The average difference between the values under "Obs." calculated from the rough moment values and plotted as circles in Fig. 1 and those calculated from the electronegativity equation (3) is only half as great as that between "Obs." and "Calcd. (1)," obtained from the electronegativity equation (1). It thus seems worth while to use equation (3) for the construction of a table which may be employed to estimate the approximate amount of ionic character of a bond from the electronegativity difference of the two bonded atoms. In Table IV, the amounts of ionic character calculated from equation (3) are multiplied by 100 to give the percentage of ionic character. The values in the latter part of the table are even more approximate than the others since they are the result of an extrapolation. Although equation (3) gives a reasonable enough value for the ionic character of cesium fluoride, it would give more than 100% ionic character for hypothetical electronegativity differences greater than 3.5 and is obviously not to be applied at the extreme limits of the electronegativity difference, where, in any event, the approximate character of the underlying theory renders meaningless the calculation of a very small amount of covalent character or a very small amount of ionic character.

TABLE IV

RELATION OF AMOUNT OF IONIC CHARACTER OF A BOND A–B TO THE DIFFERENCE IN THE ELECTRONEGATIVITIES ($x_A - x_B$) OF THE ATOMS

($x_A - x_B$)	% Ionic	($x_A - x_B$)	% Ionic
0.2	3	1.8	40
.4	7	2.0	46
.6	11	2.2	52
.8	15	2.4	58.5
1.0	19.5	2.6	65
1.2	24	2.8	72
1.4	29	3.0	79.5
1.6	34.5	3.2	87

Summary

The dipole moment of hydrogen fluoride has been measured in the vapor state.

The moment value, which is numerically identical with the electronegativity difference between hydrogen and fluorine calculated from energy data, shows the hydrogen–fluorine bond to have 43% ionic character.

A new table is constructed for the estimation of the approximate amount of ionic character in a bond from the difference in the electronegativities of the two bonded atoms.

PRINCETON, N. J. RECEIVED OCTOBER 23, 1945

The Heat Capacities, Heats of Transition, Heats of Fusion and Entropies of Cyclopentane, Methylcyclopentane and Methylcyclohexane[1]

BY DONALD R. DOUSLIN[2] AND HUGH M. HUFFMAN[3]

The Bureau of Mines has begun recently a research program to obtain precise and accurate values of the thermodynamic constants of hydrocarbons and related compounds. In this paper we present the results of our low temperature investigation of three naphthenes. All of these compounds have been investigated by other workers. Cyclopentane was studied by Jacobs and Parks[4] from 90° K. to room temperature and also by Aston, Fink and Schuman[5] over the temperature range 12 to 291° K. We have thought it desirable to repeat the measurements because of the importance of the experimental value of the entropy in helping to decide on the configuration of this molecule and also as a further check on the agreement of thermal data from this Laboratory and Penn State. Methylcyclopentane[6] and methylcyclohexane[7] were also studied by the Stanford workers from about 90° K. to room temperature.

Description of Materials

The samples of API–NBS hydrocarbons have been made available by the American Petroleum Institute and the National Bureau of Standards through the A. P. I. Research Project 44. The samples were purified at the National Bureau of Standards by A. P. I. Research Project 6 under the supervision of F. D. Rossini, from material supplied by several laboratories.

Cyclopentane, by the A. P. I. Research Project 45 on the "Synthesis and Properties of Hydrocarbons of Low Molecular Weight" at the Ohio State University, under the supervision of Cecil E. Boord.

Methylcyclopentane, by the Houdry Process Corporation, through the courtesy of E. A. Smith.

Methylcyclohexane, by the A. P. I. Research Project 45 at the Ohio State University, and the Barrett Division of the Allied Chemical and Dye Corporation.

In the course of our calorimetric investigation, we have also studied the melting points of these compounds, under equilibrium conditions in the usual manner. The experimental and certain derived data for these compounds are summarized in Table I. Since the measurements were made on the compounds in a sealed calorimeter under their own vapor pressure, the observed temperatures are triple points. In determining the temperatures corresponding to a given fraction in the liquid form, the calorimeter and environment were kept at the same temperature (as indicated by a copper–constantan difference couple) and

---

[1] Published by permission of the Director of the Bureau of Mines, U. S. Dept. of the Interior. Not copyrighted.

