

2. Hägg carbide and cementite have narrow ranges of composition and apparently do not form intermediate metastable solid solutions.

3. The reaction  $3\text{Fe}_2\text{C}-\text{Hägg} \rightarrow 2\text{Fe}_3\text{C}+\text{C}$  becomes appreciable only at about  $450^\circ$ , while the

reaction  $\text{Fe}_2\text{C}-\text{Hägg}+\text{Fe} \rightarrow \text{Fe}_3\text{C}$  (described elsewhere) starts below  $300^\circ$ .

4. The "unstable" or "labile" carbide of Kölbl and co-workers is simply Hägg carbide.

BRUCETON, PA.

RECEIVED MARCH 23, 1950

[CONTRIBUTION NO. 19 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

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

BY D. W. SCOTT, H. L. FINKE, W. N. HUBBARD, J. P. McCULLOUGH, M. E. GROSS, K. D. WILLIAMSON, GUY WADDINGTON AND H. M. HUFFMAN<sup>2</sup>

The hydrocarbon spiropentane, first prepared in a relatively pure state by Murray and Stevenson,<sup>3</sup> is of interest because of its highly condensed structure, and it seemed desirable to have accurate values of certain of its thermodynamic properties. Therefore, an investigation of spiropentane was included in the program of the Bureau of Mines for studying the thermodynamic properties of hydrocarbons and related substances. The present paper reports experimental values of the heat capacity in the solid, liquid, and vapor states, heats of fusion and vaporization, vapor pressure, and entropy, and in addition gives values of the thermodynamic functions calculated from spectroscopic and molecular structure data for selected temperatures up to  $1500^\circ\text{K}$ .

### Experimental

**The Material.**—The spiropentane used for the calorimetric and vapor-pressure studies was purified from crude material, most of which was prepared in this Laboratory but which also included two smaller quantities obtained from outside sources. The preparation was carried out by reducing pentaerythrityl tetrabromide with zinc in an ethanol-water mixture containing sodium carbonate and sodium iodide, as described by Slabey.<sup>4</sup> Batchwise reduction of 44.2 moles (17.2 kg.) of pentaerythrityl tetrabromide in this manner yielded 2.47 kg. (3.36 l.) of hydrocarbon product, which was then distilled in an efficient fractionating column to separate the spiropentane from the methylenecyclobutane, 2-methyl-1-butene, and other by-products of the reduction. Distillation fractions having refractive indices,  $n_D^{20}$ , between 1.399 and 1.418 were combined to give 870 ml. of crude spiropentane. To this was added about 75 ml. of spiropentane obtained in part from Dr. Ralph Spitzer, of the State College of Oregon, and in part from the Automotive Section of the National Bureau of Standards through the courtesy of Frank L. Howard. The combined material was treated with bromine to convert the olefinic impurities into higher-boiling brominated compounds. (Bromine was added until the yellow color would persist for a number of seconds after the addition of a single drop.) The spiropentane was then separated from the brominated materials by a second fractional distillation. Center cuts from this distillation, all having refractive indices,  $n_D^{20}$ , between 1.41193 and 1.41201, were combined into two samples. Sample A,

having a volume of about 160 ml., was used for the heat-of-vaporization measurements and the initial series of vapor-heat-capacity measurements. Its purity, as determined by the time-temperature freezing-point method, was 99.67%. Sample B, having a volume of about 65 ml., was used for the first series of low-temperature studies and for the vapor-pressure measurements. From observations of the melting point as a function of the fraction melted, its purity was found to be 99.69%. In the ebulliometric vapor-pressure studies, the difference between the boiling and condensation temperatures of this sample at the normal boiling point was observed to be  $0.009^\circ$ . After completion of the measurements with these two samples, they were combined and further purified by repeated fractional crystallization. The crystallization was done in a closed, all-glass apparatus, which will be described in detail in a forthcoming publication from the Chemistry and Refining Section of this Station. The product from the fractional crystallization, Sample C (about 70 ml.), was used for the second series of low-temperature studies. Its purity was 99.87%, as determined by the change of melting point with fraction melted. A summary of the melting-point data for Sample C is given in Table I. The larger volume of less pure material rejected in the fractional crystallization, Sample D, was used for the final series of vapor-heat-capacity measurements.

