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Low-temperature Thermal Data for Some C_7H_{14} Alkylcyclopentanes

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Low-temperature thermal measurements were made on the following compounds in the solid and liquid states: 1,1-dimethylcyclopentane (I), 1,*cis*-2-dimethylcyclopentane (II), 1,*trans*-3-dimethylcyclopentane (III) and ethylcyclopentane [crystals A(IV) and B(V)]. Values of some of the thermodynamic properties determined are: triple points, 203.68 (I), 219.45 (II), 139.48 (III), 134.73 (IV) and 134.0°K. (V); heats of fusion, 258 (*I*), 396 (*II*), 1768 (*III*), 1642 (IV) and 1889 cal. mole^{-1} (V); entropies for the liquid state at 298.16°K., 63.34 (I), 64.33 (II), 64.90 (III), 66.90 (IV) and 66.89 cal. deg.$^{-1}$ mole^{-1} (V). Isothermal transitions were observed in 1,1-dimethylcyclopentane (1551 cal. mole^{-1} at 146.80°K.) and in 1,*cis*-2-dimethylcyclopentane (1594 cal. mole^{-1} at 141.50°K.). Incomplete studies were made on 1,*trans*-2-dimethylcyclopentane and 1,*cis*-3-dimethylcyclopentane.

As a part of the continuing program of this Laboratory to measure thermodynamic properties of hydrocarbons of interest to the petroleum industry, low-temperature thermal studies have been made on ethylcyclopentane, 1,1-dimethylcyclopentane, 1,*cis*-2-dimethylcyclopentane and 1,*trans*-3-dimethylcyclopentane. Measurements were attempted on the two other C_7H_{14} alkylcyclopentanes, namely 1,*trans*-2-dimethylcyclopentane and 1,*cis*-3-dimethylcyclopentane, but the thermal studies could not be completed.

Apparatus and Method.—The measurements were made in the calorimetric apparatus described by Ruehrwein and Huffman.[2] Very briefly, the procedure was as follows: About 0.42 mole of the material under investigation was sealed in a copper calorimeter, which was mounted in the adiabatic calorimetric system. The calorimeter contained approximately 30 horizontal perforated copper disks in contact with the thermometer well and the outer wall of the calorimeter. These disks promoted rapid attainment of thermal equilibrium and prevented settling of the solid during the study of the melting point. For the determination of heat capacities a measured amount of electrical energy was supplied to the calorimeter, and the initial and final temperatures were measured by means of a strain-free platinum resistance thermometer. At all times the temperature of the surrounding shield was maintained at that of the calorimeter to minimize heat interchange. 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 6 saturated cadmium cells, which had been certified by the National Bureau of Standards. Time measurements were made with an electric stopclock driven by alternating current that was obtained from the amplified output of a vacuum-tube precision fork. The frequency of the current was constant within ±0.001%. The precision of the measurements was, in general, within ±0.1%; above 30°K. it is believed that the accuracy uncertainty, unless otherwise stated, should not be greater than ±0.2%.

When the calorimeter containing 1,1-dimethylcyclopentane was removed from the cryostat, it was found that the wall of the calorimeter had partly collapsed. The lower two-thirds of the calorimeter exhibited numerous small dents. No collapse resulted from studies made in a similar calorimeter containing 1,1-dimethylcyclopentane, which was not cooled below 118°K. (These studies were discontinued because of an electrical short in the thermometer.) Since the calorimeter was suspended in a vacuum, the deforming force must have been inside the calorimeter. Apparently, as the calorimeter and compound cooled through some temperature range below 118°K., the compound did not readily develop cracks or shrink away from the wall of the calorimeter but, instead, pulled in the wall of the calorimeter as much as the internal disks would allow. In this Laboratory, 2,2-dimethylbutane also caused the partial collapse of the wall of a copper calorimeter.

Materials.—The materials used in this investigation were A.P.I. Research samples prepared by A.P.I. Research Project 6.[3]

Physical Constants and Units.—The data presented in this paper are based on a molecular weight of 98.182 for C_7H_{14} that was derived from the 1951 International Atomic Weights.[4] The following definitions were accepted: 1 cal. = 4.1833 int. j. = 4.1840 abs. j., and 0°C. = 273.16°K.