[2] Associate Chemist, Bureau of Mines, Petroleum Experiment Station, Bartlesville, Okla.

[3] Principal Physical Chemist, Bureau of Mines, Petroleum Experiment Station, Bartlesville, Oklahoma.

[4] Jacobs and Parks, THIS JOURNAL, **58**, 2354 (1936).

[5] Aston, Fink and Schuman, *ibid.*, **65**, 341 (1943).

[6] Huffman, Parks and Barmore, *ibid.*, **53**, 3876 (1931).

[7] Parks and Huffman, *ibid.*, **52**, 4381 (1930).

the temperature of the calorimeter was observed periodically until there was no significant drift.

TABLE I

MELTING POINT SUMMARY

0°C. = 273.16°K. Cyclopentane; $N_x = 0.00227\ \Delta T$

% Melted	$T_{(obs.)}$, °K.	ΔT	N_x	$N_{(calcd.)}$	$T_{(calcd.)}$, °K.
37.2	179.666	0.047	0.000106	0.000039	179.658
59.5	179.678	.035	.000079	.000047	179.678
90.6	179.690	.023	.000052	.000047	179.690
100.0		(.021)			179.692
Pure					179.713
Triple point pure cyclopentane					179.71 ± 0.05
Impurity in this sample					0.005 ± 0.002 mole %

Methylcyclopentane; $N_x = 0.0488\ \Delta T$

% Melted	$T_{(obs.)}$, °K.	ΔT	N_x	$N_{(calcd.)}$	$T_{(calcd.)}$, °K.
21.5	130.660	0.066	0.00322	0.00069	130.638
51.1	130.689	.037	.00182	.00093	130.689
70.5	130.699	.027	.00133	.00094	130.699
89.9	130.705	.021	.00102	.00092	130.705
100.0		(.019)		.00093	130.707
Pure					130.726
Triple point pure methylcyclopentane					130.73 ± 0.05
Impurity in this sample					0.093 ± 0.003 mole %

Methylcyclohexane; $N_x = 0.0378\ \Delta T$

% Melted	$T_{(obs.)}$, °K.	ΔT	N_x	$N_{(calcd.)}$	$T_{(calcd.)}$, °K.
9.5	146.552	0.0240	0.000907	0.000086	146.545
28.0	146.565	.0106	.000401	.000112	146.565
49.2	146.570	.0060	.000227	.000112	146.570
75.7	146.572	.0039	.000147	.000111	146.572
94.2	146.573	.0032	.000121	.000114	146.573
100.0		(.0030)		.000112	146.573
Pure					146.576
Triple point pure methylcyclohexane					146.58 ± 0.05
Impurity in this sample					0.011 ± 0.002 mole %

The temperatures were recorded to 0.0001° and at equilibrium usually showed alternations of only a few 0.0001° from the mean value. The observed temperature was plotted against $1/F$, where F is the fraction melted, and the curve extrapolated to $1/F = 0$ to obtain the melting point of the pure material. To obtain N_x, the mole fraction of impurity corresponding to a given fraction melted, we have used the simplified expression $N_x = K\Delta T$[8] since in no case was N_x or ΔT large.

A study of Table I shows that in all cases the observed melting point, corresponding to the smallest fraction melted, does not agree with the calculated temperature, which may indicate that Raoult's law is not obeyed over the entire range of liquid-solid ratios. For this reason, there is a certain arbitrariness in the selection of the "true" melting point and the mole per cent. of impurity present in the 100% liquid material. We feel, however, that this uncertainty will have no significant effect on the thermal studies we have made.

The materials were placed in a glass container connected to a high vacuum system and were alternately frozen and melted *in vacuo* to remove any dissolved gases. They were then distilled into the copper calorimeter which was joined to the glass system by means of a Housekeeper seal. When the calorimeter was filled, the small (1.0 mm. O.D.) filling tube was pinched off and immediately closed with soft solder.

