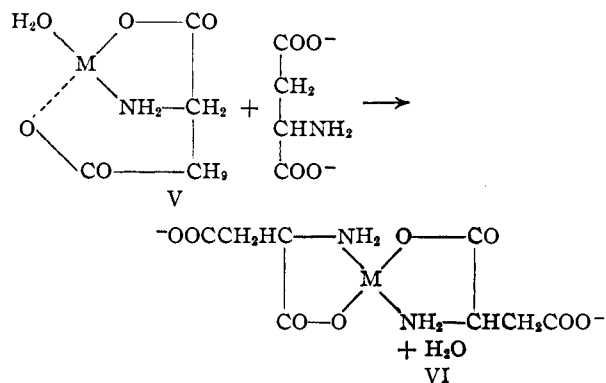


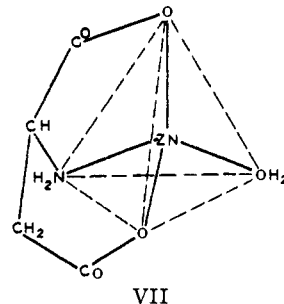
It is apparent from the results in Table II that except for the aspartic acid chelates the ratio of the first to the second chelate stability constant is much greater for copper than for the other metals investigated. This is due to the fact that the coordination number of copper is four, and one mole of a tridentate chelating agent satisfies all but one of the coordination requirements of the metal. Hence it is to be expected that the difference between the first and second stability constants will be much greater than normal.

In the case of aspartic acid, it is apparent from formula V that, if it behaves as a tridentate reagent, it cannot satisfy three of the square planar copper covalencies without introducing considerable strain in the chelate rings. Thus the stability of V would be less than that expected for a tridentate structure. Combination of V with a second donor anion may be considered as taking place in the manner indicated by the equation



The binary chelate VI which results contains

two very stable  $\alpha$ -amino acid rings and the equilibrium constant for the reaction would be expected to be quite large. Thus the abnormally low stability of V favors a comparatively low value for  $K_1$  and a relatively high value for  $K_2$ , compared to the behavior of other metals. Although  $Zn^{+2}$  also has a coordination number of 4, the equilibrium constants listed in Table II indicate its behavior to be more nearly normal with respect to the stability of the aspartic acid chelates. This is probably due to the fact that the structure is tetrahedral, and that the chelate rings formed involve very little, if any, strain, as is indicated by formula VII.



With the exceptions noted above, both the first and second metal chelate stability constants of iminopropionic-acetic and aspartic acids lie approximately half way between the corresponding metal chelate stability constants of the analogous compounds, iminodiacetic acid and iminodipropionic acid.

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WORCESTER, MASSACHUSETTS

[CONTRIBUTION No. 31 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

## Thiacyclopentane: Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressure, Entropy, Heat of Formation and Thermodynamic Functions<sup>1</sup>

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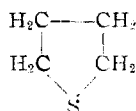
The following thermodynamic properties of thiacyclopentane were determined experimentally: heat capacity of the solid and liquid between 13 and 333°K., triple point (176.98°K.), heat of fusion (1757 cal. mole<sup>-1</sup>), vapor pressure [ $\log_{10} p = 6.99540 - 1401.939/(t + 219.607)$  ( $p$  in mm. and  $t$  in °C.)], heat of vaporization (8820, 8589 and 8279 cal. mole<sup>-1</sup> at 349.86, 370.16 and 394.28°K., respectively), heat capacity of the vapor [ $C_p^\circ = -8.23 + 0.1192T - 6.551 \times 10^{-6} T^2$  cal. deg.<sup>-1</sup> mole<sup>-1</sup> (378–487°K.)], second virial coefficient [ $B = V - RT/P = -295 - 32.37 \exp(1250/T)$  cc. mole<sup>-1</sup>], entropy of the liquid (49.67 cal. deg.<sup>-1</sup> mole<sup>-1</sup> at 298.16°K.), entropy of the vapor ( $S^\circ = 77.72, 79.22$  and  $80.92$  cal. deg.<sup>-1</sup> mole<sup>-1</sup> at 349.86, 370.16 and 394.28°K., respectively) and heat of formation [for the reaction:  $4C$  (graphite) +  $4H_2$  (g) +  $S$  (rhombic) =  $C_4H_8S$  (liq),  $\Delta H_{298.16}^\circ = -17.4$  kcal. mole<sup>-1</sup>]. The functions  $-(F^\circ - H_0^\circ)/T$ ,  $(H^\circ - H_0^\circ)/T$ ,  $H^\circ - H_0^\circ$ ,  $S^\circ$  and  $C_p^\circ$  were computed by the methods of statistical mechanics for selected temperatures up to 1000°K. Values of the heat, free energy and equilibrium constant of formation of thiacyclopentane were obtained for the same temperatures.