Results

Melting-point Studies.—Equilibrium melting temperatures and the corresponding fraction of sample melted were obtained for each compound in a manner described in a previous publication from this Laboratory.[5] These data and the percentage impurities and triple points calculated from them are given in Table I. Under the usual assumptions that the impurities are solid-insoluble and liquid-soluble and that the liquid is an ideal solution, the plot of the observed temperature against the reciprocal of the fraction of the sample melted should be a straight line. Such plots for 1,1-dimethylcyclopentane and 1,*cis*-2-dimethylcyclopentane deviate considerably from linearity. It is quite possible that the deviations are caused by the presence of solid solutions which are readily formed in hydrocarbons that have small heats of fusion, as these do.[6]

Ethylcyclopentane can be obtained in either of two crystalline forms; the melting point of each form was studied. The value of N^*_2, the mole fraction of impurity in the entire sample, should be the same for each form. The difference between the values obtained (0.025 ± 0.003 for crystals A and 0.031 ± 0.006 for crystals B) is attributed to experimental error.

Heat Capacities.—The heat capacity of each compound was measured between 13 and 300°K., with the results shown in Table II. The temperatures listed in the table are the mean temperatures of the individual measurements. C_{sat} is the heat capacity of the condensed phase under its own vapor pressure. The temperature rises of the measurements near the melting points are given in footnotes. The reported values of heat capacity have not been corrected for

(1) Deceased. Reprint requests should be sent to Guy Waddington of this Laboratory. Article not copyrighted.

(2) R. A. Ruehrwein and H. M. Huffman, THIS JOURNAL, **65**, 1620 (1943).

(3) These samples of A.P.I. Research hydrocarbons, made available through the American Petroleum Institute Research Project 44 on the "Collection, Analysis, and Calculation of Data on Properties of Hydrocarbons," were purified by the American Petroleum Institute Research Project 6 on the "Analysis, Purification, and Properties of Hydrocarbons" from materials supplied by the following laboratories: ethylcyclopentane, one-half by the A.P.I. Research Project 45 on the "Synthesis and Properties of Hydrocarbons of Low Molecular Weight," at The Ohio State University and one-half by the Hydrocarbon Laboratory at The Pennsylvania State College; 1,1-dimethylcyclopentane, 1,*cis*-2-dimethylcyclopentane, and 1,*trans*-2-dimethylcyclopentane, by the Hydrocarbon Laboratory of The Pennsylvania State College through the operations of the American Petroleum Institute Committee on Hydrocarbons for Spectrometer Calibration; 1,*cis*-3-dimethylcyclopentane and 1,*trans*-3-dimethylcyclopentane, by the A.P.I. Research Project 45 at The Ohio State University.

(4) Edward Wichers, THIS JOURNAL, **74**, 2447 (1952).

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

(6) *E.g.*, H. L. Finke, M. R. Cines, F. E. Frey and J. G. Aston, *ibid.*, **69**, 1501 (1947); G. L. Evans, K. W. Greenlee, J. M. Derfer and C. E. Boord, *ibid.*, **71**, 361 (1949).

TABLE I

SUMMARY OF MELTING POINT DATA FOR SOME C_7H_{14} ALKYLCYCLOPENTANES

Each value of per cent. impurity was obtained from the equation $N^*/F = A\Delta T$, where N^* is the mole fraction of impurity in the entire sample, F is the fraction of the sample in the liquid state, A is the cryoscopic constant given in Table III, and ΔT is $T_{T.P.} - T_{obsd.}$

