mental measurements and calculations and Mr. M. L. Sagenkahn for preparing the liquid hydrogen. The Grants-in-Aid of the National Research Council with which much of the apparatus was purchased and financial aid from the Standard Oil Development Company and the Research Corporation made this work possible.

Summary

1. The heat capacity of solid and liquid cyclohexane has been measured from 12.6 to 293.8°K.

2. The equilibrium temperatures of the transition and the fusion, together with their heats, have been determined.

3. The heat of vaporization has been determined at 298.16°K. The experimental vapor pressure equation over the range 280 to 294°K. has been used to calculate the value of the heat of vaporization at 298.10°K.

4. Comparisons of the experimental entropy with that calculated from statistical and molecular data afford a means to assign the lowest vibration frequencies. The result which was based on a "chair" configuration for the cyclohexane molecule is in good agreement with previous assignments on similar molecules.

STATE COLLEGE, PENNSYLVANIA
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[CONTRIBUTION FROM THE WILLIAM G. KERCKHOFF LABORATORIES OF THE BIOLOGICAL SCIENCES, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Thermal Data. XVI. The Heat Capacity and Entropy of Isopentane. The Absence of a Reported Anomaly

BY GEORGE B. GUTHRIE, JR., AND HUGH M. HUFFMAN

In two recent papers[1] Aston and co-workers have reported the results of their low temperature studies on isopentane. During this investigation they obtained certain anomalous results in their heat capacity and vapor pressure measurements. These anomalous results were especially evident in the temperature interval 180 to 240°K. Aston has attempted to account for these results on the basis of a hysteresis in the establishment of equilibrium between isomeric forms due to hindered rotation. The heat capacity of isopentane was also measured in 1930 by Parks, Huffman and Thomas,[2] who did not observe any irregularities in the heat capacity.

Because of the great importance of such a phenomenon and the great effect its existence would have upon similar experimental and theoretical studies on other hydrocarbon molecules, it is of paramount importance that its actual existence be established beyond any reasonable doubt.

We have accordingly reinvestigated the heat capacity of isopentane over the temperature range 13 to 300°K. Unfortunately, the design of our apparatus did not permit the simultaneous observation of the vapor pressure.

Experimental

The Material.—Measurements were made on two different samples of isopentane. The first was purified for us by the Shell Development Company, who state that the entire sample, 300 cc., boiled at 27.92 ± 0.01°C. The second sample was the isopentane that Aston, *et al.*,[1] had used in their calorimeter and was kindly sent to us by Professor Aston. From data obtained during the melting point determinations we have calculated that the liquid-soluble, solid-insoluble impurity in the first (Shell) sample was 0.013 mole per cent. and that in the second (Aston) sample was 0.008 mole per cent.

The Apparatus.—Our heat capacity measurements were carried out in an adiabatic calorimetric system which will be described in detail in a later publication. The calorimeter proper was of copper and had an internal volume of approximately 60 cc.

The isopentane was transferred to the calorimeter by distillation through a glass system to which the calorimeter was connected by a glass to metal seal. This system was connected to the high vacuum line and to the source of helium by means of stopcocks, which were greased with Apiezon grease M. The stopcocks were so placed as to be out of the direct distillation path. In transferring the first sample (Shell) to the calorimeter it was necessary to expose the isopentane to the air for a short time hence precautions were taken to remove any water, which might have gotten into the sample, by several distillations from phosphorus pentoxide in the closed system. The second sample (Aston) was received in a container that could be sealed directly into the transfer system before opening. In both cases the system and the sample were carefully outgassed by pumping with an oil diffusion pump while the isopentane was frozen in liquid air. After outgassing the

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[1] (a) Aston and Schumann, THIS JOURNAL, **64**, 1034 (1942); (b) Schumann, Aston and Sagenkahn, *ibid.*, **64**, 1039 (1942).