This Laboratory is engaged in an investigation of the thermodynamic properties of organic sulfur compounds because of their importance in petroleum technology. The program entails making detailed studies of individual compounds that are

(1) This investigation was 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.

representative of the types of sulfur compounds that occur in crude petroleum or are produced in refining processes. The investigations on a given compound include a variety of experimental measurements, mostly calorimetric, the results of which, whenever possible, are correlated and extended by the methods of statistical mechanics to give relatively completely thermodynamic information for the whole temperature range of practical interest.

This paper presents the results of such a study of the cyclic sulfide, thiacyclopentane<sup>2</sup>



This compound and its two monomethyl derivatives have been identified in petroleum from several sources.<sup>3</sup> The related molecule, thiophene,<sup>4</sup> and its oxygen analog, furan,<sup>5</sup> have also been studied in this Laboratory.

### Experimental

The experimental part of this investigation consisted of determinations of the heat capacity in the solid, liquid and vapor states, heats of fusion and vaporization, vapor pressure, entropy and heat of formation. The results of these measurements are presented in the following sections. The molecular weight of thiacyclopentane was taken to be 88.170, the ice point (0°) was taken to be 273.16°K., and measurements of electrical energy, in terms of international joules, were converted to calories by dividing by 4.1833.

**The Material.**—The thiacyclopentane used for the experimental measurements consisted of a small sample of highly purified material which was used for low temperature calorimetry and for vapor pressure and heat of combustion studies, and a second, larger sample of somewhat less pure material which was used for the heat of vaporization and vapor heat capacity studies. Both samples were prepared at the Laramie Station of the Bureau of Mines in connection with A.P.I. Research Project 48A (see ref. 1). The purity of the first sample was determined during the low temperature studies by measuring its melting point as a function of the fraction melted. The purity was found to be  $99.987 \pm 0.005$  mole per cent. This determination involved the usual assumptions of liquid-soluble, solid-insoluble impurities and ideal solutions. The purity of the second sample was determined at the Laramie Station by the time-temperature freezing point method to be 99.8 mole per cent. Since thiacyclopentane may have a slight tendency to polymerize during storage, the samples were subjected to bulb-to-bulb distillations to free them from any accumulated polymer immediately prior to use in each of the experimental studies.

**Low Temperature Studies.**—The heat capacity of solid and liquid thiacyclopentane was measured between 13 and 333°K., with the results shown in Table I. The temperatures listed in the table are the mean temperatures of the individual measurements.  $C_{\text{sat}}$  is the heat capacity of the condensed phase under its own vapor pressure. The temperature increments used for the measurements (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 heat capacity with temperature. The values of  $C_{\text{sat}}$  in Table I for temperatures immediately below the melting point are not corrected for premelting.

The measurements were made with an apparatus similar to that described by Ruehrwein and Huffman.<sup>6</sup> The calorimeter was constructed of platinum and was equipped with horizontal disks of gold to promote more rapid attainment

(2) In the literature this compound is called by at least five other names—thiolane, thiophane, tetramethylene sulfide, tetrahydrothiophene and 1,4-epithiobutane. For discussion of the nomenclature of sulfur compounds, see J. S. Ball and W. F. Haines, *Chem. Eng. News*, **24**, 2765 (1946).

(3) E. H. Thierry, *J. Chem. Soc.*, **127**, 2756 (1925); I. Teutsch, *Petroleum Z.*, **30**, No. 20, 1 (1934); O. L. Polly, A. C. Byrnes and W. E. Bradley, *Ind. Eng. Chem.*, **34**, 755 (1942); W. Friedman and C. Canseco, *Pet. Refiner*, **22**, 1 (1943); W. Friedman and C. Rodriguez, *ibid.*, **25**, 53 (1946).

(4) 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).

(5) G. B. Guthrie, Jr., D. W. Scott, W. N. Hubbard, C. Katz, J. P. McCullough, M. E. Gross, K. D. Williamson and Guy Waddington, *ibid.*, **74**, 4662 (1952).

(6) R. A. Ruehrwein and H. M. Huffman, *ibid.*, **65**, 1620 (1943).

