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Cycloheptane, Cycloöctane and 1,3,5-Cycloheptatriene. Low Temperature Thermal Properties, Vapor Pressure and Derived Chemical Thermodynamic Properties

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From determinations of the low temperature thermal properties and vapor pressure of cycloheptane, cycloöctane and 1,3,5-cycloheptatriene, values of the entropy in the liquid and vapor states and the heat of vaporization, all at 298.16°K., were obtained. These results and values of the heats of formation derivable from literature data were used to compute values of ΔHf°, ΔFf°, ΔSf° and $\log_{10} Kf$ for all three compounds in the liquid and vapor states at 298.16°K. In the solid state the thermal behavior of each substance is complex; there are transitions between four different crystalline forms of cycloheptane, three of cycloöctane and two of 1,3,5-cycloheptatriene.

Studies of low temperature thermal properties have been reported for several of the simpler saturated and unsaturated cyclic hydrocarbons: cyclopropane,[1] cyclobutane,[2] cyclopentane,[3] cyclohexane,[4] cyclopentene,[5] cyclohexene[5] and cycloöctatetraene.[6] In this research similar studies wer made with three more cyclic hydrocarbons: the two saturated cycloalkanes, cycloheptane and cycloöctane and the unsaturated compound 1,3,5-cycloheptatriene (hereafter simply called cycloheptatriene).

Current interest in higher cyclic structures and the recent identification of cycloheptane in petroleum[7] suggest the need of thermodynamic data for these compounds with seven- and eight-membered rings. Details of the molecular structure of cycloheptatriene, such as the configuration of the ring (planar or non-planar) are unknown at present. The calorimetric value of the entropy reported here may contribute to the eventual determination of the molecular structure.

The results of low temperature calorimetric studies and vapor pressure determinations for each of the three compounds will be reported in detail later in the Experimental sections. However, the most significant results are values of the entropy in the liquid and vapor states and the heat of vaporization, all at 298.16°K., as given in Table I. These values and thermochemical data from the literature were used to compute, for all three compounds, values of the standard heat, free energy, entropy and logarithm of the equilibrium constant of formation for the liquid and vapor states at 298.16°K. These calculations of the chemical thermodynamic properties will be discussed in detail in the next section.

Chemical Thermodynamic Properties.—Kaarsemaker and Coops[8] and also Spitzer and Huffman[9] have determined the heats of combustion of cycloheptane and cycloöctane. The data obtained in the two investigations agree moderately well. However, the samples studied by Spitzer and Huffman were apparently of lower purity as indicated by the melting points (−12.2° for C_7H_{14} and 14.5° for C_8H_{16}; values for pure compounds: −8.1° and 14.8°). The results of Kaarsemaker and Coops were therefore accepted. Values of the standard heat of formation in the liquid state at 298.16°K. were calculated for cycloheptane and cycloöctane from these heat of combustion data and values of the standard heat of formation of liquid water[10] and carbon dioxide.[11] Values of the standard heat of formation in the ideal gaseous state were obtained by addition of the values of ΔHv° from Table I to the values of heat of formation in the liquid state. Conn, Kistiakowsky and Smith[12] determined calorimetrically the heat of the vapor phase hydrogenation of cycloheptatriene to cycloheptane. They report $\Delta H_{355} = -72.85 \pm 0.30$ kcal. mole^{-1}. To obtain the value of $\Delta H^\circ_{298.16}$, two assumptions were made: (a) that the value of Conn, *et al.*, does not differ significantly from the standard heat of the hydrogenation reaction and (b) that ΔC_p for the hydrogenation reaction has the constant value of −15 cal. deg.$^{-1}$ mole^{-1} between 298.16 and 355°K. The value obtained for $\Delta H^\circ_{298.16}$ is −71.99 kcal. mole^{-1}. This value and the value of ΔHf° for cycloheptane vapor yield a value of ΔHf° for cycloheptatriene vapor. Subtraction of the value of ΔHv° from Table I gives the value of ΔHf° for liquid cycloheptatriene. The derived values of ΔHf° for all three substances in the liquid and vapor states are listed in the second column of Table II.

TABLE I

MOLAL ENTROPY OF LIQUID AND VAPOR AND HEAT OF VAPORIZATION AT 298.16°K.

	$S_{\text{satd.}}$ (liquid),[a] cal. deg.$^{-1}$	S° (vapor), cal. deg.$^{-1}$	ΔHv° cal.
Cycloheptane	57.97 ± 0.12	81.82 ± 0.30	9210 ± 50
Cycloöctane	62.62 ± 0.12	87.66 ± 0.30	10360 ± 50
Cycloheptatriene	51.30 ± 0.10	75.44 ± 0.25	9250 ± 50

[a] Not significantly different from S° (liquid).

Values of the standard entropy of formation, ΔSf°, were calculated from the values of entropy

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[1] R. A. Ruehrwein and T. M. Powell, THIS JOURNAL, **68**, 1063 (1946).

[2] G. W. Rathjens, Jr., and W. D. Gwinn, *ibid.*, **75**, 5629 (1953).

[3] J. G. Aston, H. L. Finke and S. C. Schumann, *ibid.*, **65**, 341 (1943); D. R. Douslin and H. M. Huffman, *ibid.*, **68**, 173 (1946); G. J. Szasz, J. A. Morrison, E. L. Pace and J. G. Aston, *J. Chem. Phys.*, **15**, 562 (1947).

[4] (a) J. G. Aston, G. J. Szasz and H. L. Finke, THIS JOURNAL, **65**, 1135 (1943); (b) R. A. Ruehrwein and H. M. Huffman, *ibid.*, **65**, 1620 (1943).

[5] H. M. Huffman, M. Eaton and G. D. Oliver, *ibid.*, **70**, 2911 (1948).

[6] D. W. Scott, M. E. Gross, G. D. Oliver and H. M. Huffman, *ibid.*, **71**, 1634 (1949).

[7] American Petroleum Institute Research Project 6 at the Carnegie Institute of Technology, unpublished results.

[8] S. Kaarsemaker and J. Coops, *Rec. trav. chim.*, **71**, 261 (1952).

[9] R. Spitzer and H. M. Huffman, THIS JOURNAL, **69**, 211 (1947).

[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] E. J. Prosen, R. S. Jessup and F. D. Rossini, *ibid.*, **33**, 447 (1944).

[12] J. B. Conn, G. B. Kistiakowsky and E. A. Smith, THIS JOURNAL, **61** 1868 (1939).

in Table I and values of the entropy of graphite and hydrogen.[10] Values of the standard free energy of formation, $\Delta Ff°$, and of the common logarithm of the equilibrium constant of formation, $\log_{10} Kf$, were calculated from the values of $\Delta Hf°$ and $\Delta Sf°$. The calculated values of $\Delta Sf°$, $\Delta Ff°$ and $\log_{10} Kf$ are listed in the last three columns of Table II.

Table II

Molal Chemical Thermodynamic Properties at 298.16° K.