Apparatus.—The measurements were made in the apparatus described by Ruehrwein and Huffman,[9] which was loaned to the Bureau of Mines by the California Institute of Technology. Very briefly, the method is as follows: 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 heat interchange. The initial and final temperatures of the calorimeter were measured by means of a platinum resistance thermometer. The electrical measurements required for the determination of the resistance of the thermometer and for the electrical energy

TABLE II

THE MOLAL HEAT CAPACITY

0°C. = 273.16°K.

Cyclopentane, molecular weight = 70.130

T, °K.	ΔT	C_p cal./mole
Crystals I		
11.88	2.362	0.437
13.84	1.487	.692
15.63	2.063	.995
18.60	3.836	1.580
22.18	3.317	2.397
26.16	4.617	3.372
31.23	5.506	4.631
36.77	5.548	5.941
42.06	5.037	7.077
47.96	6.765	8.205
54.94	7.207	9.370
55.71	5.574	9.486
61.51	6.027	10.325
67.29	5.531	11.064
72.64	5.176	11.664
78.46	6.466	12.295
80.70	6.324	12.525
85.47	7.545	13.009
92.32	6.158	13.655
99.30	7.802	14.265
106.91	7.417	14.922
113.72	6.213	15.548
118.98	4.294	16.054
Crystals II		
125.09	2.270	22.626
125.57	1.744	22.658
128.49	4.524	22.598
129.99	7.091	22.609
130.40	2.275	22.398
134.24	5.420	22.475
135.30	3.536	22.492
Crystals III		
141.39	3.992	21.671
143.07	7.245	21.608
146.04	5.316	21.535
150.31	7.234	21.453
157.53	7.212	21.378
163.83	5.393	21.327
169.17	6.571	21.305
169.22	5.379	21.302
174.58	5.355	21.320
Liquid		
185.75	8.458	24.023
189.55	5.213	24.126
195.20	10.417	24.284
197.31	10.307	24.376
205.54	10.280	24.642
207.54	10.153	24.722
217.60	9.967	25.181
227.48	9.792	25.652
237.19	9.624	26.126
246.72	9.444	26.667
256.07	9.260	27.246
265.23	9.064	27.903
274.21	8.889	28.523
283.03	8.724	29.122
291.66	8.543	29.818
300.12	8.388	30.448

---

(8) Mair, Glasgow and Rossini, *J. Research Natl. Bur. Standards*, **26**, 591 (1941).

(9) Ruehrwein and Huffman, THIS JOURNAL, **65**, 1620 (1943).

TABLE II (*Concluded*)

T, °K.	ΔT	C_p cal./mole	T, °K.	ΔT	C_p cal./mole
Methylcyclopentane, molecular weight = 84.156					
Crystals				Liquid	
12.80	3.262	0.807	126.58[a]	11.135	29.871
15.45	1.949	1.340	136.10	6.623	29.862
17.53	2.128	1.822	137.65	10.998	29.900
20.92	4.622	2.732	140.03	10.934	29.903
25.13	3.771	3.922	144.89	10.933	29.913
28.95	3.846	5.002	148.59	10.871	29.945
32.81	3.880	6.052	150.90	10.800	30.012
37.60	5.646	7.232	155.75	10.794	30.078
43.03	5.215	8.434	159.38	10.730	30.131
49.18	7.075	9.633	161.64	10.763	30.163
55.78	6.148	10.773	170.05	10.595	30.357
62.09	6.466	11.727	180.56	10.440	30.671
69.22	7.787	12.676	190.94	10.311	30.955
76.67	7.120	13.615	201.17	10.163	31.364
83.53	6.606	14.501	211.26	9.998	31.847
89.52	9.044	15.188	215.77	19.788	32.058
89.96	6.235	15.218	221.17	9.836	32.365
92.45	6.629	15.476	230.93	9.668	32.878
99.14	8.390	16.221	235.23	19.137	33.168
100.94	10.357	16.390	241.01	10.457	33.531
108.66	10.659	17.265	251.36	10.261	34.226
109.05	5.867	17.292	254.04	18.476	34.425
114.80	5.639	17.990	261.52	10.067	34.946
117.74	7.500	18.402	268.65	10.759	35.556
120.32	5.401	18.822	271.50	9.873	35.695
123.82	6.966	19.476	279.31	10.544	36.367
124.97	6.963	20.050	281.27	9.682	36.486
125.57	5.095	20.156	289.74	10.338	37.171
			291.29	10.336	37.400
			299.14	8.448	37.997
			301.52	10.152	38.162
			307.52	8.299	38.770
Methylcyclohexane, molecular weight = 98.182					
Crystals			91.36	6.713	14.859
12.19	2.358	0.780	98.65	7.883	15.739
13.59	1.340	1.020	106.84	8.509	16.782
14.28	2.358	1.158	116.06	9.948	17.932
16.03	3.495	1.547	125.69	9.345	19.102
16.69	2.405	1.689	135.63	10.561	20.339
19.92	4.243	2.492	137.39	5.221	20.543
20.02	4.208	2.516	142.51	5.037	21.378
23.96	3.652	3.540			
24.21	4.297	3.599		Liquid	
24.84	9.124	3.769	155.09	10.327	33.690
28.00	4.406	4.576	160.61	10.252	33.970
28.73	4.729	4.753	165.32	10.142	34.161
32.33	5.845	5.620	170.76	10.057	34.521
32.39	4.341	5.639	175.37	9.943	34.778
37.60	4.687	6.780	180.74	9.890	35.032
43.20	6.519	7.859	186.20	11.715	35.347
49.42	5.916	8.949	197.80	11.482	36.010
50.93	7.645	9.189	209.16	11.257	36.681
55.82	6.893	9.958	221.21	12.840	37.520
58.07	6.621	10.302	233.90	12.533	38.474
65.06	7.354	11.339	246.28	12.233	39.469
71.87	6.272	12.257	259.22	13.633	40.554
77.91	5.811	13.070	272.67	13.270	41.750
84.41	7.191	13.963	285.76	12.927	42.936