TABLE I  
MOLAL HEAT CAPACITY OF THIACYCLOPENTANE

$T$ , °K.	$C_{\text{sat}}$ , cal. deg. <sup>-1</sup>	$T$ , °K.	$C_{\text{sat}}$ , cal. deg. <sup>-1</sup>	$T$ , °K.	$C_{\text{sat}}$ , cal. deg. <sup>-1</sup>
Solid					
77.12	0.962	77.14	12.137	184.85	28.89
13.12	0.962	80.38	12.427	188.82	28.93
14.11	1.186	85.85	12.909	190.05	28.96
15.43	1.479	88.12	13.092	190.37	28.98
16.05	1.625	92.15	13.384	194.59	29.07
17.08	1.883	99.09	13.878	201.96	29.24
19.05	2.390	106.18	14.390	210.09	29.45
19.57	2.532	113.43	14.915	218.94	29.73
21.22	2.959	116.66	15.135	228.50	30.06
23.34	3.527	120.43	15.435	237.93	30.47
23.68	3.628	122.51	15.582	247.24	30.86
26.65	4.388	128.72	16.057	256.81	31.30
27.78	4.694	135.24	16.583	260.76	31.50
32.50	5.850	135.83	16.625	266.43	31.76
37.21	6.877	141.76	17.141	266.62	31.80
42.41	7.874	142.07	17.163	272.03	32.05
47.63	8.745	148.69	17.770	282.20	32.62
52.91	9.515	148.93	17.786	293.12	33.22
54.38	9.713	156.30	18.523	302.49	33.74
59.59	10.375	163.41	19.335	303.43	33.82
64.44	10.935	169.44	20.174	312.87	34.34
69.40	11.435	173.96	21.799	324.08	35.02
72.91	11.752	Liquid		333.40	35.54
74.84	11.925	180.17	28.80		

of thermal equilibrium and to prevent settling of the solid phase during melting studies. Above 30°K. the accuracy uncertainty of the heat capacity data probably does not exceed 0.2%; below 30°K., mainly because of the decrease in the sensitivity of the resistance thermometer at lower temperatures, the accuracy uncertainty is greater. The heat capacity of the liquid as a function of temperature may be represented by the equation

$$C_{\text{sat}} = 40.70 - 0.16812T + 6.944 \times 10^{-4}T^2 - 7.093 \times 10^{-7}T^3 \quad (1)$$

a plot of which deviates less than 0.05% from a visually smoothed curve through the experimental points.

Equilibrium melting temperatures, as a function of the fraction melted, were determined by the method described in an earlier publication.<sup>7</sup> The results are summarized in Table II. The value obtained for the triple point was

TABLE II

### THIACYCLOPENTANE, MELTING-POINT SUMMARY

$T_{\text{T.P.}} = 176.98 \pm 0.05^\circ\text{K.}$ ; impurity,  $0.013 \pm 0.005$  mole per cent.; this value was obtained from the equation  $N_2^*/F = 0.0282\Delta T$ , 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  $\Delta T$  is  $T_{\text{T.P.}} - T_{\text{obsd.}}$ .

Melted, %	1/F	Obsd. $T$ , °K.	Graph. <sup>b</sup>
11.3	8.84	176.9502	176.9430
24.3	4.11	176.9680	176.9644
46.0	2.17	176.9732 <sup>a</sup>	176.9732
69.9	1.43	176.9764	176.9776
91.6	1.09	176.9781 <sup>a</sup>	176.9781
100.0	1.00		176.9796
Pure	0.00		176.9831

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

176.98°K. The data of Table II were obtained at the beginning of the low temperature studies. To investigate whether or not any polymerization or other contamination

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

of the sample had occurred during the low temperature studies, a similar melting point study was made after all of the other data had been obtained. The second study gave values for the triple point and purity which were identical with those obtained the first time.

Duplicate determinations of the heat of fusion both gave the value 1757.2 cal. mole<sup>-1</sup>. For calculation of this value of the heat of fusion (and also for the entropy calculation of Table V) appropriate corrections for premelting were applied to the heat capacities of Table I and the heat absorbed in premelting was added as a correction to the heat of fusion. The cryoscopic constant,  $\Delta H_{\text{fusion}}/RT_{\text{T.P.}}$ , calculated from the heat of fusion and triple point is 0.0282 deg.<sup>-1</sup>.

**Vapor Pressure Measurements.**—The vapor pressure of thiacyclopentane was measured by a comparative ebulliometric method with the results given in Table III. Water

TABLE III  
VAPOR PRESSURE OF THIACYCLOPENTANE

Water B.p., °C.	Thiacyclo- pentane	Pressure, mm.	
		Obsd.	Calcd.
60.000	71.182	149.41	149.36
65	77.278	187.57	187.60
70	83.405	233.72	233.73
75	89.580	289.13	289.15
80	95.803	355.22	355.29
85	102.056	433.56	433.50
90	108.365	525.86	525.81
95	114.716	633.99	633.91
100	121.114	760.00	759.94
105	127.558	906.06	906.05
110	134.046	1074.6	1074.6
115	140.574	1268.0	1267.9
120	147.163	1489.1	1489.4
125	153.775	1740.8	1740.6
130	160.451	2026.0	2026.0

was used as the standard substance. The apparatus was similar to that described previously,<sup>4</sup> but was modified by having the heating element in a re-entrant well so that the sample came in contact with nothing but glass. The difference between the boiling and condensation temperatures of the sample was measured at each pressure studied and was always found to be small (less than 0.011°). This observation indicates that no significant amount of decomposition or polymerization occurred during the measurements. The vapor pressure data were correlated by means of the Antoine equation

$$\log_{10} p = 6.99540 - 1401.939/(t + 219.607) \quad (2)$$

the constants of which were obtained by a least-squares adjustment.<sup>8</sup> In equation (2),  $p$  is the vapor pressure in mm. and  $t$  is the temperature in °C. Values of the vapor pressure calculated by means of this equation are included in Table III for comparison with the experimental values. The normal boiling point is calculated to be 121.12°.