[2] Parks, Huffman and Thomas, *ibid.*, **52**, 1032 (1930).

calorimeter was immersed in a bath of solid carbon dioxide and alcohol and the isopentane distilled in. When the transfer was completed helium was admitted and the system allowed to warm to room temperature. The monel metal filling tube, 1.0 mm. o. d., was then pinched off close to the calorimeter and quickly made gas tight by the application of a small drop of soft solder. The pressure of helium in the calorimeter was approximately 40 mm. at room temperature. In the first case (Shell sample) the amount of isopentane in the calorimeter was 35.598 g. (0.49341 mole) and the gas space at 300°K. was 2.28 cc. In the second case the amount of isopentane in the calorimeter was 24.884 g. (0.34491 mole) and the gas space at 300°K. was 10.67 cc. This undesirably large gas space was due to the limited amount of material that was available.

It is of considerable importance to note that after the isopentane was sealed into the calorimeter there was no chance for it to be transferred to any other part of the calorimetric system, hence the mass of the isopentane upon which observations were made was constant.

Temperature measurements were made with a platinum resistance thermometer, H-8, which had been compared against the laboratory standard platinum thermometer, H-25, which in turn had been calibrated by the Bureau of Standards over the temperature range 14°K. to the boiling point of sulfur. The energy measurements were made in terms of the international joule by utilizing resistors and standard cells which had been compared with others certified by the Bureau of Standards. The observed energies in international joules were converted to calories by dividing by 4.1833.

TABLE I

MOLAL HEAT CAPACITY OF ISOPENTANE, ARRANGED CHRONOLOGICALLY

Molecular weight = 72.146, 0°C. = 273.16°K.

T, °K.	C_p, cal./degree
Series I, solid	
84.78	16.07
87.69	16.57
90.97	17.13
94.58	17.78
98.08	18.42
101.44	19.11
104.70	19.77
107.85	20.44
110.94	21.23
Liquid	
120.05	29.67
124.44	29.84
Series II, solid	
58.74	12.11
62.08	12.82
65.22	13.52
68.19	14.29
70.99	15.19
71.33	15.60
Series III, solid	
54.79	11.30
58.59	12.06
62.59	12.91
66.31	13.77
69.24	14.54
71.44	15.52
73.58	15.11
76.01	14.79
78.95	15.14
82.56	15.71
86.47	16.37
90.52	17.08
95.44	17.94
101.42	19.10
107.68	20.51
Series IV, liquid	
115.67	29.48
122.87	29.76
133.94	30.19
149.26	30.79
159.80	31.19
170.16	31.63
180.35	32.05
190.38	32.51
200.25	32.98
Series V, liquid	
171.33	31.66
181.50	32.09
191.51	32.54
201.36	33.02
211.05	33.51
220.60	34.02
230.00	34.56
239.26	35.12
248.37	35.69
257.34	36.29
267.90	37.08
Series VI, liquid	
209.78	33.43
219.34	33.95
Series VII, liquid	
184.60	32.22
Series VIII, liquid	
231.34	34.65
Series IX, liquid	
186.49	32.33
192.67	32.60
Series X, liquid	
188.13	32.40
197.01	32.81
206.76	33.29
216.34	33.80
225.78	34.31
235.08	34.86
Series XI, solid	
67.21	14.01
69.46	14.67
Series XII, solid	
71.46	15.30
Series XIII, solid	
52.92	10.95
56.98	11.77
Series XIV, liquid	
188.66	32.42
198.50	32.87
208.18	33.36
217.70	33.87
227.08	34.39
Series XV, liquid	
189.41	32.46
199.25	32.94
208.93	33.41
219.40	33.97
230.62	34.61
Series XVI, liquid	
253.56	36.04
262.79	36.69
271.88	37.38
280.38	38.00
288.76	38.62
297.00	39.28
Series XVII, liquid	
297.81	39.31
Series XVIII, solid	
13.20	1.119
14.61	1.482
16.42	1.956
19.20	2.750
22.90	3.861
26.94	5.034
31.92	6.390
37.65	7.821
43.41	9.072
49.20	10.24
55.03	11.38
Series XIX, solid	
15.75	1.814
18.62	2.590
22.51	3.745
27.10	5.083
32.17	6.424
37.98	7.894
44.20	9.238
49.50	10.29
Series XX, liquid	
184.29	32.220
194.20	32.664
203.97	33.165
213.57	33.667
223.04	34.165
232.35	34.757
241.52	35.293
250.54	35.899
295.42	36.496
Series XXI, liquid	
187.58	32.400
197.45	32.858
207.16	33.328
216.71	33.844
226.12	34.380
235.38	34.919
Series XXII, liquid	
214.82	33.730
224.23	34.229
233.50	34.798
242.41	35.360
251.39	35.940
260.23	36.569
268.92	37.192
277.49	37.804
285.92	38.445
294.21	39.132
Series XXII, solid	
55.40	11.461
59.98	12.371
64.65	13.389
67.72	14.076
69.37	14.639
70.96	15.294
72.51	15.456
74.07	14.552
76.25	14.743
78.98	15.155
83.19	15.822
89.41	15.897
95.89	18.031
101.96	19.220
107.41	20.385
111.24	21.716
Liquid	
115.86	29.495
122.84	29.761
132.77	30.138
143.53	30.550
154.11	30.968
164.49	31.394
174.69	31.814