	$\Delta Hf°$, kcal.	$\Delta Ff°$, kcal.	$\Delta Sf°$, cal. deg.$^{-1}$	$\log_{10} Kf$
Cycloheptane (liquid)	−37.73	+12.96	−170.03	− 9.50
Cycloheptane (vapor)	−28.52	+15.06	−146.18	−11.04
Cycloöctane (liquid)	−40.42	+18.60	−197.96	−13.64
Cycloöctane (vapor)	−30.06	+21.50	−172.92	−15.76
Cycloheptatriene (liquid)	+34.22	+58.99	− 83.07	−43.24
Cycloheptatriene (vapor)	+43.47	+61.04	− 58.93	−44.74

Thermal Behavior in the Solid State.—In common with most of the cyclic hydrocarbons that have been studied previously,[2-5] cycloheptane, cycloöctane and cycloheptatriene all exhibit complex thermal behavior in the solid state. Details, such as heats and temperatures of transition and the heat capacity of different crystalline forms, will be reported in the Experimental sections to follow. However, a general idea of the thermal behavior in the solid state may be obtained by reference to Fig. 1, in which the heat capacity of all three substances is plotted as a function of temperature. Cycloheptane exists in four different crystalline forms. Crystals II of cycloheptane could be supercooled readily through the transition regions at 198.2 (II–III) and 134.8°K. (III–IV), but subsequent warming of the supercooled crystals II to temperatures above 134.8°K. always yielded crystals III. Crystals III were also obtained by slow cooling (over a period of about one week) through the 198.2°K. transition temperature. Cycloöctane exists in three crystalline forms; the transitions occur readily. Cycloheptatriene exists in only two crystalline forms, but the form stable at low temperatures has an anomalous curve of heat capacity *vs.* temperature. In the range 82–92°K., the heat capacity changes to a higher level in a short temperature interval in a manner characteristic of organic glasses. The transition to the form stable at higher temperatures is preceded by a range of rapidly increasing heat capacity. This behavior of cycloheptatriene is strikingly parallel to that of cyclopentene.[5] It is unlikely that the 82–92°K. anomaly involved "freezing in" of any disorder to produce residual entropy at very low temperatures. If the crystals did have residual entropy, the calorimetric values of the entropy would be uncertain by more than the experimental uncertainties listed for cycloheptatriene in Table I.

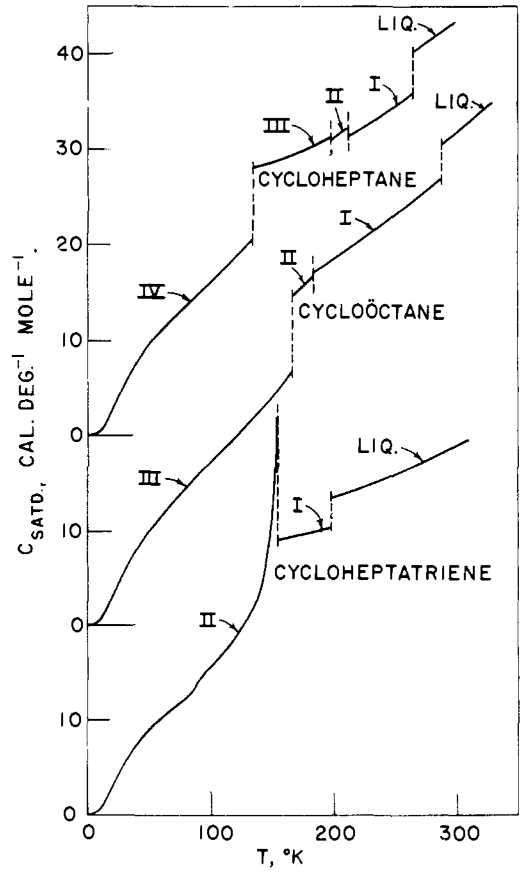

Fig. 1.—Heat capacity of cycloheptane, cycloöctane and cycloheptatriene as a function of temperature. The vertical scales are offset for clarity.

Cycloheptane, cycloöctane and cycloheptatriene all have small heats of fusion. The simpler saturated cyclic hydrocarbons, cyclobutane, cyclopentane and cyclohexane, likewise have small heats of fusion.[2-4] Studies of these latter compounds by X-ray crystallography[13-15] show a high degree of "rotational" disorder in the crystal form of each that is stable immediately below the triple point. By analogy, crystal I of cycloheptane and cyclooctane are expected to have "rotational" disorder. Crystals I of cycloheptatriene are known to be a highly disordered cubic phase.[16]

"Vapor Snake" Phenomenon.—Before introducing the samples into calorimeters for low temperature studies, the samples were thoroughly degassed by successive cycles of freezing, pumping and thawing. In the cases of cycloheptane and cycloöctane, after the initial removal of gas (mainly air), the phenomenon of "vapor snake" formation reported by Phibbs and Schiff[17] was observed during the freezing. Qualitatively, the rate of "vapor snake" formation seemed to increase with decreasing amounts of non-condensable gas present. The rate of formation of the "snake" in thoroughly degassed material was approximately that observed by Phibbs and Schiff with cyclohexane. The "vapor snake" phenomenon has been observed in this Laboratory with other compounds that have relatively high melting points and low cryoscopic constants.

Experimental

The values reported in this paper are based on the 1951 International Atomic Weights[18] and the following relations:

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(13) G. F. Carter and D. H. Templeton, *Acta Cryst.*, **6**, 805 (1953).

(14) B. Post, R. S. Schwartz and I. Fankuchen, This Journal, **73**, 5113 (1951).

(15) T. Oda, *X-Sen (X-Rays)*, **5**, 26 (1948); *cf. C. A.*, **44**, 5179 (1950).

(16) T. B. Reed and W. N. Lipscomb, *Acta Cryst.*, **6**, 108 (1953).

(17) M. K. Phibbs and H. I. Schiff, *J. Chem. Phys.*, **17**, 843 (1949).

(18) E. Wichers, This Journal, **74**, 2447 (1952).

0° = 273.16°K. and 1 cal. = 4.1840 abs. j. = 4.1833 int. j. Measurements of temperature were made with platinum resistance thermometers calibrated in terms of the International Temperature Scale[19] between 90 and 470°K. and the provisional scale[20] of the National Bureau of Standards between 11 and 90°K. Measurements of mass, energy and temperature were made in terms of standard devices calibrated at the National Bureau of Standards.

The Materials.—The samples of cycloheptatriene and cycloheptane used in this investigation were supplied through the courtesy of Dr. W. E. Doering of the Hickrill Chemical Research Foundation, Inc. The cycloheptatriene, synthesized by reaction of diazomethane with benzene, had been distilled through a 12-foot, glass, helix-packed column at slightly reduced pressure. The sample was a center cut of about 75 g. from 400 g. that had the same index of refraction. The index of refraction at 20° was determined by D. M. Richardson of the Chemistry and Refining Branch of this station for five wave lengths with the following results.