White, Barnard-Smith and Fidler<sup>9</sup> have studied the vapor pressure of thiacyclopentane by an ebulliometric method with a sample of somewhat lower purity (99.7 mole per cent.). The boiling points which they report for pressures in the range 100 to 1000 mm. are between 0.3 and 0.4° higher than those calculated by means of equation (2) of this paper. The source of this discrepancy may lie in the differences in the purity of the samples employed.

**Heat of Vaporization and Vapor Heat Capacity.**—The cycling vaporizer and flow calorimeter described previously<sup>10</sup> were used to determine the heat of vaporization and vapor heat capacity of thiacyclopentane. The heater of the vaporizer was enclosed in a glass spiral so that the boiling liquid would be in contact with nothing but glass.

(8) G. B. Willingham, W. J. Taylor, J. J. Pignocco and F. D. Rosini, *J. Research Natl. Bur. Standards*, **35**, 219 (1945).

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

(10) G. Waddington, S. S. Todd and H. M. Huffman, *THIS JOURNAL*, **59**, 22 (1947); G. Waddington and D. R. Douslin, *ibid.*, **59**, 2275 (1947).

The heat of vaporization was determined at three temperatures, with the following results: 349.86°K., 8820; 370.16°K., 8589; and 394.28°K., 8279 cal. mole<sup>-1</sup>. The value given in each case is the average of at least three separate determinations, none of which deviated from the mean by more than 4 cal. mole<sup>-1</sup>. The accuracy uncertainty of these heat of vaporization data is probably about 0.1%. The equation

$$\Delta H_{\text{vap.}} = 8418 + 12.987 T - 0.033834 T^2 \text{ cal. mole}^{-1} \quad (3)$$

may be used for interpolation within the temperature range covered by the experimental measurements.

The heat capacity of the vapor was determined at two or more pressures at each of four different temperatures with the results presented in Table IV. Linear extrapolation of the experimental data to zero pressure gave the values of  $C_p^\circ$ , the heat capacity in the ideal gas state. An accuracy uncertainty of 0.2% is assigned to the calorimetric values of  $C_p^\circ$  in Table IV. They may be represented to  $\pm 0.01$  cal. deg.<sup>-1</sup> mole<sup>-1</sup> by the equation

$$C_p^\circ = -8.23 + 0.1192 T - 6.551 \times 10^{-5} T^2 \quad (378 - 487^\circ\text{K.}) \quad (4)$$

TABLE IV

VAPOR HEAT CAPACITY OF THIACYCLOPENTANE, CAL. DEG.<sup>-1</sup> MOLE<sup>-1</sup>

T, °K.	378.25	402.20	449.20	487.20
$C_p$ (760 mm.)		29.765	32.444	34.577
$C_p$ (369 mm.)	27.979	29.435		
$C_p$ (262 mm.)			32.223	34.388
$C_p$ (184 mm.)	27.734	29.254		
$C_p^\circ$ (obsd.)	27.49	29.10	32.11	34.29
$C_p^\circ$ (calcd.) <sup>a</sup>	27.49	29.10	32.10	34.33
$(\partial C_p/\partial P)_T$ , obsd.	1.00	0.67	0.34	0.29
$(\partial C_p/\partial P)_T$ , calcd.	0.99	0.69	0.38	0.25

<sup>a</sup> As explained in the section headed "Thermodynamic Functions."

**Gas Imperfection and Second Virial Coefficient.**—Values of the second virial coefficient,  $B$ , in the equation of state  $PV = RT + BP$  and its second derivative with respect to temperature were obtained from the experimental data by use of the relationships

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

and

$$d^2B/dT^2 = -(1/T)(\partial C_p/\partial P)_T$$

where  $dP/dT$  is the temperature coefficient of the vapor pressure and  $V_L$  is the molar volume of the liquid. The results were correlated by means of the empirical equation

$$B = -295 - 32.37 e^{1280/T} \text{ cc. mole}^{-1} \quad (5)$$

The method of evaluating the constants in this equation has been described elsewhere.<sup>11</sup> The values of the second virial coefficient, -1540, -1181 and -1074 cc. mole<sup>-1</sup>, obtained from the experimental data for the temperatures 349.86, 370.16 and 394.28°K., may be compared with the values, -1448, -1243 and -1066 cc. mole<sup>-1</sup>, respectively, calculated by means of equation (5). The last two lines of Table IV compare the values of  $(\partial C_p/\partial P)_T$  from the experimental data with those calculated by means of equation (5).