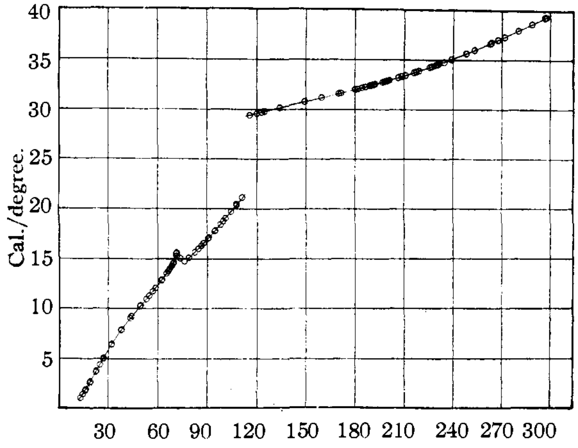

Fig. 1.—The molal heat capacity of isopentane.

The Heat Capacity.—The results of our heat capacity determinations on both samples are given in Table I and those on sample one are shown graphically in Fig. 1. The results of the heat capacity measurements on the two samples of isopentane are in complete agreement in the temperature ranges investigated. For this reason we did not feel that it was necessary to extend our measurements on the second sample (Aston) below 53°K. In view of the nature of our problem we have reported the results of each experimental series of observations as a group (Table I). In Fig. 2 we have presented graphically the (time-temperature) history of our first (Shell) sample. By reference to Fig. 2 and Table I a knowledge of the treatment of the sample preceding each series of measurements may be obtained. The time-temperature history of the second sample (Aston) is not shown on this curve. However in the temperature region 180–240°K. it was given a fast and slow cooling treatment similar to that shown for the first sample.

In the temperature region 180–240°K. repeated attempts were made to obtain evidence of an anomalous behavior. During the early part of this investigation we corresponded with Aston and asked him to suggest an experimental procedure which would cause this phenomenon to manifest itself. In reply he wrote, "We suggest that you cool across the vacuum from 290 to 180°K. in thirty-six hours (Series I), and warming to 290°K. again cool from this temperature to 180°K. in not more than four hours (Series II). In each case take measurements from 180 to 230°K. This procedure should produce a difference in heat capacity of at least 1%, Series I being higher than Series II." We carried out experiments according to these directions (our Series XIV and XV on the Shell sample and Series XX and XXI on Aston sample) except that our slow cooling required a longer time and our fast cooling was done more rapidly than suggested. The results of all of our experiments yield heat capacities that lie on a perfectly smooth curve within the precision of our measurements which is approximately 0.1% (deviation) in the region in question.