Wave length, Å.	6562.8	5892.6	5460.7	4861.3	4358.3
n at 20°	1.51845	1.52394	1.52881	1.53839	1.55069

The cycloheptane had been prepared by the reduction of cycloheptatriene with hydrogen in the presence of platinum catalyst and subsequent fractional distillation in a concentric tube column of more than 100 theoretical plates. The refractive index of the sample used in this investigation was n^{25}_{D} 1.4430.

The cycloöctane sample, obtained from General Aniline & Film Corp. through the courtesy of Dr. J. H. Bruun, had been prepared by hydrogenation of cycloöctatetraene. This material was further purified by the Chemistry and Refining Branch of this station by distillation in a Podbielniak 8-mm. × 12-inch "Heli-grid" packed column. The refractive index of the purified sample was n^{20}_{D} 1.45849.

The Heat Capacity in the Solid and Liquid States.—The low temperature calorimetric studies were made in the apparatus described by Ruehrwein and Huffman.[4b] The calorimeters used were made of copper and contained horizontal disks to facilitate attainment of thermal equilibrium and to prevent settling of the solid phase during fusion experiments. The experimental values of heat capacity in the solid and liquid states are listed in Table III. In this table T is the mean temperature of each heat capacity measurement, ΔT is the temperature increment employed and $C_{\mathrm{satd.}}$ is the heat capacity of the condensed phase under its own vapor pressure. Over the temperature range studied, $C_{\mathrm{satd.}}$ does not differ significantly from C_{p}, the heat capacity at constant pressure. The temperature increments were maintained small enough that corrections for curvature were unnecessary. The values of $C_{\mathrm{satd.}}$ immediately below the melting points are *not* corrected for premelting caused by impurities. The chronological sequence of measurements is not indicated in Table III. Generally, the precision of the results was within ±0.1%; it is estimated that above 30°K. the accuracy uncertainty is not greater than 0.2%. The values of heat capacity for the liquids may be represented by the following empirical equations. The units are $C_{\mathrm{satd.}}$ in cal. deg.$^{-1}$ mole^{-1} and T in °K.

TABLE III

MOLAL HEAT CAPACITY IN CAL. DEG.$^{-1}$

T, °K.	ΔT	$C_{\mathrm{satd.}}$	T, °K.	ΔT	$C_{\mathrm{satd.}}$
Cycloheptane					
Crystals IV			143.57	5.512	28.370
11.52	1.195	0.598	148.64	7.344	28.552
12.08	2.004	0.696	149.05	5.451	28.599
12.75	1.284	0.837	156.83	9.029	28.905
13.88	1.617	1.078	164.55	10.317	29.143
14.15	1.525	1.147	165.96	9.239	29.326
15.61	1.848	1.510	170.73	9.052	29.561
15.71	1.602	1.522	174.75	10.066	29.785
17.26	1.475	1.931	175.68	10.192	29.839
17.60	2.113	2.015	176.81	10.028	29.810
18.89	1.782	2.384	180.25	9.980	30.105
19.73	2.136	2.635	184.37	9.833	30.271
20.75	1.921	2.921	184.70	9.847	30.396
22.03	2.451	3.295	184.92	9.819	30.374
23.02	2.623	3.582	188.55	10.722	30.607
24.59	2.626	4.039	189.37	15.153	30.674
25.57	2.451	4.296	189.56	8.638	30.658
27.42	3.035	4.811	190.13	9.779	30.705
28.09	2.595	4.990	191.09	8.527	30.770
30.46	3.054	5.610	193.03	7.475	30.929
33.53	3.072	6.380	194.14	8.499	30.978
36.61	3.094	7.081	194.98	10.705	31.063
39.88	3.448	7.759	Crystals II		
43.78	4.355	8.523	202.92	4.811	31.509
47.92	3.908	9.261	203.23	2.618	31.531
52.09	4.444	9.957	204.27	4.117	31.619
55.75	4.957	10.519	206.84	4.061	31.804
56.74	4.864	10.683	207.20	3.245	31.733
60.87	5.274	11.296	208.24	2.064	31.983
66.28	5.542	12.057	208.37	4.076	31.950
72.04	5.993	12.807	Crystals I		
75.85	6.875	13.300	215.70	3.149	31.681
78.28	6.485	13.618	219.61	4.684	31.943
82.47	6.371	14.164	225.04	6.175	32.330
84.97	6.889	14.486	226.45	10.249	32.449
88.65	5.990	14.934	232.10	7.939	32.886
91.65	6.478	15.290	234.06	9.908	33.000
96.72	6.784	15.852	235.82	3.907	33.065
98.74	7.706	16.096	236.58	10.024	33.268
103.34	6.443	16.631	242.82	6.162	33.743
106.23	7.287	16.971	244.32	10.627	33.906
109.64	6.160	17.358	249.36	6.908	34.359
115.67	5.910	18.093	255.25	4.869	34.887
116.19	5.736	18.167	260.09	4.811	35.382
116.60	7.787	18.207	Liquid		
121.47	5.693	18.805	269.31	6.665	40.582
123.75	6.505	19.084	272.92	5.136	40.907
125.94	7.164	19.364	276.34	7.398	41.198
127.07	5.496	19.510	278.87	6.770	41.431
129.68	5.364	19.877	284.89	9.698	41.983
Crystals III			293.32	7.157	42.754
138.49	4.643	28.167	300.42	7.060	43.407
Cycloöctane					
Crystals III			127.69	6.231	21.051
11.34	1.251	0.608	127.89	6.308	21.071
11.48	1.171	0.651	133.80	6.003	21.876
12.62	1.323	0.867	134.68	7.268	22.003
12.87	1.644	0.929	141.80	6.982	22.984
13.91	1.306	1.163	148.65	6.724	23.978
14.79	2.213	1.384	151.66	8.762	24.432
15.52	1.924	1.572	155.79	7.543	25.084
16.88	1.965	1.936	159.20	6.308	25.629
17.55	2.112	2.134	Crystals II		
18.91	2.092	2.529	174.50	2.063	35.582
20.15	3.069	2.897	176.64	6.473	36.011
21.13	2.342	3.197	176.75	2.457	35.854
23.22	3.048	3.827	179.17	2.441	36.087
23.91	3.219	4.026	181.58	2.420	36.426
26.43	3.363	4.752	Crystals I		
27.43	3.777	5.024	192.37	5.929	37.804
29.78	3.301	5.657	196.18	6.129	38.074
30.88	3.110	5.942	203.17	7.848	38.661
34.21	3.549	6.771	210.95	7.713	39.357
37.54	3.112	7.534	216.78	9.550	39.809
40.84	3.478	8.231	226.23	9.338	40.719

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

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

TABLE III (*Continued*)