% melted	1/F	T, °K. Obsd.	T, °K. Graph.[b]
Ethylcyclopentane, Crystals A			
20.03	4.99	134.6996	134.6991
40.02	2.50	134.7128[a]	134.7128
70.02	1.43	134.7186	134.7187
90.02	1.11	134.7205[a]	134.7205
100	1.00		134.7211
Pure	0.00		134.7266
$T_{T.P.} = 134.73 \pm 0.05$°K. Impurity, 0.025 ± 0.003 mole per cent.			
Ethylcyclopentane, Crystals B			
18.50	5.41	133.9976[a]	133.9976
35.98	2.78	134.0134	134.0130
62.19	1.61	134.0192	134.0199
79.66	1.26	134.0219[a]	134.0219
100	1.00		134.0234
Pure	0.00		134.0293
$T_{T.P.} = 134.03 \pm 0.05$°K. Impurity, 0.031 ± 0.006 mole per cent.			
1,1-Dimethylcyclopentane			
11.18	8.94	203.6359	203.6092
25.02	4.00	203.6514	203.6480
45.84	2.18	203.6623[a]	203.6623
73.56	1.36	203.6684	203.6687
94.38	1.06	203.6711[a]	203.6711
100	1.00		203.6716
Pure	0.00		203.6794
$T_{T.P.} = 203.68 \pm 0.05$°K. Impurity, 0.002 ± 0.001 mole per cent.			
1,*cis*-2-Dimethylcyclopentane			
17.59	5.68	219.3886	219.3338
43.26	2.31	219.4076	219.4033
68.99	1.45	219.4210[a]	219.4210
91.02	1.10	219.4282[a]	219.4282
100	1.00		219.4303
Pure	0.00		219.4508
$T_{T.P.} = 219.45 \pm 0.05$°K. Impurity, 0.008 ± 0.004 mole per cent.			
1,*trans*-3-Dimethylcyclopentane			
11.70	8.55	139.4464	139.4450
23.55	4.25	139.4620[a]	139.4620
41.37	2.42	139.4693	139.4692
65.13	1.54	139.4727[a]	139.4727
82.95	1.21	139.4751	139.4740
100	1.00		139.4748
Pure	0.00		139.4787
$T_{T.P.} = 139.48 \pm 0.05$°K. Impurity, 0.02 ± 0.01 mole per cent.			

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

premelting. In general, the increments taken above 50°K. were between 5 and 10°, and below 50°K. were between 10 and 15% of the absolute temperature. Below 50°K. a few measurements were corrected for the curvature of the

TABLE II

MOLAL HEAT CAPACITIES OF SOME C_7H_{14} ALKYLCYCLOPENTANES, CAL. DEG.$^{-1}$

T, °K.	C_{sat}	T, °K.	C_{sat}	T, °K.	C_{sat}
Ethylcyclopentane Crystals A					
12.15	1.069	32.14	7.197	86.73	17.220
13.71	1.480	35.20	8.051	90.47	17.690
13.94	1.576	39.99	9.289	93.94	18.113
15.64	2.021	45.04	10.456	98.41	18.630
15.88	2.102	49.89	11.452	104.07	19.281
18.08	2.770	54.75	12.392	105.93	19.533
18.51	2.941	54.92	12.400	109.40	19.932
21.24	3.810	60.67	13.434	110.66	20.098
21.25	3.812	66.77	14.430	113.77	20.514
23.98	4.713	67.35	14.519	117.03	20.910[a]
24.76	4.960	73.12	15.336	117.72	21.011[a]
27.11	5.699	74.96	15.600	121.27	21.517[a]
28.41	6.088	79.79	16.263	124.33	21.968[a]
30.88	6.825	82.73	16.687	126.87	22.342[a]
Crystals B					
12.64	0.807	31.04	5.726	79.56	15.710
14.45	1.168	35.60	7.004	86.46	16.741
14.57	1.201	40.30	8.220	87.09	16.841
16.67	1.691	45.10	9.380	94.02	17.707
16.83	1.727	50.27	10.544	94.62	17.795
19.58	2.443	55.97	11.712	102.23	18.725
19.62	2.458	60.17	12.541	110.30	19.702
23.02	3.428	65.80	13.562	112.09	19.905
23.03	3.431	65.97	13.594	118.00	20.636[b]
26.77	4.517	72.22	14.594	119.71	20.817[b]
26.78	4.520	72.36	14.619	122.78	21.233[b]
30.61	5.633	79.30	15.686	124.55	21.476[b]
Liquid					
140.24	35.091	178.80	35.999	247.79	39.978
142.76	35.130	188.40	36.368	257.60	40.778
145.96	35.160	198.32	36.817	267.23	41.593
149.56	35.238	208.10	37.326	276.69	42.428
154.07	35.304	217.73	37.879	285.97	43.274
160.17	35.444	227.64	38.505	294.34	44.104
169.54	35.688	237.81	39.212	301.83	44.843
1,1-Dimethylcyclopentane					
Crystals I					
12.48	0.953	32.77	6.954	91.87	17.166
14.27	1.422	37.63	8.153	96.78	17.881
14.27	1.420	43.84	9.485	99.39	18.230
16.38	2.018	49.60	10.586	103.94	18.877
17.68	2.415	54.70	11.481	107.50	19.373
18.99	2.823	56.80	11.842	112.62	20.119
21.62	3.673	61.54	12.626	115.07	20.473
22.01	3.803	63.62	12.966	121.69	21.472
24.98	4.739	69.78	13.926	123.18	21.691
26.19	5.111	75.89	14.826	126.94	22.225
28.55	5.793	82.44	15.816	131.73	23.041
31.86	6.710	89.71	16.899	139.06	24.331
Crystals II					
158.53	32.055	178.58	32.840[c]	198.28	33.930[c]
168.19	32.322	189.31	33.379[c]		
Liquid					
205.90	36.652	249.89	40.087	279.99	42.896
212.49	37.126	258.82	40.886	284.66	43.375
222.10	37.817	267.60	41.733	292.99	44.155
231.54	38.537	271.61	42.157	299.81	44.783
240.80	39.300	276.20	42.588		

