carboxyl substituents. A calculation has been made of the variation in the apparent entropy of dimerization produced by variations in the translational and rotational entropy of dimerization for the several lower aliphatic acids—ignoring the contribution of the dimer ring vibrations, comprehensive data on which are unavailable. This calculation does not afford a satisfactory explanation of the variation in the observed entropies of dimerization. It seems improbable that the correlation of dimer dissociation constant with electronegativity of the carboxyl substituent is entirely fortuitous. Vapor phase data are available for relatively few acids, but solution phase studies have been carried out

on a large number of substances; and Maryott, Hobbs and Gross' hypothesis that there is a correlation of dimer dissociation constant in a nonpolar solvent with acid ionization constant in a polar solvent draws strength from the recently reported work of Barton and Kraus.[8] How the variation in electronegativity of the carboxyl substituents is effective in producing a coördinated variation in the entropy (and free energy) of dimerization is a question that can be resolved only by further study.

(8) B. C. Barton and C. A. Kraus, THIS JOURNAL, **73**, 4561 (1951).

CAMBRIDGE 38, MASS.

3-Thiapentane: Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressure, Entropy, Heat of Formation and Thermodynamic Functions[1]

BY D. W. SCOTT, H. L. FINKE, W. N. HUBBARD, J. P. MCCULLOUGH, G. D. OLIVER, M. E. GROSS, C. KATZ, K. D. WILLIAMSON, GUY WADDINGTON AND H. M. HUFFMAN[2]

The following thermodynamic properties of 3-thiapentane were determined experimentally: heat capacity of the solid and liquid between 15 and 320°K., triple point (169.21°K.), heat of fusion (2845 cal. mole^{-1}), vapor pressure [$\log_{10} p = 6.92836 - 1257.833/(t + 218.662)$ (p in mm. and t in °C.)], heat of vaporization (8185, 7906 and 7591 cal. mole^{-1} at 324.70, 344.16 and 365.26°K., respectively, heat capacity of the vapor [$C_p^\circ = 2.76 + 9.4965 \times 10^{-2} T - 3.794 \times 10^{-5} T^2$ cal. deg.$^{-1}$ mole^{-1} (350 to 490°K.)], second virial coefficient of the vapor [$B = V - RT/P = -385 - 26.76 \exp(1250/T)$ cc. mole^{-1}], entropy of the liquid (64.36 cal. deg.$^{-1}$ mole^{-1} at 298.16°K.), entropy of the vapor (90.43, 92.17 and 94.02 cal. deg.$^{-1}$ mole^{-1} at 324.70, 344.16 and 365.26°K., respectively) and the heat of formation [for the reaction: $4C(\text{graphite}) + 5H_2(g) + S$ (rhombic) $= (C_2H_5)_2S$ (liq), $\Delta H_{298.16}^\circ = -28.5$ kcal. mole^{-1}]. The functions $-(F^\circ - H_0^\circ)/T$, $(H^\circ - H_0^\circ)/T$, $H^\circ - H_0^\circ$, S° and C_p° were computed from spectroscopic and molecular structure data. Values of the height of the potential barriers hindering internal rotation, which were required for these calculations, were evaluated from the experimental entropy and heat capacity data. The heat, free energy and equilibrium constant of formation of 3-thiapentane were computed for selected temperatures up to 1000°K.

Because the alkane sulfides constitute one of the classes of organic sulfur compounds that occur in petroleum, selected members of that class have been included in the program of this Laboratory for studying the thermodynamic properties of sulfur compounds which occur in or are derivable from petroleum. Before this program was begun, the simplest alkane sulfide, 2-thiapropane (dimethyl sulfide), had been studied calorimetrically by Osborne, Doescher and Yost,[3] who obtained a value of the entropy of the vapor. Tables of the thermodynamic functions of 2-thiapropane were subsequently published by Barrow and Pitzer[4] and by Binder.[5] The first alkane sulfide studied in this Laboratory was the next higher homolog, 2-thiabutane (methyl ethyl sulfide). The results of that study, which included experimental values of the entropy and heat capacity of the vapor and calculated values of the thermodynamic functions,

were the subject of a recent publication.[6] The present paper presents the results of a similar investigation of a third alkane sulfide, 3-thiapentane (diethyl sulfide). Successful development of a rotating-bomb calorimeter for determining the heats of combustion of organic sulfur compounds has made it possible to include in this paper an experimental value of the heat of formation of 3-thiapentane and tables of the heat, free energy and equilibrium constant of formation at selected temperatures.

Experimental

The experimental work described in the following sections consisted of calorimetric and vapor pressure studies of 3-thiapentane which yielded values of the heat capacity in the solid, liquid and vapor states, the heats of fusion and vaporization, the vapor pressure, the entropy of the liquid and vapor, and the heat of formation.

The Material.—The 3-thiapentane used for the experimental measurements consisted of a small sample of highly purified material and a larger sample of material of somewhat lower purity. These were purified at the Laramie Station of the Bureau of Mines as part of A.P.I. Research Project 48A. The sample of higher purity was used for low temperature studies and for measurements of the vapor pressure and heat of combustion. Its purity was determined during the low temperature studies by measuring the melting point as a function of the fraction melted. The

(1) This investigation was performed as part of the work of American Petroleum Institute Research Project 48A on "The Production, Isolation and Purification of Sulfur Compounds and Measurement of Their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

(2) Deceased.

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

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

(5) J. L. Binder, *J. Chem. Phys.*, **18**, 77 (1950).

