$Fe(OH)^{+}_{2}$, $Fe(OH)_3$, as reported by Lamb and Jacques,[22] has been suggested to be due to less purely ionic binding.[20]

Using the method of continuous variations, with a light filter transmitting around 5000 Å., Babko[4] found that for aqueous molybdenum thiocyanate solutions the ratio for maximum absorbancy was near 1:5. He concluded that this was also the Mo:CNS ratio for the amber complex. However, if the stability constants for the aqueous complexes are assumed to be roughly of the orders now reported for 60% acetone–water, it can be shown mathematically, as discussed earlier, that the observed maximum occurs at a significantly higher thiocyanate ratio than is found in A.

Although Hiskey and Meloche reported[2] a Mo:CNS ratio of 1:3 for the complex they studied, over the range 1–2 *M* hydrochloric acid, it is doubtful that their complex was A. The slow, uniform rate of formation of the complex, reaching a maximum after about one hour, contrasts with the very rapid development of color when A is formed under comparable conditions, nor is it consistent with the catalyzed oxidation of lower valence molybdenum such as can follow the reduction of molybdates by stannous chloride in the absence of iron and copper.[5] The absorption curves of Hiskey and Meloche show a maximum near 5100 Å. which is absent from A, while the data indicate significantly less complete formation of the complex at high thiocyanate concentrations in 1 *M* hydrochloric acid than was found for A in the present work. Finally, application to the present results of the mathematical treatment of Hiskey and Meloche, for the dependence of absorbancy on thiocyanate concentration gave, at 4600 Å., good agreement for $n = 1$, corresponding to the conversion of Y to A at the high thiocyanate concentrations involved. The value of $n = 3$, reported by Hiskey and Meloche, is incompatible with the equilibria proposed in the present work.

HAMILTON, NEW ZEALAND

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[22] A. B. Lamb and A. G. Jacques, THIS JOURNAL, **60**, 1215 (1938).

[CONTRIBUTION NO. 68 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

2,3-Dithiabutane, 3,4-Dithiahexane and 4,5-Dithiaoctane: Chemical Thermodynamic Properties from 0 to 1000°K.[1]

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Thermodynamic properties of the first three members of the symmetrical alkane disulfide series were investigated. Measurements were made of the heat of vaporization and vapor heat capacity of 2,3-dithiabutane; the low temperature thermal properties, vapor pressure and entropy of 4,5-dithiaoctane; and the heats of combustion and formation of 2,3-dithiabutane, 3,4-dithiahexane and 4,5-dithiaoctane. The new experimental data were used in revising previously published tables of thermodynamic functions for 2,3-dithiabutane and 3,4-dithiahexane. A table of thermodynamic functions for 4,5-dithiaoctane was calculated by an incremental method. Values of the heat, free energy and logarithm of the equilibrium constant of formation between 0 and 1000°K. were computed for the three compounds. The S–S thermochemical bond energy is the same in the three disulfides as in S_8 within experimental uncertainty.

Chemical thermodynamic studies of alkane disulfides are included in the program of American Petroleum Institute Research Project 48A in this Laboratory. Earlier publications reported experimental thermodynamic studies and tables of thermodynamic functions for 2,3-dithiabutane (dimethyl disulfide)[2] and 3,4-dithiahexane (diethyl disulfide).[3] This paper reports additional experimental studies for those two compounds and the next higher symmetrical alkane disulfide, 4,5-dithiaoctane (di-*n*-propyl disulfide). The experimental work included: for 2,3-dithiabutane, vapor flow calorimetry and combustion calorimetry; for 3,4-dithiahexane, combustion calorimetry; and for 4,5-dithiaoctane, low temperature calorimetry, comparative ebulliometry and combustion calorimetry. Detailed results are presented later in the Experimental section. However, the more pertinent results, to which reference will be made in the subsequent discussion, are collected for ready reference in Table I.

The experimental results were used in calculating more reliable tables of thermodynamic functions for 2,3-dithiabutane and 3,4-dithiahexane. A similar table for 4,5-dithiaoctane was obtained by an incremental method. The values of $\Delta Hf°_{298.16}$ were used to calculate the standard heat, standard free energy and logarithm of the equilibrium constant of formation for all three substances over the temperature range of interest. Finally, values $\Delta Hf°_{298.16}$ for the related symmetrical alkane sulfides, also determined in this Laboratory, made possible calculations of the S–S thermochemical bond energy. The several calculations are discussed in the next section.

Chemical Thermodynamic Properties

Thermodynamic Functions of 2,3-Dithiabutane.—The thermodynamic functions given for 2,3-

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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. The authors wish to acknowledge the assistance of Thelma C. Kincheloe with the low temperature calorimetry, James P. Dawson with the comparative ebulliometry and Frankie R. Frow with the combustion calorimetry.

[2] D. W. Scott, H. L. Finke, M. E. Gross, G. B. Guthrie and H. M. Huffman, THIS JOURNAL, **72**, 2424 (1950).

[3] D. W. Scott, H. L. Finke, J. P. McCullough, M. E. Gross, R. E. Pennington and Guy Waddington, *ibid.*, **74**, 2478 (1952).

TABLE I

OBSERVED AND CALCULATED MOLAL THERMODYNAMIC PROPERTIES FOR THE VAPOR STATE

2,3-Dithiabutane

	Entropy, $S°$, cal. deg. $^{-1}$			Heat capacity, $C_p°$, cal. deg. $^{-1}$	
T, °K.	Obsd.	Calcd.	T, °K.	Obsd.	Calcd.
340.80	83.57	83.58	369.20	25.24	25.22
360.40	84.91	84.95	392.20	26.06	26.07
382.90	86.44	86.48	420.20	27.07	27.08
			450.20	28.15	28.14
			500.20	29.81	29.81

$$2C(c, \text{graphite}) + 3H_2(g) + S_2(g) = C_2H_6S_2(g)$$

$$\Delta Hf°_{298.16}(\text{obsd.}) = -36.59 \pm 0.25 \text{ kcal.}$$

3,4-Dithiahexane

	Entropy, $S°$, cal. deg. $^{-1}$			Heat capacity, $C_p°$, cal. deg. $^{-1}$	
T, °K.	Obsd.	Calcd.	T, °K.	Obsd.	Calcd.
373.73	107.31[a]	107.28	408.20	41.41[a]	41.44
400.04	109.96[a]	110.00	428.25	42.71[a]	42.75

$$4C(c, \text{graphite}) + 5H_2(g) + S_2(g) = C_4H_{10}S_2(g)$$

$$\Delta Hf°_{298.16}(\text{obsd.}) = -48.26 \pm 0.29 \text{ kcal.}$$

4,5-Dithiaoctane

$S°_{298.16}(\text{obsd.}) = 118.3$ cal. deg. $^{-1}$

$S°_{298.16}(\text{calcd.}) = 118.3$ cal. deg. $^{-1}$

$$6C(c, \text{graphite}) + 7H_2(g) + S_2(g) = C_6H_{14}S_2(g)$$

$$\Delta Hf°_{298.16}(\text{obsd.}) = -58.61 \pm 0.30 \text{ kcal.}$$

[a] From ref. 3.

