Summary

1. The vapor pressures of anthracene, naphthalene and hexachlorobenzene were measured in the region 0.01–1.0 mm. by a Rodebush manometer.

2. The data were fitted to vapor pressure equations.

3. Only in one case (naphthalene) was a quantitative comparison with previous workers possible. The agreement was satisfactory.

Durham, North Carolina Received August 2, 1948

[Contribution No. 14 from the Thermodynamics Laboratory, Petroleum Experiment Station, Bureau of Mines]

Cycloöctatetraene: Low-Temperature Heat Capacity, Heat of Fusion, Heat of Vaporization, Vapor Pressure and Entropy

By D. W. Scott, M. E. Gross, G. D. Oliver[1] and H. M. Huffman

During the past decade Reppe and his coworkers made extensive studies of acetylene chemistry, and one of the interesting results of these studies was a method for the synthesis of cycloöctatetraene.[2] This compound is of considerable interest, both to the theoretical chemist and to the industrial chemist. Because of this it appeared desirable to make accurate determinations of its thermodynamic properties.

This paper presents the results of low-temperature thermal studies and vapor-pressure measurements which yield a value for the entropy of cycloöctatetraene vapor. This entropy value will aid in the eventual decision as to the structure of the cycloöctatetraene molecule, since any proposed structure must have moments of inertia, symmetry number, and vibrational frequencies consistent with the observed entropy.

Experimental

The Material.—The cycloöctatetraene used in this investigation was a composite sample purified by the Chemistry and Refining Section of this station. A batch of approximately 90 cc. having a boiling range of about 5° was obtained from the General Aniline & Film Co. through the courtesy of Dr. P. G. Stevens. The second 60 cc. lot was obtained by Dr. Karl Kammermeyer at the I. G. Farbenindustrie plant at Ludwigshafen, Germany, and transmitted to this Bureau through the courtesy of Dr. Julius Alsberg of the Office of Technical Service, U. S. Department of Commerce.

The crude material, after preliminary distillation under reduced pressure, was purified by repeated fractional crystallization from *n*-pentane, followed by a second distillation under reduced pressure to remove residual solvent. A detailed description of the purification process will be given in another publication from the Chemistry and Refining Section of this station.

During the course of the low-temperature studies, a routine investigation was made of the melting point of this material. The data obtained in this investigation are given in Table I. If Raoult's law is obeyed, a plot of the equilibrium temperature against the reciprocal of the fraction melted should give a straight line. The data obtained in this study do not follow this straight-line relation, as shown by the lack of agreement between $T_{\text{calcd.}}$ and $T_{\text{obs.}}$ Hence any conclusions drawn from the data are somewhat arbitrary. An analysis of the data on the basis of the phase rule showed that the presence of a small amount of water, less than saturation concentration, could account for the observed behavior. In fact, in the vapor pressure measurements, an anomalous behavior was observed which disappeared after the material was dried by passing the vapors over magnesium perchlorate. For this reason a second study of the melting point was made with a sample dried in this manner. Unfortunately these measurements were made on a small sample, because the bulk of the material had been returned to the donors, and the results were too erratic to yield reliable values for the melting point and mole fraction of impurity. However, the general trend of this second set of measurements leads one to believe that the melting point and mole fraction of impurity given in Table I are reasonably reliable. The small amount of water that may have been present in the first sample would not have affected the heat-capacity measurements by any significant amount.

Table I

Melting Point Summary, 0°C. = 273.16°K.

Melted, %	T, °K. Obs.	T, °K. Calcd.
18.8	268.337	268.257
37.9	.387	.368
57.1[a]	.405	.405
76.3	.417	.423
90.7[a]	.432	.432
100		.436
Pure		.478
Triple point		268.48 ± 0.05

$N_2/F^b = 0.0188\Delta T$

$N_2 = 0.0008 \pm 0.0005$

[a] Calculation based on these points. [b] F = fraction of sample in liquid form.

Under the conditions of these heat capacity experiments some polymerization occurred, as was evidenced by the inability to remove all of the sample from the calorimeter by distillation. The amount polymerized, approximately 0.04%, was so small that it is believed to have had no significant effect on the thermal measurements.

Apparatus and Methods.—The low-temperature measurements were made in the apparatus described by Ruehrwein and Huffman.[3] Very briefly, the method is as follows: About 0.44 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 environment was maintained at that of the calorimeter to prevent

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(2) Reppe, (a) "Cyclopolyolefins," BIOS Final Report No. 137; (b) "Polymerization of Acetylene to Cycloöctatetraene," FIAT Final Report 967, Appendix 5.

(3) Ruehrwein and Huffman, This Journal, **65**, 1620 (1943).

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.

The vapor pressure measurements were made by the static method in the apparatus described in another publication from this Laboratory.[4] Two measurements were made at each temperature, one on the 80% of the sample remaining after 20% had been pumped off and another on the 20% of the sample remaining after another 60% had been pumped off. Agreement of the two sets of measurements is taken as evidence that the sample was adequately outgassed and contained insignificant amounts of impurity of different volatility.