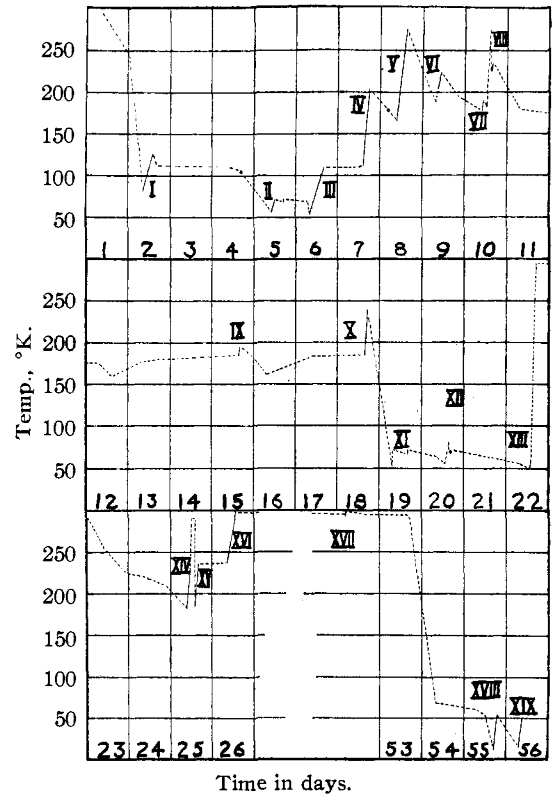

Fig. 2.—Time-temperature history of isopentane: solid lines ascending to right indicate heat capacity measurements, Series I–XIX consecutively. Dashed lines indicate temperature of the isopentane in the intervals between heat capacity measurements. Break in lower section of graph indicates a period of 27 days when isopentane was at room temperature.

The Heat of Fusion.—Two measurements of the heat of fusion were made on the Shell sample, one of which was in conjunction with the melting point determination. The value obtained for the heat of fusion was 1232.2 cal./mole with an estimated uncertainty of less than 1 calorie. A single value of the heat of fusion of sample two (Aston) was calculated from data obtained during the melting point determination. The value of the heat of fusion found was 1229.2 calories per mole. This value is about 0.2% lower than the value found for the first sample and is probably less reliable due to the experimental method.

We have calculated the melting point of pure isopentane from data obtained when various fractions of the two samples were melted. The first sample (Shell) gave a melting point of 113.371°K. and the second (Aston) 113.368°K. from which we conclude that the melting point of pure isopentane is 113.37 ± 0.05°K. This is in excellent agreement with Aston's value 113.39 ± 0.05°K.

The Entropy.—We have also calculated the entropy of isopentane from our data. The results of these calculations are summarized in Table III.

Discussion

Aston's plot of his experimental data indicates an anomalous behavior especially in the temperature intervals 20–60°K. and 180–240°K. Our measurements in both of these temperature regions show no anomalous results. In cooling the isopentane through the 70° transition zone we cooled both rapidly and slowly. The measurements in Series II were made after rapid cooling, all of the other measurements below 73°K., with one exception, were made after the isopentane had been allowed to cool slowly, approximately 0.4–0.5° per hour, in the region 71 to 60°K. The single measurement in Series XII was made after cooling rapidly (twenty-five minutes) from 80.4 to 69.8°K. in an attempt to get a point on an extrapolation of the high temperature curve as we have been able to do in the case of a similar transition found in sebacic acid (unpublished investigation). The attempt was unsuccessful. Below 69°K. all of the experimental results were in complete agreement. In the region 69 to 77°K. the points did not lie on any regular curve; this may be due to the fact that the temperature increments were too large and that they did not cover the same portion of the temperature scale or to the fact that the energy absorption in this region is a function of the history of the sample. The measurements on sample two (Aston) in this region gave approximately the same temperature (72°) for the maximum energy absorption but the total energy absorbed is definitely lower than in the case of sample one.

Aston made four series of measurements on the solid at liquid hydrogen temperatures and found evidence for hysteresis. We made two series of measurements between 13 and 55°K. and several additional series of measurements between 53 and 70°K. without finding any evidence of an anomalous behavior. We are unable to compare our data with Aston's experimental points since he has only published the values taken from a smoothed curve, However, we submitted our data to Aston prior to publication and in a communication to Dr. A. B. Lamb he states that his low curve between 10 and 55°K. is essentially in agreement with our curve.