TABLE II

THE MOLAL THERMODYNAMIC PROPERTIES OF 2,3-DITHIABUTANE[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	−32.65	−32.65	Infinite
273.16	−63.07	15.44	4.219	78.52	21.59	−36.32	−17.34	13.88
298.16	−64.46	16.00	4.771	80.46	22.54	−36.59	−15.60	11.43
300	−64.56	16.04	4.813	80.60	22.61	−36.61	−15.47	11.27
400	−69.47	18.15	7.260	87.62	26.36	−37.54	− 8.28	4.52
500	−73.73	20.15	10.07	93.88	29.80	−38.28	− 0.88	0.38
600	−77.59	22.00	13.20	99.59	32.82	−38.86	6.65	−2.42
700	−81.10	23.74	16.62	104.84	35.41	−39.26	14.28	−4.46
800	−84.38	25.35	20.28	109.72	37.66	−39.50	21.94	−5.99
900	−87.44	26.83	24.14	114.27	39.60	−39.62	29.64	−7.20
1000	−90.34	28.20	28.20	118.53	41.31	−39.61	37.34	−8.16

[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 of formation by the reaction: $2C(c, \text{graphite}) + 3H_2(g) + S_2(g) = C_2H_6S_2(g)$.

dithiabutane in Table IX of ref. 2 were revised to accord with the new experimental values of $S°$ and $C_p°$. Minor changes in the set of fundamental vibrational frequencies were made in view of more recent spectroscopic data.[4,5] The set used was 239, 272, 509, 689(2), 954(4), 1305(2), 1425(4), 2910(2) and 2985(4). Values of the moments and reduced moments of inertia given in ref. 2 were used unchanged. The following values of the parameters used to compute the contributions of internal rotation and anharmonicity were chosen simultaneously to give agreement between calculated and observed values of $S°$ and $C_p°$ (see Table I): effective barrier height for rotation about the S–S bond, 6800 cal. mole^{-1}; effective barrier height for methyl rotation, 1500 cal. mole^{-1}; and empirical anharmonicity parameters,[6,7] ν = 1100 cm.$^{-1}$ and Z = 0.80 cal. deg.$^{-1}$ mole^{-1}. If rotation about the S–S bond did not interact with the methyl rotations or the molecular vibrations, a barrier height of 6800 cal. mole^{-1} would correspond to a torsional frequency of 98 cm.$^{-1}$ The fact that the observed torsional frequency is somewhat higher (*ca.* 120 cm.$^{-1}$) indicates significant interaction. However, the assumption that the internal rotations are independent is satisfactory for the calculation of thermodynamic functions if the effective barrier heights are evaluated from the calorimetric data.

The calculated thermodynamic functions of 2,3-dithiabutane are listed in columns 2–6 of Table II.

Thermodynamic Functions of 3,4-Dithiahexane.—The thermodynamic functions given for 3,4-dithiahexane in Table VII of ref. 3 were revised to take advantage of the more reliable value of the effective barrier height for rotation about the S–S bond that was obtained from the study of 2,3-dithiabutane. All degrees of freedom were treated as described in ref. 3 except rotation about the S–S bond and rotation of the two ethyl groups. For rotation about the S–S bond the effective barrier height of 6800 cal. mole^{-1} was taken from 2,3-dithiabutane. The following potential function for rotation of an ethyl group (Fig. 1) was then selected to give satisfactory agreement between calculated and observed values of $S°$ and $C_p°$ (see Table I)

$$\begin{aligned} V &= (4500/2)(1 + \cos 3\phi) + (1200/2)(1 - \cos 2\phi) && 0 < \phi < \pi/3 \\ &= (1200/2)(1 - \cos 2\phi) && \pi/3 < \phi < \pi \\ &= (4500/2)(1 + \cos \phi) && \pi < \phi < 2\pi \end{aligned}$$

The units are V in cal. mole^{-1}. This potential function implies a reasonable energy difference of 0.9 kcal. mole^{-1} between the *trans*-configuration and lower-energy *skew*-configuration of an ethyl group. Anharmonicity was neglected because not enough experimental values of $C_p°$ were available for evaluating the empirical anharmonicity

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(4) R. Vogel-Högler, *Acta Phys. Austriaca*, **1**, 311 (1948).

(5) American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology, Catalog of Infrared Spectral Data, Serial Nos. 1247 and 1615.

(6) 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).

(7) R. E. Pennington and K. A. Kobe, *J. Chem. Phys.*, **22**, 1442 (1954).

TABLE III

THE MOLAL THERMODYNAMIC PROPERTIES OF 3,4-DITHIAHEXANE[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.	logKf[b]
0	0	0	0	0	0	−41.81	−41.81	Infinite
273.16	− 74.26	21.92	5.988	96.18	32.01	−47.83	−16.30	13.04
298.16	− 76.23	22.85	6.812	99.07	33.78	−48.26	−13.40	9.82
300	− 76.37	22.92	6.874	99.28	33.91	−48.29	−13.18	9.60
400	− 83.45	26.54	10.62	109.99	40.90	−49.81	− 1.24	0.68
500	− 89.75	30.05	15.03	119.81	47.08	−50.99	11.05	− 4.83
600	− 95.53	33.33	20.00	128.87	52.24	−51.87	23.54	− 8.57
700	−100.90	36.36	25.45	137.26	56.57	−52.49	36.16	−11.29
800	−105.93	39.11	31.29	145.04	60.19	−52.89	48.86	−13.35
900	−110.69	41.62	37.46	152.32	63.30	−53.10	61.59	−14.96
1000	−115.20	43.92	43.92	159.13	65.97	−53.12	74.33	−16.24

[a] See footnote a, Table II. [b] The standard heat, standard free energy and common logarithm of the equilibrium constant of formation by the reaction: $4C(c, graphite) + 5H_2(g) + S_2(g) = C_4H_{10}S_2(g)$.

