum reservoirs, it is reasonable to conclude that these substances are not in thermodynamic equilibrium in the Wasson crude.

Table VII

The Isomerization Equilibria between Ethanethiol and 2-Thiapropane

T, °K.	$\Delta Hi°$, kcal. mole^{-1}	$\Delta Fi°$, kcal. mole^{-1}	$\log_{10} Ki$[a]	$C_t:C_e$[b]
0	1.90	1.90	Infinite	
273.16	2.03	2.71	−2.17	1:148
298.16	2.05	2.79	−2.05	1:112
300.00	2.05	2.78	−2.03	1:107
400	2.06	3.02	−1.65	1:45
500	2.05	3.25	−1.42	1:26
600	2.04	3.50	−1.27	1:19
700	2.03	3.76	−1.17	1:15
800	1.98	3.98	−1.09	1:12
900	1.96	4.22	−1.02	1:10.5
1000	1.95	4.50	−0.98	1:9.6

[a] The standard heat, free energy and equilibrium constant for the isomerization reaction, ethanethiol → 2-thiapropane. [b] The ratio of the concentration of 2-thiapropane to that of ethanethiol in a mixture in thermodynamic equilibrium.

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