(6) 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).

value of the purity obtained was 99.995 ± 0.002 mole per cent. This determination involved the usual assumptions of liquid-soluble, solid-insoluble impurities and ideal solutions. The less pure sample was used for heat of vaporization and vapor heat capacity measurements, which require a larger sample and are not sensitive to small amounts of impurity. The purity of this second sample, determined at the Laramie Station by the time-temperature freezing point method, was reported to be 99.6 ± 0.3 mole per cent.

Low Temperature Studies.—Measurements of the heat capacity of 3-thiapentane in the solid and liquid states and its melting point and heat of fusion were made in an apparatus similar to that described by Ruehrwein and Huffman.[7] The platinum calorimeter used to contain the sample was equipped with horizontal perforated discs of gold to promote more rapid attainment of thermal equilibrium and to prevent settling of the solid phase during melting studies.

The results of the heat capacity measurements are given in Table I. C_{sat} is the heat capacity of the condensed phase under its own vapor pressure. The temperatures listed in Table I are the mean temperatures of the individual measurements. The temperature increments employed (6–10° above 100°K., 5–6° from 50 to 100°K., and less than 10% of the absolute temperature below 50°K.) were small enough that no correction was necessary for non-linear variation of C_{sat} with temperature. The precision of the measurements was, in general, better than 0.1%; above 30°K. the accuracy uncertainty of the heat capacity data probably does not exceed 0.2%. The heat capacity of the liquid as a function of temperature may be represented by the equation

$$C_{sat} = 46.028 - 0.10894T + 3.8800 \times 10^{-4}T^2 - 2.6667 \times 10^{-7}T^3 \quad (1)$$

a plot of which deviates less than 0.1% (less than 0.03% above 210°K.) from a visually smoothed curve through the experimental points.

TABLE I

MOLAL HEAT CAPACITY OF 3-THIAPENTANE[a]

T, °K.	C_{sat}, cal. deg.$^{-1}$	T, °K.	C_{sat}, cal. deg.$^{-1}$	T, °K.	C_{sat}, cal. deg.$^{-1}$
Solid		71.50	13.142	196.60	37.62
15.98	1.292	73.49	13.476	200.06	37.65
16.63	1.430	77.66	14.156	206.90	37.75
17.70	1.645	78.85	14.374	210.32	37.80
18.23	1.756	83.94	15.178	217.12	37.95
20.17	2.184	84.26	15.234	220.51	38.01
20.56	2.273	89.73	16.062	227.28	38.18
23.09	2.865	90.32	16.132	230.62	38.26
23.10	2.869	96.84	17.002	237.33	38.45
25.87	3.516	103.09	17.820	240.65	38.56
26.93	3.771	109.58	18.624	247.31	38.78
28.92	4.252	116.26	19.435	250.59	38.89
30.87	4.734	122.69	20.190	257.19	39.14
34.41	5.572	128.92	20.897	260.43	39.26
38.01	6.419	134.96	21.570	266.97	39.53
42.17	7.355	141.31	22.263	270.18	39.67
46.99	8.414	147.97	22.996	276.66	39.94
51.97	9.476	153.99	23.660	279.82	40.08
54.13	9.931	159.41	24.262	286.71	40.41
57.62	10.615	Liquid		289.36	40.53
60.02	11.081	181.96	37.50	295.77	40.85
62.89	11.633	186.24	37.52	305.99	41.36
68.18	12.590	189.74	37.54	316.09	41.95

[a] The conversions 0°C. = 273.16°K., molecular weight of 3-thiapentane = 90.186, and 1 calorie = 4.1833 international joules were used throughout this research.

Equilibrium melting temperatures, as a function of the fraction melted, were determined by the method described in an earlier publication.[8] The results are summarized in

Table II. The value obtained for the triple point is 169.21°K. Duplicate determinations of the heat of fusion gave the values 2845.0 and 2845.5 cal. mole^{-1}. The cryoscopic constant ($\Delta H_{fusion}/RT^2_{T.P.}$), calculated from these data is 0.0500 deg.$^{-1}$.

TABLE II

3-THIAPENTANE, MELTING POINT SUMMARY

		T, °K.	
Melted, %	$1/F$	Obsd.	Graph.[b]
10.39	9.62	169.1998	169.1986
25.72	3.89	.2046	.2046
51.25	1.95	.2066[a]	.2066
71.69	1.39	.2072	.2071
93.83	1.07	.2075[a]	.2075
100.00	1.00		.2076
Pure	0.00		.2086

[a] A straight line through these points was extrapolated to $1/F = 0$ to obtain the triple point ($T_{T.P.}$). [b] These are values of T on the straight line of footnote a.

Vapor Pressure Measurements.—The vapor pressure of 3-thiapentane for temperatures between 46 and 122° was measured by the ebulliometric method that has been described in a previous publication from this Laboratory.[9] $T_{T.P.} = 169.21 \pm 0.05°K$. Impurity: 0.005 ± 0.002 mole per cent. This value is obtained from the equation $N_2*/F = 0.0500\Delta T$, where N_2* is the mole fraction of impurity in the whole sample, F is the fraction of the sample in the liquid state, and ΔT is $T_{T.P.} - T_{obsd}$.

In this method, the boiling point of the substance is compared with the boiling point of water at the same pressure. The results of the measurements are given in Table III. These data were correlated by means of the Antoine equation

$$\log_{10} p = 6.92836 - 1257.833/(t + 218.662) \quad (2)$$

the constants of which were obtained by a least squares adjustment.[10] In this equation p is the vapor pressure in mm. and t is the temperature in °C. Values of the vapor pressure calculated by means of equation (2) are included in Table III for comparison with the experimental values. The normal boiling point, as given by equation (2), is 92.10°. The difference between the boiling and condensation temperatures of the sample at a pressure of 1 atmosphere was 0.006°.