**Entropy.**—The entropy of thiacyclopentane was computed from the experimental data both for the liquid state at 298.16°K. and for the vapor state at the three temperatures at which the heat of vaporization was measured. The calculations are summarized in Table V. For extrapolating the heat capacity of the solid below 13°K., a Debye function for five degrees of freedom with  $\theta = 119.9^\circ$  was used. For extrapolating the heat capacity of the liquid to the temperatures at which experimental values of the heat of vaporization had been obtained, equation (1) was used; the integrals,  $\int_{298.16}^T C_{\text{obs}} d \ln T$ , were evaluated analytically. The corrections for gas imperfection, which are given by  $P(dB/dT)$  in terms of the second virial coefficient, were obtained by means of equation (5).

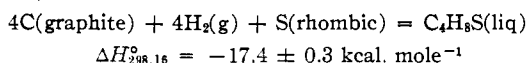
(11) D. W. Scott, G. Waddington, J. C. Smith and H. M. Huffman, *J. Chem. Phys.*, **15**, 565 (1947).

TABLE V

ENTROPY OF THIACYCLOPENTANE, CAL. DEG. <sup>-1</sup> MOLE <sup>-1</sup>			
0-13°K.	Debye extrapolation		0.324
13-176.98°	Solid, graphical $\int C_{\text{sat}} d \ln T$		23.528
176.98°	Fusion, 1757.2/176.98		9.929
176.98-298.16°	Liquid, graphical $\int C_{\text{sat}} d \ln T$		15.887
Entropy ( $\pm 0.10$ ) of liquid at 298.16°K.			49.67
T, °K.	349.86	370.16	394.28
Entropy of liquid at 298.16°			49.67
Liquid, $\int_{298.16}^T C_{\text{sat}} d \ln T$	5.59	7.68	10.10
Vaporization, $\Delta H_{\text{vap}}/T$	25.21	23.20	21.00
Gas imperfection	0.07	0.10	0.15
Compression, $R \ln (p/760)$	-2.82	-1.43	0.00
Entropy ( $\pm 0.20$ ) of ideal gas at 1 atm.			77.72
	79.22	80.92	

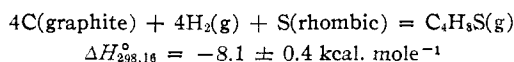
**Heat of Formation.**—The heat of formation of thiacyclopentane was determined by combustion calorimetry in the following manner. First, the heat of combustion of the compound to give water, carbon dioxide and aqueous sulfuric acid was determined directly. Second, the heat of combustion of rhombic sulfur to give aqueous sulfuric acid of the same concentration was determined by measuring the heat of combustion of mixtures of rhombic sulfur and a hydrocarbon oil whose heat of combustion was known from previous experiments. From the results of these measurements and the accurately known values of the heats of combustion of hydrogen and graphite, the heat of formation of thiacyclopentane was calculated.

The experimental measurements were made with a rotating combustion bomb and associated calorimetric apparatus that have recently been developed in this Laboratory for determining the heats of combustion of organic sulfur compounds. A very brief description of the calorimetric apparatus and methods has been given previously.<sup>12</sup> It is planned to give a more complete description in a future publication, which will also include the detailed heat of combustion data for thiacyclopentane and rhombic sulfur and a comparison with the results of Sunner,<sup>13</sup> who has also studied the heat of combustion of these substances. Therefore, only the derived value of the heat of formation will be reported here. This is, for the reaction



The uncertainty given equals twice the final "over-all" standard deviation.<sup>14</sup>

A short extrapolation of the experimental heat of vaporization data [using equation (3)] gives 9.28 kcal. mole<sup>-1</sup> 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 9.29 kcal. mole<sup>-1</sup>. Adding this to the value of the heat of formation of the liquid gives for the standard heat of formation of the gas



### Thermodynamic Functions

The thermodynamic functions,  $-(F^\circ - H_0^\circ)/T$ ,  $(H^\circ - H_0^\circ)/T$ ,  $H^\circ - H_0^\circ$ ,  $S^\circ$  and  $C_p^\circ$ , for thiacyclopentane were computed for selected temperatures up to 1000°K. by the methods of statistical mechanics. Because detailed information about

(12) D. W. Scott, H. L. Finke, W. N. Hubbard, J. P. McCullough, G. D. Oliver, M. E. Gross, C. Katz, K. D. Williamson, G. Waddington and H. M. Huffman, *THIS JOURNAL*, **74**, 4656 (1952).

(13) S. Sunner, Dissertation, Lund, 1949, "Studies in Combustion Calorimetry applied to Organo-Sulfur Compounds," Carl Bloms Boktryckerie, Lund, Sweden, 1949.

(14) F. D. Rossini and W. E. Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

the molecular structure was lacking and because there was some uncertainty in the assignment of the vibrational frequencies, the treatment adopted was necessarily in part empirical. However, this treatment included the correct number and kinds of degrees of freedom and gave a satisfactory fit to the calorimetric values of the entropy and heat capacity over the temperature ranges covered by the experimental measurements.