T, °K.	ΔT	$C_{satd.}$	T, °K.	ΔT	$C_{satd.}$
44.79	4.408	9.006	235.47	9.152	41.585
48.98	3.965	9.764	244.54	8.976	42.451
53.21	4.504	10.502	254.30	10.549	43.435
55.84	6.666	10.934	254.88	3.424	43.238
57.54	4.134	11.219	259.30	5.408	43.903
62.15	5.937	11.972	264.73	10.319	44.499
68.37	6.481	12.904	265.47	6.937	44.546
74.58	5.955	13.836	272.81	10.178	45.341
80.34	5.550	14.700	273.20	8.522	45.417
86.15	6.071	15.566	280.40	4.994	46.236
86.67	5.279	15.649	281.64	8.366	46.369
92.05	5.740	16.363		Liquid	
92.23	5.840	16.388	294.61	4.627	51.140
97.93	5.562	17.131	295.56	7.633	51.241
103.75	6.066	17.906	299.71	4.588	51.624
109.68	5.806	18.681	303.88	9.019	52.102
115.38	5.580	19.435	312.83	8.878	53.007
121.45	6.566	20.242	321.64	8.735	53.959
		Cycloheptatriene			
Crystals II			109.86	5.287	17.176
11.34	0.461	0.866	111.53	5.717	17.424
12.06	0.952	1.040	113.84	7.326	17.751
12.87	1.058	1.214	115.23	5.467	17.960
13.28	1.454	1.328	117.57	6.358	18.333
14.04	1.285	1.495	120.96	6.912	18.918
14.78	1.517	1.687	121.00	6.079	18.924
15.38	1.389	1.834	124.18	6.864	19.534
16.32	1.537	2.068	124.36	6.843	19.571
16.94	1.693	2.242	130.22	9.676	20.916
17.87	1.533	2.468	130.83	6.440	21.046
18.74	1.857	2.709	130.99	6.418	21.053
19.51	1.725	2.908	137.06	6.012	22.741
20.82	2.280	3.264	138.97	7.830	23.416
21.46	2.164	3.432	143.17	6.211	25.402
23.23	2.508	3.897	145.48	5.192	27.326
23.76	2.419	4.031		Crystals I	
25.80	2.638	4.532	157.35	5.397	29.090
26.50	3.039	4.720	159.72	5.404	29.201
28.65	3.031	5.238	162.71	5.343	29.299
31.90	3.462	5.967	165.02	6.446	29.320
35.51	3.745	6.717	166.21	6.294	29.435
39.36	3.961	7.417	168.03	5.300	29.463
43.92	5.159	8.131	171.42	6.375	29.574
49.24	5.476	8.892	177.76	6.305	29.790
54.46	4.951	9.546	184.04	6.249	30.028
54.96	4.140	9.615	188.91	8.326	30.256
56.78	9.951	9.824		Liquid	
56.82	8.662	9.826	201.50	4.732	33.664
59.34	4.612	10.134	203.82	4.712	33.764
61.91	4.539	10.413	206.66	5.600	33.873
63.92	5.530	10.654	212.25	5.582	34.118
64.15	4.999	10.688	217.81	5.537	34.370
66.58	9.643	10.937	223.78	6.406	34.640
67.62	5.284	11.056	230.61	7.252	34.952
69.31	5.330	11.251	237.83	7.175	35.331
74.17	7.789	11.748	245.82	8.865	35.738
74.79	5.611	11.838	254.65	8.750	36.216
80.78	5.407	12.519	264.20	10.346	36.764
80.86	3.582	12.533	269.12	10.077	37.075
85.22	3.413	13.156	274.47	10.181	37.393
88.92	5.779	14.019	279.13	9.925	37.684
88.94	4.024	14.019	288.98	9.775	38.309
95.05	6.475	15.010	298.68	9.626	38.937
101.34	6.100	15.934	302.75	9.485	39.220
104.45	5.523	16.437	308.23	9.480	39.606
105.67	6.001	16.604	312.16	9.327	39.880
107.29	5.791	16.814			

Cycloheptane (±0.05%, 265–300°K.)

$$C_{satd.} = 17.231 + 8.309 \times 10^{-2}\,T + 1.3348 + 10^{-5}\,T^2 \quad (1)$$

Cycloöctane (±0.05%, 288–322°K.)

$$C_{satd.} = 36.127 + 2.350 \times 10^{-3}\,T + 1.6500 \times 10^{-4}\,T^2 \quad (2)$$

Cycloheptatriene (±0.1%, 198–312°K.)

$$C_{satd.} = 35.309 - 6.6933 \times 10^{-2}\,T + 3.4778 \times 10^{-4}\,T^2 - 2.7778 \times 10^{-7}\,T^3 \quad (3)$$

The Heat of Fusion and Cryoscopic Constants.—Duplicate determinations of the heats of fusion of each compound were made, with the results listed in Table IV, column 3. For calculating these values of ΔH_{fusion} approximate corrections were applied for the effect of premelting caused by impurities. Kaarsemaker and Coops[8] report values (±5%) of 453 and 601 cal. mole^{-1} for the heats of fusion of cycloheptane and cycloöctane, respectively.

Values of the first and second cryoscopic constants, $A = \Delta H_{fusion}/RT_{T.P.}^{\,2}$ and $B = 1/T_{T.P.} - \Delta C_{fusion}/2\Delta H_{fusion}$, calculated from the observed values of ΔH_{fusion} and values of the triple point temperature, $T_{T.P.}$, and of ΔC_{fusion}, are also listed in Table IV.

TABLE IV

MOLAL HEAT OF FUSION AND CRYOSCOPIC CONSTANTS

	$T_{T.P.}$, °K.	ΔH_{fusion}, cal.	A, deg.$^{-1}$	B, deg.$^{-1}$
Cycloheptane	265.12	449.8 ± 0.1[a]	0.00322	−0.00100
Cycloöctane	287.98	575.9 ± 0.0[a]	.00349	+0.00041
Cycloheptatriene	197.92	277.4 ± 0.2[a]	.00356	−0.00046

[a] Deviation from the mean of duplicate determinations.

The Triple Point and Purity of Sample.—For determination of the triple point temperatures and purity of the samples a study of the "equilibrium" melting temperature, T_{obsd}, as a function of fraction of total sample melted, F, was made for each substance by the procedure outlined in an earlier publication.[21] Table V presents the results of these studies. In each instance, plots of $T_{obsd.}$ *vs.* $1/F$ are not linear, as they would be if the impurities formed ideal solutions in the liquid and were insoluble in the solid. Instead, the plots deviate from linearity in the direction to be expected if the impurities formed a solid solution with the major component. The loosely bound crystal structures associated with the small heats of fusion of the three compounds are favorable to solid solution formation.

When impurities form a solid solution with the major component, a quantitative measure of sample purity cannot be obtained from calorimetric melting point studies, because (a) equilibrium may not be established between solid and liquid phases in the time of the measurements and (b) if there are several impurities with different distribution coefficients between solid and liquid, there are more unknowns than can be evaluated from the experimental data. However, a somewhat arbitrary value of sample purity may be calculated if it is assumed that (a) equilibrium is established between the liquid and solid phases and (b) that the impurity has a single value, less than 1, of the Henry's law constant, K, for distribution between the solid and liquid phases. A convenient method of treating calorimetric melting point data on the basis of these assumptions has been given by Mastrangelo and Dornte.[22] Treatment of the data of Table V by this method leads to values of sample purity of 99.951 mole % for cycloheptane, 99.982 mole % for cycloöctane and 99.986 mole % for cycloheptatriene. The values selected for the triple point temperatures are 265.12, 287.98 and 197.92°K. (−8.04, +14.82 and −75.24°) for cycloheptane, cycloöctane and cycloheptatriene, respectively. For comparison, literature values of the melting points are: (a) cycloheptane, −8.1°[8] and −7.98°[12]; (b) cycloöctane, 14.8°[8] and 14.5°[9]; (c) cycloheptatriene, −79.49°.[23]

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[21] S. S. Todd, G. D. Oliver and H. M. Huffman, THIS JOURNAL, **69**, 1519 (1947).