TABLE IV

THE MOLAL THERMODYNAMIC PROPERTIES OF 4,5-DITHIAOCTANE[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	−49.64	−49.64	Infinite
273.16	− 86.10	28.44	7.770	114.5	41.9	−57.99	−14.09	11.28
298.16	− 88.67	29.66	8.844	118.3	44.3	−58.61	−10.06	7.38
300	− 88.83	29.78	8.932	118.6	44.5	−58.64	− 9.76	7.11
400	− 98.04	34.72	13.89	132.8	54.5	−60.83	6.90	− 3.77
500	−106.3	39.60	19.80	145.9	63.5	−62.55	24.03	−10.50
600	−114.0	44.24	26.54	158.2	71.3	−63.81	41.46	−15.10
700	−121.1	48.60	34.03	169.7	78.0	−64.66	59.08	−18.45
800	−127.9	52.61	42.09	180.5	83.7	−65.16	76.80	−20.98
900	−134.3	56.36	50.72	190.7	88.8	−65.30	94.51	−22.95
1000	−140.4	59.84	59.84	200.2	93.2	−65.12	112.3	−24.55

[a] See footnote a, Table II. [b] The standard heat, standard free energy and common logarithm of the equilibrium constant of formation by the reaction: $6C(c, graphite) + 7H_2(g) + S_2(g) = C_6H_{14}S_2(g)$.

parameters. For independent rotation about the S–S bond, a barrier height of 6800 cal. mole^{-1} would correspond to a torsional frequency of 82 cm.$^{-1}$. The observed torsional frequency is 115 cm.$^{-1}$. As in the case of 2,3-dithiabutane, the higher value of the observed frequency indicates significant interaction with other degrees of freedom.

The calculated thermodynamic functions of 3,4-dithiahexane are listed in columns 2–6 of Table III.

Thermodynamic Functions of 4,5-Dithiaoctane.—Thermodynamic functions of 4,5-dithiaoctane were estimated by the addition of two CH_2 increments to the corresponding functions of 3,4-dithiahexane in Table III. The CH_2 increments appropriate for replacement of an ethyl group bonded to sulfur with a n-propyl group were obtained as the difference in the thermodynamic functions of 1-propanethiol[8] and ethanethiol.[9] The formula used was then

$$G°(\text{4,5-dithiaoctane}) = G°(\text{3,4-dithiahexane}) + 2G°(\text{1-propanethiol}) - 2G°(\text{ethanethiol})$$

In the foregoing $G°$ represents any one of the functions $(F° - H°_0)/T$, $(H° - H°_0)/T$, $H° - H°_0$, $S°$ or $C_p°$. The comparison in Table I shows that the value of $S°_{298.16}$ as calculated by the incremental method is concordant with the experimentally determined value. The exact agreement must be regarded as fortuitous in view of the uncertainties in both values.

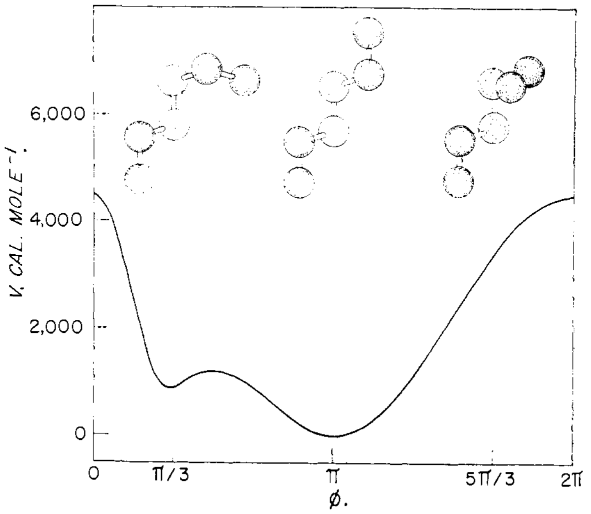

Fig. 1.—Potential function for rotation of an ethyl group in 3,4-dithiahexane. Sketches of molecular configuration (hydrogen atoms not shown) show position of upper ethyl group for $\phi = \pi/3$, π and $5\pi/3$.

The calculated thermodynamic functions of 4,5-dithiaoctane are listed in columns 2–6 of Table IV.

The Heat, Free Energy and Equilibrium Constant of Formation.—The calculated values of the

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(8) R. E. Pennington, D. W. Scott, H. L. Finke, J. P. McCullough, J. F. Messerly, I. A. Hossenlopp and Guy Waddington, THIS JOURNAL, **78**, 3266 (1956).

(9) J. P. McCullough, W. N. Hubbard, F. R. Frow, I. A. Hossenlopp and Guy Waddington, *ibid.*, **79**, 561 (1957).

thermodynamic functions, the experimental values of $\Delta Hf°_{298.16}$ (Table I) and values of the thermodynamic functions of C(c, graphite),[10] $H_2(g)$[10] and $S_2(g)$[11] were used to compute $\Delta Hf°$, $\Delta Ff°$ and $\log_{10} Kf$ at selected temperatures from 0 to 1000°K. The computed values are listed in columns 7–9 of Tables II, III and IV.

The S–S Thermochemical Bond Energy

The hypothetical reaction of an alkane disulfide to give the corresponding sulfide and a normal ^3P sulfur atom involves loss of one S–S bond. The standard heat of the reaction (at 298.16°K.) is simply the S–S thermochemical bond energy, E(S–S), as customarily defined.

$$\text{R–S–S–R}'(g) = \text{R–S–R}'(g) + S(g)$$

$$\Delta H°_{298.16} = \Delta Hf°_{298.16}(\text{R–S–R}') + \Delta Hf°_{298.16}(S) - \Delta Hf°_{298.16}(\text{R–S–S–R}') = E(\text{S–S})$$

In addition to the values of $\Delta Hf°_{298.16}$ in Table I, values for the corresponding sulfides, 2-thiapropane, 3-thiapentane and 4-thiaheptane are also available from work in this Laboratory. Values of $[E(\text{S–S}) - \Delta Hf°_{298.16}(S)]$ from the three pairs may be compared without need for the value of $\Delta Hf°_{298.16}(S)$, which is controversial. Such a comparison is made in Table V. The value from the heat of formation of $S_8(g)$[12] is also included in the table. Within experimental uncertainty, the same value of $[E(\text{S–S}) - \Delta Hf°_{298.16}(S)]$ is obtained from each of the three pairs of sulfides and disulfides. This value, in turn, is the same, within experimental uncertainty, as that obtained from the heat of formation of $S_8(g)$. The calculations for the sulfides and the disulfides involve only two heats of formation determined in the same laboratory by the same method; therefore, any systematic errors in the determination of the heats of formation should tend to cancel. Also, these calculations are independent of the C–C, C–H and C–S thermochemical bond energies and, incidentally, of the heats of atomization of carbon or hydrogen.