TABLE I  
SPIROPENTANE MELTING POINT SUMMARY  
 $0^\circ\text{C.} = 273.16^\circ\text{K.}, N_2/F = 0.0280\Delta T^a$

Melted, %	Obsd. $T, ^\circ\text{K.}$	Calcd.
10.3	165.6969	165.6848
50.4 <sup>b</sup>	166.0450	166.0450
70.8	.0722	.0716
91.1 <sup>b</sup>	.0860	.0860
100		.0907
Pure		.1373

Triple point =  $166.14 \pm 0.05^\circ\text{K}$ .  
Impurity = 0.13 mole %.

<sup>a</sup>  $N_2$  = mole fraction of impurity;  $F$  = fraction of sample in liquid form. <sup>b</sup> These points used to obtain calculated values.

**Low-Temperature Heat Capacity.**—The low-temperature measurements were made in the apparatus described by Ruehrwein and Huffman.<sup>5</sup> Very briefly, the method is as follows: About 0.61 mole of the material under investigation was contained in a sealed copper calorimeter, which was mounted in the adiabatic calorimetric system. A measured amount of electrical energy was supplied to the calorimeter, and at all times the temperature of the

(1) Not subject to copyright.

(2) Deceased.

(3) Murray and Stevenson, *THIS JOURNAL*, **66**, 314 (1944); *ibid.*, p. 812.

(4) Slabey, *ibid.*, **68**, 1285 (1946)

(5) Ruehrwein and Huffman, *ibid.*, **65**, 1620 (1942).

environment was maintained at that of the calorimeter to prevent heat interchange. The initial and final temperatures of the calorimeter were measured by means of a platinum resistance thermometer. The electrical measurements required for determining the resistance of the thermometer and the electrical energy were made on a "White" double potentiometer in conjunction with a high-sensitivity galvanometer and accurately calibrated resistances. The potential was in terms of a bank of six saturated cadmium cells, which had been certified by the National Bureau of Standards. Time measurements were made with an electric stop clock, which was operated by an a.c. power supply, the frequency of which was accurate to 0.001%. The precision of the measurements was, in general, better than 0.1%, and above 30°K. it is believed that the accuracy uncertainty should not be greater than 0.2%. The energy measurements were made in terms of the international joule and converted to calories by dividing by 4.1833.

Two complete sets of low-temperature measurements were made, one with Sample B and one with Sample C. The two sets of data did not differ significantly, except in the premelting region, and they yielded virtually identical values for the entropy of the liquid at 298.16°K. Only the data obtained with the purer material, Sample C, will

TABLE II  
THE MOLAL HEAT CAPACITY OF SPIROPENTANE  
0°C. = 273.16°K., mol. wt. = 68.114.

T, °K.	$\Delta T$	$C_{sat.}$ cal. deg. <sup>-1</sup>	T, °K.	$\Delta T$	$C_{sat.}$ cal. deg. <sup>-1</sup>
12.56	1.511	0.649	102.07	6.801	13.256
14.12	1.597	0.919	103.53	6.706	13.365
15.88	1.929	1.262	105.34	6.604	13.507
16.99	2.595	1.504	109.19	7.430	13.800
18.21	2.730	1.776	110.10	6.438	13.864
19.65	2.733	2.120	116.42	6.201	14.356
21.12	3.088	2.480	116.46	7.119	14.350
22.54	3.052	2.835	122.52	6.003	14.800
24.46	3.601	3.309	123.86	7.692	14.900
25.82	3.497	3.643	128.43	5.820	15.246
28.10	3.671	4.205	131.61	7.819	15.498
29.41	3.691	4.515	134.56	6.442	15.753
31.49	3.107	4.984	139.29	7.529	16.104
33.26	4.016	5.393	140.91	6.250	16.249
37.52	4.498	6.262	146.68	7.256	16.745
41.73	3.920	7.020	153.78	6.945	17.605
45.88	4.374	7.697	159.95	5.396	19.993
50.43	4.729	8.344			Liquid
54.48	5.593	8.870	176.44	5.698	25.944
55.08	5.569	8.941	176.84	5.701	25.956
59.83	5.109	9.494	182.12	5.658	26.076
60.90	6.063	9.614	184.40	9.420	26.125
65.22	5.668	10.067	194.69	11.154	26.402
66.72	5.585	10.222	205.76	10.979	26.781
70.70	5.298	10.594	216.64	10.795	27.224
72.55	6.080	10.766	227.35	10.610	27.700
76.26	5.808	11.115	237.86	10.413	28.240
78.44	5.695	11.336	248.17	10.220	28.804
81.90	5.475	11.658	258.29	10.020	29.426
84.60	6.615	11.904	268.21	9.814	30.068
87.32	5.359	12.131	277.94	9.643	30.708
89.91	5.319	12.332	287.49	9.460	31.366
91.04	6.270	12.423	294.55	4.865	31.890
93.07	6.151	12.578	297.20	7.701	32.089
95.62	6.099	12.767	301.91	10.687	32.428
97.17	5.998	12.889	312.11	9.719	33.194
99.09	5.897	13.032			