[a] Supercooled liquid.

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 frequently compared against a stop watch. The precision of our measurements was in general better than 0.1% and above 30° K. we believe the accuracy uncertainty should not be greater than 0.2%. The energy measurements were made in terms of the international joule and were converted to calories by dividing by 4.1833.

The results of the heat capacity measurements are given in Table II. In Table III we have listed the values at integral temperatures as selected from a smooth curve through the experimental data.

TABLE III

MOLAL HEAT CAPACITY VALUES AT INTEGRAL TEMPERATURES

	C_p		
T, °K.	Cyclopentane	Methylcyclopentane	Methylcyclohexane
12	0.45	0.66	0.75
13	.57	.84	.91
14	.72	1.04	1.10
15	.88	1.25	1.32
20	1.89	2.48	2.52
25	3.08	3.90	3.81
30	4.33	5.30	5.07
35	5.53	6.60	6.23
40	6.64	7.79	7.26
45	7.66	8.83	8.18
50	8.56	9.78	9.04
55	9.37	10.64	9.81
60	10.11	11.42	10.60
70	11.37	12.78	12.00
80	12.45	14.04	13.36
90	13.44	15.24	14.68
100	14.32	16.30	15.92
110	15.20	17.37[a]	17.18
120	16.14	18.44[a]	18.41
130	22.58	19.51[a]	19.64
140	21.72	29.89	20.86
150	21.56	29.98	33.44
160	21.46	30.14	33.94
170	21.35	30.35	34.46
180	23.88	30.61	35.00
190	24.14	30.92	35.56
200	24.45	31.31	36.14
210	24.84	31.78	36.76
220	25.28	32.29	37.43
230	25.76	32.85	38.17
240	26.28	33.46	38.96
250	26.87	34.13	39.78
260	27.52	34.84	40.62
270	28.22	35.60	41.50
280	28.93	36.40	42.40
290	29.68	37.22	43.33
300	30.44	38.09	44.28

[a] These values taken from extrap. curve after making allowance for premelting.

Cyclopentane undergoes two transitions in the solid state. We have made studies of the temperature at which these transitions occur and the data are given in Table IV.

TABLE IV

CYCLOPENTANE; TRANSITION TEMPERATURE SUMMARY

Lower transition % in high temp. form	T, °K.
7.2	122.380
40.0	122.384
80.0	122.387

Transition temp. = 122.39 ± 0.05 K.

Upper transition % in high temp. form	T, °K.
40.0	138.062
85.0	138.077

Transition temp. = 138.08 ± 0.05° K.