[22] S. V. R. Mastrangelo and R. W. Dornte, *ibid.*, **77**, 6200 (1955).

[23] E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, *ibid.*, **61**, 1057 (1939).

TABLE V

SUMMARY OF MELTING POINT STUDIES[a]

Cycloheptane

$T_{\text{T.P.}} = 265.12 \pm 0.05$°K. $A = 0.003220$ deg.$^{-1}$
$K = 0.249$ $N_2{}^* = 0.000492$ mole fraction

Melted, %	$[F + K/(1 - K)]^{-1}$	T, °K. Obsd.	T, °K. Calcd.[b]
13.65	2.136	264.785	264.793
27.60	1.646	.869	.868
51.56	1.180	.939	.939
70.97	.960	.971	.972
90.47	.809	.995	.995
100.00	.751		265.004
Pure			.119

Cyclooctane

$T_{\text{T.P.}} = 287.98 \pm 0.05$°K. $A = 0.003494$ deg.$^{-1}$
$K = 0.189$ $N_2{}^* = 0.000183$ mole fraction

11.06	2.910	287.829	287.829
58.73	1.219	.921	.919
74.85	1.019	.928	.929
94.18	.851	.938	.938
100.00	.811		.940
Pure			.983

Cycloheptatriene

$T_{\text{T.P.}} = 197.92 \pm 0.05$°K. $A = 0.003564$ deg.$^{-1}$
$K = 0.128$ $N_2{}^* = 0.000143$ mole fraction

11.49	3.821	197.766	197.764
25.36	2.598	.817	.817
49.85	1.550	.854	.855
70.49	1.174	.869	.870
89.11	.963	.879	.878
100.00	.872		.882
Pure			.917

[a] $T_{\text{T.P.}}$ is the triple point temperature, A is the first cryoscopic constant, K is the Henry's law constant for distribution of the impurity between the solid and liquid phases and $N_2{}^*$ is the mole fraction of impurity in the sample. [b] Calculated from the relationship

$$T_{\text{obsd}} = T_{\text{T.P.}} - (N_2{}^*/A)[F + K/(1 - K)]^{-1}$$

The Transition Temperatures and Heats of Transition.—Transition temperatures were studied by transposing successive fractions of the form stable below the transition temperature and observing the equilibrium temperature. From a plot of equilibrium temperature *vs.* fraction of the sample in the high temperature form, the temperature corresponding to 100% transposed was determined and chosen as the transition temperature. Duplicate determinations were made of each heat of transition. The results are given in Table VI.

TABLE VI

TRANSITION TEMPERATURES AND HEATS OF TRANSITION

	Transition temp., °K.	Heat of transition, cal. mole^{-1}
Cycloheptane	134.8	1187.0 ± 0.1[a]
	198.2	69.2 ± 0.2[a]
	212.4	107.5 ± 0.1[a]
Cyclooctane	166.5	1507.1 ± 0.4[a]
	183.8	114.3 ± 0.2[a]
Cycloheptatriene	153.98	560.9 ± 0.0[a]

[a] Deviation from the mean of duplicate determinations.

Collapse of Calorimeter Containing Cyclooctane.—The copper calorimeter that contained the cyclooctane sample was degassed before sealing by successive cycles of freezing, pumping and thawing. After rapid cooling to liquid air temperature and subsequent warming the calorimeter wall was partly collapsed as though by a contractive force. Similar damage to copper calorimeters has occurred in this Laboratory with two other compounds that have a large heat of transition and a small heat of fusion: 1,1-dimethylcyclopentane and 2,2-dimethylbutane.[24]

Thermodynamic Properties in the Solid and Liquid States.—Values of the free energy function, heat content function, heat content and entropy at selected even temperatures are listed in Tables VII, VIII and IX, with smoothed values of

TABLE VII

MOLAL THERMODYNAMIC PROPERTIES OF CYCLOHEPTANE

T, °K.	$-(F_{\text{satd.}} - H_0^\circ)/T$, cal. deg.$^{-1}$	$(H_{\text{satd.}} - H_0^\circ)/T$, cal. deg.$^{-1}$	$H_{\text{satd.}} - H_0^\circ$, cal.	$S_{\text{satd.}}$, cal. deg.$^{-1}$	$C_{\text{satd.}}$, cal. deg.$^{-1}$
		Crystals IV			
10	0.03	0.11	1.07	0.14	0.43
15	0.12	0.35	5.28	0.47	1.34
20	0.27	0.77	15.32	1.04	2.71
25	0.50	1.30	32.45	1.80	4.14
30	0.78	1.89	56.57	2.67	5.50
35	1.12	2.49	87.20	3.61	6.72
40	1.49	3.09	123.5	4.58	7.78
45	1.89	3.66	164.8	5.55	8.74
50	2.30	4.22	210.8	6.52	9.62
60	3.17	5.25	314.9	8.42	11.17
70	4.05	6.19	433.6	10.24	12.54
80	4.93	7.07	565.5	12.00	13.84
90	5.82	7.89	710.4	13.71	15.10
100	6.68	8.67	866.9	15.35	16.23
110	7.55	9.41	1035	16.96	17.41
120	8.39	10.13	1215	18.52	18.62
130	9.23	10.83	1408	20.06	19.91
134.8	9.63	11.16	1505	20.79	20.56
		Crystals III			
134.8	9.63	19.97	2692	29.60	28.04
140	10.40	20.27	2838	30.67	28.23
150	11.82	20.81	3122	32.63	28.61
160	13.18	21.31	3410	34.49	29.04
170	14.49	21.78	3703	36.27	29.54
180	15.74	22.23	4001	37.97	30.09
190	16.95	22.66	4305	39.61	30.70
198.2	17.92	23.00	4559	40.92	31.26
		Crystals II			
198.2	17.92	23.35	4628	41.27	30.99
200	18.12	23.43	4685	41.55	31.21
210	19.28	23.81	5001	43.09	32.09
212.4	19.55	23.91	5079	43.46	32.27
		Crystals I			
212.4	19.55	24.41	5186	43.96	31.47
220	20.41	24.67	5427	45.08	31.98
230	21.52	25.00	5751	46.52	32.72
240	22.59	25.34	6082	47.93	33.54
250	23.62	25.69	6422	49.31	34.41
260	24.64	26.04	6770	50.68	35.38
265.12	25.15	26.23	6952	51.38	35.92
		Liquid			
265.12	25.15	27.92	7402	53.07	40.21
270	25.66	28.15	7601	53.81	40.65
273.16	25.98	28.30	7731	54.28	40.93
280	26.70	28.61	8011	55.31	41.54
290	27.71	29.07	8431	56.78	42.46
298.16	28.52	29.45	8780	57.97	43.20
300	28.70	29.53	8860	58.23	43.36

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(24) M. E. Gross, G. D. Oliver and H. M. Huffman, THIS JOURNAL, **75**, 2801 (1953).