be presented in detail. The results of the heat-capacity measurements are given in Table II, and the values of  $C_{sat.}$  at integral temperatures, as selected from a smooth curve through all the data, are given in Table III. Two measurements of the heat of fusion gave the same value, 1537.6 cal./mole.

TABLE III  
MOLAL HEAT CAPACITY OF SPIROPENTANE AT INTEGRAL TEMPERATURES

T, °K.	$C_{sat.}$ cal. deg. <sup>-1</sup>	T, °K.	$C_{sat.}$ cal. deg. <sup>-1</sup>	T, °K.	$C_{sat.}$ cal. deg. <sup>-1</sup>
12	0.555	80	11.480	180	26.020
13	.720	85	11.935	190	26.265
14	.895	90	12.340	200	26.570
15	1.080	95	12.725	210	26.945
20	2.210	100	13.100	220	27.365
25	3.435	110	13.860	230	27.830
30	4.645	120	14.615	240	28.350
35	5.750	130	15.370	250	28.910
40	6.720	140	16.125	260	29.530
45	7.560	150	16.885	270	30.180
50	8.285	160	17.640	280	30.850
55	8.930	166.14	18.110	290	31.550
60	9.510		Liquid	298.16	32.150
65	10.050	166.14	25.740	300	32.280
70	10.530	170	25.810	310	33.030
75	11.000				

Vapor Heat Capacities and Heats of Vaporization.—Measurements of vapor heat capacities and heats of vaporization were carried out with a flow calorimeter and cycling vaporizer as described in previous publications from this laboratory.<sup>6</sup> The glass cycling vaporizer formerly used has been replaced by one made of metal. This will be described in a forthcoming publication.

Sample A was used in the determination of the heat of vaporization. As the 0.33% of volatile impurity present in this sample probably was similar in physical properties to spiro-pentane, it is believed that it had a negligible effect upon the heat of vaporization. From three experiments at each of the three temperatures 10.00, 25.00 and 38.98° the mean values  $6753 \pm 5$ ,  $6572 \pm 4$  and  $6393 \pm 1$  cal./mole were obtained. The uncertainties listed are maximum deviations from the mean. The accuracy of these values is believed to be about  $\pm 0.1\%$ . For interpolation within the temperature range covered by the experimental measurements, the following equation may be used

$$\Delta H_{vap.} = 8023 + 2.727T - 2.547 \times 10^{-2}T^2 \quad (1)$$

The heat capacity of the vapor was determined at two or more pressures at each of five temperatures ranging from 318 to 488° K. Two complete series of measurements were made. The first of these, made on sample A, was rejected because of inconsistencies and a lack of precision in the data indicative of experimental difficulties of unknown nature. The second series was made on Sample D, which at the beginning of the measurements contained approximately 0.4 mole per cent. of volatile impurity but during the measurements suffered an additional contamination of 0.6 mole per cent. of non-volatile impurity. The non-volatile impurity affected the heat of vaporization by an amount mainly due to a heat of mixing term. The cycling process involved the vaporization of the volatile material and its return in liquid form to the vaporizer. An analysis of the heat effects attending the changes of state entering into the cycling process indicated that the presence of the small percentage of non-volatile material had little effect upon the flow rates determined from the power input and the heats of vaporization of the uncontaminated sample. The quantity of sample available was insufficient

(6) (a) Waddington, Todd and Huffman, *THIS JOURNAL*, **69**, 22 (1947); (b) Waddington and Doulin, *ibid.*, **69**, 2275 (1947).

to repeat the measurements on a repurified sample; hence, the results of the second series are reported here in Table IV. An accuracy uncertainty of  $\pm 0.4\%$  is assigned to these results instead of the usual value of  $\pm 0.2\%$ .