TABLE V

S–S THERMOCHEMICAL BOND ENERGY

R	$\Delta Hf°_{298.16}$, kcal. mole^{-1a} R–S–R	$\Delta Hf°_{298.16}$, kcal. mole^{-1a} R–S–S–R	E(S–S) − $\Delta Hf°_{298.16}(S)^a$, kcal.
Methyl	-24.40^b	-36.59	12.2
Ethyl	-35.19^c	-48.26	13.1
n-Propyl	-45.63^d	-58.61	13.0
From heat of formation of $S_8(g)$			12.4

[a] Reference state for sulfur is $S_2(g)$. [b] Ref. 9. [c] More recent experimental value that supersedes that of ref. 20. [d] Unpublished datum from this Laboratory.

In the preparation of an internally consistent set of thermochemical bond energies, once a value has been selected for the heat of formation of atomic sulfur in the normal ^3P state from $S_2(g)$, the S–S thermochemical bond energy may be obtained at once from the equation

$$E(\text{S–S}) = \Delta Hf°_{298.16}(S) + (12.7 \pm 0.5) \text{ kcal.}$$

The values of $\Delta Hf°_{298.16}$ in Table V may also be used with kinetic, electron impact and other data in the preparation of an internally consistent set of *dissociation* bond energies as, for example, D (RS–SR) for the process, R–S–S–R(g) = 2 R–S·(g).

Experimental

The reported data are based on the 1951 International Atomic Weights[13] and the relations: 0° = 273.16°K. and 1 cal. = 4.1840 abs. j. = 4.1833 int. j. The 1951 fundamental physical constants[14] were used in all calculations. Measurements of temperature were made with platinum resistance thermometers calibrated in terms of the International Temperature Scale[15] between 90 and 500°K. and the provisional scale of the National Bureau of Standards[16] between 11 and 90°K. All electrical and mass measurements were referred to standard devices calibrated at the National Bureau of Standards.

The basic experimental techniques used in this research are discussed in published descriptions of apparatus and methods for low temperature calorimetry,[17] vapor flow calorimetry,[18] comparative ebulliometry[19] and combustion calorimetry.[20]

The Materials.—The samples of 2,3-dithiabutane, 3,4-dithiahexane and 4,5-dithiaoctane used for low temperature calorimetry, comparative ebulliometry and combustion calorimetry were parts of Standard Samples of Sulfur Compounds, designated NBS 907, NBS 908 and API-USBM 33, respectively. These were prepared and purified at the Laramie, Wyo., Station of the Bureau of Mines. The purities of these samples, as determined by calorimetric studies of melting point as a function of fraction melted, were 99.97,[2] 99.92[3] and 99.97 mole %, respectively. For vapor flow calorimetry, which required a larger volume of material, a sample of 2,3-dithiabutane of somewhat lower purity was provided by the Laramie Station.

Vapor Flow Calorimetry of 2,3-Dithiabutane.—Vapor flow calorimetry of 2,3-dithiabutane yielded the experimental values of heat of vaporization and vapor heat capacity listed in Tables VI and VII. The estimated accuracy uncertainty of the values of ΔHv and $C_p°$ are 0.1 and 0.2%, respectively. The empirical equations selected to represent the results are

$$\Delta Hv = 12932 - 12.131T - 1.615 \times 10^{-3}T^2 \text{ cal. mole}^{-1} \text{ (341–383°K.)} \quad (1)$$

$$C_p° = 9.173 + 4.971 \times 10^{-2}T - 1.688 \times 10^{-5}T^2 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \text{ (369–500°K.)} \quad (2)$$

TABLE VI

THE MOLAL HEAT OF VAPORIZATION AND SECOND VIRIAL COEFFICIENT OF 2,3-DITHIABUTANE

T, °K.	P, atm.	ΔHv, cal.	$B_{\text{obsd.}}$, cc.	$B_{\text{calcd.}}$,^{a} cc.
340.80	0.250	8610 ± 2^b	−1331	−1353
360.40	.500	8350 ± 5^b	−1208	−1185
382.90	1.000	8050 ± 4^b	−1030	−1040

[a] Calculated from eq. 3. [b] Maximum deviation from the mean of three determinations.

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

(11) W. H. Evans and D. D. Wagman, *ibid.*, **49**, 141 (1952).

(12) G. B. Guthrie, Jr., D. W. Scott and Guy Waddington, THIS JOURNAL, **76**, 1488 (1954).

(13) E. Wichers, *ibid.*, **74**, 2447 (1952).

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

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

(16) H. J. Hoge and F. G. Brickwedde, *ibid.*, **22**, 351 (1939).

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(18) Guy Waddington, S. S. Todd and H. M. Huffman, *ibid.*, **69**, 22 (1947); J. P. McCullough, D. W. Scott, R. E. Pennington, I. A. Hossenlopp and Guy Waddington, *ibid.*, **76**, 4791 (1954).

(19) Guy 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).

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

TABLE VII

THE MOLAL VAPOR HEAT CAPACITY OF 2,3-DITHIABUTANE IN CAL. DEG.$^{-1}$

T, °K.	369.20	392.20	420.20	450.20	500.20
C_p(1.000 atm.)		26.637	27.474	28.427	29.980
C_p(0.500 atm.)	25.584	26.316			
C_p(0.250 atm.)	25.410	26.210	27.169	28.221	29.850
$C_p°$(obsd.)	25.24	26.06	27.07	28.15	29.81
$-T(d^2B/dT^2)$, obsd.^{a}	0.70	0.57	0.41	0.28	0.17
$-T(d^2B/dT^2)$, calcd.^{b}	.76	.56	.39	.28	.17

^{a} Units: cal. deg.$^{-1}$ mole^{-1} atm.$^{-1}$. ^{b} Calculated from eq. 3.