The experimental values for the heats of fusion and heats of transition are given in Tables V and VI.

TABLE V

FUSION DATA SUMMARY, ΔH CAL./MOLE

Exp.	Cyclopentane	Methyl[a] cyclopentane	Methyl-cyclohexane
1	145.20	1655.7	1614.2
2	145.88	1656.4	1612.6
Mean	145.54 ± 0.34	1656.0 ± 0.4	1613.4 ± 0.8

[a] These values have been corrected for the 0.093 mole % impurity.

TABLE VI

TRANSITION DATA CYCLOPENTANE, ΔH CAL./MOLE

Exp.	Lower trans.	Upper trans.
1	1167.3	82.13
2	1165.5[a]	82.50
Mean	1167.3 ± 1.0	82.32 ± 0.19

[a] This value was obtained from data taken during the determination of the transition temperature. The shield was known to be hot part of the time; consequently, this datum was given no weight in obtaining mean value.

The above data have been used to calculate the entropies of the three compounds at 298.16° K. and in the liquid form. The results of these calculations are summarized in Table VII.

Discussion

The data obtained in this Laboratory can be compared with those from the Stanford and Penn State Laboratories. However, since the Stanford work is admittedly not of the same order of accuracy, little is to be gained from such a comparison. In the case of cyclopentane, the specific heat measurements from this Laboratory and Penn State have differences ranging from −1.3 to +1.7% except in the region below 30° K. where the difference reaches a maximum of 5.3%.

TABLE VII

SUMMARY OF THE MOLAL ENTROPY DATA

Cyclopentane	
S_{12° (Debye, 6° θ = 151.6)	0.153
$\Delta S_{12^\circ - 122.39^\circ}$ (graphical)	16.032
$\Delta S_{122.39^\circ}$ (1167.3/122.39)	9.537
$\Delta S_{122.39^\circ - 138.09^\circ}$ (graphical)	2.723
$\Delta S_{138.09^\circ}$ (82.32/138.09)	0.596
$\Delta S_{138.09^\circ - 179.71^\circ}$ (graphical)	5.642
$\Delta S_{179.71^\circ}$ (145.54/179.71)	0.810
$\Delta S_{179.71^\circ - 298.16^\circ}$ (graphical)	13.293
$S_{298.16^\circ}$ liquid	48.786 ± 0.10
Methylcyclopentane	
S_{13° (Debye, 6°, θ = 134.0°)	0.280
$\Delta S_{13^\circ - 130.73^\circ}$ (graphical)	19.800
$\Delta S_{130.73^\circ}$ (1656.0/130.73)	12.667
$\Delta S_{130.73^\circ - 296.16^\circ}$ (graphical)	26.473
$S_{298.16^\circ}$ liquid	59.220 ± 0.10
Methylcyclohexane	
S_{12° (Debye, 4°, θ = 111.5°)	0.254
$\Delta S_{12^\circ - 146.58^\circ}$ (graphical)	21.447
$\Delta S_{146.58^\circ}$ (1613.4/146.58)	11.007
$\Delta S_{146.58 - 298.16^\circ}$ (graphical)	26.546
$S_{298.16^\circ}$ liquid	59.254 ± 0.10

The entropy values from all three laboratories are in excellent agreement, with the exception of the Stanford value for cyclopentane. The values of the transition and fusion temperatures of cyclopentane, as determined by us and by Penn State are in excellent agreement.

This would indicate that the source of the discrepancies between the two laboratories is not due to the temperature scale. Furthermore, the continuing presence of these discrepancies may be offered as an argument that steps should be taken to find their source and to eliminate it.

Acknowledgment.—We wish to express our thanks to Dr. J. W. Knowlton, of this Laboratory, who assisted with the measurements and grateful acknowledgment is made to the American Petroleum Institute and the National Bureau of Standards for the loan of the samples measured.

Summary

Heat capacity data on cyclopentane, methylcyclopentane and methylcyclohexane have been given over the range 12 to 300° K.

Values of the melting points and temperatures of transition have been given.

The heats of fusion and transition were determined.

Entropy values for the liquid state at 298.16° K. were calculated.

BARTLESVILLE, OKLAHOMA RECEIVED SEPTEMBER 10, 1945