TABLE IV  
VAPOR HEAT CAPACITY OF SPIROPENTANE IN CAL./DEG./MOLE

T, °K.	318.65	367.65	407.15	449.20	487.20
$C_p$ (760 mm.)	23.285	26.650	29.395	32.151	34.471
$C_p$ (458 mm.)	23.023				
$C_p$ (249 mm.)	22.841	26.423	29.233	32.030	34.417
$C_p^\circ$ (expt.)	22.63	26.31	29.16	31.97	34.39
$C_p^\circ$ (calcd.)	22.64	26.27	29.04	31.82	34.15
$C_p^\circ - C_p^\circ$ (expt.)	0.66	0.34	0.24	0.18	0.08
$(\partial C_p/\partial P)_T$ (calcd.)	0.66	0.35	0.24	0.16	0.11

Values of  $C_p^\circ$ , the heat capacity in the ideal gas state, were obtained at each temperature by linear extrapolation to zero pressure of plots of heat capacity vs. pressure. Over the temperature range of the experiments the calorimetric values of  $C_p^\circ$  are represented to better than  $\pm 0.1\%$  by the empirical equation

$$C_p^\circ = -7.078 + 0.10850T - 4.799 \times 10^{-5}T^2 \quad (2)$$

**Vapor Pressure.**—The vapor pressure of spiropentane was measured from 3 to 71° by an ebulliometric method with the apparatus that has been described in previous publications from this laboratory.<sup>7</sup> The results of the measurements are tabulated in Table V. These data were fitted to an Antoine equation by a least-squares adjustment, and the equation obtained is

$$\log_{10} p = 6.91794 - 1090.589/(t + 231.165)$$

The normal boiling point given by this equation is 38.98°. Values of the vapor pressure calculated by means of the above equation are listed in the fourth column of Table VI for comparison with the observed values.

**Gas Imperfection and Second Virial Coefficients.**—Values of the second virial coefficient,  $B$ , which is defined by the equation  $PV = RT + BP$ , 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  $(\partial C_p/\partial P)_T = -T(\partial^2 B/$

TABLE V

Boiling point, °C.		Pressure, mm.	
Water	Spiropentane	Obs.	Calcd.
65	3.632	187.57	187.55
70	8.565	233.72	233.72
75	13.537	289.13	289.16
80	18.546	355.22	355.25
85	23.592	433.56	433.55
90	28.679	525.86	525.84
95	33.808	633.99	634.00
100	38.977	760.00	760.05
105	44.181	906.06	906.05
110	49.429	1074.6	1074.5
115	54.714	1268.0	1267.9
120	60.045	1489.1	1489.1
125	65.421	1740.8	1741.0
130	70.829	2026.0	2026.0

(7) (a) Waddington, Knowlton, Scott, Oliver, Todd, Hubbard, Smith and Huffman, *This Journal*, **71**, 797 (1949); (b) Scott, Waddington, Smith and Huffman, *ibid.*, **71**, 2767 (1949).

$\partial T^2)_P$ . These data were correlated by means of the empirical equation

$$B = -57 - 136.7e^{860/T} \text{ cc./mole} \quad (3)$$

The method of evaluating the constants in this equation has been described elsewhere.<sup>8</sup>

At 283.16, 298.16 and 312.14° K. the values of  $B$  derived from the experimental data are  $-1424$ ,  $-1253$  and  $-1157$  cc./mole, respectively. These agree well with the values  $-1413$ ,  $-1267$  and  $-1154$  calculated from equation 3. The last two rows of Table IV give a comparison of the values of  $C_p^\circ - C_p^\circ$  obtained from the experimental data with the values of  $(\partial C_p/\partial P)_T$  calculated using this equation for the second virial coefficient.

**Entropy.**—The calorimetric data were utilized to calculate the entropy of spiropentane in both the liquid and vapor states. A summary of the entropy calculations is given in Table VI. For calculating the correction for gas imperfection, which is given by  $P(\partial B/\partial T)_P$  in terms of the second virial coefficient, eq. 3 was used.