Equation 2 represents the experimental values of $C_p°$ within 0.1%. The effects of gas imperfection were correlated by the procedure described in an earlier publication from this Laboratory.[21] The empirical equation obtained for B, the second virial coefficient in the equation of state, $PV = RT(1 + B/V)$, is

$$B = -215 - 60.5 \exp (1000/T) \text{ cc. mole}^{-1} \quad (341\text{–}500\text{°K.}) \qquad (3)$$

Comparisons of "observed" values of B and $-T(d^2B/dT^2) = \lim_{P \to 0} (\partial C_p/\partial P)_T$ with those calculated from eq. 3 are given in Tables VI and VII.

TABLE VIII

THE MOLAL ENTROPY OF 2,3-DITHIABUTANE IN CAL. DEG.$^{-1}$

T, °K.	340.80	360.40	382.90
S_{satd}(liq.)	61.00^a	63.03^b	65.27^b
$\Delta Hv/T$	25.26	23.17	21.03
S(ideal) − S(real)^c	0.06	0.09	0.14
Compression, $R \ln P^d$	−2.75	−1.38	0.00
$S°$(obsd.)(±0.20)^e	83.57	84.91	86.44

^{a} Ref. 2. ^{b} Extrapolated by use of the equation for the heat capacity of the liquid: $C_{satd} = 45.894 - 11.840 \times 10^{-2}T + 3.532 \times 10^{-4}T^2 - 2.667 \times 10^{-7}T^3$. ^{c} Calculated by use of eq. 3. ^{d} From the Cox equation selected to represent the vapor pressure data of ref. 2: $\log_{10} P = A(1 - 382.899/T)$; $\log_{10} A = 0.846998 - 6.8647 \times 10^{-4}T + 6.4468 \times 10^{-7}T^2$. ^{e} Estimated accuracy uncertainty.

The entropy in the ideal gaseous state at 1 atm. pressure was calculated as indicated in Table VIII.

Low Temperature Calorimetry of 4,5-Dithiaoctane.—Low temperature calorimetry of 4,5-dithiaoctane was done with 53.286 g. of sample in a platinum calorimeter with helium (3 cm. pressure at room temperature) added to promote thermal equilibration. The observed values of heat capacity, C_{satd}, are listed in Table IX. Above 30°K., the accuracy uncertainty is estimated to be no greater than 0.2%. The heat capacity curve for the solid (C_{satd} *vs.* T) has the normal sigmoid shape. The heat capacity curve for the liquid between 225 and 350°K. may be represented by the empirical equation

$$C_{satd} \text{ (liq.)} = 85.568 - 0.32092\,T + 1.1675 \times 10^{-3}T^2 - 1.1667 \times 10^{-6}T^3 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \qquad (4)$$

Three determinations of the heat of fusion, ΔH_{fusion}, gave the values 3299.8, 3302.1 and 3297.5 cal. mole^{-1}. The average value with the uncertainty taken as the maximum deviation is 3300 ± 3 cal. mole^{-1}.

The results of a study of the melting temperature, T_{obsd}, as a function of fraction of total sample melted, F, are listed in Table X. Also listed in Table X are the values obtained for the triple point temperature, $T_{T.P.}$, the mole fraction of impurity in the sample, N_2^*, and the cryoscopic constants,[22] $A = \Delta H_{fusion}/RT_{T.P.}^2$ and $B = 1/T_{T.P.} - \Delta C_{fusion}/2\Delta H_{fusion}$ calculated from the observed values of $T_{T.P.}$, ΔH_{fusion} and ΔC_{fusion} (17.95 cal. deg.$^{-1}$ mole^{-1}).

TABLE IX

THE MOLAL HEAT CAPACITY OF 4,5-DITHIAOCTANE IN CAL. DEG.$^{-1}$

T, °K.^{a}	C_{satd}^{b}	T, °K.^{a}	C_{satd}^{b}	T, °K.^{a}	C_{satd}^{b}
Crystals		53.59	15.691	162.69	36.076^c
12.07	1.261	55.49	16.230	167.87	36.954^c
12.58	1.358	58.42	17.043	168.93	37.177^c
13.65	1,681	63.73	18.483	175.02	38.277^c
14.28	1.895	69.60	19.900	Liquid	
15.13	2.155	75.57	21.274	193.63	58.47
15.76	2.375	81.19	22.517	201.84	58.59
16.53	2.595	86.93	23.739	202.06	58.59
17.33	2.871	89.14	24.173	207.24	58.71
18.14	3.159	94.81	25.214	213.24	58.83
19.02	3.467	100.79	26.249	224.35	59.13
20.14	3.881	107.08	27.310	235.38	59.48
20.87	4.149	113.04	28.303	246.33	59.94
22.40	4.733	119.01	29.245	255.75	60.39
23.00	4.959	124.72	30.136	257.19	60.44
24.66	5.613	130.28	31.002	266.77	60.93
25.40	5.895	136.14	31.885	277.68	61.49
27.12	6.561	142.30	32.830	288.50	62.14
28.38	7.052	148.30	33.749^c	299.22	62.77
30.02	7.681	151.18	34.209^c	309.81	63.50
33.17	8.891	154.17	34.680^c	320.30	64.26
36.77	10.236	154.82	34.787^c	330.50	64.90
40.88	11.692	156.84	35.112^c	330.67	64.92
45.26	13.139	161.43	35.873^c	341.61	65.62
50,11	14.662			351.22	66.31

^{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} Not corrected for the effects of premelting caused by impurities.

TABLE X

4,5-DITHIAOCTANE: MELTING POINT SUMMARY

Triple point temperature, $T_{T.P.}$ = 187.66 ± 0.05°K.; indicated mole fraction of impurity, $N_2^* = AF(T_{T.P.} - T_{obsd}) = 0.0003$; cryoscopic constants, $A = 0.04716$ deg.$^{-1}$ and $B = 0.00261$ deg.$^{-1}$

Melted, %	1/F	T_{obsd}, °K.	T_{graph}, °K.^{b}
11.55	8.658	187.6344	187.60
27.49	3.638	187.6464	187.636
53.44	1.871	187.6507	187.649
73.39	1.363	187.6529^a	187.6529
93.33	1.071	187.6551^a	187.6551
100.00	1.000		187.6556
Pure	0		187.6632

^{a} A straight line through these points on a plot of T_{obsd} *vs.* $1/F$ was extrapolated to $1/F = 0$ to obtain the triple point temperature, $T_{T.P.}$. ^{b} Temperatures read from the straight line of footnote *a*.