TABLE III

VAPOR PRESSURE OF 3-THIAPENTANE

Boiling point, °C.		Pressure, mm.	
Water	3-Thiapentane	Obsd.	Calcd.
60.000	45.920	149.41	149.39
65	51.536	187.57	187.56
70	57.204	233.72	233.76
75	62.905	289.13	289.13
80	68.659	355.22	355.27
85	74.452	433.56	433.59
90	80.286	525.86	525.81
95	86.169	633.99	633.91
100	92.100	760.00	759.94
105	98.073	906.06	905.96
110	104.098	1074.6	1074.6
115	110.165	1268.0	1268.1
120	116.279	1489.1	1489.3
125	122.433	1740.8	1740.7

Vapor pressure data for 3-thiapentane in excellent agreement with the present results have recently been reported by White, Barnard-Smith and Fidler,[11] who also used an ebulliometric method. Over the range of their measurements (100 to 1000 mm.), the vapor pressures calculated

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

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

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

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

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

from the Antoine equation by which they represent their data and from equation (2) of this paper differ by less than 0.2%.

Heat of Vaporization and Vapor Heat Capacity.—Measurements of the heat of vaporization and vapor heat capacity of 3-thiapentane were made with a cycling vaporizer and flow calorimeter as described in previous publications from this Laboratory.[12] A metal vaporizer was used in place of the glass vaporizer described in ref. 12.

The values found for the heat of vaporization at 324.70, 344.16 and 365.26°K. were 8185, 7906 and 7591 cal. mole^{-1}. These are averages of at least three separate determinations whose maximum deviations from the mean were ±3, ±4 and ±4 cal. mole^{-1}, respectively. The accuracy of the heat of vaporization data is thought to be about ±0.1%. For interpolation within the temperature range covered by the experimental measurements, the following equation may be used.

$$\Delta H_{vap.} = 11,298 - 5.0897T - 1.3849 \times 10^{-2}T^2 \quad (3)$$

The heat capacity of the vapor was determined at two or more pressures at each of five temperatures ranging from 350.20 to 487.20°K. The results of these measurements are listed in Table IV. Values of C_p^0, the heat capacity in the ideal gas state, were obtained at each temperature

TABLE IV

VAPOR HEAT CAPACITY OF 3-THIAPENTANE, CAL. DEG.$^{-1}$ MOLE^{-1}

T, °K.	350.20	381.40	413.30	449.20	487.20
C_p (760 mm.)		34.260	35.998	38.089	40.189
C_p (385 mm.)	32.017	33.838			
C_p (188 mm.)	31.680	33.650	35.662	37.824	40.065
C_p^0 (obsd.)	31.36	33.45	35.55	37.74	40.02
C_p^0 (calcd.)^a	31.37	33.35	35.34	37.49	39.64
$(\partial C_p/\partial P)_T$, obsd.	1.29	0.81	0.45	0.35	0.16
$(\partial C_p/\partial P)_T$, calcd.	1.30	0.78	0.49	0.31	0.20

^{a} From spectroscopic and molecular structure data.

by linear extrapolation to zero pressure of plots of heat capacity vs. pressure. An accuracy uncertainty of ±0.2% is assigned to these values of C_p^0. They may be represented to within 0.1% by the following equation, which of course is valid only over the temperature range of the experimental measurements.

$$C_p^0 = 2.76 + 9.4965 \times 10^{-2} T - 3.794 \times 10^{-5}T^2 \quad (4)$$

Gas Imperfection and Second Virial Coefficient.—Values of the second virial coefficient, B, in the equation of state $PV = RT + BP$ were obtained at three temperatures from the heat of vaporization and vapor pressure data with the aid of the exact form of the Clapeyron equation. The relationship used was

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

where V_L is the molar volume of the liquid. In addition, the values of C_p as a function of pressure at five temperatures yielded values of the second derivative of B with respect to temperature, since $(\partial C_p/\partial p)_T = -T(d^2B/dT^2)$. These data were correlated by means of the empirical equation

$$B = -385 - 26.76e^{1250/T} \text{ cc. mole}^{-1} \quad (5)$$

The method of evaluating the constants in this equation has been described elsewhere.[13] The values of the second virial coefficient, -1524, -1389 and -1240 cc. mole^{-1}, obtained from the experimental data for the temperatures 324.70, 344.16 and 365.26°K., may be compared with the values, -1642, -1396 and -1205 cc. mole^{-1}, respectively, calculated by means of equation (5). The last two lines in Table IV compare the observed values of $(\partial C_p/\partial P)_T$ with those calculated by use of equation (5).

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

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

Entropy.—The calorimetric and vapor pressure data were utilized to calculate the entropy of 3-thiapentane in both the liquid and vapor states. The entropy calculations are summarized in Table V. For extrapolating the heat capacity of the solid below 15°K., a Debye function for 4.2 degrees of freedom with $\theta = 122.0°$ was used. This function fits the experimental heat capacity data between 15 and 21°K. within 0.01 cal. deg.$^{-1}$ mole^{-1}. For extrapolating the heat capacity of the liquid to the temperatures at which the heat of vaporization was measured, equation (1) was used; the integrals, $\int_{298.16}^{T} C_{sat}$ d ln T, were evaluated analytically. Equation (5) for the second virial coefficient was employed in calculating the correction for gas imperfection, $P(dB/dT)$.