TABLE VI

THE ENTROPY OF SPIROPENTANE, CAL./DEG./MOLE			
0–12°K.	Debye extrapolation, $\theta = 141$ , 6 degrees of freedom		
12–166.14°	Solid, graphical		0.190
166.14°	Fusion, 1537.6/166.14		9.255
166.14–298.16°	Liquid, graphical		16.354
Entropy of liquid at 298.16°K.			46.29 $\pm$ 0.10
T, °K.	283.16	298.16	312.14
Entropy of liquid	44.65	46.29	47.78
Vaporization, $\Delta H_{vap}/T$	23.85	22.04	20.48
Compression, $R \ln (p/760)$	-2.22	-1.01	0.00
Gas imperfection	0.09	0.13	0.18
Entropy of ideal gas at 1 atm.	66.37	67.45	68.44
	$\pm 0.15$	$\pm 0.15$	$\pm 0.15$

### Vibrational Assignment and Thermodynamic Functions

**Vibrational Assignment.**—In order to extend the calorimetric data to other thermodynamic functions and to higher temperatures, a complete set of vibrational frequencies was necessary. With the vapor-heat-capacity and entropy data as guides, a vibrational assignment was made, which, although not certain in every detail, is adequate for the purpose of computing thermodynamic functions.

The Raman and infrared spectra of spiropentane have been studied by Cleveland, Murray and Gallaway.<sup>9</sup> As an aid in interpreting the spectroscopic data and in estimating the unobserved fundamental frequencies, a normal coordinate treatment was carried out. It was considered desirable to be able to transfer as many force constants as possible from the structurally related molecule cyclopropane. Therefore, the same coordinates were used to describe the motions of the CH<sub>2</sub> groups and the three-membered rings that were used by C. S. Lu, C. W. Beckett and K. S. Pitzer of the University of California in their normal coordinate treatment of cyclopropane.<sup>10</sup> Wilson's G F matrix method was employed, and the C–H stretching motions were reduced out immediately.<sup>11</sup> The highest order matrix remaining was then of the sixth order.

A potential-energy function was used that included all the interaction terms that were found to be important in

(8) Scott, Waddington, Smith and Huffman, *J. Chem. Phys.*, **15**, 565 (1947).

(9) Cleveland, Murray and Gallaway, *ibid.*, **15**, 742 (1947).

(10) Private communication from Dr. C. W. Beckett.

(11) Wilson, (a) *J. Chem. Phys.*, **7**, 1047 (1939); (b) **9**, 76 (1941).

cyclopropane. The force constants were either transferred from cyclopropane or selected to fit observed frequencies of spiropentane, with the exception of a force constant for  $\text{CH}_2$  twisting that could not be obtained from either source. This one force constant was selected to yield calculated  $\text{CH}_2$  twisting frequencies consistent with the calorimetric vapor heat-capacity data.

Initial calculations using the generally accepted vibrational assignment for cyclopropane,<sup>12</sup> gave calculated  $\text{CH}_2$  rocking frequencies for spiropentane inconsistent with the observed spectra and the calorimetric vapor heat capacity data. This discrepancy was resolved by using a different assignment for the two lowest frequencies of cyclopropane, namely, by assigning the 740  $\text{cm}^{-1}$  Raman line to ring deformation,  $E'$ , and the 866  $\text{cm}^{-1}$  Raman line to  $\text{CH}_2$  rocking,  $E''$ . This latter assignment is supported by the existence of a weak band at 740  $\text{cm}^{-1}$  in the infrared spectrum of cyclopropane.<sup>13</sup>

As it is unlikely that any of the new force constants obtained for spiropentane could be transferred to other molecules, it does not seem desirable to present the normal coordinate calculations in detail. Consequently only the final results will be given. The calculated frequencies are listed in column 3 of Table VII for comparison with the observed values listed in column 4. The observed frequencies used to evaluate force constants are enclosed in parentheses. The secular equations of second and third order were expanded and solved by numerical computation; those of fourth and sixth order were solved with a resistance-network computer recently constructed in this laboratory. This computer is similar to that described by Frost and Tamres<sup>14</sup> but is modified as suggested by Wilson<sup>15</sup> to make it more adaptable to molecular-vibration problems.