Since cycloöctatetraene polymerizes slowly even in the absence of oxygen at moderate temperatures, it was necessary to take precautions that the vapor-pressure measurements were not affected by polymerization of the sample. The measurements were made in several series, starting each time with sample freshly distilled into the sample container and making measurements as rapidly as was feasible. Between each series of measurements, the sample was transferred to a storage bulb, air was admitted to the sample container, and the sample container was heated to 150°. This was done to cause any traces of polymer remaining in the sample container to undergo further polymerization to material insoluble in the liquid monomer. The presence of insoluble polymer will, of course, have no effect on the vapor pressure. The vapor pressure measured at the highest temperature, 75°, seems somewhat out of line with the remainder of the data and may be slightly low because of polymer formation. For all the other temperatures, the general consistency of the data and the satisfactory agreement of the results with 80% and with 20% of the sample make it appear unlikely that the vapor pressure was affected significantly by polymer formation.

TABLE II

CYCLOÖCTATETRAENE MOLAL HEAT CAPACITY, CAL. DEGREE^{-1}, 0°C. = 273.16°K.

T, °K.	ΔT	$C_{\text{sat.}}$	T, °K.	ΔT	$C_{\text{sat.}}$
12.80	1.338	1.022	155.50	10.867	21.275
13.99	1.583	1.299	166.14	10.400	22.355
14.22	1.509	1.365	176.33	9.992	23.393
15.91	1.884	1.816	185.48	10.131	24.313
16.07	2.574	1.856	186.14	9.631	24.410
18.44	3.186	2.524	195.43	9.764	25.398
19.28	3.846	2.774	195.61	9.307	25.416
21.89	3.715	3.543	205.03	9.440	26.449
23.20	3.994	3.924	214.88	10.262	27.550
25.70	3.898	4.624	224.97	9.928	28.675
26.92	3.462	4.935	234.74	9.607	29.832
29.64	3.978	5.611	242.75	8.300	30.782
30.55	3.796	5.835	244.71	10.330	31.048
34.45	3.999	6.723	250.94	8.068	31.871
38.52	4.152	7.542	254.86	9.971	32.442
43.27	5.345	8.392	255.88	8.966	32.552
48.75	5.602	9.272	258.40	6.862	33.001
54.46	5.812	10.102	263.43	3.188	34.616
54.76	6.450	10.149	266.14	2.239	41.592
60.28	5.849	10.914		Liquid	
60.88	5.797	10.990	272.97	3.983	42.805
66.95	6.344	11.789	274.43	6.386	42.895
73.06	5.865	12.538	278.92	7.912	43.126
79.17	6.369	13.293	287.57	9.390	43.624
85.42	6.125	14.074	296.90	9.278	44.183
91.95	6.933	14.786	300.33	9.129	44.395
99.24	7.640	15.553	306.13	9.167	44.740
107.18	8.255	16.390	309.40	9.018	44.968
116.18	9.739	17.330	315.62	9.809	45.311
125.66	9.221	18.296	318.74	9.651	45.545
135.05	9.552	19.243	325.36	9.684	45.929
144.95	10.246	20.231	328.33	9.531	46.139

Results

The results of the low-temperature heat-capacity measurements are given in Table II, and Table III lists values of $C_{\text{sat.}}$ at integral temperatures as selected from a smooth curve through all of the data. Two experimental values of the heat of fusion were determined and are given in Table IV.

TABLE III

CYCLOÖCTATETRAENE SMOOTHED MOLAL HEAT CAPACITY, CAL. DEGREE^{-1}

t. °K.	$C_{\text{sat.}}$	T, °K.	$C_{\text{sat.}}$
12	0.84	140	19.73
13	1.07	150	20.73
14	1.30	160	21.73
15	1.56	170	22.74
20	2.98	180	23.76
25	4.43	190	24.82
30	5.70	200	25.90
35	6.84	210	27.00
40	7.82	220	28.11
45	8.68	230	29.26
50	9.46	240	30.45
55	10.18	250	31.63[a]
60	10.87	260	32.81[a]
65	11.54	268.5	33.81[a]
70	12.17	Liquid	
75	12.79	268.5	42.54
80	13.40	270	42.63
85	14.00	280	43.19
90	14.57	290	43.77
95	15.11	298.16	44.26
100	15.64	300	44.37
110	16.67	310	45.00
120	17.70	320	45.61
130	18.73	330	46.23
		340	46.84[a]

[a] Extrapolated values.

TABLE IV

MOLAL HEAT OF FUSON, ΔH, CALORIES

Expt. 1	Expt. 2	Mean
2694.2	2695.1	2694.6 ± 0.5[a]

[a] Precision uncertainty.