TABLE II (*Continued*)

T, °K.	C_{sat}	T, °K.	C_{sat}	T, °K.	C_{sat}
1,*cis*-2-Dimethylcyclopentane					
Crystals I					
12.31	0.771	31.57	6.369	94.92	17.349
13.38	1.009	36.29	7.602	100.08	18.013
14.32	1.240	41.50	8.802	104.27	18.493
15.86	1.647	46.93	9.944	106.89	18.767
16.55	1.840	52.86	11.091	113.20	19.543
19.22	2.630	56.85	11.801	115.22	19.776
19.34	2.678	58.53	12.093	120.77	20.421
22.55	3.684	63.37	12.888	124.03	20.790
23.36	3.944	70.17	13.947	127.60	21.209
26.24	4.822	78.11	15.095	129.02	21.359
27.37	5.162	86.23	16.268	132.79	21.776
30.04	5.943	94.79	17.346	134.18	21.961
Crystals II					
146.85	32.186	174.01	33.200	195.51	34.302[d]
149.39	32.327	175.86	33.288	202.65	34.745[d]
154.27	32.472	182.79	33.612	202.97	34.759[d]
157.66	32.588	184.16	33.681	205.34	34.916[d]
163.69	32.793	185.51	33.752	210.70	35.295[d]
166.56	32.903	192.81	34.143	213.09	35.466[d]
173.10	33.083	194.14	34.231[d]		
Liquid					
223.08	38.793	244.34	40.386	274.44	42.977
227.80	39.110	244.45	40.393	284.07	43.820
230.06	39.300	249.62	40.807	293.54	44.682
235.69	39.708	254.64	41.228	302.84	45.567
239.49	40.008	264.63	42.083		
1,*trans*-3-Dimethylcyclopentane					
Crystals					
12.49	0.858	28.48	5.420	86.36	15.905
12.98	.965	30.56	6.012	93.95	16.894
14.46	1.268	33.23	6.749	101.48	17.870
14.77	1.347	38.84	8.136	104.37	18.253
16.74	1.860	44.92	9.420	109.11	18.882
17.23	1.991	51.01	10.588	112.37	19.325
19.47	2.650	57.17	11.648	115.09	19.674
20.51	2.974	58.79	11.910	119.94	20.339[e]
22.89	3.720	65.51	12.933	123.27	20.782[e]
24.33	4.161	72.09	13.849	127.15	21.383[e]
26.67	4.874	79.07	14.856	133.19	22.425[e]
Liquid					
143.70	34.552	180.86	36.118	251.15	40.773
146.90	34.659	190.80	36.645	254.73	41.081
151.06	34.815	200.58	37.212	260.81	41.593
154.26	34.939	210.67	37.813	264.27	41.895
159.89	35.170	221.07	38.494	274.51	42.806
162.57	35.274	231.28	39.225	284.54	43.729
171.28	35.657	241.30	39.990	294.38	44.676
				304.03	45.617

[a] The temperature rises of these measurements are in order of increasing T, °K.: 8.287, 6.626, 6.494, 6.321 and 4.696°. [b] The temperature rises of these measurements are in order of increasing T, °K.: 6.668, 8.287, 6.676 and 6.407°. [c] The temperature rises of these measurements are in order of increasing T, °K.: 10.836, 10.630 and 7.319°. [d] The temperature rises of these measurements are in order of increasing T, °K.: 9.885, 9.916, 9.758, 7.786, 9.739, 7.669 and 5.755°. [e] The temperature rises of these measurements are in order of increasing T, °K.: 7.378, 7.330, 7.034 and 5.052°.

heat capacity *vs.* temperature curve within the temperature rise; above 50°K. no correction was necessary. The correction was never larger than 0.01 cal. deg.$^{-1}$ mole^{-1}.