TABLE V

ENTROPY OF 3-THIAPENTANE, CAL. DEG.$^{-1}$ MOLE^{-1}

0–15 °K.	Debye extrapolation	0.392
15–169.21°	Solid, graphical $\int C_{sat}$ d ln T	25.356
169.21°	Fusion, 2845/169.21	16.813
169.21–298.16°	Liquid, graphical $\int C_{sat}$ d ln T	21.796

Entropy (±0.10) of liquid at 298.16°K.		64.36

T, °K.	324.70	344.16	365.26
Entropy of liquid at 298.16°K.	64.36	64.36	64.36
Liquid $\int_{298.16}^{T} C_{sat}$ d ln T	3.55	6.06	8.69
Vaporization, $\Delta H_{vap.}/T.$	25.21	22.97	20.78
Compression, R ln $(p/760)$	−2.78	−1.35	0.00
Gas imperfection	0.09	0.13	0.19
Entropy (±0.20) of ideal gas at 1 atm.	90.43	92.17	94.02

Heat of Formation.—The heat of formation of 3-thiapentane was obtained from determinations of its heat of combustion. These were performed with a rotating combustion bomb and associated calorimetric apparatus recently developed in this Laboratory for the purpose of determining the heats of combustion of sulfur compounds. The combustion experiments were conducted in a platinum-lined bomb containing 10 ml. of liquid water. The bomb was charged with oxygen to a total pressure of 30 atmospheres without removing the air initially present in it. Oxides of nitrogen formed during the combustion (from the nitrogen of the air left in the bomb) effectively catalyzed the oxidation of sulfur-containing products of combustion to sulfuric acid. After the combustion had occurred, the bomb was rotated simultaneously about two axes for 90 seconds. The rotation had the two purposes of rinsing condensed sulfuric acid from the interior surfaces of the bomb to ensure that the final solution was homogeneous and of agitating the solution to promote equilibrium with respect to solution of the bomb gases. Appropriate corrections to the observed heat were applied for extraneous heat effects (such as the formation of nitrogen acids) and for reducing the results for the actual combustion reaction to those for the reaction involving the reactants and products in their standard states (Washburn corrections).
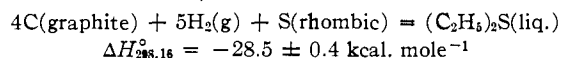
Calculation of the heat of formation from the heat of combustion data required a value of the heat of the reaction

$$H_2O(liq) + S(rhombic) + 3/2O_2(g) = H_2SO_4 \text{ (aqueous)}$$
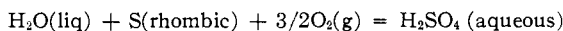
when the sulfuric acid produced is at the same concentration as that obtained in the heat of combustion experiments with 3-thiapentane. To obtain this datum, heat of combustion determinations were performed with mixtures of rhombic sulfur and a hydrocarbon oil, the heat of combustion of which was known from previous experiments. Determination of the heat of combustion of a sulfur compound and of elemental sulfur under nearly identical experimental conditions has the advantage that systematic errors tend to cancel in computing the heat of formation of the former.
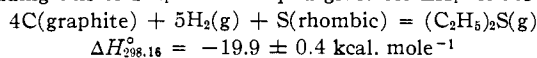
It is planned to include the detailed presentation of the heat of combustion data for 3-thiapentane and rhombic sulfur as part of the publication of a more complete description of the calorimetric apparatus and techniques. Therefore,

only the derived value of the heat of formation will be reported here. This is, for the reaction

$$4C(\text{graphite}) + 5H_2(g) + S(\text{rhombic}) = (C_2H_5)_2S(\text{liq.})$$
$$\Delta H^\circ_{298.16} = -28.5 \pm 0.4 \text{ kcal. mole}^{-1}$$

The uncertainty given is equal to twice the final "over-all" standard deviation.

A short extrapolation of the experimental heat of vaporization data [using equation (3)] gives 8.55 kcal. mole^{-1} at 298.16°K. for the heat of vaporization to the real gas at saturation pressure. When a small correction for gas imperfection is applied, the value obtained for the heat of vaporization to the gas in its standard state is 8.57 kcal. mole^{-1}. Adding this to ΔH_f° of the liquid gives for ΔH_f° of the gas

$$4C(\text{graphite}) + 5H_2(g) + S(\text{rhombic}) = (C_2H_5)_2S(g)$$
$$\Delta H^\circ_{298.16} = -19.9 \pm 0.4 \text{ kcal. mole}^{-1}$$

Thermodynamic Functions

The thermodynamic functions of 3-thiapentane were calculated from spectroscopic and molecular structure data by the usual formulas of statistical mechanics. Certain parameters required for these calculations were selected to give agreement between the calculated and observed values of the entropy and heat capacity. The treatment of the thermodynamic functions of 3-thiapentane reported here closely parallels that for 2-thiabutane reported in an earlier paper.[6] However, the greater complexity of the 3-thiapentane molecule as compared with the 2-thiabutane molecule makes the present treatment somewhat more approximate than that for the lower homolog. The more significant additional complexities are: (a) There are three spectroscopically important rotational isomers of 3-thiapentane as compared with the two of 2-thiabutane. Consequently, the spectra are more complex, and the assignment of observed frequencies to individual isomers is less straightforward. (b) Certain configurations of the 3-thiapentane molecule involve steric repulsion between the terminal methyl groups. The method selected to take account of these high energy configurations is somewhat artificial. (c) The cross terms in the kinetic energy of internal rotation, which are neglected in treating the rotations independently, are more important for 3-thiapentane than for 2-thiabutane. These circumstances will be discussed more fully in the appropriate places in the following sections.