Values of thermodynamic properties for the condensed phases were computed from the calorimetric data for selected temperatures between 10 and 360°K. The results are given in Table XI. The values at 10°K. were computed from a Debye function for 5.5 degrees of freedom with $\theta = 104.1°$; these parameters were evaluated from the heat capacity data between 12 and 20°K. Corrections for the effects of premelting have been applied to the "smoothed" data recorded in Table XI.

Comparative Ebulliometry of 4,5-Dithiaoctane.—Observed values of the vapor pressure of 4,5-dithiaoctane are listed in Table XII. Water was used as the primary reference substance, and at the lower pressures benzene was used as a secondary reference substance. Because of thermal instability of the sample, measurements were limited to temperatures below 175°. Even in the temperature range of

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[21] J. P. McCullough, H. L. Finke, J. F. Messerly, R. E. Pennington, I. A. Hossenlopp and Guy Waddington, THIS JOURNAL, **77**, 6119 (1955).

[22] A. R. Glasgow, Jr., A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

TABLE XI

THE MOLAL THERMODYNAMIC PROPERTIES OF 4,5-DITHIAOCTANE IN THE SOLID AND LIQUID STATES[a]

T, °K.	$-(F_{\text{satd.}} - H^\circ_0)/T$, cal. deg.$^{-1}$	$(H_{\text{satd.}} - H^\circ_0)/T$, cal. deg.$^{-1}$	$H_{\text{satd.}} - H^\circ_0$, cal.	S_{satd}, cal. deg.$^{-1}$	C_{satd}, cal. deg.$^{-1}$
		Crystals			
10	0.063	0.187	1.873	0.250	0.739
15	.207	0.589	8.837	0.796	2.109
20	.453	1.176	23.518	1.629	3.824
25	.791	1.895	47.38	2.686	5.746
30	1.206	2.696	80.89	3.902	7.671
35	1.685	3.545	124.08	5.230	9.573
40	2.215	4.414	176.55	6.629	11.389
45	2.786	5.282	237.71	8.068	13.055
50	3.387	6.139	306.9	9.526	14.628
60	4.653	7.796	467.7	12.449	17.482
70	5.974	9.365	655.5	15.339	19.990
80	7.322	10.836	866.8	18.158	22.263
90	8.679	12.223	1100.0	20.902	24.336
100	10.035	13.524	1352.4	23.559	26.113
110	11.381	14.746	1622.0	26.127	27.800
120	12.714	15.902	1908.1	28.616	29.398
130	14.031	17.000	2209.9	31.03	30.96
140	15.330	18.051	2527	33.38	32.47
150	16.609	19.064	2859	35.67	34.02
160	17.871	20.049	3207	37.92	35.62
170	19.116	21.015	3572	40.13	37.33
180	20.344	21.971	3954	42.31	39.11
187.66	21.275	22.698	4259	43.97	40.47
		Liquid			
187.66	21.275	40.283	7559	61.55	58.42
190	21.77	40.50	7696	62.28	58.44
200	23.87	41.40	8281	65.28	58.56
210	25.91	42.22	8867	68.14	58.75
220	27.89	42.98	9456	70.88	59.00
230	29.82	43.68	10048	73.51	59.29
240	31.69	44.34	10642	76.04	59.66
250	33.52	44.96	11241	78.48	60.10
260	35.29	45.55	11845	80.85	60.58
270	37.02	46.12	12453	83.15	61.09
273.16	37.56	46.29	12646	83.86	61.25
280	38.71	46.66	13067	85.38	61.63
290	40.36	47.19	13686	87.55	62.22
298.16	41.67	47.61	14196	89.28	62.73
300	41.96	47.70	14311	89.67	62.85
310	43.54	48.20	14943	91.74	63.51
320	45.08	48.69	15582	93.77	64.19
330	46.58	49.17	16227	95.76	64.87
340	48.06	49.64	16879	97.70	65.55
350	49.50	50.11	17538	99.61	66.22
360	50.92	50.56	18204	101.49	66.91

[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 measurements, very slight but detectable decomposition occurred. The results in Table XII are therefore somewhat less reliable than those obtained with stable samples under similar conditions. The Antoine and Cox equations selected to represent the results are

$$\log_{10} p(\text{mm.}) = 6.97529 - 1603.793/(t + 195.848) \quad (5)$$

and

$$\log_{10} P(\text{atm.}) = A(1 - 469.008/T) \quad (6)$$

$$\log_{10} A = 0.917975 - 8.01926 \times 10^{-4}T + 6.76813 \times 10^{-7}T^2.$$

In these equations, t is in °C. and T in °K. Comparisons of the observed and calculated vapor pressure for both the Antoine and Cox equations are given in Table XII. The normal boiling point, calculated by extrapolation with either equation, is 195.85° (469.01°K.).

TABLE XII

THE VAPOR PRESSURE OF 4,5-DITHIAOCTANE

Boiling point, °C.		p(obsd.), mm.	p(obsd.) − p(calcd.), mm.	
Water	4,5-Dithiaoctane		Eq. 5	Eq. 6
45.000	117.472	71.87	−0.01	0.00
47.5	120.869	81.64	+ .11	+ .08
50	124.340	92.52	− .03	− .02
52.5	127.798	104.63	− .06	− .05
55	131.251	118.06	− .03	− .03
57.5	134.732	132.95	− .04	− .04
60	138.207	149.41	+ .03	+ .03
65	145.223	187.57	+ .04	+ .04
70	152.297	233.72	+ .05	+ .06
75	159.426	289.13	+ .03	+ .04
80	166.604	355.22	+ .04	.00
85	173.848	433.56	− .10	− .06

Comparative ebulliometry of 4,5-dithiaoctane was done previously by White, Barnard-Smith and Fidler,[23] who also observed thermal decomposition. In the range of experimental measurements, values of vapor pressure calculated by their Antoine equation and either eq. 5 or 6 differ by less than 0.06%.

The heat of vaporization to the real gas, $\Delta Hv_{298.16}$ = 12940 cal. mole^{-1}, was computed by using eq. 6, the exact form of the Claperon equation and an estimated value of −10 l. mole^{-1} for the second virial coefficient. The standard heat of vaporization, $\Delta Hv^\circ_{298.16}$, is not significantly different.

Entropy of 4,5-Dithiaoctane in the Ideal Gaseous State.—The entropy of 4,5-dithiaoctane in the ideal gaseous state at 1 atm. pressure and 298.16°K. was calculated as shown below.