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[4] Waddington, Knowlton, Scott, Oliver, Todd, Hubbard, Smith and Huffman, THIS JOURNAL, **71**, 797 (1949).

TABLE V

VAPOR PRESSURE OF CYCLOÖCTATETRAENE

t, °C.	p(obs.), mm. 80% of sample	p(obs.), mm. 20% of sample	p(calcd.), mm. From eq. 1
0	1.51	1.48	1.54
15	4.29	4.22	4.26
20	5.84	5.76	5.81
25	7.84	7.80	7.82
30	10.43	10.43	10.41
35	13.72	13.71	13.71
40	17.91	17.83	17.85
45	23.06	22.98	23.02
50	29.45	29.43	29.40
55	37.26	37.13	37.22
60	46.79	46.65	46.71
65	58.20	58.12	58.16
70	71.89	71.84	71.88
75	88.13[a]	88.08[a]	88.18

[a] May be low because of polymer formation.

TABLE VI

ENTROPY OF CYCLOÖCTATETRAENE, CAL./DEG./MOLE

$S_{12°}$	Debye, 6° freedom, Θ = 122.5	0.289
$\Delta S_{12-268.48°}$	Solid, graphical	37.776
$\Delta S_{268.48°}$	Fusion, 2694.6/268.48	10.037
$\Delta S_{268.48-298.16°}$	Liquid, graphical	4.545
Entropy of the liquid at 298.16°K.		52.65 ± 0.10
$\Delta S_{298.16°}$	Vaporization, 10,300/298.16	34.54
$\Delta S_{298.16°}$	Compression, $R \ln P/760$	−9.09
$\Delta S_{298.16°}$	Gas imperfection	0.00
Entropy in the ideal gas state at 1 atm. and 298.16°K.		78.10 ± 0.35

The results of the vapor-pressure measurements are given in Table V. These data were all obtained after drying the sample by passing the vapors over magnesium perchlorate. The Antoine equation

$$\log_{10} P = 7.06926 - \frac{1504.036}{t + 218.534} \qquad (1)$$

the constants of which were determined by the method of least squares,[5] was found to fit the data satisfactorily. In the least-squares adjustment, no weight was given to the values at 75°.

The heat of vaporization at 25° was calculated from the vapor-pressure data by means of the Clapeyron equation. No equation of state or values of the critical constants are available for cycloöctatetraene, but since, at the low vapor pressure at 25°, the volume of the saturated vapor deviates very little from the ideal gas volume, only a rough estimate of this deviation is required. The approximation used was to employ the Berthelot equation of state with estimated critical constants; the critical constants were taken to be the same as those of *o*-xylene,[6] a C_8 hydrocarbon whose boiling point is close to that of cycloöctatetraene. The calculated heat of vaporization at 25° is 10,300 ±75 cal./mole.

The experimental data have been utilized to compute the entropy of cycloöctatetraene at 298.16°K., for both the liquid and the vapor state. These entropy calculations are summarized in Table VI.

Discussion

Since the completion of this work, Pink and Ubbelohde[7] have published the results of their investigations of certain properties of cycloöctatetraene. From time–temperature studies, these workers found evidence for a transition at about 98°K. They further substantiated this transition by visual observation of a color change, yellow to white, upon cooling through this same region.

The heat capacity measurements reported in this paper show no anomalies in the neighborhood of 98° K. In addition to the heat capacity data given here, two other preliminary series of measurements were made on a sample of cycloöctatetraene which contained considerable impurity (about 1%). These measurements likewise showed no evidence of a transition in the solid. After the authors learned of Pink and Ubbelohde's observations, a portion of the sample used for the heat capacity measurements was cooled with liquid air to about 85° K. After four hours at this temperature, the crystals still had a yellow color.

From these results, it appears as though the transition reported by Pink and Ubbelohde requires conditions not realized in this investigation.

Summary

The heat capacity of cycloöctatetraene was measured from 12 to 330° K. The triple point (268.48±0.05° K.) and heat of fusion (2694.6±0.5 cal./mole) were determined. The vapor pressure was measured over the temperature range 0–75° and the following equation was found to fit the data

$$\log_{10} P \text{ (mm.)} = 7.06926 - \frac{1504.036}{t + 218.534}$$

The heat of vaporization calculated from the vapor pressure equation is 10,300±75 cal./mole. The entropy of the liquid at 298.16° K. is 52.65± 0.10 cal./deg./mole and the entropy of the vapor in the ideal gas state at 1 atm. and 298.16° K. is 78.10±0.35 cal./deg./mole.

BARTLESVILLE, OKLA. RECEIVED NOVEMBER 12, 1948

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(5) Willingham, Taylor, Pignocco and Rossini, *J. Research Natl. Bur. Standards*, **35**, 219 (1945).

(6) Altschul, *Z. physik. Chem.*, **11**, 577 (1893).

(7) Pink and Ubbelohde, *Trans. Faraday Soc.*, **44**, 708 (1948).