Vibrational Assignment.—The vibrational assignment used for the thermodynamic calculations was based on the spectroscopic data listed in Table VI. Since these observed frequencies may arise from several different rotational isomers, a consideration of the possible rotational isomers is a necessary prerequisite to the discussion of the vibrational assignment. Different combinations of *trans-* and *skew-*configurations of the two ethyl groups can result in four spectroscopically distinguishable isomers whose point group symmetry, symmetry number and classification according to whether or not they exist in d and l forms are as follows:

Point group symmetry	Symmetry number	d-and l-forms
C_{2v}	2	No
C_1	1	Yes
C_2	2	Yes
C_s	1	No

These rotational isomers are illustrated in Fig. 1.

TABLE VI

SPECTRA OF 3-THIAPENTANE BELOW 1500 CM.$^{-1}$

Abbreviations used: $\bar{\nu}$, Raman displacement in cm.$^{-1}$; ν, infrared frequency in cm.$^{-1}$; I, intensity; ρ, depolarization factor; s, strong; m, medium; w, weak; vw, very weak.

Raman (liq.)[a]			Infrared (liq.)[b]		Assignment
$\bar{\nu}$	I	ρ	ν		
187	w				C-S-C bend., C_{2v}
256	vw				C-S-C bend., C_1 & C_2
305	m	0.29	308	s	C-C-S bend., C_{2v}
334	m	.44			C-C-S bend., C_1
			345	s	C-C-S bend., C_2
383	m	.62	379	s	C-C-S bend., C_{2v}, C_1 & C_2
639	s	.14	640	m	C-S str., C_2
657	s		660	m	C-S str., C_1
693	s	.63	693	m	C-S str., C_{2v} (double)
			738	m	CH$_2$ rock.
764	vw		764	m	C-S str., C_1
778	vw		781	m	C-S str., C_2
975	s	.88	973	s	C-C str.
1017	w				381 + 639 = 1020
1047	s	.29	1047	w	CH$_3$ rock.
1074	m		1074	m	CH$_3$ rock.
1249	w		1259	s	CH$_2$ wag.
1274	w				2 × 639 = 1278
			ca. 1310	vw	CH$_2$ twist.
1382	w		1377	s	CH$_3$ bend., sym.
1427	s	.87			CH$_3$ bend. and
1450	s		1451	s	CH$_3$ bend., unsym.

[a] Raman displacements and intensities from unpublished measurements by Dr. J. Rud Nielsen, Dept. of Physics, Univ. of Okla.; polarization data of ref. 14g. [b] KRS-5 region—unpublished measurements by Mr. T. G. Burke, Physics Dept., Carbide and Carbon Chemicals Division, K-25 Plant Laboratory, Oak Ridge, Tenn.; KBr region—ref. 14f; rocksalt region—ref. 14h.

The C_s form involves close approach of the terminal methyl groups and probably has a much higher energy than the other forms because of steric repulsion; it is unlikely that it exists in sufficient concentration for any of its vibrational frequencies to be observed spectroscopically. Therefore only the other three forms need be considered in interpreting the observed spectra.
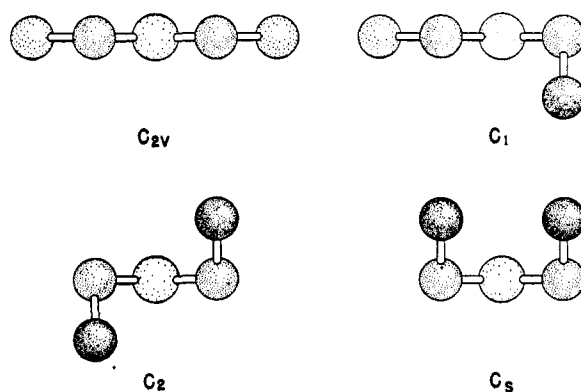

Fig. 1.—Rotational isomers of 3-thiapentane. The large spheres represent sulfur atoms and the smaller spheres carbon atoms. The hydrogen atoms are not shown. Only one enantiomorph of the C_1 and of the C_2 form is depicted.

The skeletal bending and C-S stretching modes of vibration will be considered first. Each rotational isomer has 5 such modes, and the 3 isomers together have a total of 15, all of which would be expected to have frequencies below 800 cm.$^{-1}$. Examination of the spectroscopic data which were

available at the time this work was undertaken[14] showed that in the region below 800 cm.$^{-1}$ there were only 10 observed frequencies, one of which had to be assigned to an internal ethyl group mode. A reinvestigation of the spectra with special effort to locate the six "missing" frequencies, therefore, seemed desirable. At the suggestion of A.P.I. Research Project 48A, Dr. J. Rud Nielsen of the University of Oklahoma redetermined the Raman spectrum and Mr. T. G. Burke of the Carbide and Carbon Chemicals Division extended the infrared measurements through the KRS-5 region (450–250 cm.$^{-1}$). This attempt to locate the six "missing" frequencies was only partly successful. One additional frequency was observed as a very weak Raman line at 256 cm.$^{-1}$, and a second was observed as a strong infrared band at 345 cm.$^{-1}$. The failure to observe all of the skeletal bending and C–S stretching frequencies suggested that some were so nearly coincident that they were unresolved in the observed spectra.