TABLE VII

CALCULATED AND OBSERVED FREQUENCIES OF SPIROPENTANE, SYMMETRY:  $V_d \equiv D_{2d}$

Class	Motion	Calculated	Observed
	$\text{CH}_2$ bend.	1480	....
$A_1$	Ring str.	1150	(1150) R
$R(p), -$	$\text{CH}_2$ wag.	1025	1033 $R(p)$
	Ring def.	581	(581) $R(p)$
$A_2$	$\text{CH}_2$ twist.	1198	....
$-, -$	$\text{CH}_2$ rock.	853	852 from combination
	$\text{CH}_2$ twist.	1203	....
$B_1$	$\text{CH}_2$ rock.	872	(872) $R(d)$
$R(d), -$	Frame twist.	272	(272) from combination
	$\text{CH}_2$ bend.	1481	....
$B_2$	Ring str.	1397	(1397) $R(d)$
$R(d),$	$\text{CH}_2$ wag.	1024	993 $IR(\parallel)$
$IR(\parallel)$	Ring def.	870	(870) $IR(\parallel)$
	$\text{CH}_2$ bend.	1425	1430 $R(d), IR(\perp)$
	$\text{CH}_2$ twist.	1157	(1157) $IR$
$E$	$\text{CH}_2$ wag.	1087	1053 $IR(\perp)$
$R(d),$	$\text{CH}_2$ rock.	872	896 $IR$
$IR(\perp)$	Ring def.	810	778 $R(?)$ , $IR(\perp)$
	Frame bend.	305	(305) $R(d)$

The direct assignment from spectroscopic data will now be discussed. The selection rules are given in the first

(12) Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 352.

(13) Catalog of Infrared Spectral Data, American Petroleum Institute Research Project 44 at the National Bureau of Standards. Serial No. 445, cyclopropane (gas), contributed by the Shell Development Co.

(14) Frost and Tamres, *J. Chem. Phys.*, **15**, 383 (1947).

(15) Wilson, *ibid.*, **15**, 736 (1947).

column of Table VII, where the abbreviations have the following meanings: R, Raman active; IR, infrared active; p, polarized; d, depolarized;  $\parallel$ , parallel band contour; and  $\perp$ , perpendicular band contour. The E symmetry class will be considered first. The infrared bands at 778, 1053, and 1430  $\text{cm}^{-1}$  are readily assigned to this class on the basis of their perpendicular band contour. The infrared band at 1157  $\text{cm}^{-1}$  with a double-minimum contour unlike either a parallel or perpendicular band is interpreted as resulting from Fermi resonance between an E fundamental and a combination band of the same species. The Raman line at 305  $\text{cm}^{-1}$  must be assigned to the E symmetry class, as its first overtone appears in both the Raman and infrared spectra.<sup>16</sup> For the remaining E vibration, the normal coordinate calculation indicates a frequency somewhat less than 900  $\text{cm}^{-1}$ ; the shoulder at 896  $\text{cm}^{-1}$  on the stronger infrared band at 870  $\text{cm}^{-1}$  is assigned to this mode.

The  $A_1$  and  $B_2$  symmetry classes are conveniently considered together, as the same types of motion occur in both classes; in the  $A_1$  modes, the two halves of the molecule vibrate in phase and in the  $B_2$  modes they vibrate out of phase. The ring deformation and  $\text{CH}_2$  wagging frequencies are readily assigned from the observed spectra. Those in  $A_1$  appear as strong polarized Raman lines at 581 and 1033  $\text{cm}^{-1}$ , and those in  $B_2$  as intense infrared bands with parallel contour at 870 and 993  $\text{cm}^{-1}$ . The assignment of the ring-stretching frequencies is less straightforward. In cyclopropane the ring-stretching frequency is 1189  $\text{cm}^{-1}$ , and in spiropentane the  $B_2$  frequency would be expected to be greater and the  $A_1$  frequency less than this value. The depolarized Raman line at 1397  $\text{cm}^{-1}$  is assigned to the  $B_2$  vibration, and the very weak Raman line at 1150  $\text{cm}^{-1}$  to the  $A_1$  vibration. The latter assignment is particularly questionable from a spectroscopic standpoint, as it is not supported by polarization data and as the 1150  $\text{cm}^{-1}$  Raman line nearly coincides with an infrared band. However, a significantly higher frequency for the  $A_1$  ring-stretching mode would require an unreasonably high value for the C-C stretching force constant, and a significantly lower value would make it impossible to fit the calorimetric vapor heat-capacity data with any reasonable values for the two unobserved  $\text{CH}_2$  twisting frequencies. The  $\text{CH}_2$  bending frequencies in the  $A_1$  and  $B_2$  symmetry classes are apparently unobserved, for there is no Raman line nor infrared band strong enough to assign as a fundamental in the region of the spectra near 1500  $\text{cm}^{-1}$  where these modes would be expected to appear.