Heat capacity measurements on 1,1-dimethylcyclopentane and 1,*cis*-2-dimethylcyclopentane between the transition temperature and the melting point may be less accurate than the other heat capacity measurements because, in the region between the transition temperature and the melting point, equilibration was slow and may not have been complete. This phenomenon has been observed in other compounds.[7] The uncertainty in the heat capacity does not significantly affect the calculated value of the entropy.

Heats of Fusion.—Table III lists mean values for the duplicate determinations of the heat of fusion of each compound together with the calculated values of the cryoscopic constants ($\Delta H_{fusion}/RT^2_{T.P.}$).

TABLE III

HEATS OF FUSION AND CRYOSCOPIC CONSTANTS OF SOME C_7H_{14} ALKYLCYCLOPENTANES

Compound	ΔH_{fusion}, cal. mole^{-1}	Cryoscopic constant, deg.$^{-1}$
Ethylcyclopentane, A	1641.8 ± 0.5[a]	0.0455
Ethylcyclopentane, B	1889.2 ± 2.0	.0529
1,1-Dimethylcyclopentane	257.8 ± 0.2	.00313
1,*cis*-2-Dimethylcyclopentane	396.1 ± 0.1	.00414
1,*trans*-3-Dimethylcyclopentane	1768.2 ± 0.3	.0457

[a] Precision uncertainty.

Transitions.—1,1-Dimethylcyclopentane and 1,*cis*-2-dimethylcyclopentane have isothermal transitions. The transition temperature for each was obtained by transposing successive fractions of the form stable below the transition (approximately 25, 60 and 90%) and observing an approximate equilibrium temperature for each fraction. The change in temperature observed between 25 and 90% transposed for 1,1-dimethylcyclopentane was less than 0.03° and for 1,*cis*-2-dimethylcyclopentane less than 0.06°. This small change in temperature may have been caused by solid solutions, the presence of which in the form stable above the transition was indicated by the melting point studies. For each compound the highest equilibrium temperature was chosen for the transition temperature. These values are 146.80 ± 0.05°K. for 1,1-dimethylcyclopentane and 141.50 ± 0.1°K. for 1,*cis*-2-dimethylcyclopentane. The heat of transition of 1,1-dimethylcyclopentane was found to be 1551.0 cal. mole^{-1} (average of two determinations, 1551.3 and 1550.8 cal. mole^{-1}); of 1,*cis*-2-dimethylcyclopentane 1593.9 cal. mole^{-1} (average of two determinations, 1593.7 and 1594.2 cal. mole^{-1}).

Entropies.—Table IV summarizes the calculations of the entropy of each compound at 298.16°K. in the liquid state. For each compound a visually smoothed curve of heat capacity *vs.* temperature was used to obtain values of C_{sat} for graphical evaluation of the entropy integral ($\int C_{sat}\, d \ln T$).

Discussion

All C_7H_{14} alkylcyclopentanes but one (1,*trans*-3-dimethylcyclopentane) exhibit some kind of polymorphism. 1,1-Dimethylcyclopentane and 1,*cis*-2-dimethylcyclopentane are enantiotropic. 1,*cis*-3-Dimethylcyclopentane, one of the two compounds on which studies were not completed[8] is mono-

(7) *E.g.*, J. E. Kilpatrick and K. S. Pitzer, THIS JOURNAL, **68**, 1066 (1946); G. J. Szasz, J. A. Morrison, E. L. Pace and J. G. Aston, *J. Chem. Phys.*, **15**, 562 (1947).

(8) Although measurements on 1,*cis*-3-dimethylcyclopentane were not satisfactorily completed, values of the heat of fusion (1738 ± 20 cal. mole^{-1} and the triple point (139.27 ± 0.05°K.)) were obtained. This value of the heat of fusion is thought to be more reliable than an earlier value of 1700 cal. mole^{-1} from this Laboratory reported in American Petroleum Institute Research Project 44, Selected Values of Properties of Hydrocarbons, Table 6 Z (Part III) April 30, 1946; May 31, 1947; August 31, 1949.