The set of vibrational frequencies used for calculating the thermodynamic functions was based on spectroscopic data from a number of sources. The Raman data employed were from an investigation by Dr. E. J. Rosenbaum of the Sun Oil Company, the results of which have been included in the A.P.I. 44 catalog of Raman data.<sup>15</sup> These Raman data were obtained with somewhat better resolution and with a sample better characterized as to purity than in the earlier investigation of Yur'ev, Tatevskii and Gragerov.<sup>16</sup> Six infrared spectrograms of thiacyclopentane for various wave length regions have been submitted to the A.P.I. 44 catalog of infrared data.<sup>17</sup>

The spectroscopic data were interpreted on the basis of the structure which seemed most likely in view of the present knowledge of related molecules, particularly the parent molecule, cyclopentane, the molecular structure of which has been treated in detail by Kilpatrick, Pitzer and Spitzer.<sup>18</sup> These investigators showed that the five-membered ring of the cyclopentane molecule is puckered and that the puckering is of an indefinite type because the minimum potential energy is essentially the same for all types of puckering. The two degrees of freedom associated with puckering of the ring may be described as "first, an ordinary vibration in which the amount of puckering oscillates about a most stable value and second, a pseudo one-dimensional rotation in which the phase of the puckering rotates around the ring." The latter is not a real rotation, as there is no angular momentum about the axis of rotation, but the energy levels and contributions to the thermodynamic functions are identical with those of a one-dimensional rotation.

Substituting a sulfur atom for a CH<sub>2</sub> group in going from cyclopentane to thiacyclopentane must change this situation somewhat. In particular, with the symmetry of the cyclopentane molecule destroyed by substitution of the sulfur atom, the minimum potential energy for thiacyclopentane is probably no longer independent of the phase of puckering. In other words, potential barriers must be surmounted as the phase of puckering rotates around the ring. It seems appropriate, therefore, to consider the degree of freedom of thiacyclopentane corresponding to the pseudo

(15) American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology, Catalog of Raman Spectral Data, Serial No. 185. The Raman spectrum was obtained with a sample of the same highly purified thiacyclopentane that was used in this research.

(16) Yu. K. Yur'ev, B. M. Tatevskii and I. P. Gragerov, *Zhur. Fiz. Khim.*, **22**, 783 (1948).

(17) American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology, Catalog of Infrared Spectral Data, Serial No.'s. 542 (2-15 $\mu$ ), 962 (15-22 $\mu$ ), 1155 (2-15 $\mu$ ), 1156 (2.5-5 $\mu$ ), 1157 (15-22 $\mu$ ) and 1249 (2-15 $\mu$ ).

(18) J. E. Kilpatrick, K. S. Pitzer and R. Spitzer, *THIS JOURNAL*, **69**, 2483 (1947).

rotation of cyclopentane as a *restricted pseudo rotation* whose contributions to the thermodynamic functions are identical with those of an ordinary restricted internal rotation. The other degree of freedom associated with puckering of the thiacyclopentane ring may be regarded as an ordinary vibration, just as in the case of cyclopentane. This description of the ring puckering is of course a simplification, for purposes of thermodynamic calculations, of what must actually be a much more complex situation.

Depending on the instantaneous type of puckering of the ring, the point-group symmetry of the thiacyclopentane molecule may be either  $C_{2v}$ ,  $C_2$  or  $C_1$ , in each of which cases all frequencies are active in both the Raman and infrared spectra. Selection rules were therefore of no assistance in making a vibrational assignment, and the set of vibrational frequencies for thermodynamic calculations was selected largely by making use of known regularities in the frequencies of structurally related molecules. The set of frequencies is given in Table VI. The 297  $\text{cm}^{-1}$  frequency, observed as a weak, diffuse Raman line, is ascribed to the ring-puckering vibration because it is close to the frequency of the analogous vibration in cyclopentane, 288  $\text{cm}^{-1}$ . This choice is somewhat arbitrary, as the 297  $\text{cm}^{-1}$  Raman line has an alternative interpretation as a difference combination. Of the other 19 frequencies below 1400  $\text{cm}^{-1}$  in Table VI, 15 appear

TABLE VI

VIBRATIONAL FREQUENCIES USED FOR THERMODYNAMIC CALCULATIONS,  $\text{CM}^{-1}$

Ring puckering	297, restricted pseudo rotation
Ring deformation	471, 520
S-C stretching	632, 688
C-C stretching	884, 960, 1036
$\text{CH}_2$ rocking	770, 820, 960, 1022
$\text{CH}_2$ wagging	1064, 1098, 1196, 1258
$\text{CH}_2$ twisting	1136, 1183, 1307, 1333
$\text{CH}_2$ bending	1442 (2), 1466 (2)
C-H stretching	2950(8)

strongly in one or both spectra, and their assignment as fundamentals is quite certain. The use of weak Raman lines and infrared bands and an assumed coincidence for the other four is somewhat schematic. Average values are used for the thermodynamically unimportant  $\text{CH}_2$  bending and C-H stretching frequencies, which are not fully resolved in the observed spectra.