The remaining spectroscopically active class is  $B_1$ . The strong Raman line at 872  $\text{cm}^{-1}$  is assigned to the  $\text{CH}_2$  rocking mode of this class. The frame-twisting frequency has not been observed in the Raman spectrum; a value near 275  $\text{cm}^{-1}$  is required to fit the calorimetric entropy. A spectroscopic value for this frequency is obtained from the combination band observed at 1325  $\text{cm}^{-1}$  in the infrared spectrum. This band cannot be explained as an overtone or combination arising from any of the observed fundamentals but may be interpreted as a combination of 1053  $\text{cm}^{-1}$  (E) with a frame-twisting frequency of 272  $\text{cm}^{-1}$ . The  $B_1$   $\text{CH}_2$  twisting frequency is unobserved.

The double minimum contour of the infrared band at 1157  $\text{cm}^{-1}$  assigned as an E fundamental has been interpreted as resulting from Fermi resonance with a combination band. The only sum combination of the proper species that could appear at 1157  $\text{cm}^{-1}$  is the combination of the inactive  $\text{CH}_2$  rocking frequency ( $A_2$ ) and 305  $\text{cm}^{-1}$  (E). This gives a spectroscopic value of 852  $\text{cm}^{-1}$  for the  $A_2$   $\text{CH}_2$  rocking frequency, which is in good agreement with the calculated value. This completes the direct assignment from spectroscopic data. All prominent features in the spectra below 1600  $\text{cm}^{-1}$  have been mentioned except the infrared band at 1340  $\text{cm}^{-1}$ , which is interpreted as the combination band 305 + 1033 ( $A_1 \times E$ ).

(16) N. G. Adams and Dorothy Richardson, of this station, studied the infrared spectra of liquid spiropentane between 400 and 700  $\text{cm}^{-1}$  and found a very weak band at about 610  $\text{cm}^{-1}$ .

The complete set of vibrational frequencies used for thermodynamic calculations is listed in Table VIII. An average value of 1200  $\text{cm}^{-1}$  for the two unobserved  $\text{CH}_2$  twisting frequencies was selected to fit the calorimetric vapor-heat-capacity data. The calculated values for the two unobserved  $\text{CH}_2$  bending frequencies were rounded off to 1500  $\text{cm}^{-1}$ . No detailed assignment was attempted for the thermodynamically unimportant C-H stretching modes; four frequencies of 2990  $\text{cm}^{-1}$  and four of 3050  $\text{cm}^{-1}$  were employed for the thermodynamic calculations.

TABLE VIII

VIBRATIONAL FREQUENCIES OF SPIROPENTANE USED FOR THERMODYNAMIC CALCULATIONS

Motion	Frequency, $\text{cm}^{-1}$	Degeneracy
C-H stretching	3050	4
	2990	4
$\text{CH}_2$ bending	1500	2
	1430	2
$\text{CH}_2$ twisting	1200	2
	1157	2
$\text{CH}_2$ wagging	1053	2
	1033	1
	993	1
$\text{CH}_2$ rocking	896	2
	872	1
	852	1
Ring stretching	1397	1
	1150	1
Ring deformation	870	1
	778	2
	581	1
Frame bending	305	2
Frame twisting	272	1

**Thermodynamic Functions.**—Values of the functions  $(H_0^0 - F_0^0)/T$ ,  $(H_T^0 - H_0^0)/T$ ,  $S^0$ , and  $C_p^0$  were calculated for a range of temperatures. The moments of inertia were computed from the electron diffraction results of Donohue, Humphrey and Schomaker<sup>17</sup> to be  $I_A = 77.28 \times 10^{-40}$  g.  $\text{cm}^2$  and  $I_B = I_C = 199.63 \times 10^{-40}$  g.  $\text{cm}^2$ .