TABLE IV

ENTROPIES OF SOME C_7H_{14} ALKYLCYCLOPENTANES, CAL. DEG.$^{-1}$ MOLE^{-1}

Ethylcyclopentane, Crystals A		
0–13 °K.	Debye extrapolation 6 degrees of freedom, θ = 115.0 °K.	0.439
13–134.73	Solid, graphical, $\int C_{sat}$ d ln T	24.195
134.73	Fusion, 1641.8/134.73	12.186
134.73–298.16	Liquid, graphical, $\int C_{sat}$ d ln T	30.081
Entropy (±0.13) of liquid at 298.16 °K.		66.901
Ethylcyclopentane, Crystals B		
0–13 °K.	Debye extrapolation, 6 degrees of freedom, θ = 132.1 °K.	0.293
13–134.03	Solid, graphical, $\int C_{sat}$ d ln T	22.245
134.03	Fusion, 1889.2/134.03	14.095
134.03–298.16	Liquid, graphical, $\int C_{sat}$ d ln T	30.262
Entropy (±0.13) of liquid at 298.16 °K.		66.895
1,1-Dimethylcyclopentane		
0–12 °K.	Debye extrapolation, 6 degrees of freedom, θ = 120.7 °K.	0.302
12–146.80	Solid, graphical, $\int C_{sat}$ d ln T	25.232
146.80	Transition, 1551.0/146.80	10.565
146.80–203.68	Solid, graphical, $\int C_{sat}$ d ln T	10.708
203.68	Fusion, 257.8/203.68	1.266
203.68–298.16	Liquid, graphical, $\int C_{sat}$ d ln T	15.270
Entropy (±0.13) of liquid at 298.16 °K.		63.34
1,*cis*-2-Dimethylcyclopentane		
0–12 °K.	Debye extrapolation, 7 degrees of freedom, θ = 135.0 °K.	0.253
12–141.50	Solid, graphical, $\int C_{sat}$ d ln T	23.572
141.50	Transition, 1593.9/141.50	11.264
141.50–219.45	Solid, graphical, $\int C_{sat}$ d ln T	14.716
219.45	Fusion, 396.1/219.45	1.805
219.45–298.16	Liquid, graphical, $\int C_{sat}$ d ln T	12.718
Entropy (±0.13) of liquid at 298.16 °K.		64.33
1,*trans*-3-Dimethylcyclopentane		
0–13 °K.	Debye extrapolation, 6 degrees of freedom, θ = 127.4 °K.	0.326
13–139.48	Solid, graphical, $\int C_{sat}$ d ln T	22.900
139.48	Fusion, 1768.2/139.48	12.678
139.48–298.16	Liquid, graphical, $\int C_{sat}$ d ln T	28.999
Entropy (±0.13) of liquid at 298.16 °K.		64.90

tropic; it crystallized in an unstable form, which required several days to transpose to a form melting about 7° higher. Incomplete studies on 1,*trans*-2-dimethylcyclopentane[9] indicated polymorphism. Information obtained from the method of crystallization, from the values for the heat of fusion and from behavior during studies of the melting point suggest that this compound can crystallize in either of two forms whose melting points do not differ by more than 0.1°.

Ethylcyclopentane could be obtained at will in either of the two crystalline forms previously mentioned. The rate at which the liquid was cooled below the melting point determined in which form it crystallized. Crystals A were obtained by cooling the sample rapidly from above the melting point to 85°K. (in 3 hours) and then heating to about 105°K., at which temperature crystallization definitely started. Crystallization was completed by allowing the sample to warm to the melting point by evolution of its heat of fusion. To obtain crystals B, the sample was allowed to cool slowly from above the melting point until it crystallized.

The two values obtained for the entropy of ethylcyclopentane in the liquid state at 134.73°K. from the data for crystals A and B differ by only 0.006 cal. deg.$^{-1}$ mole^{-1}. The agreement between the two values is well within the precision uncertainty of the measurements and is in excellent accord with the third law of thermodynamics.

From the measured heat capacities and heats of fusion for each crystalline form of ethylcyclopentane the free energy of each form relative to that of the liquid at 134.73°K. can be calculated for temperatures below the melting points. The value calculated for the temperature at which the two forms have the same free energy is somewhat sensitive to the values chosen for heat capacities below the melting point. From the observed heat capacities uncorrected for premelting, 126°K. is obtained for the transition temperature; from the corrected heat capacities, from which the entropy was calculated, 129.5°K. is obtained. Crystals B are thermodynamically stable below the transition temperature. All attempts to observe the transition were unsuccessful. Neither form showed any tendency to transpose to the other form at any temperature. Even during the melting point study of crystals B that required 6 hours no evidence of transposition was observed.

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(9) Incomplete studies indicate a heat of fusion for 1,*trans*-2-dimethylcyclopentane of 1660 ± 50 cal. mole^{-1} with a triple point of 155.7 ± 0.1°K. These values are uncertain due to lack of definition of the state of the crystals.