The moments of inertia of thiacyclopentane were calculated for a planar ring model with the following bond distances and angles: S-C distance, 1.82 Å.; C-C distance, 1.54 Å.; C-H distance, 1.09 Å.; C-S-C angle 98°; H-C-H angle, H-C-C angles and H-C-S angles equal for the  $\alpha$ -methylene group; and H-C-H angle and H-C-C angles equal for the  $\beta$ -methylene group. The product of the three principal moments of inertia for this model is  $8.72 \times 10^{-114} \text{ g}^3 \text{ cm}^6$ . The value for the actual molecule with a puckered ring will be approximately the same.

Two parameters are required to describe the restricted pseudo rotation— $V$ , the height of the

restricting potential barrier (assumed to be of the simple cosine type) and the ratio  $I/n^2$ , where  $I$  is essentially the effective moment of inertia and  $n$  is the number of potential minima in a complete pseudo rotation. (For the present purpose,  $n$  itself may remain unspecified, as only the ratio  $I/n^2$  is required. However, as indistinguishable configurations occur twice for each complete pseudo rotation, the most likely value for  $n$  is 2.) The two parameters were selected empirically to fit the calorimetric entropy and heat capacity data with the results

$$V = 2800 \text{ cal. mole}^{-1}$$

$$I/n^2 = 2.665 \times 10^{-40} \text{ g. cm}^2$$

The satisfactory empirical fit that was obtained may be judged by the comparison of the observed and calculated values of the heat capacity in Table IV and the following comparison of the observed and calculated values of the entropy.

$T$ , °K.	349.86	370.16	394.28
$S^\circ$ , cal. deg. $^{-1}$ mole $^{-1}$ (obsd.)	77.72	79.22	80.92
$S^\circ$ , cal. deg. $^{-1}$ mole $^{-1}$ (calcd.)	77.71	79.19	80.94

The excellent fit of the heat capacity data over the entire range of the experimental measurements is particularly gratifying and gives increased confidence in the reliability of the treatment just described for extending the calorimetric data to higher temperatures and to other thermodynamic functions.

The computed values of the functions,  $-(F^\circ - H_0^\circ)/T$ ,  $(H^\circ - H_0^\circ)/T$ ,  $H^\circ - H_0^\circ$ ,  $S^\circ$  and  $C_p^\circ$ , at selected temperatures up to 1000°K. are given in Table VII. In some places in the table the last digit is retained for reasons of internal consistency although its retention is not justified by the absolute accuracy of the value of the function.

TABLE VII

THERMODYNAMIC FUNCTIONS OF THIACYCLOPENTANE

$T$ , °K.	$-(F^\circ - H_0^\circ)/T$ , cal. deg. $^{-1}$ mole $^{-1}$	$(H^\circ - H_0^\circ)/T$ , cal. deg. $^{-1}$ mole $^{-1}$	$H^\circ - H_0^\circ$ , kcal. mole $^{-1}$	$S^\circ$ , cal. deg. $^{-1}$ mole $^{-1}$	$C_p^\circ$ , cal. deg. $^{-1}$ mole $^{-1}$
273.16	59.59	12.52	3.419	72.11	19.90
298.16	60.73	13.21	3.939	73.94	21.72
300	60.81	13.26	3.979	74.07	21.85
400	65.04	16.31	6.526	81.35	28.95
500	69.02	19.46	9.732	88.48	35.04
600	72.84	22.49	13.49	95.33	40.05
700	76.52	25.31	17.72	101.8	44.20
800	80.07	27.88	22.31	108.0	47.66
900	83.49	30.25	27.23	113.7	50.60
1000	86.80	32.42	32.42	119.2	53.14

### Heat, Free Energy and Equilibrium Constant of Formation

The heat, free energy and equilibrium constant of formation of thiacyclopentane at selected temperatures were computed from the value of  $\Delta H_f^\circ$  at 298.16°K. and the thermodynamic functions of this paper, the thermodynamic functions for graphite and hydrogen given by Wagman, *et al.*,<sup>19</sup> and the thermodynamic functions for sulfur given in

(19) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **54**, 143 (1945).