TABLE IX

THERMODYNAMIC FUNCTIONS OF SPIROPENTANE

T, °K.	$(H_0^0 - F_0^0)/T$		$S^0$ cal./deg./mole	$C_p^0$ cal./deg./mole
	cal./deg./mole	cal./deg./mole		
298.16	54.92	3.739	67.46	21.06
300	55.00	3.775	67.59	21.19
400	59.03	6.266	74.70	28.55
500	62.88	9.451	81.78	34.91
600	66.60	13.21	88.62	40.10
700	70.22	17.44	95.13	44.36
800	73.72	22.06	101.30	47.91
900	77.11	27.01	107.12	50.93
1000	80.40	32.23	112.63	53.51
1100	83.58	37.70	117.83	55.73
1200	86.62	43.36	122.76	57.64
1300	89.58	49.22	127.44	59.29
1400	92.45	55.22	131.89	60.73
1500	95.22	61.35	136.12	61.98

(17) Donohue, Humphrey and Schomaker, THIS JOURNAL, **67**, 432 (1945).

The symmetry number is 4. Values of the physical constants given by Wagman, *et al.*,<sup>18</sup> were used. No corrections for anharmonicity, rotational stretching or interaction between rotation and vibration were included, as the last two effects were estimated to be negligible, and insufficient data are available for any adequate treatment of anharmonicity.

The values calculated for the entropy at 283.16, 298.16, and 312.14° K., 66.40, 67.46 and 68.45 cal./deg./mole agree well with the calorimetric values of 66.37, 67.45 and 68.44 cal./deg./mole from Table VI. The values calculated for the heat capacity are compared with those determined experimentally in Table IV. The differences at the higher temperatures between the observed and calculated values of  $C_p^0$  are no greater than is to be expected from the neglect of anharmonicity in computing the latter.

Table IX lists the values of the thermodynamic functions for selected temperatures up to 1500° K. Some entries in the table are given to more decimal places than is justified by their absolute accuracy in order to retain internal consistency among the several functions.

**Acknowledgment.**—The authors wish to thank J. W. Moore and R. L. Hopkins of the Chemistry and Refining Section of this station for assistance in the synthesis of the compound. The fractional distillations were done by H. J. Coleman of that section.

### Summary

The heat capacity of spiro-pentane in the solid and liquid states was measured over the temperature range 12–298° K. The melting point ( $166.14 \pm 0.05^\circ$  K.) and heat of fusion (1538 cal./mole) were determined. The heat of vaporization was measured at three temperatures, and the values found were 6753, 6572 and 6393 cal./mole, at 10.00, 25.00 and 38.98°, respectively. The heat capacity of the vapor was measured at five different temperatures in the range 318 to 487° K. The experimental values of  $C_p$ , the heat capacity in the ideal gas state, may be represented by the equation:  $C_p^0 = -7.078 + 0.10850T - 4.799 \times 10^{-5}T^2$ . The vapor pressure was measured over the temperature range from 3 to 71°, and the following equation was found to fit the vapor-pressure data:  $\log_{10}p = 6.91794 - 1090.589/(t + 231.165)$ . An equation for the second virial coefficient,  $B$ , in the equation of state  $PV = RT + BP$  was obtained from thermal data. This equation is  $B(\text{cc.}) = -57 - 136.7 \exp(650/T)$ . The entropy of liquid spiro-pentane is  $46.29 \pm 0.10$  cal./deg./mole, and the entropy of the vapor in the ideal gas state at one atmosphere pressure is  $67.45 \pm 0.15$  cal./deg./mole, both at 298.16° K.

A vibrational assignment was made for spiro-pentane with the aid of detailed normal coordinate calculations. Using this vibrational assignment and other molecular structure data, values of the functions  $(H_0^0 - F_0^0)/T$ ,  $H_T^0 - H_0^0$ ,  $S^0$  and  $C_p^0$  were computed for selected temperatures up to 1500° K.

BARTLESVILLE, OKLA.

RECEIVED APRIL 24, 1950

(18) Wagman, Kùpatrick, Taylor, Pitzer and Rossini, *J. Research Natl. Bur. Standards*, **54**, 143 (1945).