S_{satd}(liq.)	89.28
$\Delta Hv/T$ = 12940/298.16	43.40
S(ideal) − S(real)	Negligible
Compression, R ln P	−14.38
S°(obsd.), cal. deg.$^{-1}$ mole^{-1}	118.30

Combustion Calorimetry.—Series of combustion and comparison experiments were performed for 2,3-dithiabutane, 3,4-dithiahexane and 4,5-dithiaoctane. The first compound required a slight modification in method because of the high sulfur content—the highest of any organic sulfur compound for which combustion calorimetry has been done in this Laboratory. Normally, only enough auxiliary oil for ignition of the sample is used in a combustion experiment. Comparison experiments are then made with samples of sulfur and oil to produce the same amounts of sulfuric acid and carbon dioxide as in the combustion experiment. When the customary comparison experiments were made for 2,3-dithiabutane, the sulfur–oil ratio required was so high that the combustion reaction did not convert all of the sulfur to sulfuric acid but always produced at least traces of sulfur dioxide as well. The modification in method consisted of the use of less 2,3-dithiabutane and more oil as sample, so that the composition of the final contents of the bomb was brought within the range accessible to comparison experiments.

The total number of satisfactory experiments for the three compounds, including calibration experiments with benzoic acid, was 44. It is impractical to report all 44 experiments in detail, but experiments selected as typical of each of the several series are summarized in Table XIII. Combustion of the samples, contained in Pyrex ampoules, took place in the bomb, which initially contained 10 g. of water and was charged with oxygen to 30 atm. total pressure without removal of the air initially present. Corrections to standard

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

TABLE XIII

SUMMARY OF TYPICAL CALORIMETRIC EXPERIMENTS[a,b]

	2,3-Dithiabutane (Series A)	2,3-Dithiabutane (Series B)	3,4-Dithiahexane	4,5-Dithiaoctane
	Combustion experiments			
m', mass of compound, g.	0.74860	0.52506	0.96823	1.03931
m'' mass of auxiliary oil, g.	0.02385	0.28248	0.07498	0.04450
$\Delta t_c = t_f - t_i - \Delta t_{corr}$, deg.	1.41437	1.73898	2.18249	2.39755
$\mathcal{E}$(Calor.)($-\Delta t_c$), cal.	−5528.77	−6797.67	−8531.35	−9372.02
$\mathcal{E}$(Cont.)($-\Delta t_c$),[c] cal.	−19.43	−23.96	−30.19	−33.42
$\Delta E_{ign.}$, cal.	1.35	1.35	1.35	1.35
ΔE^f_{dec} (HNO_3 + HNO_2), cal.	5.01	8.24	11.40	12.17
ΔE, cor. to st. states,[d] cal.	−2.17	1.62	0.13	1.72
$-n''\Delta Ec°$(auxiliary oil), cal.	261.95	3102.66	823.58	488.72
$-n'''\Delta Ec°$(fuse), cal.	16.20	15.10	16.08	15.65
$n'\Delta Ec°$(compound), cal.	−5265.86	−3692.66	−7709.00	−8885.83
$\Delta Ec°/M$(compound), cal. g.$^{-1}$	−7034.28	−7032.83	−7961.95	−8549.74
	Comparison experiments			
m', mass of sulfur, g.	....	0.35747	0.50810	0.44337
m'', mass of auxiliary oil, g.	....	0.43764	0.51586	0.62214
$\Delta t_c = t_f - t_i - \Delta t_{corr.}$, deg.	....	1.63940	2.02760	2.25338
$\mathcal{E}$(Calor.)($-\Delta t_c$), cal.	....	−6408.41	−7925.89	−8808.46
$\mathcal{E}$(Cont.)($-\Delta t_c$),[c] cal.	....	−21.94	−27.38	−30.54
$\Delta E_{ign.}$, cal.	....	1.35	1.35	1.35
$\Delta E^f_{dec.}$(HNO_3 + HNO_2), cal.	....	11.13	9.51	12.20
ΔE, cor. to st. states,[d] cal.	....	1.95	0.69	2.24
$-n''\Delta Ec°$(auxiliary oil), cal.	....	4807.04	5666.21	6833.58
$-n'''\Delta Ec°$(fuse), cal.	....	16.63	16.01	16.20
$n'\Delta Ec°$(sulfur), cal.	....	−1592.25	−2259.50	−1973.43
$\Delta Ec°/M$(sulfur), cal. g.$^{-1}$	....	−4454.22	−4446.96	−4450.98

[a] The symbols and abbreviations in this Table are those used in ref. 24. [b] Auxiliary data: $\mathcal{E}$(Calor.) = 3909.0 ± 0.1 cal. deg.$^{-1}$ as determined by eight calibration experiments with benzoic acid (NBS Sample 39g); V(bomb) = 0.347 l.; $\Delta Ec°/M$(auxiliary oil) = 10984 cal. g.$^{-1}$; physical properties at 25° of 2,3-dithiabutane, 3,4-dithiahexane and 4,5-dithiaoctane, respectively—ρ = 1.057, 0.983 and 0.953 g. ml.$^{-1}$, $(\partial E/\partial P)_T$ = −0.0072, −0.0072 and −0.007 cal. g.$^{-1}$ atm.$^{-1}$, c_p = 0.371, 0.399 and 0.417 cal. deg.$^{-1}$ g.$^{-1}$. [c] $\mathcal{E}_i$(Cont.)($t_i - 25°$) + $\mathcal{E}^f$(Cont.) ($25° - t_f + \Delta t_{corr}$). [d] Items 81–85, incl., 87–91, incl., 93 and 94 of the computation form of ref. 24.

states[24] were applied to the results of all calorimetric experiments. The values of $\Delta Ec°/M$(compound) in Table XIII apply to the idealized combustion reaction I at 298.16°K.

$$C_aH_bS_2(liq) + (a + b/4 + 3)O_2(g) + (92 - b/2)\ H_2O(liq) = aCO_2(g) + 2(H_2SO_4{\cdot}45H_2O)(liq) \quad (I)$$

and the values of $\Delta Ec°/M$ (sulfur) apply to the idealized combustion reaction II at 298.16°K.