TABLE VIII  
HEAT, FREE ENERGY AND LOGARITHM OF EQUILIBRIUM  
CONSTANT FOR FORMATION OF THIACTYCLOPENTANE

$T$ , °K.	$\Delta H_f^\circ$ , kcal. mole <sup>-1</sup>	$\Delta F_f^\circ$ , kcal. mole	$\log_{10} K_f$
4C(graphite) + 4H <sub>2</sub> (g) + S(rhombic) = C <sub>4</sub> H <sub>8</sub> S(liq)			
298.16	-17.4	+9.0	-6.56
4C(graphite) + 4H <sub>2</sub> (g) + 1/2S <sub>8</sub> (g) = C <sub>4</sub> H <sub>8</sub> S(g)			
0	-17.3	-17.3	Infinite
298.16	-23.5	+1.4	-1.05
300	-23.5	1.6	-1.16
400	-25.1	10.2	-5.58
500	-26.4	19.2	-8.40
600	-27.4	28.4	-10.35

700	-28.1	37.8	-11.80
800	-28.6	47.2	-12.90
900	-28.9	56.7	-13.78
1000	-29.1	66.3	-14.48

reference 20. Diatomic sulfur gas was adopted as the reference state for elemental sulfur for temperatures other than 298.16°K. The computed values are presented in Table VIII.

(20) (a) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D. C., 1949, *et seq.*, Series I, Tables 14-1 and Series 111 [S<sub>2</sub>(g)]; (b) National Bureau of Standards Report No. 1037.

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## The Specific Heat of Small Particles at Low Temperatures

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The theory is developed for the specific heat of a very finely divided solid at low temperatures. Each particle is treated as if it were a separate molecule but the usual theory of vibrations of a solid is used to estimate the frequencies of the normal modes. Numerical values are given for 100 Å. cubes of aluminum in the range 1-6°K. At 1°K. the gross translation and rotation of whole particles make the principal contributions. It is concluded that the heat capacity of a finely divided solid will be higher than that of the infinite crystal up to the temperature at which the vibrations become classical.

To the temperature at which the internal vibrations of a solid become essentially classical, the heat capacity of a solid is a function of the particle size. The smaller the crystal size, the higher the heat capacity at a given temperature. Another parameter of importance is the shape of the crystal. Experimentally, this effect is illustrated by the heat capacity of MgO. Parks and Kelley<sup>1</sup> measured the heat capacity of very large crystals, while Giaque and Archibald<sup>2</sup> made similar measurements on a sample whose average cube size was 200 Å. The data of the latter authors are as much as 7% higher than for the large crystals. In this paper we treat the heat capacity only at very low temperatures, *i.e.*, up to a few degrees Kelvin.

Montroll<sup>3</sup> recently gave the first-order corrections to the Debye specific heat equation for small particles. We are taking a more drastic point of view in treating small particles essentially as molecules. This brings in detailed consideration of the translation and rotation of each particle. Also we avoid the assumption of a continuous distribution of vibration frequencies, although we retain the same equations that Debye used for the calculation of the frequencies of given modes of oscillation in terms of the macroscopic elastic constants.

The translation and rotation of particles in a powder will be limited by some restoring forces. There are certainly gravity and the ever present repulsive forces between atoms at small distances. Presumably there will also be attractive forces of an atomic character at slightly larger interatomic

distances. For the usual reason, the net force is necessarily harmonic for very small amplitudes, and only such amplitudes will be involved at the very low temperatures where these translational and rotational modes make a substantial contribution. Thus we can use the harmonic oscillator formula for these heat capacity terms. However, the mass of even the smallest solid particle of interest will be several orders of magnitude larger than an atomic mass so that at presently attainable temperatures these motions can be regarded as classical.

Then for a gram atom of a solid, composed of  $q$  particles, each particle containing  $N/q$  atoms, the heat capacity is given by the expression

$$C = q \left[ 6k + \sum_1^{3N/q-6} g(u_\nu) \right] \quad (1)$$

where  $g(u)$  is the usual harmonic oscillator or Einstein function

$$g(u) = ku^2 e^u / (e^u - 1)^2 \quad (2)$$

$k$  is the Boltzmann constant and  $u_\nu = h\nu_\nu/kT$  with  $\nu_\nu$  the frequency of the  $\nu$ -th normal mode of vibration.

For convenience in evaluating  $\nu_\nu$ , we assume that the crystal is a rectangular parallelepiped. If  $a_x$ ,  $a_y$  and  $a_z$  are the edges of this crystal, then, neglecting possible end corrections, the frequencies of the transverse normal modes are

$$\nu_l = (c_l/2)[(l/a_x)^2 + (m/a_y)^2 + (n/a_z)^2]^{1/2} \quad (3)$$

where  $l$ ,  $m$  and  $n$  are positive integers or zero. The corresponding expression is obtained for the longitudinal vibrations by substituting  $c_l$  for  $c_t$ . At the low temperatures under discussion, the usual averaging of the transverse and longitudinal vibrations

(1) G. S. Parks and K. K. Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

(2) W. F. Giaque and R. C. Archibald, *THIS JOURNAL*, **59**, 561 (1937).

(3) E. W. Montroll, *J. Chem. Phys.*, **18**, 183 (1950).