TABLE VIII

MOLAL THERMODYNAMIC PROPERTIES OF CYCLOÖCTANE

T, °K.	$-(F_{satd.} - H_0^\circ)/T$, cal. deg.$^{-1}$	$(H_{satd.} - H_0^\circ)/T$, cal. deg.$^{-1}$	$H_{satd.} - H_0^\circ$, cal.	$S_{satd.}$, cal. deg.$^{-1}$	$C_{satd.}$, cal. deg.$^{-1}$
			Crystals III		
10	0.04	0.11	1.14	0.15	0.46
15	0.12	0.38	5.64	0.50	1.44
20	0.29	0.81	16.27	1.10	2.85
25	0.53	1.37	34.32	1.90	4.35
30	0.83	1.98	59.51	2.81	5.71
35	1.19	2.61	91.24	3.80	6.96
40	1.57	3.22	128.8	4.79	8.06
45	1.99	3.81	171.6	5.80	9.04
50	2.42	4.38	219.2	6.80	9.95
60	3.31	5.45	327.3	8.76	11.63
70	4.23	6.44	451.1	10.67	13.15
80	5.14	7.38	590.1	12.52	14.65
90	6.07	8.27	744.0	14.34	16.10
100	6.98	9.12	911.5	16.10	17.41
110	7.89	9.93	1092	17.82	18.73
120	8.79	10.72	1286	19.51	20.06
130	9.68	11.48	1493	21.16	21.36
140	10.55	12.24	1713	22.79	22.73
150	11.42	12.99	1948	24.41	24.18
160	12.29	13.73	2197	26.02	25.75
166.5	12.85	14.22	2368	27.07	26.79
			Crystals II		
166.5	12.85	23.27	3875	36.12	34.62
170	13.34	23.51	3997	36.85	35.05
180	14.69	24.19	4354	38.88	36.25
183.8	15.20	24.44	4492	39.64	36.71
			Crystals I		
183.8	15.20	25.07	4607	40.27	37.08
190	16.08	25.46	4838	41.54	37.57
200	17.37	26.09	5218	43.46	38.40
210	18.65	26.70	5606	45.35	39.26
220	19.91	27.29	6003	47.20	40.16
230	21.13	27.87	6409	49.00	41.07
240	22.33	28.44	6825	50.77	42.02
250	23.51	29.00	7250	52.51	43.00
260	24.65	29.56	7685	54.21	44.01
270	25.78	30.11	8130	55.89	45.05
273.16	26.13	30.29	8274	56.42	45.07
280	26.89	30.66	8586	57.55	46.11
287.98	27.75	31.10	8957	58.85	46.95
			Liquid		
287.98	27.75	33.10	9533	60.85	50.48
290	27.99	33.22	9635	61.21	50.68
298.16	28.91	33.71	10052	62.62	51.50
300	29.12	33.82	10147	62.94	51.68
310	30.23	34.42	10669	64.65	52.71
320	31.34	35.00	11201	66.34	53.78
330	32.42	35.59	11744	68.01	54.86

TABLE IX

MOLAL THERMODYNAMIC PROPERTIES OF CYCLOHEPTATRIENE

T, °K.	$-(F_{satd.} - H_0^\circ)/T$, cal. deg.$^{-1}$	$(H_{satd.} - H_0^\circ)/T$, cal. deg.$^{-1}$	$H_{satd.} - H_0^\circ$, cal.	$S_{satd.}$, cal. deg.$^{-1}$	$C_{satd.}$, cal. deg.$^{-1}$
			Crystals II		
10	0.05	0.16	1.59	0.21	0.63
15	0.18	0.49	7.37	0.67	1.74
20	0.38	0.96	19.28	1.34	3.05
25	0.65	1.51	37.79	2.16	4.34
30	0.98	2.09	62.57	3.06	5.55
35	1.34	2.66	93.04	4.00	6.62
40	1.73	3.21	128.5	4.95	7.52
45	2.14	3.73	168.0	5.88	8.29
50	2.56	4.23	211.3	6.79	8.99
60	3.41	5.12	307.4	8.54	10.21
70	4.26	5.93	415.0	10.19	11.31
80	5.10	6.67	533.7	11.78	12.43
90	5.93	7.40	665.6	13.33	14.18
100	6.75	8.16	815.6	14.91	15.78
105	7.16	8.54	896.3	15.69	16.50
110	7.56	8.91	980.5	16.48	17.19
115	7.97	9.29	1068	17.26	17.92
120	8.37	9.67	1160	18.04	18.74
125	8.77	10.05	1256	18.82	19.72
130	9.18	10.44	1357	19.62	20.84
135	9.58	10.85	1465	20.42	22.10
140	9.98	11.28	1579	21.26	23.80
145	10.38	11.76	1705	22.14	26.86
150	10.79	12.36	1854	23.15	33.38
153.98	11.12	13.01	2003	24.13	41.90
			Crystals I		
153.98	11.12	16.65	2564	27.77	29.01
155	11.23	16.73	2593	27.96	29.04
160	11.77	17.12	2739	28.89	29.21
170	12.83	17.84	3033	30.67	29.54
180	13.87	18.50	3330	32.37	29.87
190	14.88	19.10	3630	33.99	30.20
197.92	15.68	19.55	3870	35.23	30.46
			Liquid		
197.92	15.68	20.96	4148	36.63	33.52
200	15.89	21.09	4217	36.98	33.60
210	16.94	21.69	4555	38.63	34.02
220	17.96	22.26	4898	40.22	34.46
230	18.96	22.80	5245	41.77	34.94
240	19.94	23.32	5597	43.26	35.44
250	20.91	23.81	5954	44.72	35.96
260	21.85	24.29	6316	46.14	36.52
270	22.78	24.76	6684	47.53	37.12
273.16	23.06	24.90	6802	47.96	37.32
280	23.68	25.21	7058	48.89	37.74
290	24.58	25.65	7439	50.23	38.37
298.16	25.29	26.01	7754	51.30	38.90
300	25.45	26.09	7826	51.54	39.03
310	26.32	26.52	8220	52.83	39.72
320	27.16	26.94	8621	54.10	40.45

the heat capacity. The functions were computed by appropriate numerical integration of the experimental heat capacity data and the inclusion of the experimental values of the heat and entropy of transition and fusion. The thermodynamic properties at 10°K. were computed from Debye functions with the following parameters: for cycloheptane, 6 degrees of freedom with $\theta = 129.5°$; for cycloöctane, 6.1 degrees of freedom with $\theta = 127.2°$; for cycloheptatriene, 4 degrees of freedom with $\theta = 98.8°$. The parameters of these Debye functions were evaluated from heat capacity data below 30°K. Approximate corrections for the effects of premelting caused by impurities have been applied to the "smoothed" values in Tables VII, VIII and IX. Some entries in these tables are given to one more decimal place than is justified by the absolute accuracy in order to retain internal consistency throughout the tables.