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

The results of all the combustion and comparison experiments are listed in Table XIV, and the derived results are listed in Table XV. Only the results of Series B for 2,3-dithiabutane were used in obtaining the derived results because comparison experiments could not be done for Series A. The assigned uncertainty in Table XV is the uncertainty interval equal to twice the final "over-all" standard deviation.[25] The values of $\Delta Hc°$ for each compound and rhombic sulfur and values of the heat of formation of carbon dioxide and water[10] were used in computing the heats of formation of the liquids. Determination of the heat of combustion of rhombic sulfur under nearly identical conditions in the comparison experiments has the advantage that any systematic errors would be expected to cancel largely in computation of the heat of formation. Values of the standard heat of vaporization, $\Delta Hv°$, were calculated from the thermodynamic data for each compound and used in computing the heats of formation in the gaseous state. Values of the entropy of the compounds in the liquid and vapor states and of graphite,[10] hydrogen[10] and rhombic sulfur[11] were used in computing the values of the entropy, free energy and logarithm of the equilibrium constant of formation, also included in Table XV.

TABLE XIV

RESULTS OF COMBUSTION AND COMPARISON EXPERIMENTS

	2,3-Dithiabutane (Series A)	2,3-Dithiabutane (Series B)	3,4-Dithiahexane	4,5-Dithiaoctane
		Combustion experiments		
$\Delta Ec°/M$ (compd.), cal. g.$^{-1}$	−7035.41	−7035.89	−7962.15	−8548.46
	−7035.98	−7036.12	−7958.63	−8550.02
	−7034.28	−7038.81	−7959.77	−8549.74
	−7037.06	−7035.53	−7961.95	−8550.12
	−7036.13	−7034.75	−7959.75	−8549.99
		−7032.83	−7958.96	−8549.53
Mean	−7035.77	−7035.66	−7960.20	−8549.64
Stnd. dev. of the mean	±0.46	±0.80	±0.61	±0.25
		Comparison experiments		
$\Delta Ec°/M$ (sulfur), cal. g.$^{-1}$		−4451.87	−4446.96	−4447.73
		−4451.19	−4444.81	−4446.17
		−4453.06		−4450.98
		−4450.31		−4448.51
		−4454.22		−4446.17
				−4452.26
Mean		−4452.13	−4445.89	−4448.64
Stnd. dev. of the mean		±0.69		±1.02

Finally, the heat of formation of S_2(g) from rhombic sulfur[11] was used in computing the heats of formation from S_2(g), as given in Table I.

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(24) W. N. Hubbard, D. W. Scott and Guy Waddington, "Experimental Thermochemistry," F. D. Rossini, editor, Interscience Publishers, Inc., New York, N. Y., 1956, Chapter 5, pp. 75–128.

(25) F. D. Rossini, ref. 24, Chapter 14, p. 319.

Table XV

Derived Thermochemical Data at 298.16°K.[a,b]

	2,3-Dithiabutane	3,4-Dithiahexane	4,5-Dithiaoctane
$\Delta Ec°$ (compound)	-662.76 ± 0.17	-973.15 ± 0.19	-1285.05 ± 0.17
$\Delta Hc°$ (compound)	-665.43 ± 0.17	-976.41 ± 0.19	-1288.90 ± 0.17
$\Delta Hc°$ (sulfur)	-143.65 ± 0.05	-143.45 ± 0.07	-143.54 ± 0.07
$\Delta Hf°$, liquid	-14.93 ± 0.20	-28.28 ± 0.24	-40.71 ± 0.24
$\Delta Sf°$, liquid	-55.33	-103.83	-152.60
$\Delta Ff°$, liquid	$+1.57$	$+2.68$	$+4.79$
$\log_{10} Kf$, liquid	-1.15	-1.96	-3.51
$\Delta Hv°$	9.18 ± 0.03^c	10.86 ± 0.05^c	12.94 ± 0.10^c
$\Delta Hf°$, gas	-5.75 ± 0.20	-17.42 ± 0.25	-27.77 ± 0.26
$\Delta Sf°$, gas	-31.13	-77.66	-123.6
$\Delta Ff°$, gas	$+3.53$	$+5.73$	$+9.08$
$\log_{10} Kf$, gas	-2.59	-4.20	-6.66

[a] Reference state for sulfur is S(c, rhombic). [b] Units: ΔEc^0, ΔHc^0, ΔHf^0, ΔFf^0 and ΔHv^0, kcal. mole^{-1}; ΔSf^0, cal. deg.$^{-1}$ mole^{-1}. [c] Estimated accuracy uncertainty.

The only previous thermochemical data for alkane disulfides are the results of Franklin and Lumpkin,[26] who used a static bomb method less adapted to organic sulfur compounds. Their values of −16.4 and −32.5 kcal. mole^{-1} for the heat of formation of liquid 2,3-dithiabutane and 3,4-dithiahexane, respectively, may be compared with the values −14.93 and −28.28 kcal. mole^{-1} from Table XV.

BARTLESVILLE, OKLA.

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[26] J. L. Franklin and H. E. Lumpkin, THIS JOURNAL, **74**, 1023 (1952).

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Characteristic Vibrational Frequencies of Organic Sulfur Compounds[1]

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Calorimetric and spectroscopic data were used previously to make complete vibrational assignments for 10 organic sulfur compounds that contain only the CH_3S, C_2H_5S, $(CH_3)_2CHS$ and $(CH_3)_3CS$ groups. These assignments were used in calculating values of thermodynamic properties reported in earlier papers. In this paper, regularities found in the spectra of the 10 compounds are discussed. Characteristic fundamental frequencies of one alkyl group attached to sulfur are affected little by the nature of a second attached group. Incomplete vibrational assignments, based on limited spectroscopic data, are given for five other sulfur compounds to illustrate the utility of this correlation of characteristic frequencies with molecular structure.

In the last 10 years, experimental thermodynamic studies of about 35 organic sulfur compounds have been made in this Laboratory as part of American Petroleum Institute Research Project 48A. Complete vibrational assignments were made for many of these compounds and were used in calculating thermodynamic functions at temperatures inaccessible to calorimetric measurements. Significant regularities noted in the fundamental vibrational frequencies of related sulfur compounds will be discussed in this paper.

Vibrational assignments have been reported from this Laboratory for these several ten compounds: methanethiol,[2] 2-thiapropane,[3] 2,3-dithiabutane,[4] 2-thiabutane,[2,5] 3-methyl-2-thiabutane,[6] ethanethiol,[7] 3-thiapentane,[8] 3,4-dithiahexane,[9] 2-propanethiol[10] and 2-methyl-2-propanethiol.[11] The assignments for these compounds form the basis for the present discussion. Details of the assignments and reference to earlier work can be found in the articles cited. All of the assignments were based on good Raman and infrared spectroscopic

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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.

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