In the temperature region 180–240°K. our re-

TABLE II

MOLAL HEAT CAPACITY OF ISOPENTANE AT ROUNDED TEMPERATURES

	C_p, cal./degree			% diff. from H. and G.	
T, ° K.	H. and G.	S., A. and S.	P., H. and T.	S., A. and S.	P., H. and T.
			Crystals		
13	1.07				
15	1.58				
20	3.00	3.25		8.3	
25	4.49	4.82		7.3	
30	5.86	6.00		2.4	
35	7.18	7.24		0.8	
40	8.34	8.41		.8	
45	9.40	9.46		.6	
50	10.39	10.41		.2	
55	11.38	11.36		− .2	
60	12.37	12.38		.1	
70	(14.8)[b]	15.00			
80	15.24	15.19	15.58	− .3	2.2
90	16.99	16.96	17.14	− .2	.9
100	18.79	18.81	19.54	.1	4.0
110	20.99	20.75		−1.0	
			Liquid		
115	29.46				
120	29.66	29.68	29.55	0.07	−0.37
130	30.04	29.99	29.95	− .17	− .30
140	30.42	30.38	30.34	− .13	− .26
150	30.80	30.72	30.74	− .26	− .20
160	31.20	31.06	31.14	− .45	− .19
170	31.61	31.48	31.55	− .41	− .19
180	32.04	31.95	32.00	− .28	− .10
190	32.48		32.46		− .06
200	32.96		33.00		.12
210	33.46		33.50		.12
220	34.00		34.04		.12
230	34.58		34.60		.09
240	35.18	35.20	35.20	.06	.06
250	35.82	35.89	35.80	.20	− .06
260	36.52	36.59	36.48	.19	− .11
270	37.24	37.37	37.10	.35	− .38
280	37.98	38.31	37.75[a]	.87	− .61
290	38.75	40.49[a]		4.49	
300	39.55				

[a] Extrapolated values. [b] In transition zone, actual value not certain.

sults show no evidence of an anomalous behavior in either of the two samples that we have studied. These results lead us to the belief that the hysteresis in the liquid observed by Aston is not characteristic of isopentane. We have sent Aston a portion of the Shell isopentane upon which he will repeat his measurements.

Another noteworthy result of this reinvestigation of the heat capacity of isopentane is the lack of agreement between our results and those of Aston, even in the temperature regions in which Aston reports no anomalous results. In Table II we have compared the data taken from a smooth curve through our data with those from Aston's smoothed table. For sake of completeness we have also included the data of Parks, Huffman and Thomas. The accuracy (1%) claimed by the latter authors is not high, neither did they make any estimate of the impurity in their sample, so little weight should be given to the apparent discrepancies between their results and those of the other two investigations.

TABLE III

THE MOLAL ENTROPY OF ISOPENTANE

S (13.21, Debye, 6° freedom)	= 0.385	± 0.040
ΔS (13.21 − 113.37)	= 19.174	± .019
ΔS (113.37, fusion)	= 10.869	± .011
ΔS (113.37 − 298.16)	= 31.812	± .032
S (298.16, liquid)	= 62.240	± .10

An examination of the data in Table II shows that at 20°K. Aston's results are about 8% higher than those of this investigation; this difference becomes progressively less as the temperature is increased. From 55 to 100°K. the heat capacity measurements are essentially in agreement. Above the melting point the discrepancies range from −0.45 at 160°K. to 4.5% at 290°K. The above discrepancies are of such a magnitude as to suggest that the accuracy claimed in one or the other or both of these investigations is entirely fictitious. This suggests that perhaps the accuracy claimed by other laboratories may be open to question.

We should like to propose that workers in this field select a substance whose heat capacity has been accurately determined which may be used as a standard test substance.

The discrepancies in the experimental observations have very little effect on the agreement of the values of the entropies calculated from the two sets of data. Our value for the entropy of liquid isopentane at 298.16°K. is only 0.15 unit lower than that reported by Aston, which is well within the error assigned by him.

Summary

1. The heat capacity of isopentane has been measured over the temperature range 13 to 300°K.
2. The melting point and heat of fusion of isopentane have been measured.
3. We believe that the results of this investigation indicate that certain anomalous results reported by Aston are not characteristic of isopentane.
4. The entropy of liquid isopentane at 291.16°K., calculated from the data of this research, is 62.24 ± 0.10 cal. degree^{-1} mole^{-1}.
5. It is suggested that thermochemists should check their methods so that the accuracy assigned to the experimental results will have a real significance.

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