Approximate normal coördinate calculations were used to guide the assignment of the lower frequencies to particular rotational isomers and to indicate where near coincidences were to be expected. A five atom chain approximation was used, that is, point masses of 14 and 15 atomic weight units were substituted for the CH$_2$ and CH$_3$ groups, respectively. Wilson's G-F matrix method[15] was employed and the C–C stretching frequencies were factored out at once. The force constants selected were 2.2 × 10^5 dynes cm.$^{-1}$ for C–S stretching, 1.3 × 10^{-11} erg radian^{-2} for C–C–S bending and 0.9 × 10^{-11} erg radian^{-2} for C–S–C bending. The calculated frequencies for the three rotational isomers and the assignment of the observed frequencies made by analogy with the calculated values are:

	Calculated			Observed		
	C$_{2v}$	C$_i$	C$_2$	C$_{2v}$	C$_i$	C$_2$
C–S–C bend	184 p	221 p	224 p	187	256	256
C–C–S bend. (sym.)	295 p	315 p	415 p	305	334	381
C–C–S bend. (unsym.)	407 d	403 p	356 d	381	381	345
C–S str. (sym.)	708 p	671 p	633 p	693	657	639
C–S str (unsym.)	668 d	695 p	711 d	693	761	780

The designations "symmetrical" and "unsymmetrical" apply only to the C$_{2v}$ and C$_2$ forms. The Raman polarizations required by the selection rules are indicated by p, polarized, and d, depolarized. The interpretation made here implies that there are pairs of unresolved frequencies near 256 and 693 cm.$^{-1}$ and three unresolved frequencies near 381 cm.$^{-1}$. It is noteworthy that the 383 and 693 cm.$^{-1}$ Raman lines that are assumed to have polarized and depolarized components have higher depolarization factors than the 305, 334, 639 and 657 cm.$^{-1}$ lines that are assumed to be

single polarized lines. Sirkar and Bishui[14e] observed that, upon crystallization, the 639- and 657-cm.$^{-1}$ Raman lines (C$_2$ and C$_i$ forms) disappear and the 693-cm.$^{-1}$ line (C$_{2v}$ form) persists; 3-thiapentane therefore exists as the C$_{2v}$ form in the solid state.

The remaining frequencies to be considered are the internal frequencies of the ethyl groups. The assignment of these, as given in the last column of Table VI, was made by comparison with the corresponding frequencies of the ethyl groups bonded to sulfur in ethanethiol and 2-thiabutane.[6] These frequencies apparently have values so nearly the same for the different rotational isomers and for each of the two ethyl groups of the same isomer that they are not resolved in the observed spectra. The use of a very weak infrared band for the CH$_2$ twisting frequency is somewhat arbitrary. The thermodynamically unimportant CH$_2$ bending, unsymmetrical CH$_3$ bending and C–H stretching frequencies were assigned average values of 1445 cm.$^{-1}$ for the first two and 2950 cm.$^{-1}$ for the latter.

For thermodynamic calculations it is sufficient to use the vibrational assignment for one rotational isomer if the moments of inertia for over-all and internal rotation are calculated for the same configuration. The C$_{2v}$ form was selected for the moment of inertia calculations. The following complete set of vibrational frequencies of this form was therefore employed for thermodynamic calculations: 187, 305, 381, 693(2), 738(2), 974(2), 1047(2), 1074(2), 1254(2), 1310(2), 1380(2), 1445(6) and 2950(10) cm.$^{-1}$. The spectroscopic data on which the present assignment was based, with the exception of the Raman polarizations and the two infrared bands in the KBr region, were obtained with some of the same highly purified sample of 3-thiapentane that was used for the calorimetric studies of this investigation.

Moments and Reduced Moments of Inertia.— The methods of Kilpatrick and Pitzer[16] for molecules with compound internal rotation were used to compute the moments and reduced moments of inertia of the 3-thiapentane molecule. The bond distances and angles were estimated by analogy with structurally related molecules to be as follows: S–C distance, 1.82 Å.; C–C distance, 1.54 Å.; C–H distance, 1.09 Å.; C–S–C angle, 105°; all other angles, 109° 28'. The value obtained for the product of the three principal moments of inertia was 1.504 × 10^{-113} g.^{3} cm.^{6}. The off-diagonal elements of the internal rotational kinetic energy matrix were neglected, and the diagonal elements were taken as the reduced moments of inertia. These were 4.934 × 10^{-40} g. cm.^{2} for methyl rotation and 28.63 × 10^{-40} g. cm.^{2} for ethyl rotation. Neglect of the off-diagonal elements in this case is a rather poor approximation, as the square root of the determinant of the matrix differs by 12% from the square root of the product of the diagonal elements. However, error from this source is effectively compensated by using barriers to internal rotation selected to give agreement with the calorimetric value of the entropy.

(14) (a) S. Venkateswaren, *Indian J. Physics*, **6**, 51 (1931); (b) F. Matossi and H. Aderhold, *Z. Physik*, **68**, 683 (1931); (c) V. N. Thatte and A. S. Ganesan, *Nature*, **127**, 306 (1931); *Phil. Mag.*, **15**, 51 (1933); (d) P. Donzelot and M. Chaix, *Compt. rend.*, **202**, 851 (1936); (e) S. C. Sirkar and B. M. Bishui, *Science and Culture*, **9**, 90 (1943); (f) I. F. Trotter and H. W. Thompson, *J. Chem. Soc.*, **481** (1946); (g) R. Vogel-Högler, *Acta Phys. Austriaca*, **1**, 311 (1948); (h) Infrared data obtained at this Station and included in the Catalog of Infrared Spectral Data, American Petroleum Institute Research Project 44 at Carnegie Institute of Technology, Serial No. 790.

(15) E. B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).