Vapor Pressure.—The vapor pressures of cycloheptane and cycloöctane were measured from 150 to 2026 mm. by an ebulliometric method, and the vapor pressure of cycloheptatriene was measured from 5 to 144 mm. by a static method.

Both methods have been described in a previous publication from this Laboratory.[25] The results are listed in Tables X and XI.

TABLE X

THE VAPOR PRESSURE OF CYCLOHEPTANE AND CYCLOÖCTANE (EBULLIOMETRIC METHOD)

Boiling point, °C. Water	Sample	p (obsd.), mm.	p (obsd.) − p (calcd.) Antoine eq.	Cox eq.
		Cycloheptane		
60.000	68.204	149.41	−0.01	0.00
65	74.338	187.57	.00	+ .01
70	80.529	233.72	.00	.00
75	86.771	289.13	+ .02	.00
80	93.068	355.22	+ .02	− .01
85	99.416	433.56	+ .06	+ .01
90	105.820	525.86	+ .06	+ .01
95	112.281	633.99	.00	− .03
100	118.793	760.00	+ .01	.00
105	125.364	906.06	− .11	− .07
110	131.985	1074.6	− .1	.0
115	138.665	1268.0	− .2	− .1
120	145.387	1489.1	+ .1	+ .2
125	152.178	1740.8	+ .1	.0
130	159.022	2026.0	+ .2	− .3
		Cycloöctane		
60.000	96.711	149.41	+0.01	0.00
65	103.318	187.57	− .02	− .02
70	109.977	233.72	.00	+ .01
75	116.694	289.13	+ .02	+ .02
80	123.472	355.22	− .02	− .02
85	130.301	433.56	+ .02	+ .01
90	137.190	525.86	+ .01	− .01
95	144.133	633.99	+ .06	+ .04
100	151.146	760.00	− .10	− .11
105	158.203	906.06	− .03	− .01
110	165.321	1074.6	+ .1	+ .1
115	172.502	1268.0	.0	+ .1
120	179.738	1489.1	.0	+ .1
125	187.040	1740.8	.0	.0
130	194.397	2026.0	.0	− .2

TABLE XI

THE VAPOR PRESSURE OF CYCLOHEPTATRIENE (STATIC METHOD)

t, °C.	p (obsd.), mm. 1st	2d	Mean	p (mean) − p (calcd.), mm.
0.00	5.52	5.48	5.50	+0.04
15.00	13.66	13.56	13.61	− .01
20.00	18.03	17.96	18.00	− .01
25.00	23.58	23.45	23.52	− .02
30.00	30.49	30.40	30.44	.00
35.00	39.06	38.92	38.99	+ .01
40.00	49.52	49.37	49.44	.00
45.00	62.23	62.07	62.15	.00
50.00	77.57	77.34	77.46	− .01
55.00	95.92	95.70	95.81	+ .02
60.00	117.66	117.44	117.55	− .01
65.00	143.35	143.08	143.22	− .02

In the ebulliometric method, observations were made of the boiling and condensation temperatures of the sample and of water as the two substances boiled simultaneously at a common pressure. The pressures corresponding to the observed boiling points of water were obtained from the tabulation of Osborne, Stimson and Ginnings.[26] The platinum resistance thermometer used for temperature measurements agreed within a few milli-degrees, before and after the vapor-pressure determinations, with the certified temperature, 122.360°, of a benzoic acid triple point cell.

In the study of cycloheptatriene by the static method, two series of measurements were made. The data of the 1st series were obtained after material had been distilled out of the sample container until about four-fifths of the original sample remained; the data of the 2d series were obtained after additional material was distilled out until only about one-fifth of the original sample remained. Comparison of the two series shows that the observed values of vapor pressure were decreased a few tenths of a per cent. by distilling out the additional material. This behavior indicates that the sample contained a small amount of impurity of different volatility. The presence of such impurity introduces some uncertainty into the experimental values of vapor pressure but has little effect on the value of the heat of vaporization calculated from the vapor pressure data, because both series of measurements give almost identical values of $d \log p/d(1/T)$.

The following Antoine equations were obtained from the vapor pressure data by a least squares adjustment.[27] The units are p in mm. and t in °C.

TABLE XII

MOLAL ENTROPY IN CAL. DEG.$^{-1}$

	Cycloheptane		
0–12°K.	Debye extrapolation	0.245	
12–134.8°	Solid, graphical, $\int C_{\text{satd.}}\, d \ln T$	20.550	
134.8°	Transition, 1187.0/134.8	8.806	
134.8–198.2°	Solid, graphical, $\int C_{\text{satd.}}\, d \ln T$	11.323	
198.2°	Transition, 69.2/198.2	0.349	
198.2–212.4°	Solid, graphical, $\int C_{\text{satd.}}\, d \ln T$	2.185	
212.4°	Transition, 107.5/212.4	0.506	
212.4–265.16°	Solid, graphical, $\int C_{\text{satd.}}\, d \ln T$	7.413	
265.12°	Fusion, 449.8/265.12	1.697	
265.12–298.16°	Liquid, graphical, $\int C_{\text{satd.}}\, d \ln T$	4.894	
	Entropy (±0.12) of liquid at 298.16°K.		57.97
298.16°	Vaporization 9210/298.16		30.89
298.16°	Gas imperfection (estimated)		0.02
298.16°	Compression, $R \ln (p/760)$		−7.06
	Entropy (±0.30) of ideal gas at 298.16°K. and 1 atm.		81.82
	Cycloöctane		
0–12°K.	Debye extrapolation	0.263	
12–166.5°	Solid, graphical, $\int C_{\text{satd.}}\, d \ln T$	26.805	
166.5°	Transition, 1507.1/166.5	9.052	
166.5–183.8°	Solid, graphical, $\int C_{\text{satd.}}\, d \ln T$	3.524	
183.8°	Transition, 114.3/183.8	0.622	
183.8–287.98°	Solid, graphical, $\int C_{\text{satd.}}\, d \ln T$	18.586	
287.98°	Fusion, 575.9/287.98	2.000	
287.98–298.16°	Liquid, graphical, $\int C_{\text{satd.}}\, d \ln T$	1.771	
	Entropy (±0.12) of liquid at 298.16°K.		62.62
298.16°	Vaporization, 10,360/298.16		34.75
298.16°	Gas imperfection (estimated)		0.01
298.16°	Compression, $R \ln (p/760)$		−9.72
	Entropy (±0.30) of ideal gas at 298.16°K. and 1 atm.		87.66
	Cycloheptatriene		
0–12°K.	Debye extrapolation	0.360	
12–153.98°	Solid, graphical, $\int C_{\text{satd.}}\, d \ln T$	23.775	
153.98°	Transition, 560.9/153.98	3.643	
153.98–197.92°	Solid, graphical, $\int C_{\text{satd.}}\, d \ln T$	7.455	
197.92°	Fusion, 277.4/197.92	1.402	
197.92–298.16°	Liquid, graphical, $\int C_{\text{satd.}}\, d \ln T$	14.669	
	Entropy (±0.10) of liquid at 298.16°K.		51.30
298.16°	Vaporization, 9250/298.16		31.02
298.16°	Gas imperfection (estimated)		0.02
298.16°	Compression, $R \ln (p/760)$		−6.90
	Entropy (±0.25) of ideal gas at 298.16°K. and 1 atm.		75.44

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

(26) N. S. Osborne, H. F. Stimson and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 261 (1939).