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

Barriers to Internal Rotation.—The environment of either ethyl group of the 3-thiapentane molecule is very similar to the environment of the single ethyl group of the 2-thiabutane molecule. In the case of 2-thiabutane, the *trans*- and *skew*-configurations of the ethyl group have essentially the same energy, and a simple threefold cosine-type potential barrier is satisfactory for calculating the thermodynamic contributions of the ethyl rotation.[6] This result was transferred to the ethyl rotations of 3-thiapentane, but it was necessary to consider the steric repulsion between the terminal methyl groups in the C_s configuration of the molecule. If this steric repulsion did not exist, the fact that the internal symmetry number for each ethyl rotation is 1 and not 3 would have required a term $2 R \ln 3 = R \ln 9$ in the contribution of the ethyl rotations to the functions S° and $-(F^\circ - H_0^\circ)/T$. This can be regarded as the entropy and free energy of mixing of the nine forms corresponding to the nine combinations of the one *trans*- and two *skew*-configurations of each of the two ethyl groups. However, two of these nine combinations correspond to the C_s configuration of the molecule. It was assumed that the C_s configuration has high enough energy relative to the other configurations so that it can be neglected in the thermodynamic calculations. Then the appropriate term in the entropy and free energy function is $R \ln 7$ instead of $R \ln 9$. This same result was obtained by calculating the entropy and free energy of mixing of the C_{2v}, C_1 and C_2 rotational isomers with due regard to the differences in symmetry number and the existence of enantiomorphs of the C_1 and C_2 isomers.

Simple, threefold, cosine-type potential barriers were used in treating the methyl roations. The barrier heights for both kinds of internal rotation were selected to give agreement between the calculated and observed values of the entropy and of the heat capacity at the lower temperatures where the effects of anharmonicity are small. The barrier heights so obtained were 1750 cal. mole^{-1} for the ethyl rotations and 3550 cal. mole^{-1} for the methyl rotations.

Thermodynamic Functions.—The functions $-(F^\circ - H_0^\circ)/T$, $(H_0^\circ - H_0^\circ)/T$, $H^\circ - H_0^\circ$, S° and C_p° were computed for selected temperatures up to 1000°K. from the vibrational assignment, moments and reduced moments of inertia, and barrier heights given in the previous sections. The symmetry number (of the C_{2v} form) is 2. The 1949 atomic weights and the values of the fundamental physical constants given by Wagman, *et al.*,[17] were used in all computations of this paper. The thermodynamic functions are given in Table VII. For reasons of internal consistency, the tabulated values are all given to four digits, although in some places in the table the retention of the last digit is not justified by the accuracy of the molecular-structure parameters used in the calculations or by the reliability of the approximations employed. The calculated thermodynamic functions are necessarily less reliable at the higher temperatures,

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

TABLE VII

MOLAL THERMODYNAMIC FUNCTIONS OF 3-THIAPENTANE

T, °K.	$-(F^\circ - H_0^\circ)/T$, cal. deg.$^{-1}$	$(H^\circ - H_0^\circ)/T$, cal. deg.$^{-1}$	$H^\circ - H_0^\circ$, kcal.	S°, cal. deg.$^{-1}$	C_p°, cal. deg.$^{-1}$
273.16	68.04	17.52	4.786	85.56	26.35
298.16	69.62	18.34	5.467	87.96	27.95
300	69.74	18.39	5.518	88.13	28.07
400	75.48	21.61	8.644	97.09	34.51
500	80.65	24.79	12.39	105.4	40.33
600	85.43	27.82	16.69	113.2	45.31
700	89.94	30.61	21.43	120.6	49.57
800	94.20	33.20	26.56	127.4	53.20
900	98.24	35.62	32.06	133.9	56.39
1000	102.1	37.83	37.83	140.0	59.17

where the contributions of the less accurately assigned higher frequencies become important and where ·the neglect of anharmonicity and other effects in the simple treatment is more serious.

The observed values of the entropy at 324.70, 344.16 and 365.26°K., 90.43, 92.17 and 94.02 cal. deg.$^{-1}$ mole^{-1} may be compared with the calculated values at these same temperatures, 90.40, 92.17 and 94.05 cal. deg.$^{-1}$ mole^{-1}. The observed and calculated values of the vapor heat capacity are compared in Table IV; the differences at the higher temperatures are no greater than is to be expected from the neglect of anharmonicity in the calculated values.

Heat, Free Energy and Equilibrium Constant of Formation

The heat, free energy and equilibrium constant of formation of 3-thiapentane at selected temperatures were computed from the value of ΔH_f° at 298.16°K. and the thermodynamic functions of this paper, the thermodynamic functions for graphite and hydrogen given by Wagman, *et al.*,[17] and the thermodynamic functions for sulfur given in "Selected Values of Chemical Thermodynamic Properties."[18] Diatomic sulfur gas was adopted

TABLE VIII

HEAT, FREE ENERGY AND LOGARITHM OF EQUILIBRIUM CONSTANT FOR FORMATION OF 3-THIAPENTANE

T, °K.	ΔH_f°, kcal. mole^{-1}	ΔF_f°, kcal. mole^{-1}	$\log_{10} K_f$
4C(graphite) + 5H$_2$(g) + S(rhombic)		= (C$_2$H$_5$)$_2$S(liq)	
298.16	−28.5	+ 2.7	−2.00
4C(graphite) + 5H$_2$(g) + ½S$_2$(g)		= (C$_2$H$_5$)$_2$S(g)	
0	−28.6	−28.6	Infinite
298.16	−35.3	− 5.3	3.87
300	−35.4	− 5.1	3.71
400	−37.1	+ 5.3	−2.88
500	−38.5	16.0	−7.01
600	−39.7	27.1	−9.85
700	−40.6	38.2	−11.94
800	−41.2	49.5	−13.53
900	−41.7	60.9	−14.80
1000	−42.0	72.3	−15.81

(18) (a) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D. C., 1949, *et seq.*, Series I, Table 14-1 and Series III [S$_2$(g)]; (b) National Bureau of Standards Report No. 1037.

as the reference state for elemental sulfur for temperatures other than 298.16°K. The computed values are presented in Table VIII.