(27) C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *ibid.*, **35**, 219 (1945).

Cycloheptane $\log_{10} p = 6.85271 - 1330.742/(t + 216.246)$ (4)

Cyclooctane $\log_{10} p = 6.86173 - 1437.682/(t + 210.003)$ (5)

Cycloheptatriene $\log_{10} p = 6.97032 - 1374.656/(t + 220.538)$ (6)

The Antoine equations, with three empirical constants, are of a form convenient for numerical computation and are satisfactory for most purposes. However, for extrapolation outside the range of experimental measurements Cox equations, with four empirical constants, are more reliable. For calculations at 298.16°K. for cycloheptane and cyclooctane, the following Cox equations were obtained from the vapor pressure data. The units are P in atm. and T in °K.

$$\text{Cycloheptane: } \log_{10} P = \mathrm{A}(1 - 391.953/T) \quad (7)$$

where $\log_{10} \mathrm{A} = 0.839609 - 6.9133 \times 10^{-4}\, T + 6.4035 \times 10^{-7}\, T^2$

$$\text{Cyclooctane: } \log_{10} P = \mathrm{A}(1 - 424.300/T) \quad (8)$$

where $\log_{10} \mathrm{A} = 0.839906 - 6.2033 \times 10^{-4}\, T + 5.1773 \times 10^{-7}\, T^2$

The differences between the observed values of the vapor pressure and those calculated from the foregoing equations are listed in Tables X and XI.

The normal boiling points calculated from the equations are 118.79° for cycloheptane, 151.14° for cyclooctane and 115.60° for cycloheptatriene. The extrapolated value for cycloheptatriene is much less reliable than the directly measured values for the other two compounds. Other reported values for the boiling points are 118.48° for cycloheptane,[8] 150.70° for cyclooctane[8] and 115.50° for cycloheptatriene.[23]

The Heat of Vaporization.—Values of the heat of vaporization, at saturation pressure at 298.16°K., were computed by use of eq. 7, 8 and 6 and the exact form of the Clapeyron equation. The equation of state, $PV = RT + BP$, was assumed for the vapor; values of the second virial coefficient, B, were estimated from a correlation published previously[28] to be −2.7, −4.2 and −2.3 liters at 298.16°K. for cycloheptane, cyclooctane and cycloheptatriene, respectively. The values obtained for the heat of vaporization are 9210, 10360 and 9250 cal. mole^{-1} for cycloheptane, cylooctane and cycloheptatriene, respectively, each with an estimated uncertainty of ±50 cal. mole^{-1}.

The Entropy in the Ideal Gaseous State.—The experimental and derived results given in the foregoing sections were used to compute "observed" values of the entropy in the ideal gaseous state at 1 atm. pressure. These calculations are summarized in Table XII.

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

BARTLESVILLE, OKLAHOMA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS]

The Vapor Pressure and Heat of Sublimation of Chromous Iodide. The Chromium–Iodine Bond Energy in Chromous Iodide*

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The vapor pressure of CrI_2 has been determined from 943 to 1054°K. For sublimation at 298.16°K., $\Delta F° = 54.0$ kcal./mole, $\Delta H° = 71.4$ kcal./mole, and $\Delta S° = 58.4$ cal./deg. mole. The average chromium-iodine bond energy in CrI_2 has been found to be 55.7 kcal./mole. Experimental bond energies of this and other group VIa halides ($CrCl_2$, $CrCl_3$, $CrCl_4$, MoI_2 and WCl_6) are compared with bond energies calculated theoretically.

The chromium–iodine bond energy in CrI_2 may be calculated from the heat of formation of CrI_2(c), the heats of atomization of chromium and iodine, and the heat of sublimation of CrI_2. Only the latter quantity has not been measured previously. It was determined from the change in vapor pressure of CrI_2 with temperature, using the transpiration method (saturated vapor flow method).

Experimental

Chromous iodide was prepared from the elements by the method of Handy and Gregory,[1] using Fisher chromium powder (98% pure) and Mallinckrodt iodine (A.R.). Analysis for iodine by ignition to Cr_2O_3 gave 82.9% I (stoichiometric for CrI_2, 83.0% I). Operations with the CrI_2 were conducted in a dry box under a nitrogen atmosphere.

The CrI_2 was sublimed into a transpiration tube of the type described by MacLaren and Gregory.[2] Fused quartz glass was used for those parts of the apparatus within the furnace. The end of the collector tube extending into the transpiration chamber was made of 1.5 mm. bore capillary tubing to decrease diffusion of CrI_2 into the collector. Dow Corning silicone high vacuum grease was used on stopcocks and ground joints.

Measurements were made on two samples of CrI_2. The first was sublimed into the transpiration chamber from a mixture of chromous iodide and unreacted chromium. The second was sublimed from pure CrI_2. In each case the sample bulb was left attached to the transpiration chamber. During the initial state of sublimation of the second sample, a temporary leak developed in the vacuum system. Air from this source oxidized a small amount of the CrI_2. The oxidation product (green in color, probably Cr_2O_3) was not volatile at the temperature of the vapor pressure measurements.

Argon (Linde Air Products Co.) was used as the carrier gas. It was passed through a flowmeter of the capillary type which was fitted with an overflow tube. Oxygen and water vapor were removed by means of hot copper and magnesium perchlorate, respectively.

The furnace (Hevi-Duty, Type HDT-1712) was lined with a nickel tube of one-quarter inch wall thickness, and the ends were insulated with asbestos. Temperature control was provided by a chromel–alumel thermocouple, located between the nickel tube and the heating coils, and a Minneapolis–Honeywell controller. Along the last three inches of the transpiration chamber the temperature was constant to within ±1°.

A chromel–alumel thermocouple, calibrated with a National Bureau of Standards certified platinum *vs.* platinum–rhodium thermocouple, was used for temperature measurement in the first set of experiments. After that, the platinum *vs.* platinum–rhodium thermocouple was used directly. The hot junction was placed next to the transpiration chamber.

After the nitrogen in the transpiration tube was replaced with argon, the furnace was heated rapidly. When the temperature had reached 100° below the set temperature, the flow of argon was stopped. It was started again when the temperature was constant at the desired value. The experiment was stopped by shutting both stopcocks and re-

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[1] L. L. Handy and N. W. Gregory, THIS JOURNAL, **72**, 5049 (1950).

[2] R. O. MacLaren and N. W. Gregory, *J. Phys. Chem.*, **59**, 184 (1955).