Acknowledgments.—The authors wish to thank Dr. J. Rud Nielsen, of the Physics Department, University of Oklahoma, Norman, Oklahoma, and Mr. T. G. Burke, of the Physics Department, Carbide and Carbon Chemicals Division, Oak Ridge, Tennessee, for making available spectroscopic data which were essential to this investigation. The assistance of Mr. Robert Robinson in some of the experimental measurements is gratefully acknowledged.

BARTLESVILLE, OKLAHOMA

Thermodynamic Properties of Furan

By G. B. Guthrie, Jr., D. W. Scott, W. N. Hubbard, C. Katz, J. P. McCullough, M. E. Gross, K. D. Williamson and Guy Waddington

A sample of furan was purified and used for calorimetric studies and for measurement of vapor pressure, density, refractive index, infrared spectrum ($2-15\mu$) and mass spectrum. The heat of formation of liquid furan ($-\Delta H_f = 14.90$ kcal. mole^{-1}) was derived from heat of combustion measurements. Low temperature thermal studies included measurement of the heat capacity of the solid, transition temperature (150.0°K.), heat of transition (489.2 cal. mole^{-1}), triple point (187.55°K.), heat of fusion (908.8 cal. mole^{-1}) and heat capacity of the liquid. The entropy of the liquid at 298.16°K., calculated from these data is 42.22 cal. deg.$^{-1}$ mole^{-1}. The observed vapor pressures between 2 and 62° are represented by the equation $\log_{10} p$ (mm.) $= 6.97523 - 1060.851/(t + 227.740)$. The heat of vaporization at the normal boiling point (31.36°) is 6474 cal. mole^{-1}. The vapor heat capacity, measured at five temperatures between 317 and 488°K., is given by the equation $C_p^0 = -7.55 + 9.352 \times 9.352 \times 10^{-2}T - 5.287 \times 10^{-5} T^2$ cal. deg.$^{-1}$ mole^{-1}. The equation $B = -279 - 22.6 \exp(950/T)$ cc. mole^{-1} was derived for the second virial coefficient from calorimetric data. A vibrational assignment which was partly empirical was made and used with molecular structure data to compute thermodynamic functions of the ideal gas to 1500°K. The heat, free energy and equilibrium constant of formation at temperatures to 1500° were calculated using appropriate calorimetric data and thermodynamic functions.

An investigation of the thermodynamic properties of furan was included in the research program of this Laboratory following a recent study of its sulfur analog, thiophene.[1] Derivatives of furan are used widely in the petroleum industry and are important items in the chemical trade. This investigation, in addition to supplying thermodynamic data for furan itself, has provided fundamental information which will be needed for future studies of the various derivatives of furan.

The several phases of this investigation, in the order of their presentation in this paper, were: (1) purification of the material and determination of the infrared spectrum of the liquid and of some of its physical properties including the triple point, density and refractive index; (2) measurement of the vapor pressure as a function of temperature; (3) determination of the heat of combustion and heat of formation; (4) measurement of the heat capacity of the solid and liquid and the heats of transition and fusion; (5) measurement of the heat of vaporization and the vapor heat capacity; (6) calculation of the entropy of the liquid and of the ideal gas from the appropriate experimental data; and (7) calculation of the thermodynamic functions and the heat, free energy and equilibrium constant of formation of the ideal gas at selected temperatures from molecular structure, spectroscopic and calorimetric data.

Units and Conversion Factors.—In this paper the defined calorie (1 cal. = 4.18 40 abs. j.) is used throughout for the unit of energy. Celsius temperatures are converted to Kelvin temperatures by adding 273.16°. The molecular weight of furan calculated from the 1949 atomic weights is 68.072.

The Material and Its Physical Properties

Purification and Purity.—About 1.2 l. of technical furan was distilled through a 70-plate column packed with steel helices. An atmosphere of nitrogen was maintained in the still at all times, and an inhibitor (hydroquinone) was added to each fraction when it was removed. Two 70-ml. heart cuts, samples A and B, were used for low-temperature and vapor pressure measurements, respectively, and portions of both samples were used for determining the heat of combustion. Later these two samples were combined for the determinations of the density, refractive index and infrared spectrum. Several other cuts, totaling about 300 ml., were combined into a third sample (C), which was used for the heat of vaporization and vapor heat capacity measurements. Each sample of furan was separated from the inhibitor and dried by a bulb-to-bulb distillation under its own vapor pressure in which the vapors passed over anhydrous magnesium perchlorate. The samples were stored in sealed ampoules under their own vapor pressure.

In the course of the low temperature thermal measurements, the purity of sample A was determined to be 99.98 ± 0.01 mole %.[2] The purity of sample B was not determined quantitatively. Since the boiling and condensation temperatures observed in the vapor pressure measurements differed by only 2 millidegrees at the normal boiling point, it is evident that sample B did not contain enough impurity of different volatility to have any significant effect on the vapor pressure measurements. The heat of combustion of this sample was indistinguishable from that of sample A. Since this measurement is sensitive to about 0.05 mole % of C₅-hydrocarbons (the most probable impurities), it is believed that sample B was more than 99.9 mole % pure. The mass spectra of samples A and C were determined.[3] Isopentane (0.01 mole %) and a trace of an unidentified impurity (peak at 85) were found in sample A. Sample C showed 0.04 mole % isopentane and a somewhat larger trace of the same unidentified impurity. This analysis sug-

---

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